



# Hazardous Chemical Waste Management in the Laboratory (*Advanced 1-Day Workshop*)

**Bangkok, Thailand  
September 9, 2011**



International Year of  
**CHEMISTRY**  
**2011**

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# *Course topics*

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- **Hazardous waste definitions and characteristics**
- **Chemical management**
- **Hazardous waste survey – Deficiency recognition**
- **Hazardous waste – Collection, segregation, storage, labeling, recycling, lab treatment (including peroxides) and pickup**
- **Legacy waste and lab cleanout procedures**
- **Chemical waste accidents – Case Studies**
- **Hazardous waste disposal – technologies, policies and procedures**
- **Workshop Wrap Up**



# *Definition of waste*

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## Definition of Wastes- Basel

“substances or objects which are disposed of or are intended to be disposed of or are required to be disposed of by the provisions of national law”

## Definition of Hazardous Wastes- EPA

“ liquid, solid, contained gas, or sludge wastes that contain properties that are dangerous or potentially harmful to human health or the environment.”

**Characteristic** – Ignitable-Corrosive-Reactive-Toxic  
**Listed** – Industrial source-Type



# ***Waste management: nonhazardous waste***

- **Used oil (uncontaminated) is not considered hazardous waste. Label Containers "USED OIL", not "hazardous waste."**
- **Uncontaminated PPE (gloves, wipes)**
- **Triply rinsed glassware (bottles, droppers, pipettes)**
- **Salts (KCl, NaCl, Na<sub>2</sub>CO<sub>3</sub>)**
- **Sugars - Amino acids**
- **Inert materials (uncontaminated resins and gels)**





# Characteristic hazardous waste properties (US EPA)

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**Ignitable:** the waste will *catch fire under certain conditions.*



**Corrosive:** the waste has a very high (12.5 or greater) or low (2 or less) pH.

**Reactive:** the waste is unstable, reacts violently, explodes, and/or produces toxic fumes when mixed with water or subjected to heat or pressure.



**Toxic:** the waste is harmful or fatal when ingested or absorbed. It will leach toxic chemicals.





## ***Ignitable: the waste will catch fire under certain conditions***

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**Liquid:** has a flash point less than 60°C (this is the temperature at which enough vapor is emitted to ignite in the presence of a spark/flame).

(Example: gasoline, isopropyl alcohol)

**Non-liquid:** will cause fire via friction, absorption of moisture, or spontaneous chemical change.

(Example: metal dusts)

**Compressed Gas:** cylinders or aerosol sprays using flammable gases as a propellant. (Example: hydrogen, propane)

**Oxidizer:** initiating combustion by contributing oxygen. (Example: oxygen, peroxides, hypochlorite)



***Corrosive: pH high or low.  
Reactive: unstable – reacts violently.***

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**Corrosive:** the waste has a very high (12.5 or greater) or low (2 or less) pH.

**(Example: battery acid, rust removers, and alkaline cleaning solutions such as ammonium hydroxide.)**

**Reactive:** the waste is unstable, reacts violently, explodes, and/or produces toxic fumes when mixed with water or subjected to heat or pressure.

**(Examples: explosives, alkali metals and certain cyanides, or sulfide-bearing wastes.)**



# ***Toxic: the waste is harmful or fatal when ingested or absorbed.***

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**It will leach into the soil or groundwater if disposed in a landfill.**

**(Examples: wastes that contain high concentrations of heavy metals, such as cadmium, lead, or mercury.)**

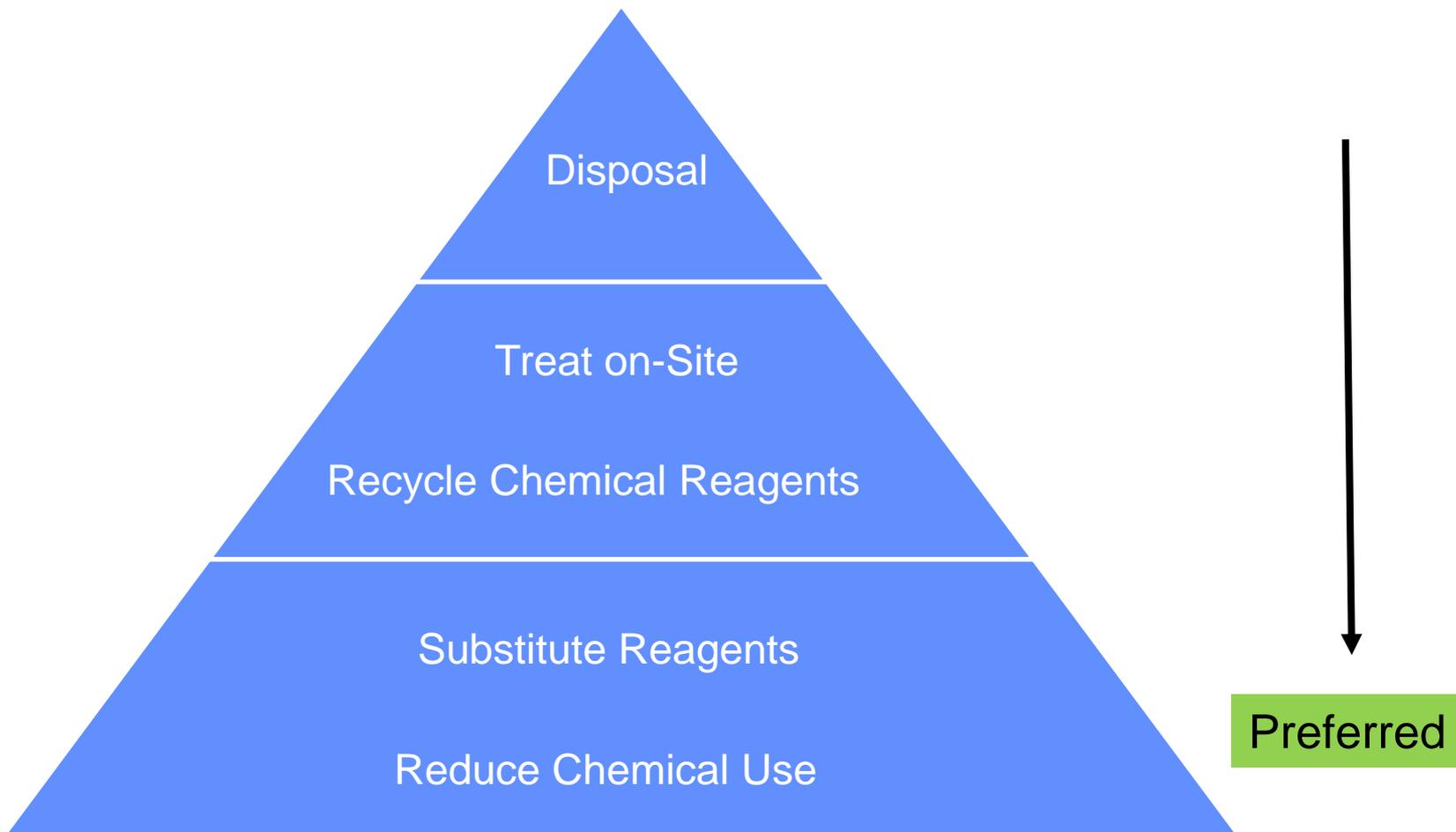
**Toxic wastes are determined through sufficient generator knowledge or with a test called the Toxicity Characteristic Leaching Procedure (TCLP-which is pronounced “T-clip.”)**

**This test will analyze the waste to determine if it exceeds allowable concentrations of 39 specific chemical compounds (found in 40 CFR 261.24).**



# *Chemical management is Intrinsic to waste management*

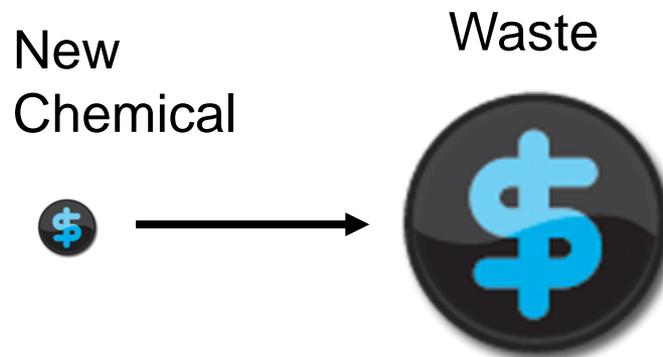
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# *Chemical management is a best practice for safety and security*

- **Reduces hazardous waste**
- **Reduces cost**
  - ✓ New purchases
  - ✓ Waste disposal
  - ✓ More efficient
- **Improves security**
  - ✓ Insider threat
  - ✓ Outsider threat
- **Facilitates environmental compliance**
- **Improves quality of research**
- **Improves quality of lab instruction**



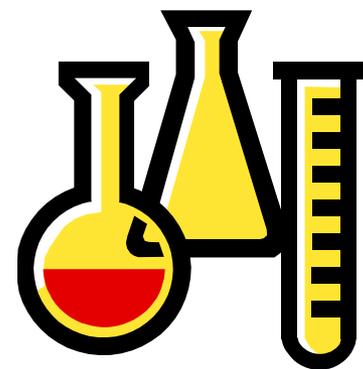


# *Proper chemical management program has several essential elements*

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## **Chemical Management Elements**

- **Source reduction**
- **Procedure for chemical ordering and disposal**
- **Inventory and tracking**
- **Storage in stockrooms**
- **Access control**
- **Recycling of chemicals, containers and packages**





# *Inventory management*

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## **Less is Better !**

- **Order only what you need**
- **Reduce size of experiment**
  - **It costs less to store**
  - **It costs less to dispose**



See reference to ACS “Less is Better” Campaign





# Ordering chemicals - chemical inventory

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- **Database or spreadsheets are tools to track the chemical inventory**
  - **Barcoding can be used**
  - **Chemicals can be found easily**
  - **Chemical ages can be tracked**
  - **Chemical standards maintain traceability**
  - **Disposal can be documented**
- **Physical reconciliation**
  - **Assures accuracy of database**
  - **Provides visual inspection of chemical condition**





# ***Best practice - ordering and stocking chemicals***

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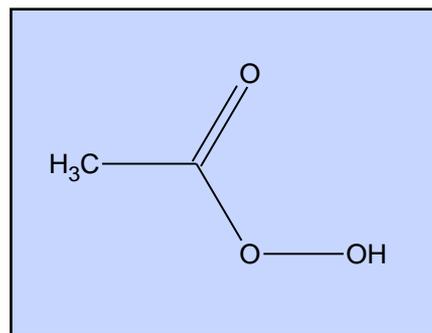
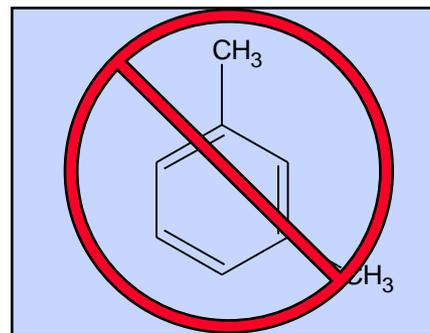
- **See if your institution already has it (surplus)**
- **Order minimum needed (large quantities are not a bargain)**
- **Check on special storage (refrigeration, dry box...)**
- **Mark the receipt /open date (unstable chemical)**
- **Can it eventually be disposed of (rad waste, mixed waste)**





## ***Best practice: replace a hazardous solvent with a non-hazardous one***

- **Citrus based solvents for xylene in histology lab**
- **Substitute nucleic acid dye for ethidium bromide**
- **Peracetic acid for formaldehyde for cleaning kidney dialysis machines**
- **Non mercury thermometers**
- **Enzyme and peroxide based cleaners for chromerge (NoChromix)**
- **When purchasing automated equipment think of chemical waste**



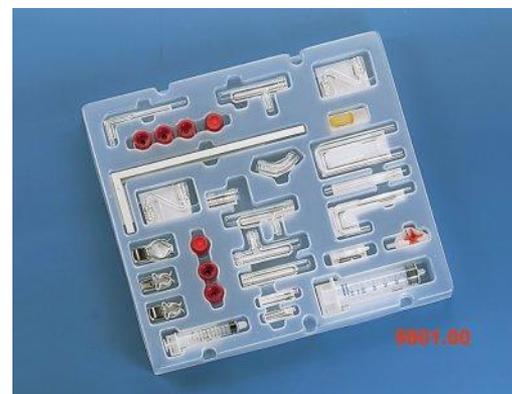
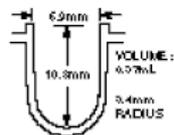
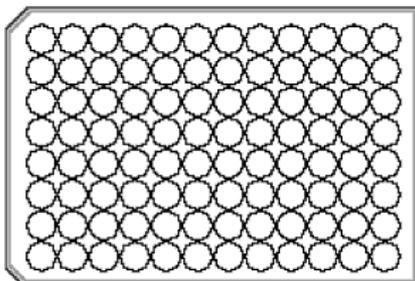


# Best practice: Reduce the size of experiments

- Reduce the size of experiment by 50%.
  - Semimicro
- Use microchemical techniques.
  - Organic
  - Inorganic
  - May allow exotic chemical use (<\$).



Small-Scale Lab:Tantayanon



HalbMikroTechnik Chemie





# *Microchemistry references*

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“Microscale Techniques for the Organic Laboratory.”

Dana W. Mayo, Ronald M. Pike, Samuel S. Butcher, Peter K. Trumper; John Wiley & Sons, 1991, ISBN 0-471-62192-7.

“Organic Chemistry Experiments Microscale & Semi-Microscale.”

Bruce N. Campbell, Jr., Monica McCarthy Ali; Books/ Cole Publishing Company, 1994, ISBN 0-534-17611-9.

“Experimental Organic Chemistry Standard and Microscale.”

L. M. Harwood, C. J. Moody, J. M. Percy; Blackwell Science, Second Edition, 1998, ISBN 0-632-04819-0.



## ***Best practice: Reduce solvent use improve teaching***

- **Reuse** products as reagents in future tests.
- Use the third cleaning wash from one test as the first wash solution for the next.
- **Zero Effluent Laboratory**
  - ✓ Limited quantity of solvent given to students.
  - ✓ Product from experiment poured into dedicated container – students alert instructor if cross-mixing occurs.
  - ✓ Teaching assistant responsible to distill and recover.

## **Zero Effluent Laboratory**





# ***Best practice in laboratory notebook***

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In addition to these precautions, we require that you look up the toxicities of all reagents and compounds you may handle in laboratory and write the information in your lab notebook before entering the laboratory. This information is to be found in CRC Handbook of Chemical Safety, the Merck Index, or the Toxic Substances List, copies of which are on 30-minute reserve at the Sciences Library.

University of California Riverside (T.H. Morton - 1983)





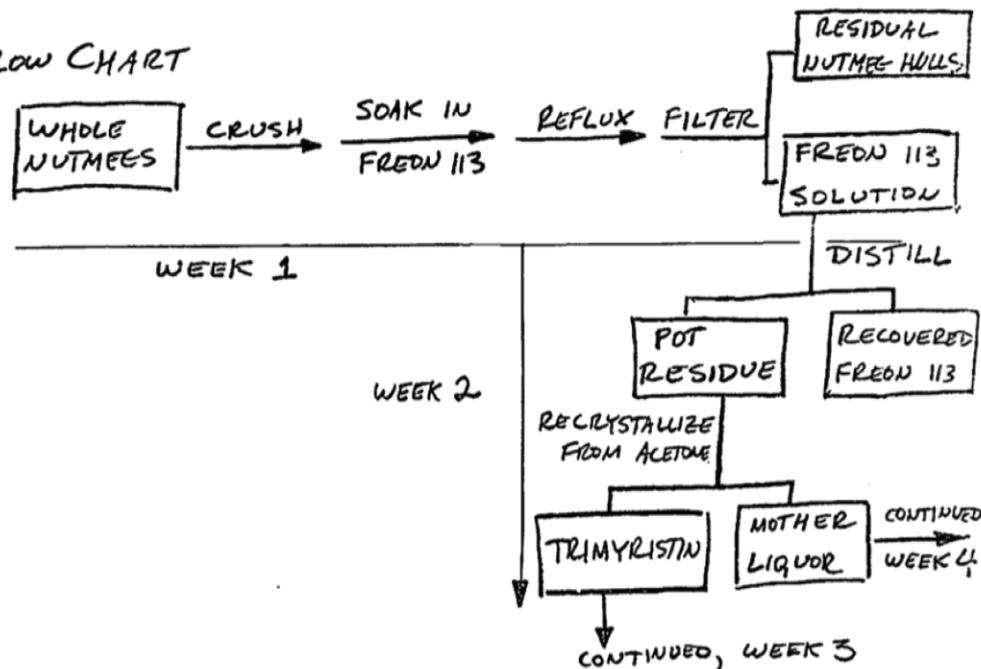
# Best Practice in Laboratory Notebook

Students required to  
look up toxicity and  
record it in notebook

University of California  
Riverside (T.H. Morton - 1983)

## ISOLATION OF NATURAL PRODUCTS FROM NUTMEG

### Flow Chart



### WEEK 1

#### TOXICITIES

FREON 113 [1,1,2-TRICHLOROTRIFLUOROETHANE, C<sub>2</sub>F<sub>3</sub>Cl<sub>3</sub>]:  
Minor inhalation toxicity hazard,  
Threshold limit value: 1000 ppm (7600  $\frac{\mu\text{g}}{\text{m}^3}$ )

NUTMEG [MYRISTICA, MELZER INDEX]:  
Ingestion of large quantities  
causes drowsiness, stupor, death.

#### DATA

# of nutmegs received:

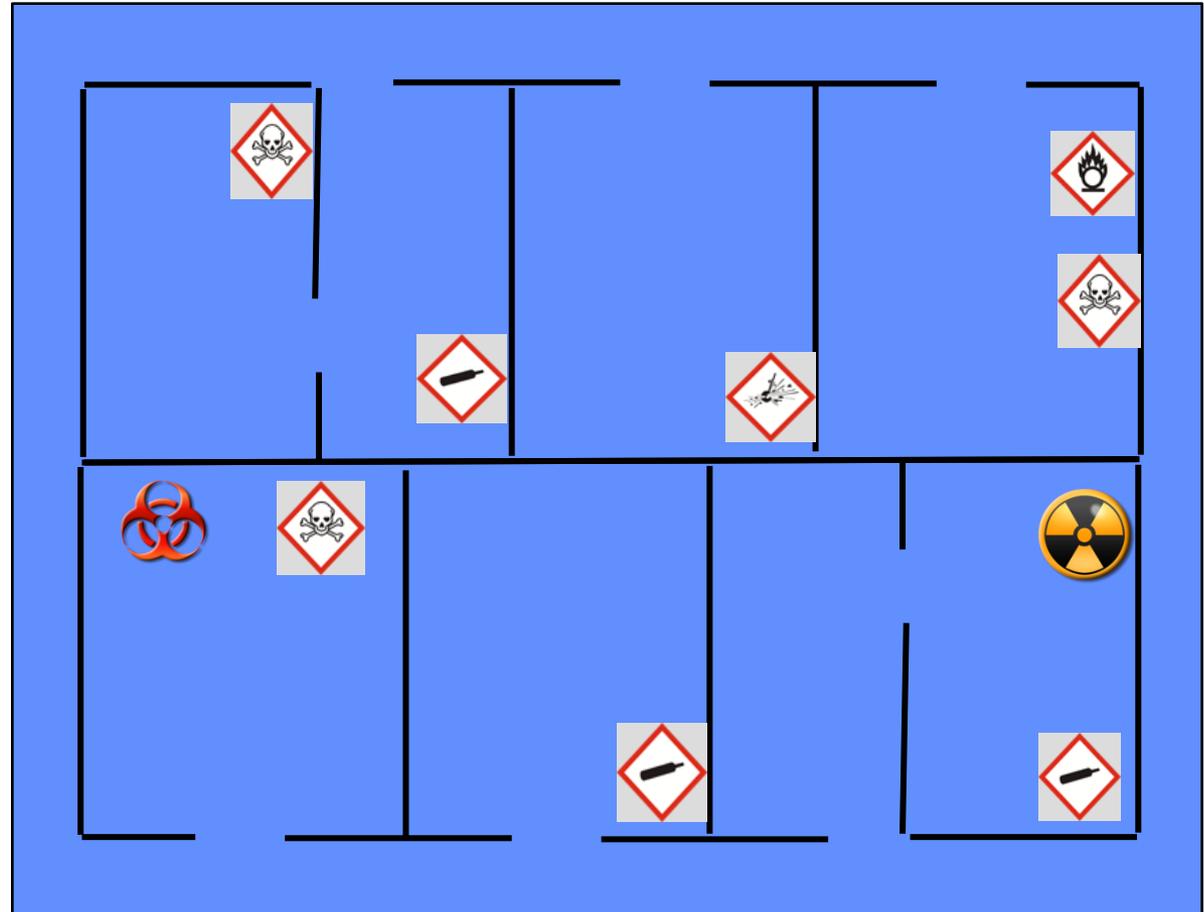
Weight:

Volume of FREON 113 used:



# Hazardous waste survey

Need to take a fresh look at where wastes are stored





# *Hazardous waste survey - deficiency recognition*

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**The waste survey is meant to be a snapshot in time to see what you are up against.**

- List the locations where hazardous waste are stored
- List the types of waste stored
- List the quantity of waste stored
- Evaluate which wastes are “legacy waste”
- List the quantity of hazardous waste stored
- Evaluate which labs or classes produce which wastes



# *Hazardous waste plan*

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**The waste plan is meant to address how you will reduce, store, treat and dispose of hazardous waste.**

- **Policy / administrative:** Establish a waste handling policy – Contact approved waste disposal company - Put in place processes for waste handling.
- **Laboratory / operations:**
  - ✓ Reduce chemical use
  - ✓ Search for non hazardous substitutions
  - ✓ Recycle solvents when possible
  - ✓ Store and segregate waste
  - ✓ Treat waste where appropriate
  - ✓ Dispose of waste promptly



# *Hazardous waste plan*

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- **Collection in the laboratory,**
- **Segregation of waste,**
- **Labeling and Log Sheets,**
- **Storage,**
- **Recycling and Treatment (as allowed),**
- **Pickup (Where does it go after it leaves the laboratory?)**



# Hazardous waste - Collection

Select the appropriate and compatible container for the specific waste. **Container should not react with the waste being stored.**

- Original containers that contained solvents or reagents can usually be used.
- Avoid **metal containers** because they **can corrode**.
- Avoid glass containers if the waste contains hydrofluoric acid (HF).
- Waste containers must be capped and closed, except during transfers. Do not leave funnel in hazardous waste container.
- If there is a concern of the waste building up pressure the container can be loosely capped until there is no longer a risk of over pressuring the container.





# ***Hazardous waste – Segregation of waste streams***

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***Wastes from incompatible hazard classes should not be mixed*** (e.g. organic solvents with oxidizers, acids and bases- unless purposeful neutralization).

**Separate into different waste streams**

- **Organics,**
- **Halogenated organics,**
- **Acids,**
- **Bases.**

***Keeping waste streams separated avoids unintended reactions and makes it easier to eventually dispose of the wastes.***



# *Hazardous waste – Labeling*

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Label wastes containers immediately and keep a log of the wastes added to the container.

The waste container label should contain the following information –

- **Hazardous Waste,**
- Contents – for example - Organic Wastes,
- Name and date – Person that started the waste container and the date when waste was first put into the container,
- A unique code that identifies the container with the waste log sheet.



# Hazardous waste – Labeling

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Example of a waste container label -

## Hazardous Waste

Contents – Organic Wastes

Date – 8 Sept. 2011

Name – *Bob Wills*

Container Identification – 080911-1A



# Hazardous waste – Labeling



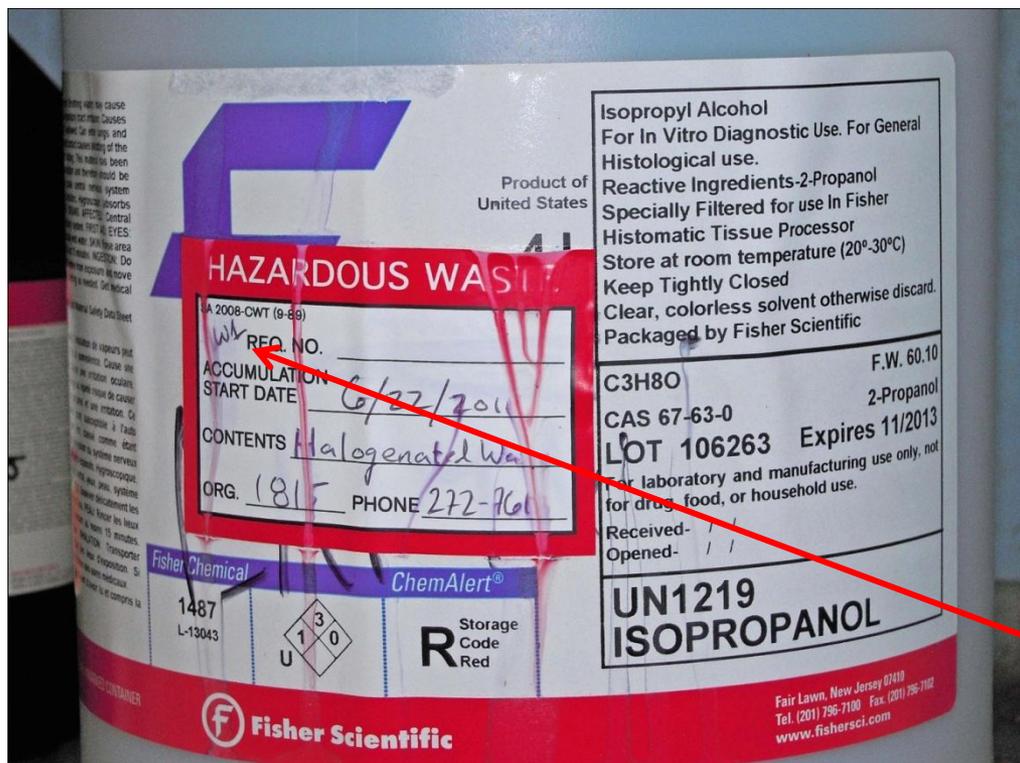
Example of a waste container –

- The container is clean,
- The label covers the old container label completely,
- Container identifier.





# Hazardous waste – Labeling



A bad example of a waste container –

- The label ink has started to run due to spillage,
- The label does not cover the old container label completely,
- There is no unique identifier for this waste container to reference it to the log sheet.



## ***Hazardous waste – Log Sheets***

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- Since there is a limited amount of space on the waste label it is necessary to keep a *Waste Log Sheet*.
- Waste log sheets describe the types of wastes that go into the waste container and the amounts.
- The waste logs are unique to each waste container.



# Hazardous waste – Waste log sheet example

## Waste Contents Organic Wastes

Bldg/Room No. IBP-2173

Organization Chemical Synthesis Lab

Phone 505-284-3016

Container designation 081211-1A

Container size 4 Litre

Container description. Bottle

Container material Plastic

Please enter the required information above. Give the container a unique designation for identification, provide container size, description (i.e. bottle, bag, box, etc.) and identify container material (i.e. glass, plastic, cardboard, etc.).

Fill out a Waste Addition Log for each waste container that is actively used to collect waste and provide the required information each time a waste is added to the container. Once the container is full or is ready for disposal the request will be entered into the WDDR system and a Disposal Request number issued. Once the Disposal request number has been issued place this number on the container. Return this page to C. A. Stewart.

Date	Qty./vol.	Description	Generator
<i>08/12/2011</i>	<i>25 ml</i>	<i>Toluene</i>	<i>CAStewart</i>
<i>08/15/2011</i>	<i>100 ml</i>	<i>Petroleum ether</i>	<i>Rich K.</i>





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**BREAK**



# Hazardous waste – Storage

- Secure and lock waste storage area
- Post signs to warn others
- Keep area well ventilated
- Provide fire extinguishers and alarms, spill kits
- Provide suitable PPE
- Provide eye wash, safety showers
- Do not work alone





# *Hazardous waste – Storage*

- **Separate incompatible chemicals**
- **Separate flammables/explosives from ignition sources**
- **Use flammable storage cabinets for large quantities of flammable solvents**
- **Do not store incompatible hazardous wastes next to each other**
- **Separate alkali metals from water**
- **Separate acids and bases**





# *Hazardous waste – Some helpful hints*

- **Individuals own their own waste**
- **Lab must be orderly and neat**
- **Waste should not be stored in aisle**
- **Stored with secondary containment**





# ***Hazardous waste – Some helpful hints***

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- **Use good quality plastic bottles for containers that are used frequently. (They are not as likely to get broken when moved in and out of the storage area.)**
- **For the Waste Label use an ink or marking pen that will not run if the ink comes in contact with the liquid wastes (and most likely it will).**
- **If possible cover the Waste Label with clear packing tape. This protects the information on the label from solvents and keeps the label from coming off.**



# ***Hazardous waste – Some helpful hints***

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- **Keep the waste containers clean and replace the caps on the containers once the waste has been added.**
- **If there is a chance that newly added waste will build up pressure loosely cap the bottle and place the container in the hood. Allow for the gases to vent. Once there is no longer the risk of pressure building up in the container then cap the container tightly.**
- **Periodically check the waste containers to make sure they are not pressurized. Make sure to take the necessary precautions when doing these checks (in the hood, safety glasses, etc.).**
- **Use a unique identifying code on the Waste Label that corresponds with the Waste Log Sheet.**



# Hazardous waste - Gas cylinders

- Secure (chain/clamp) and separate gas cylinders
- Screw down cylinder caps
- Store in well-ventilated area
- Separate & label empty cylinders
- Store empty cylinders separately
- Separate flammable from reactive/oxidizing gases





# *Chemical recycling*

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- Reuse by others in the organization or community
- An active chemical exchange program
- Beware of accepting unusable chemicals
- Reuse in experiments in the laboratory
- Exchange for credit with suppliers by agreement





# *What should not be recycled*

- **Gas cylinders past their pressure testing date**
- **Used disposable pipettes and syringes**
- **Chemicals and assay kits past their expiration**
- **Obviously degraded chemicals**
- **Used tubing, gloves and wipes**
- **Others?**





# *What should be recycled or redistributed?*

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- **Excess unopened chemicals**
- **Excess laboratory glassware (unused or clean)**
- **Consumables with no expiration**
- **Solvent that can be purified**
  - **Lower purity suitable for secondary use?**
- **Precious or toxic metals**
  - **Hg, Ag, Pt, Pd, Au, Os, Ir, Rh, Ru**
- **Others?**

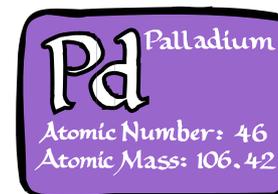
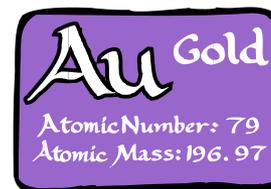




# Chemical Recycling - Precious metal

## For reuse in lab or for exchange

- Requires chemical knowledge for lab reuse
- Recover from solution - evaporate then
  - Ignite (Au, Pd, Pt)
  - Reduce with  $\text{NaBH}_4$  for metal powder or by electroless plating (Pt, Au, Pd, Ag, Rh).
  - Electroplate
  - Metal recovery Ion exchange-then ash



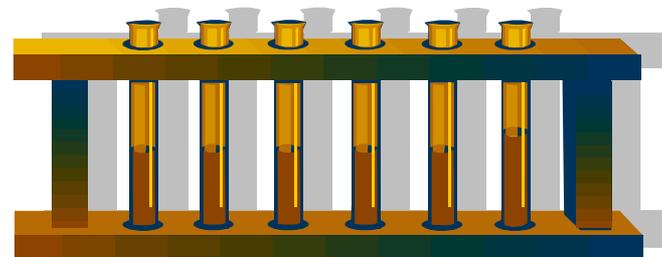
Source : Handbook of Laboratory Waste Disposal, Pitt & Pitt, John Wiley, 1986



# Solvent recycling – general guidance

## Solvent recycling requires care and organization

- Keep solvents segregated prior to separation (single product solvent)
- No unnecessary dirt due to careless handling
- Requires good labeling
- A small amount of the wrong chemical can ruin a desired separation
- Care must be taken not to concentrate peroxides





# Solvent recycling – general guidance

## Solvent recycling requires care and organization

- Try other purification methods before distillation
  - Convert to precipitate
  - Convert to water soluble
  - Use an adsorbent
- Need BP difference of  $> 10^{\circ}\text{C}$
- Can form azeotrope\*
  - water / ethanol ( $100^{\circ}\text{C} / 78.3^{\circ}\text{C}$ )
  - cyclohexane / isobutanol ( $81^{\circ}\text{C} / 108^{\circ}\text{C}$ )
- Mixture of 4 solvents not practical
- Distillation can be incorporated into curriculum



\* Consult CRC Handbook of Chemistry and Physics for list of azeotropes





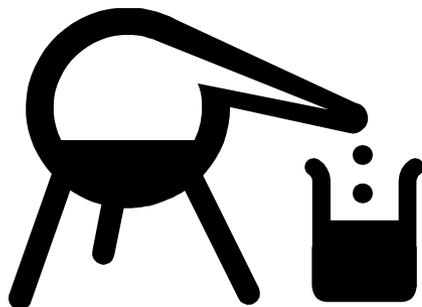
# Solvent recycling – general guidance (cont.)

- Even high efficiency stills are not perfect
- Continuous better than batch for large volumes
- Control reflux
- Monitor head temperature
- Reduce heat loss to get more efficiency
- Do not let still operate to dryness
- Use boiling chips but do not add when solvent is hot

Example: 200mm long column for separating benzene and toluene

Packing	TP
Empty	0.5
Coarse packing	1
Fine packing	5

TP = theoretical plates





# *Solvents that should not be recycled by distillation*

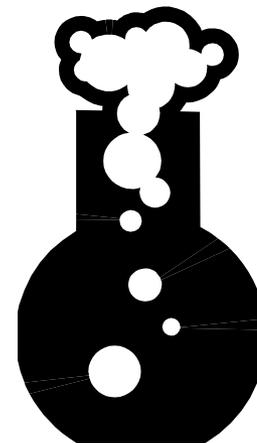
**Accidents have been reported for these distillations**

## Individual Substances

- Di-isopropyl ether (isopropyl alcohol)
- Nitromethane
- Tetrahydrofuran
- Vinylidene chloride (1,1 dichloroethylene)

## Mixtures

- Chloroform + acetone
- Any ether + any ketone
- Isopropyl alcohol + any ketone
- Any nitro compound + any amine

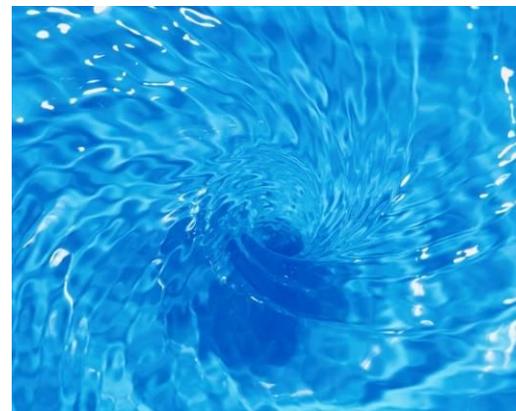




# *Waste treatment - Down the drain?*

## **If legally allowed:**

- **Deactivate & neutralize some liquid wastes yourself**
  - e.g., acids & bases
  - Don't corrode drain pipes
- **Dilute with lots of water while pouring down the drain**
- **Be sure that you do not form more hazardous substances**
  - Check reference books, scientific literature, internet





# *Treating on site – volume reduction*

## Evaporation – if not excessive

- Roto evaporation for recovery
- Do not evaporate corrosives or radioactives
- Only in laboratory hood
- Beware toxics and flammables



## Adsorption

- Activated carbon
- Ion exchange resin
- Activated alumina



## Precipitation - Extraction

Handbook of Laboratory Waste Disposal, Martin Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8





# *Treating on site – chemical conversion*

**Requires chemical expertise - may not be allowed by regulations - specific to each chemical**

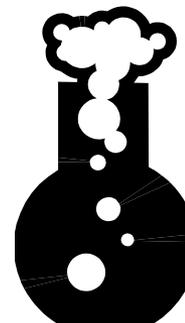
## **Dilution to reduce hazard**

- $\text{H}_2\text{O}_2$ ,  $\text{HClO}_4$ ,  $\text{HNO}_3$
- Never add water to concentrated acid
- Neutralization acid base - gentle

## **Hydrolysis (acid and base)**

- Active halogen compounds with  $\text{NaOH}$
- Carboxamides with  $\text{HCl}$

## **Oxidation-reduction**



Handbook of Laboratory Waste Disposal, Martin Pitt and Eva Pitt, 1986. ISBN 0-85312-634-8



# ***Chemical waste treatment example: sodium cyanide***

- **Wear PPE, work in hood**
- **Add sodium cyanide to a solution of 1% sodium hydroxide (~50mL/g of cyanide).**
- **Household bleach (~70mL/g of cyanide) is slowly added to the basic cyanide solution while stirring.**
- **When addition of the bleach is complete, test for the presence of cyanide using the Prussian blue test:**
  - **To 1mL of the solution to be tested, add 2 drops of a freshly prepared 5% aqueous ferrous sulfate solution.**
  - **Boil this mixture for at least 60 seconds, cool to room temperature, then add 2 drops of 1% ferric chloride solution.**
  - **Take the resulting mixture, make it acid (to litmus paper) using 6M hydrochloric acid.**
  - **If cyanide is present, a deep blue precipitate will be formed.**
- **If test is positive, add more bleach, then retest.**



From “Hazardous Laboratory Chemicals Disposal Guide”, Armour, 2003.



# ***Chemical waste treatment example: Tollens' Reagent***

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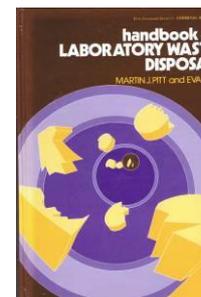
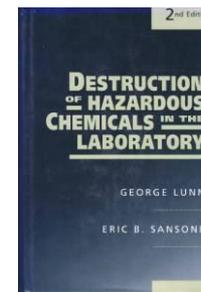
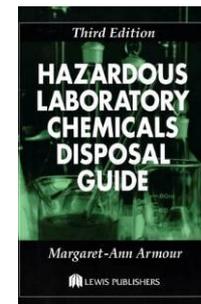
- **The reagent should be freshly prepared and stored refrigerated in a dark glass container. It has a shelf-life of ~24 hours when stored in this way.**
- **After the test has been performed, the resulting mixture should be acidified with dilute acid before disposal. These precautions are to prevent the formation of the highly explosive silver nitride.**





## Waste : Treatment in lab - references

- “Procedures for the Laboratory-Scale Treatment of Surplus and Waste Chemicals, Section 8.D in Prudent Practices in the Laboratory: Handling and Disposal of Chemicals,” National Academy Press, 2011, available online: <http://dels.nas.edu/Report/Prudent-Practices-Laboratory-Handling/12654>
- “Destruction of Hazardous Chemicals in the Laboratory, 2<sup>nd</sup> Edition”, George Lunn and Eric B. Sansone, Wiley Interscience, 1994, ISBN 978-0471573999.
- “Hazardous Laboratory Chemicals Disposal Guide, Third Edition”, Margaret-Ann Armour, CRC Press, 2003, ISBN 978-1566705677
- “Handbook of Laboratory Waste Disposal”, Martin Pitt and Eva Pitt, 1986, ISBN 0-85312-634-8





# ***Chemical waste treatment example: Peroxides***

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- **Peroxide formation of ether solvents can be a problem in a chemical laboratory.**

**This section will cover some basic information about peroxides –**

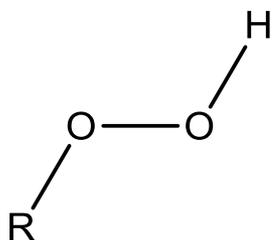
- **What are peroxides?**
- **Compounds susceptible to peroxide formation and how they are formed,**
- **Acceptable levels of peroxides,**
- **Determination of peroxide levels, and**
- **Neutralization of peroxides.**



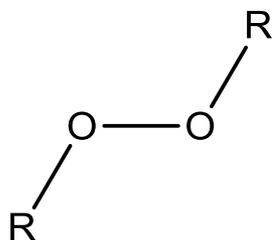
# Chemical waste treatment example: Peroxides

## What are peroxides?

- Any compound containing an oxygen-oxygen single bond is called a peroxide. Furthermore peroxides can be classified as organic peroxides or inorganic peroxides. The oxygen-oxygen bond in these peroxide compounds is relatively unstable and will easily cleave into reactive radicals.



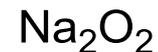
organic  
hydroperoxide



organic  
peroxide



hydrogen  
peroxide



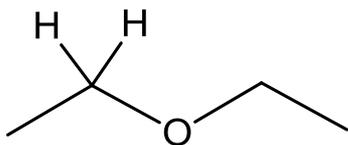
sodium  
peroxide



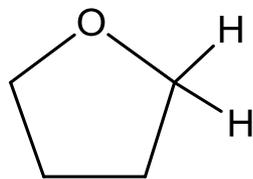


# Chemical waste treatment example: Peroxides

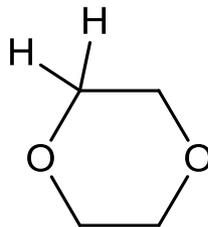
- **Compounds susceptible to peroxide formation and how they are formed.**
  - Some organic compounds are capable of undergoing auto-oxidation under mild conditions to form peroxides. Ethers are generally the compounds we think of that form peroxides;



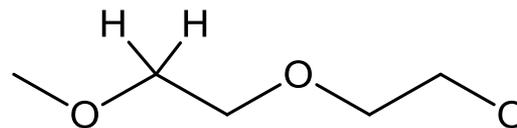
diethyl ether



tetrahydrofuran



dioxane



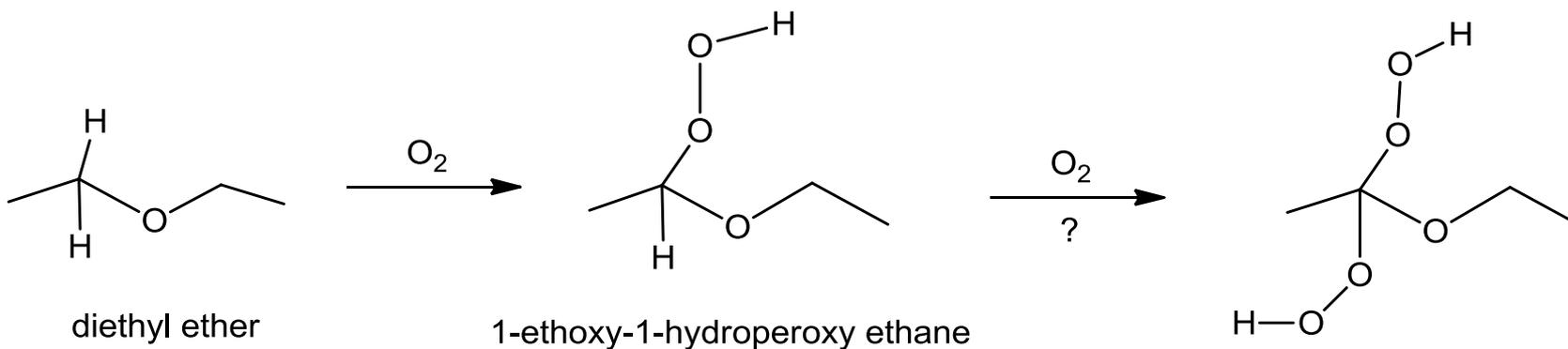
diglyme





# Chemical waste treatment example: Peroxides

- Route to the formation of peroxidized diethyl ether -





# Chemical waste treatment example: Peroxides

- **Other compounds** susceptible to peroxide formation are generally ones that have activated hydrogen bonds or weak carbon-hydrogen bonds.<sup>1</sup>
  - *Methylene groups attached to a vinyl group* ( $\text{C}=\text{C}-\text{CH}_2$ ) or a benzene ring, for example allyl compounds or benzyl compounds.
  - *Methine group between two methylene groups* ( $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), for example isopropyl compounds and decahydro-, naphthalenes.
  - *Methine groups* ( $-\text{CH}-$ ) *between two oxygen atoms*, for example an acetal ( $\text{O}-\text{CH}-\text{O}$ ).
  - *Methine groups between a benzene ring and a methylene group* ( $\text{Ph}-\text{CH}-\text{CH}_2$ ), examples include cumene, and tetrahydronaphthalene.
  - *Vinyl groups* ( $-\text{C}=\text{CH}_2$ ) vinyl compounds such as dienes, styrene and other olefinic type monomers.

1. Clark, D.E., *Peroxides and peroxide-forming compounds*. Chemical Health & Safety, 2001(September/October): p. 12 - 22.



# *Chemical waste treatment example: Peroxides*

---

- What are the acceptable levels of peroxides?

Due to the wide variety of peroxide forming compounds, the mechanisms of their formation and conditions that can lead to decomposition it is difficult to establish safe concentration levels.

In general a 100 ppm concentration is widely accepted as the control value. This value appears to be based on the old potassium iodide test.<sup>1</sup>

*The maximum level for peroxide concentration in organic compounds, at which most groups deem hazardous, is equal to or greater than **100 ppm**.*

1. Matthews, J.S. and J.F. Patchan, *Analytical Chemistry*, 1959. **31**: p. 1003.  
Foxley, G.H., *The Detection of Organic Peroxides*. *Analyst*, 1961. **86**: p. 348 - 349.





# Chemical waste treatment example: Peroxides

---

There are several ways of determining peroxide levels.

- Peroxide test strips<sup>1</sup> – *Easy*
  - *Detects hydroperoxides, dialkyl peroxides, polyperoxides and cyclic peroxides.*
  - How they work –
    - *They work by using a peroxidase enzyme, which transfers oxygen from the peroxide to an organic redox indicator.*
    - *The indicator will turn blue in the presence of peroxides.*
  - How to use them –
    - *Dip into chemical to be tested for 1 second,*
    - *Breath slowly onto test strip for 15 to 30 seconds,*
    - *Compare color of strip with color chart on bottle.*

1. Available from Merck and Sigma-Aldrich Chemical Company.



# ***Chemical waste treatment example: Peroxides***

---

- Other methods to determine peroxide levels –
  - A solution of 0.1 g NaI or KI and 1 mL of glacial acetic acid (10% wt/vol),
  - Add this NaI/glacial acetic acid solution to 1 mL of the material to be tested.
  - The color change may take up to 10 minutes.
  - A yellow color indicates a low concentration of peroxides (40 – 100 ppm),
  - A brown color indicates a much higher concentration,
  - Blanks must be prepared,
  - The NaI/glacial acetic acid solution must be used immediately due to the oxidation by air.



# ***Chemical waste treatment example: Peroxides***

---

- Neutralization of peroxides –
  - In some cases peroxides may need to be neutralized if it is permitted.
  - However, extreme caution must be used when handling peroxidized materials.
  - This includes the proper personal protective equipment, blast shields, etc.

**Do not attempt these neutralizations if you are not qualified chemist.**



# ***Chemical waste treatment example: Peroxides***

---

- Neutralization of peroxides...
  - Low levels of peroxides (less than 500) can be removed from solvents.
  - However, if the solvent shows signs of discoloration or there are crystals or layers (a viscous layer), then the neutralization procedure is too hazardous and should not be attempted.
  - Several neutralization methods are given below from the Environmental Health and Safety Website at Berkeley –

*Berkeley - Guidelines for Explosive and Potentially Explosive Chemicals Safe Storage and Handling. 2011; Available from:  
<http://www.ehs.berkeley.edu/pubs/guidelines/pecguidelines.html>*





## ***Chemical waste treatment example: Peroxides***

---

- Several methods for neutralizing peroxides –
  - Ferrous Salt Method,
  - Activated Alumina Method,
  - Blue Indicating Molecular Sieves (4-8 mesh, Type 4A).



## ***Chemical waste treatment example: Peroxides***

---

- Ferrous Salt Method will remove/destroy peroxides from water soluble solvents –
  - $\text{FeSO}_4$  (60 g) +  $\text{H}_2\text{SO}_{4(\text{conc.})}$  (6 mL) +  $\text{H}_2\text{O}$  (110 mL), or
  - $\text{FeSO}_4$  (100 g) +  $\text{HCl}_{(\text{conc.})}$  (42 mL) +  $\text{H}_2\text{O}$  (85 mL)
  - Gently shake the ferrous sulfate/acid/water solution with the peroxide containing solvent. **Caution - if the solvent contains a high concentration of peroxide the reaction can be exothermic.**



## ***Chemical waste treatment example: Peroxides***

---

- Activated Alumina Method will remove peroxides from water soluble and water insoluble solvents
  - About 100 g of alumina for 100 mL of solvent can be used.
  - This method removes the peroxides from the solvent but does not destroy them. Therefore the alumina must be washed with a dilute acid solution of KI or ferrous sulfate to destroy the peroxides on the alumina.



# Chemical waste treatment example: Peroxides

- Blue Indicating Molecular Sieves (4-8 mesh, type 4A) -
  - These types of molecular sieves can be added to peroxidized solvents in the amount of 5 – 10% (wt/vol).
  - The process is slow (1 – 30 days) but safe,
  - The peroxide is actually broken down and the indicator in the sieve consumed.
  - It is important that the blue indicating sieves are used, they contain  $\text{Co}^{2+}$  ion which is the neutralizing agent.<sup>1</sup>
  - This method is well suited for THF, diethyl ether and di-iso-propyl ether and takes several days at room temperature.
  - This does not work for dialkyl peroxides.

1. Burfield, D.R., *Deperoxidation of Ethers. A Novel Application of Self-Indicating Molecular Sieves*. Journal of Organic Chemistry, 1982. **47**(20): p. 3821 - 3824.





# ***Chemical waste treatment example: Peroxides***

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## **▪ Some useful references -**

Clark, D.E., *Peroxides and peroxide-forming compounds*. Chemical Health & Safety, 2001(September/October): p. 12 - 22.

Kelly, R.J., *Review of Safety Guidelines for Peroxidizable Organic Compounds*. Chemical Health & Safety, 1996 (September/October 1996): p. 28 - 36.

Matthews, J.S. and J.F. Patchan, *Analytical Chemistry*, 1959. 31: p. 1003.

Foxley, G.H., *The Detection of Organic Peroxides*. Analyst, 1961. 86: p. 348 - 349.

New Mexico State University - *NMSU Explosive Chemical Management Procedures*. none [cited 2009 August].

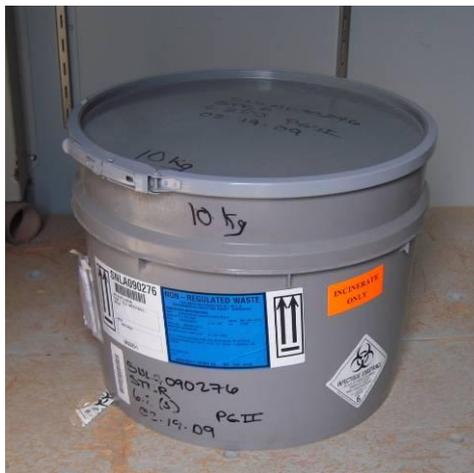
University of Iowa, *Potentially Explosive Chemicals (PECs) Guidelines for Safe Storage and Handling*.





# *Hazardous waste - Pickup and transport*

Lab packs consists of small containers of compatible waste, packed in absorbent materials.



Lab packs segregated at hazardous waste facility





# *Hazardous waste – Pickup*

- **Wear appropriate PPE for pickup.**
- **Insure against leakage; dyke area if possible.**
- **Keep gas cylinders separate.**
- **Keep radioactive material separate.**
- **Know how long waste can be stored.**
- **Provide for timely pick-up.**





# *Hazardous waste - Pickup and transport*

- Use freight elevators - not passenger elevators.
- Use appropriate handcarts and carrying trays.
- Use only approved transportation.
- Provide secondary containment during transport.
- Have a chemical manifest for shipment.





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# LUNCH



# *Legacy waste, lab cleanout procedures, disposal technologies*

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- I. What is legacy waste?**
- II. The difficulties of retaining custom made compounds,**
- III. Labeling chemical samples**
- IV. Lab cleanout procedures**
- V. Disposal of hazardous waste**
  - a. Thermal**
  - b. Landfill**
  - c. Stabilization**
  - d. Deep well injection**



# *Legacy waste*

---

## What is legacy waste?

“Legacy waste chemicals are those wastes that are left behind by the occupants of a laboratory when they leave the lab.”

**In most cases these wastes become the responsibility of the new lab owners.**



# *Legacy waste – continued...*

---

## Legacy Chemicals – **When is a gift not a gift?**

Often times we are given the opportunity to take over a chemical inventory, either through the transfer of chemicals or through inheriting a “new” laboratory.

Try to ensure the following –

- These chemicals are truly ones that you need for your research,
- They have not expired (especially ether type solvents, etc.),
- That the containers and contents are in good condition.



# *Legacy waste – continued...*

---

## Legacy Chemicals – **When is a gift not a gift?**

- Of course if the chemicals can be used then it is a benefit to all involved –
  - ✓ To those that could transfer the chemicals,
  - ✓ To those that can use them.
- However, if the chemicals cannot be used, or they are out of date or the containers are in poor condition then -
  - x they will have to be disposed of and that could cost the current “owner”.**



# ***Legacy waste – Retaining chemical compounds***

---

**The difficulties of retaining custom made compounds or specialty samples.**

**Custom made chemical samples are particularly relevant to a research synthesis lab. These are compounds that are made by graduate, undergraduate students or laboratory staff in support of research programs.**

**They are usually –**

- Intermediates in a synthetic route (i.e. natural product synthesis, ligands or other chemical components that are integral to forming a final compound),**
- The final target compound such as a catalyst that will be used for further studies or compounds to be used in special spectroscopic studies or other testing.**





## ***Legacy waste – Retaining compounds, continued..***

---

**These specialty compounds are valuable to research programs in a variety of ways -**

- **The value of the reagents used to make them,**
- **The time and expertise required to synthesize them,**
- **The availability of having them in the inventory and ready for immediate use.**

**They can be a liability when they are –**

- **Improperly labeled and referenced,**
- **Improperly stored, or**
- **When they have decomposed and need to be disposed.**



# ***Legacy waste – Retaining compounds, continued..***

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## **Labeling chemical samples**

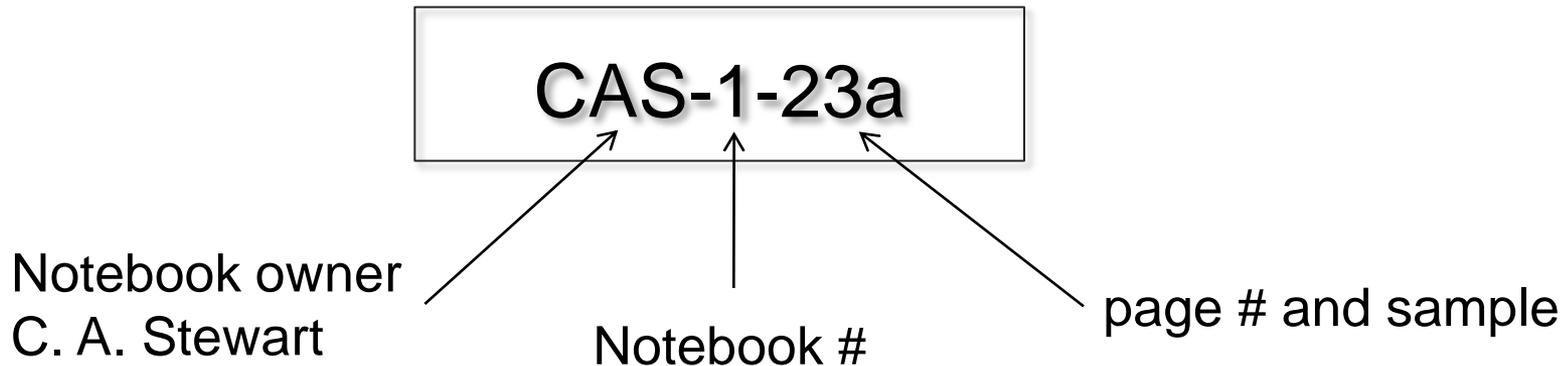
- **There are many, many ways and methods to organize one's laboratory notebook, compounds, data, etc.,**
- **The best method of course is the one that works best for the individual.**



# Legacy waste – Retaining compounds, continued..

## Some helpful hints -

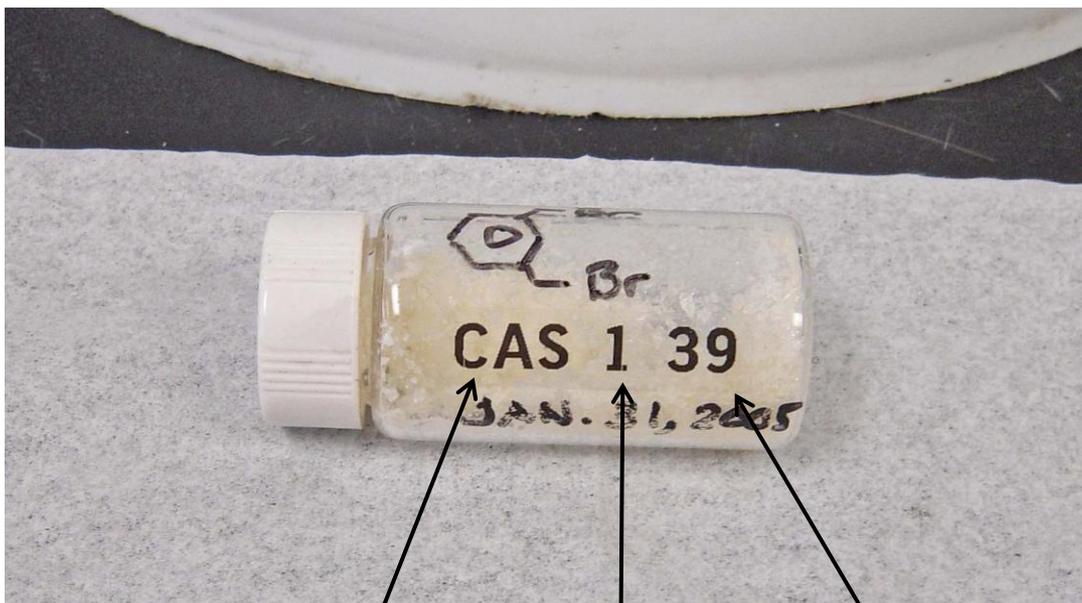
- ❑ Use a notebook with numbered pages,
- ❑ Uniquely label the notebook,
  - For example CAS-1,
- ❑ Reference compounds or samples to that notebook and specifically to that page,





# Legacy waste – Retaining compounds, continued..

## Example -



Notebook owner  
C. A. Stewart

Notebook #

page # of sample



# Legacy waste – Retaining compounds, continued..

## Bad examples –

- No name,
- No notebook reference,
- Loose tags,
- Incomplete chemical formulas.





## ***Lab Cleanout Advice***

---

**Some things to think about when it comes to laboratory cleanout, decommissioning or turning a lab over to a new owner.**

**This modified list comes from an article by Jennifer Bossleman, “Laboratory Decommissioning: Lessons Learned in the Field”, *Environmental Health & Engineering* Vol. 1(23) 2008.**



## ***Lab Cleanout Advice...***

---

### **Questions concerning the **laboratory space** –**

- **Who will be responsible for cleaning the laboratory - the researchers or a subcontractor?**
- **What was the laboratory space used for?**
  - **hazardous chemicals, biological materials or radioactive materials.**
- **Were there any spills of hazardous, biological and/or radioactive materials in this laboratory?**
- **What are the laboratory cleaning procedures? Are they appropriate for the types of hazards?**



## *Lab Cleanout Advice...*

---

### Questions concerning the **laboratory equipment** -

- **What equipment was used in the space? Did or does the equipment contain hazardous chemicals, biological materials, and/or radioactive materials? (Also consider radioactive sources in some instruments.)**
- **Who will be responsible for cleaning, disinfecting, or decontaminating the equipment?**
- **Is the equipment being disposed of, relocated to another lab, repaired (sent off site), or sent to storage?**



## ***Lab Cleanout Advice...***

---

### **Once the laboratory has been cleaned –**

- Who will determine that the lab was cleaned properly? What kind of testing should be used?
- Who will be responsible for signing off that the lab has been properly cleaned and is ready for the next occupant?
- Who is responsible for signing off on the lab equipment to make sure it was properly cleaned/decontaminated?
- Who will conduct the final “walk through” to determine if the lab was cleaned according to procedures?

**The EPA has developed support materials (see “Tools you can Use”)**





# ***Unknown waste characterization\****

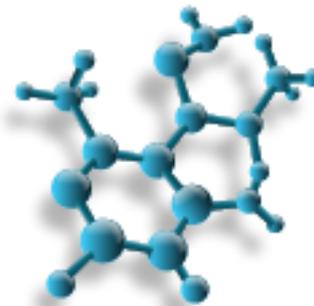
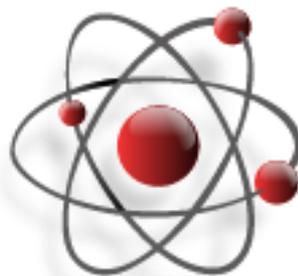
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**Physical description - Water reactivity - Water solubility**

**pH and neutralization information**

**Presence of:**

- ✓ **Oxidizer**
- ✓ **Sulfides or cyanides**
- ✓ **Halogens**
- ✓ **Radioactive materials**
- ✓ **Biohazards**
- ✓ **Toxics**



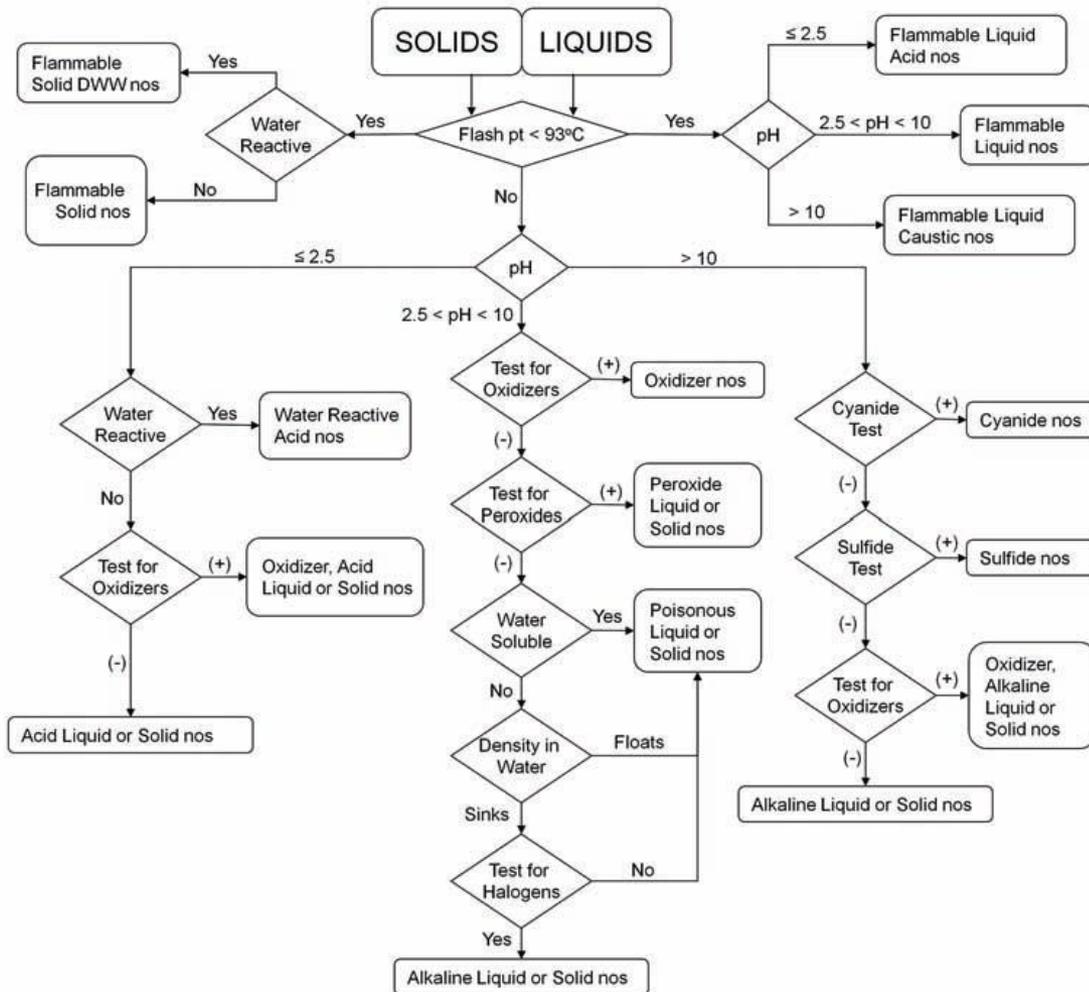
**\*Prudent Practices in the Laboratory: Handling and Disposal of Chemicals,” National Academy Press, 1995 Section 7.B.1**





# Legacy waste :Categorizing unknowns\*

\* "Prudent Practices in the Laboratory" 2011  
-See Reference





## ***Chemical waste accidents – Case study***

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### **A University in California, California, USA Incident –**

- **A graduate student was finishing up an experiment and needed to dispose of 20 mL of methanol.**
- **In the fume hood there were two waste bottles –**
  - **500 mL amber glass container for waste solvents,**
  - **500 mL clear glass container for nitric acid.**
- **Both bottles were clearly labeled.**
- **The researcher mistakenly added the methanol to the acid waste container.**

**The acid waste container exploded.**





## ***Chemical waste accidents – Case study***

---

### **A University in California, California, USA**

#### **Actions following the incident –**

- **The graduate student used the nearby safety shower and rinsed for 5 minutes,**
- **He then went to seek assistance, but he was working alone,**
- **He pulled the fire alarm and went back to the safety shower where he removed his contaminated clothing and continued to wash with water,**
- **Emergency response personnel showed up and assisted him.**



## ***Chemical waste accidents – Case study***

---

### **A University in California, California, USA Injuries –**

- **The graduate student's injuries –**
  - **Glass cuts to face and arms,**
  - **Limited acid burns,**
  - **Non-permanent injury to his right eye.**

**He was not wearing safety glasses!**



## ***Chemical waste accidents – Case study***

---

**A University in California, California, USA**

**Cause of the accident –**

- **The graduate student had taken the necessary lab safety training which included information on hazardous waste handling –**

**He admitted that he was not paying attention to what he was doing!**



## ***Chemical waste accidents – Case study***

---

### **A University in California, California, USA**

#### **Corrective actions –**

- **The lab proposed to separate organic wastes bottles from the acid waste bottles and place them in different areas,**
- **EH&S provided secondary containers to hold the glass waste containers to contain glass shrapnel in the case of an explosion.**
- **They also provided color-coded labels to waste containers to prominently differentiate chemical wastes.**



# *Waste disposal processes*

---

- **Thermal / Incineration**
  - Incineration is **NOT** the same as open burning
  - Co-fire in cement kiln has advantages
- **Landfill**
  - Must be specially constructed and permitted for hazardous waste
- **Stabilization / solidification**
- **Deep well injection**
  - Expensive, but common



# *Emissions from incineration vs. open burning*

Incineration

	Open Burn ( $\mu\text{g}/\text{kg}$ )	Municipal Waste Incinerator ( $\mu\text{g}/\text{kg}$ )
PCDDs	38	0.002
PCDFs	6	0.002
Chlorobenzenes	424150	1.2
PAHs	66035	17
VOCs	4277500	1.2



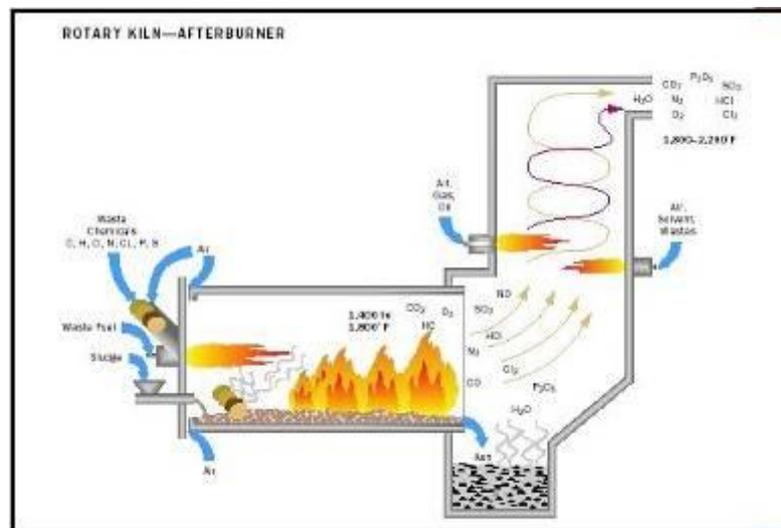
Source: EPA/600/SR-97/134 March 1998



# *Incineration is the controlled combustion of waste*

## Incineration

- **Requires 3 “T’s”:**
  - **Time:** 2 seconds minimum
  - **Temperatures:** 1000°C-1200°C
  - **Turbulence:** Mixing during burn
- **Rotary Kiln or Fixed Grate**
- **Secondary Combustion Chamber (afterburner)**
- **Rapid cooling of ash to prevent PCDD and PCDF**

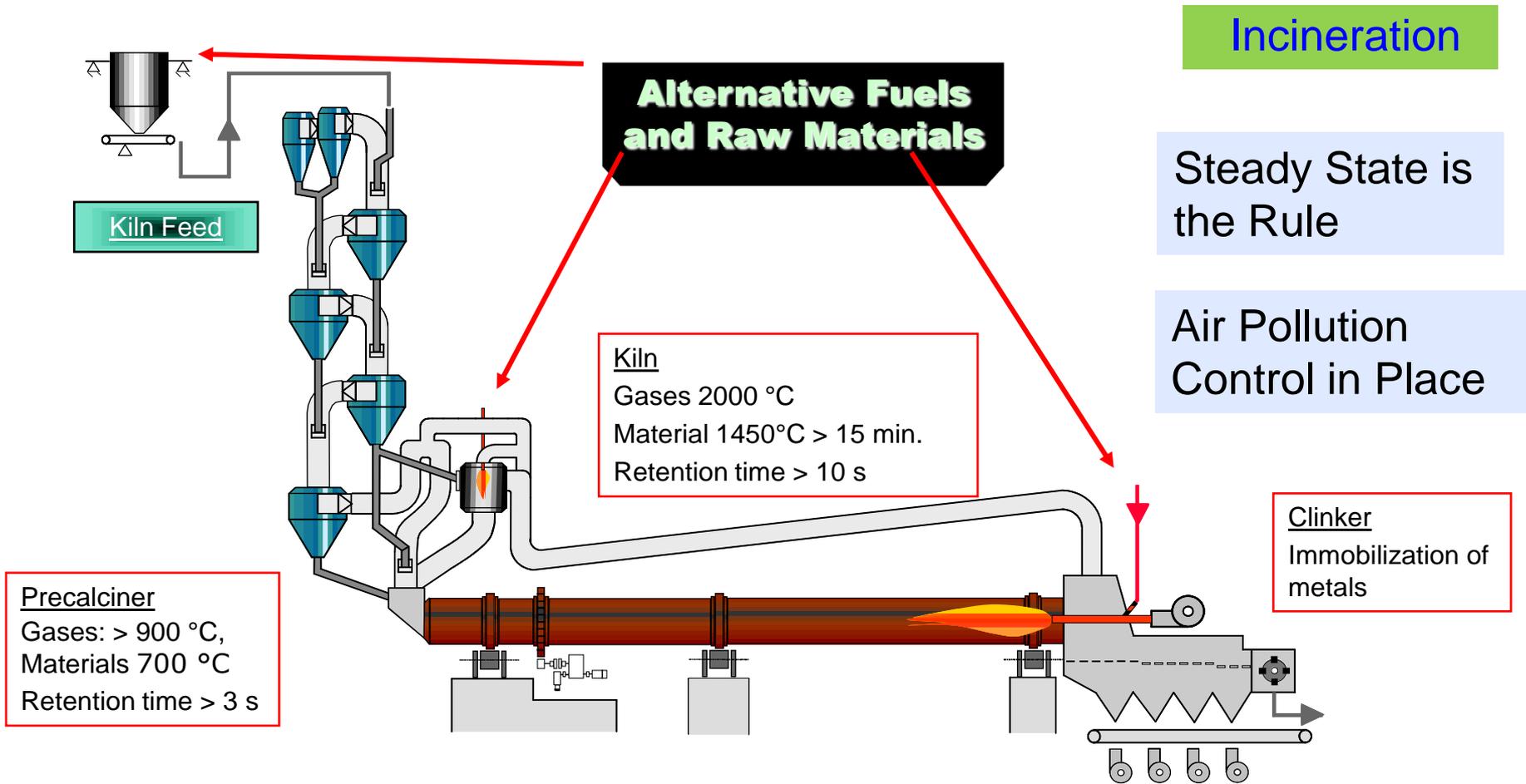


Source :<http://www.pollutionissues.com/>





# Typical dry process cement kiln





# Comparison of 95 U.S. WTE plants with EPA standard - (2001 Success story!)

Pollutant	Average Emission	EPA standard	Unit	Incineration
Dioxin/Furan (TEQ basis)	0.05	0.26	ng/dscm	
Particulate Matter	4	24	mg/dscm	
Sulfur Dioxide	6	30	ppmv	
Nitrogen Oxides	170	180	ppmv	
Hydrogen Chloride	10	25	ppmv	
Mercury	0.01	0.08	mg/dscm	
Cadmium	0.001	0.020	mg/dscm	
Lead	0.02	0.20	mg/dscm	
Carbon Monoxide	33	100	ppmv	

TEQ: Toxic Equivalents are used to report the *toxicity-weighted masses* of mixtures of dioxins (ng/dscm or mg/dscm): nanograms or milligrams per dry standard cubic meter (ppmv): parts per million by volume - Waste to Energy =WTE

Source: [http://www.energyanswers.com/pdf/awma\\_final.pdf](http://www.energyanswers.com/pdf/awma_final.pdf)

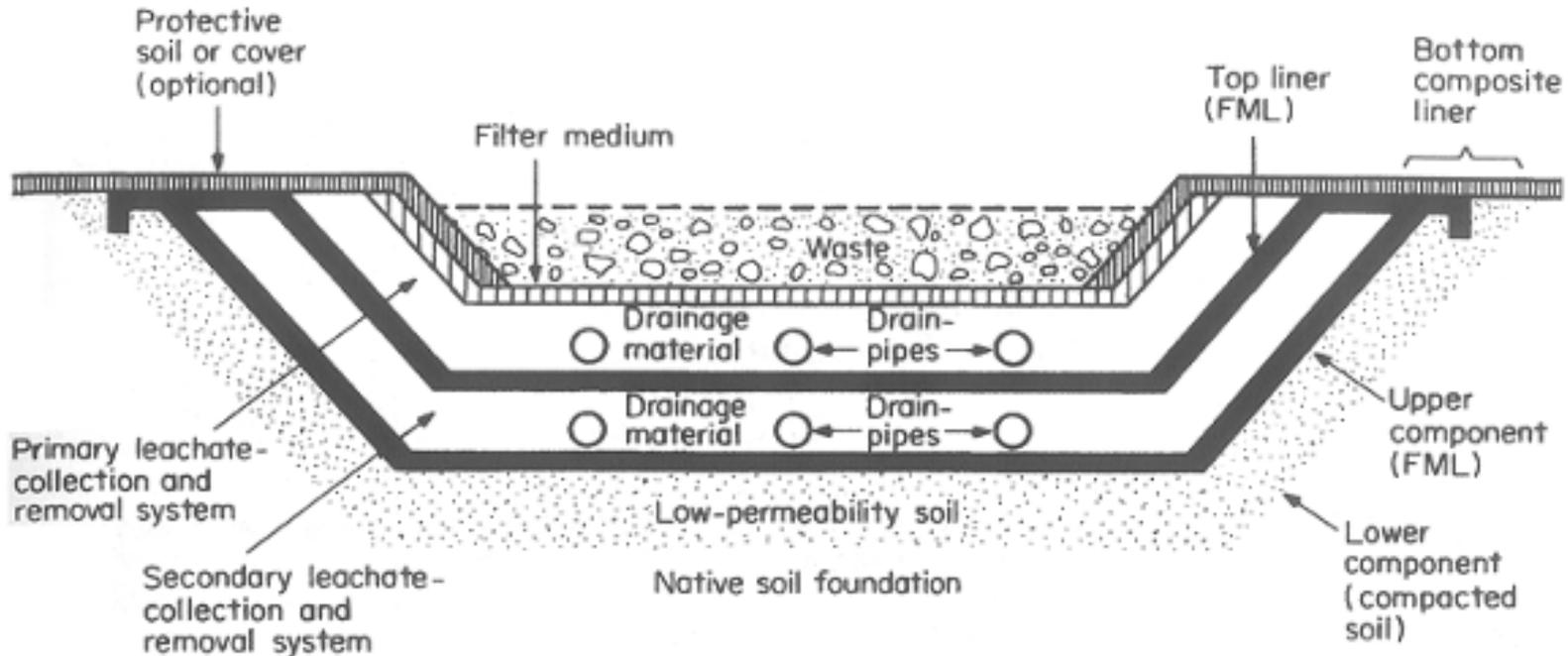




# Landfill with flexible membrane liner plus compacted soil double liner

Landfill

## LAND STORAGE AND DISPOSAL



<http://www.epa.gov/wastes/hazard/tsd/td/disposal.htm>

*Groundwater and leachate monitoring important !*





# Landfill design and construction

## Landfill

### Landfill Liners

Clay

Flexible membrane

Liner/waste compatibility

### Landfill Cap

### Leachate

Collection-Removal-Recirculation

Primary leachate

Leak detection

Surface water collection

Gas collection and removal



No free or bulk liquids

- Mixed with sorbent
- Small ampoules
- Container is item–battery
- Container is lab pack





# ***Solidification and stabilization processes***

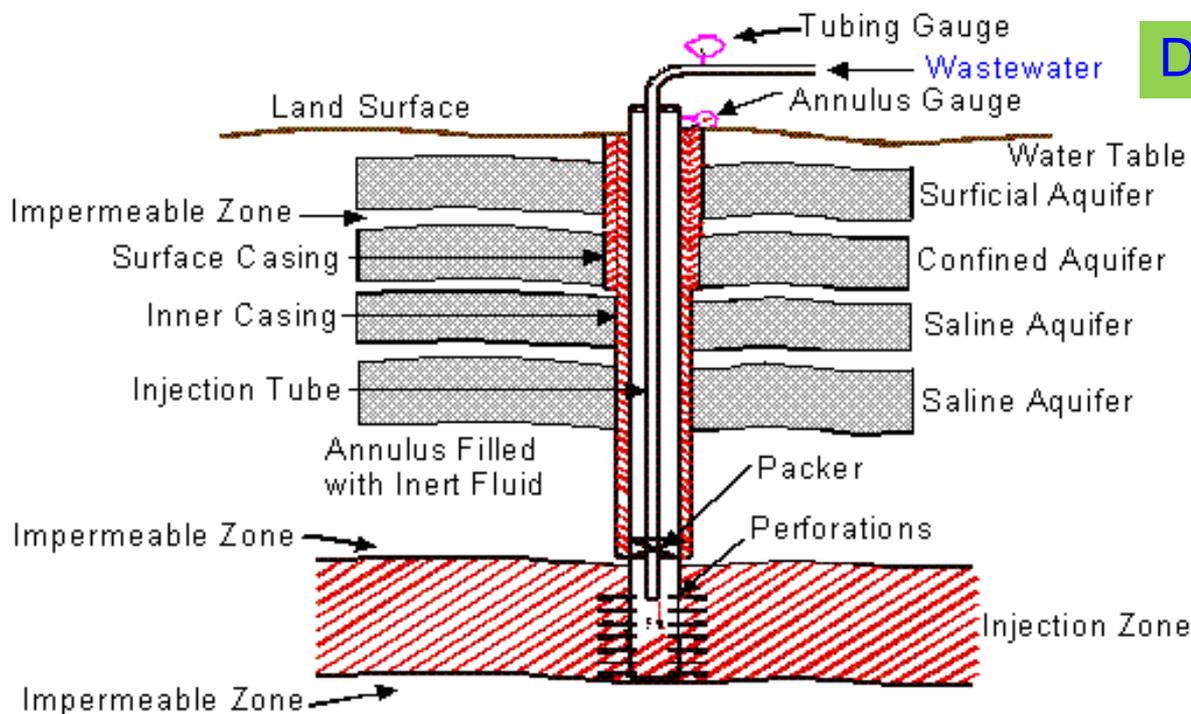
- **Solidification methods physically encapsulate hazardous waste into a solid material matrix of high structural integrity.**
  - **Stabilization techniques chemically treat hazardous waste by converting them into a less soluble, less mobile or less toxic form.**
  - **Principally used for metal-bearing wastes.**
  - **Limited applicability to organic wastes.**
  - **2 Main types of processes: **cement and pozzolanic.****
- 
- **Advantages:** low cost, low technology, suitable for many types of waste
  - **Disadvantages:** increases volume, may leak

## Stabilization

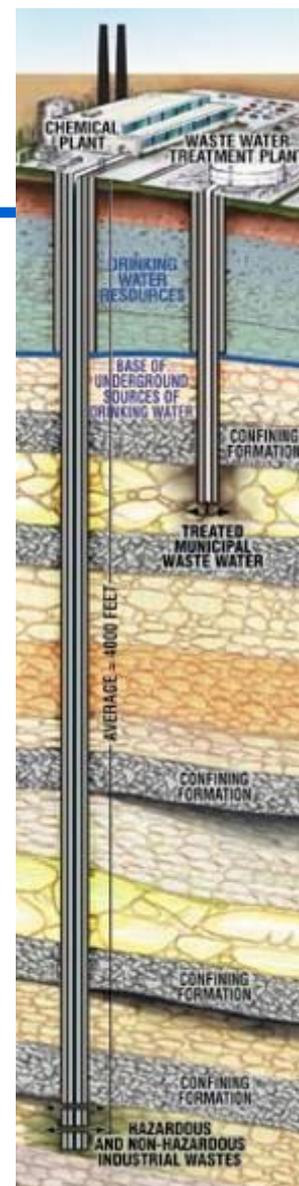




# Deep well injection is an important technology



Deep Well



- **550 Class I wells in the United States (22% for HW)**
- **43% of all HW in United States !!!**

<http://www.epa.gov/safewater/uic/index.html>



## ***Waste disposal questions to consider***

---

- **Does your government have regulations for disposal company?**
- **Does the company have requisite permits?**
- **Is disposal service licensed?**
- **How will waste be packaged?**
- **How will waste be transported?**
- **Where will material be disposed?**
- **How will it be disposed?**
- **Does your liability end? (incineration: yes, landfill: maybe not)**





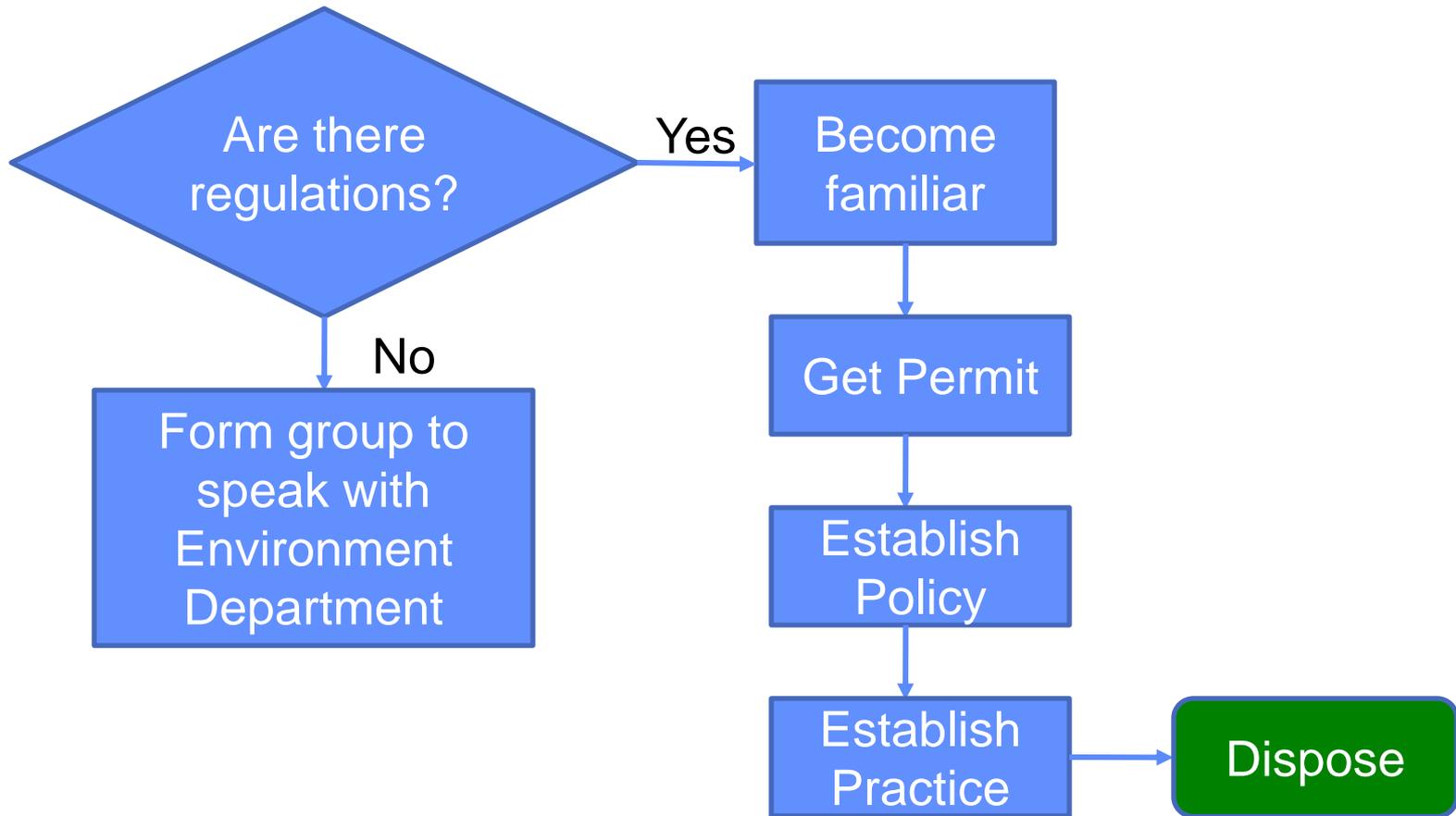
## *Issues to consider-actions to take*

- **Check with other institutions about reliability and integrity of company.**
- **Determine how to provide waste to disposal company (bulking at University or by contractor).**
- **Visit the site of the disposal.**
- **Review the company's practices and capabilities routinely.**
- **Ensure safety of shipment.**
- **Maintain written records.**





# Discussion topic- waste disposal contractor





## *Tools you can use*

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–“Training Resource Pack for hazardous waste management in developing economies”,

<http://www.unep.fr/shared/publications/cdrom/3128/menu.htm>

–“Microchemistry training curriculum”,

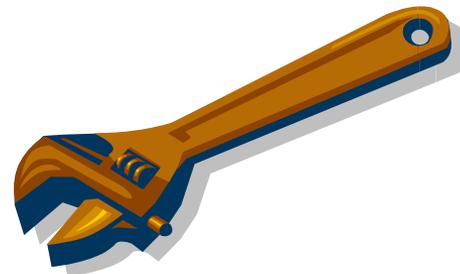
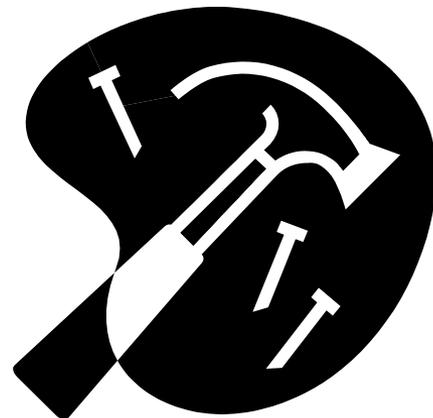
<http://www.radmaste.org.za/amicrosciencematerialchemistry.htm>

–“School cleanout campaign-US EPA”,

<http://www.epa.gov/epawaste/partnerships/sc3/index.htm>

–“International Solid Waste Association”

<http://www.iswa.org/>





# Waste management references

–“Less is Better,” American Chemical Society, Washington DC, 2003, available online:

<http://portal.acs.org/portal/acs/corg/content?nfpb=true&pageLabel=PPSUPERARTICLE&nodeid=2230&usesec=false&securlvar=region1&uuid=ef91c89e-8b83-43e6-bcd0-ff5b9ca0ca33>

–“School Chemistry Laboratory Safety Guide,” US NIOSH Publication 2007-107, Cincinnati, OH, 2006, available on-line:

<http://www.cpsc.gov/CPSCPUB/PUBS/NIOSH2007107.pdf>

–“Prudent Practices in the Laboratory: Handling and Disposal of Chemicals,” National Academy Press, 2011, available online:

<http://dels.nas.edu/Report/Prudent-Practices-Laboratory-Handling/12654>





# *Workshop wrap up*

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**Questions?  
Open Discussion**

