Presentation Title
Procedures for Chemical Safety

Description of the Presentation
This presentation will provide the critical procedures and their regulatory references which will set the operational boundaries and facilitate safe work with chemicals.

Time of Presentation
45 minutes

Biographical Information
Michael (Mike) Jaurena, *CSP, OHST* started Safety and Training Consultants, Inc. (STCI) in 2002 after working 17 years for a major oil and gas producer and has recently sold his company to Safety Management Systems, LLC out of Lafayette Louisiana. Mike has a vast array of experience in domestic and international operations, construction, health, safety & environmental program development, as well as organizational and project management. A 1983 graduate of Cal Poly San Luis Obispo, Mike began his journey towards the safety profession as a laborer in the oil fields of Coalinga, California. Mike remained in Operations & Maintenance for 12 years until making the transition into the Health, Safety and Environmental profession. Mike is most proud of these base roots and continues to focus his safety approach at the “Point of Risk”.

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Fifth Annual Bakersfield County Central Valley Chemical Safety Day

Track E – Oil and Gas

Procedures for Chemical Safety

March 7, 2013

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Central Valley Chemical Safety Day

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Procedures for Chemical Safety

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Scope of Presentation

- Basic Safety for Chemicals
- Provide Regulatory Safe Work Practices which apply to Chemical Safety
- Provide links or resources to these requirements
- Provide for a Q&A session to help facilitate answers to your questions
- Disclaimer
  - You are responsible for your own compliance and actions and solely relying on this presentation to get you there is misguided. This is a basic overview of the safety basics and ***critical*** regulations and is not an exhaustive list.

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Introduction

Base line

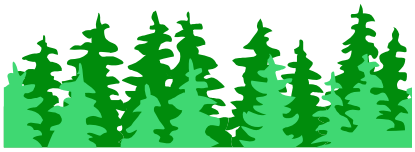
- Chemical safety starts with a basic understanding of chemistry, physics and a chemical hazard assessment process.
- Working with chemicals mandates compliance with a myriad of regulatory requirements.
- Most of these requirements are very ***prescriptive*** in nature and leave little leeway in your actions, some however are ***performance*** based. The largest variable in chemical safety is the qualifications, skills, knowledge and temperament of the agency inspector(s).
- No middle ground either you are in and shall comply or you are out and do not.
- Some of your existing programs you have in place for your primary operations can fulfill, supplement or enhance some of the requirements. You must do a gaps analysis to see.

Chemical Safety–Basic Chemistry & Physics

- It is critical for safe and effective operations for employers and workers to complete a comprehensive hazard assessment based off of education and knowledge of the chemical(s), the work practices and of the work surroundings.
- Based off the hazard assessment, mitigation techniques must be developed to eliminate or minimize the risk to acceptable levels

Chemical Safety–Basic Chemistry & Physics

- Chemistry and Physis Basic 101:
  - Normal Atmospheric Conditions
  - Oxygen Deficient / Enriched Environments
  - Toxic Environments
  - Flammable / Combustible Environments



Chemical Safety–Basic Chemistry & Physics

- Normal Atmospheric Conditions
  - 78% Nitrogen
  - 20.9% Oxygen
  - 1.1% Carbon Dioxide & other gases

Properties of Air

- Air weighs 0.075#/ft3
- Molecular Weight = 29
- Vapor Density = 1

Chemical Safety–Basic Chemistry & Physics

- **Oxygen Deficient**

  Any atmosphere that has less than 19.5% O2 by volume.

- **Oxygen Enriched**

  Any atmosphere that has greater than 23.5% O2 by volume.

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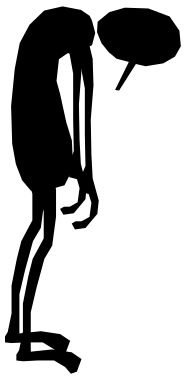
Chemical Safety–Basic Chemistry & Physics

- **Oxygen Deficient Atmospheres**
  - **Causes of Oxygen Deficiency**
    - **Displacement -- purging**
    - **Chemical Reactions -- cleaning**
    - **Bacterial Action -- bugs**
    - **Oxidation -- rust**
    - **Combustion -- welding / cutting**
    - **Absorption -- activated charcoal**



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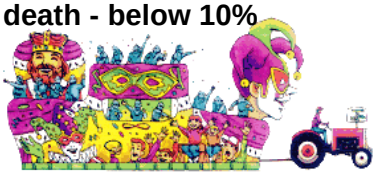
Chemical Safety–Basic Chemistry & Physics

- **Oxygen Deficient Atmospheres**
  - **Symptoms of Oxygen Deficiency**
    - increase in respiration & pulse - 16%-12%
    - loss of coordination - 16%-10%
    - blueness of lips
    - slurring of speech
    - buzzing in the ears
    - impaired judgment
    - nausea, vomiting, fainting, death - below 10%



Chemical Safety–Basic Chemistry & Physics

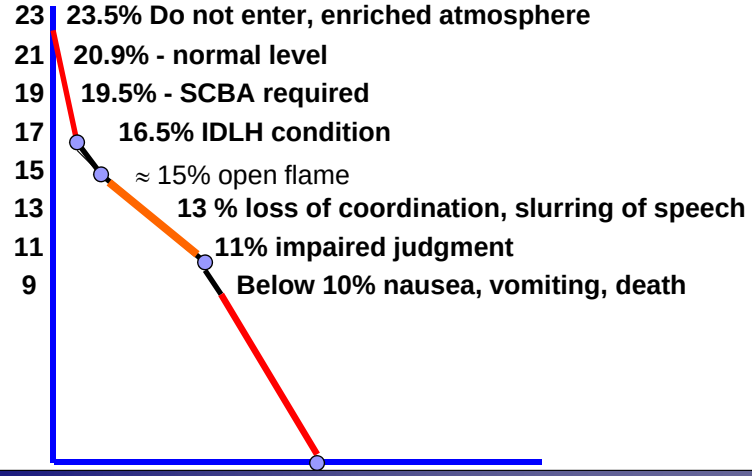
- **Oxygen Enriched Atmospheres**
  - **Causes of Oxygen Enrichment**
    - **Original vessel contents**
    - **Leaks or improper isolation**
    - **introduction of oxygen source**
  - **Oxygen enriched atmospheres must be vacated immediately & ventilated with ambient air to bring oxygen back within normal range. High O2 levels significantly increase the chance of combustion or explosion**

- Is O2 enriched atmospheres normal? –

-Where can you find this?-

Chemical Safety–Basic Chemistry & Physics

O2 %



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Chemical Safety–Basic Chemistry & Physics

Normal Vs Deficient Atmospheres

- ☺ **Normal air has 20.9% O2 or equals 1/5th of the volume of air.**
- 😐 **An atmosphere is considered deficient when the O2 is below 19.5% or a 1.4% change in the O2 level.**
- ☹ **An 1.4% change in O2 volume in the atmosphere can represent a 7% (or 70,000 ppm) change in the total atmosphere. Many materials are toxic well below this range.**

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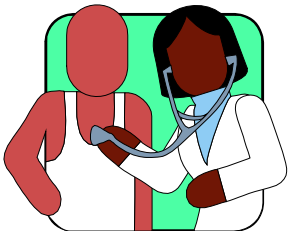
Chemical Safety–Basic Chemistry & Physics

☠ Toxic Atmospheres ☠

- An atmosphere with excessive levels of toxic gases, vapors, mists & or dusts.
- ☹ Common Toxins
  - Hydrogen Sulfide -- H2S
  - Carbon Monoxide -- CO
  - Chlorine -- Cl2
  - Ammonia -- NH3
  - Benzene -- C6H6
  - Sulfur Dioxide -- SO2
  - Welding fumes

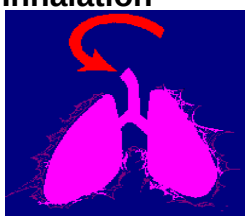


☠ Toxic Agents ☠

Primary Routes of Exposure

Absorption

Inhalation



Ingestion

Injection

Chemical Safety–Basic Chemistry & Physics

☠ Toxic Agents ☠

Local Effects -

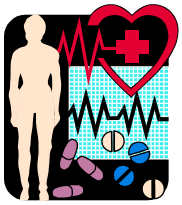
- occur at site of exposure or point of contact
  - -acid burns, lung or eye irritation

Systemic Effect -

- absorbed & distributed in body
- impact body at site other than exposure site
  - -target organ (CNS, Kidneys, liver, glands)
    - H2S, benzene, toluene

Chemical Safety–Basic Chemistry & Physics

☠ Toxic Agents ☠



Effects of Exposure

Acute -

- occurs rapidly or within a short period of time
  - allergic reaction, headaches, skin burns, nausea

Chronic -

- occurs after many years of repeated exposure
  - liver damage, CNS damage, cancer, lung damage

Chemical Safety–Basic Chemistry & Physics

☠ Toxic Agents☠

Causes / Sources of Toxins

- Original contents of space
  - hydrocarbons, caustic, ammonia, DEA,....
- Substances brought into space by workers
  - solvents, paints, blasting grits, sprays,.....
- Work performed in space
  - welding, degreasing, spraying, cleaning,.....
- Outside sources
  - motor exhausts, adjacent operations,.....

Chemical Safety–Basic Chemistry & Physics

☠ Toxic Agents ☠

Who Sets Standards

- OSHA
  - PEL - Permissible Exposure Limit
  - STEL - Short Term Exposure Limit
- NIOSH - National Institute for Occupational Safety & Health
  - IDLH - Immediately Dangerous to Life & Health
- ACGIH - American Conference of Government Industrial Hygienists
  - TLV-TWA, TLV-STEL, TLV-C

Chemical Safety–Basic Chemistry & Physics

Flammable / Combustible Atmospheres

- **Flammable -- Atmosphere containing vapors, gases, or mists in excess of 10% of it's lower explosive limit (LEL).**
  - ***Example -- Methane, butane, H2S, propane, etc.**
- **Combustible -- Airborne combustible dust at concentration that meets or exceeds (LEL)**
  - ***Example -- Grain, particulate, dust**

Chemical Safety–Basic Chemistry & Physics

Flammable / Combustible Atmospheres

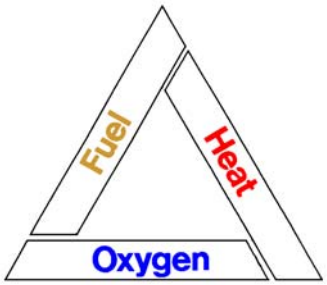
- **Flammable Range:**

  All fuels, when mixed with oxygen, have ranges in which they will ignite. This range lies between the Lower Explosive Limit (LEL) & the Upper Explosive Limit (UEL). When the mixture of fuel & oxygen is within the LEL & UEL, the conditions are prime for ignition.

Chemical Safety–Basic Chemistry & Physics

Flammable / Combustible Atmospheres

- In order for something to burn three elements must be present within the environment under the right conditions:
  - Oxygen
  - Fuel
  - Heat



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Chemical Safety–Basic Chemistry & Physics

Flammable / Combustible Atmospheres

- 100% LEL Vs. 100% concentration not the same!
- 100% LEL - minimum amount of fuel in atmosphere to allow ignition.
- 100% Concentration - complete space occupied by material.

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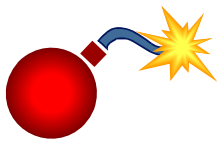
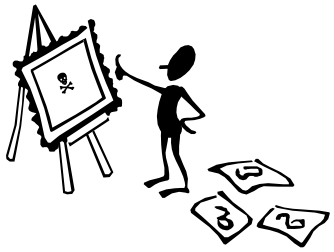
Chemical Safety–Basic Chemistry & Physics

- **Flammable / Combustible Atmospheres**
  - 1% is equal to 10,000 parts per million
  - LEL's for most Hydrocarbon gases range from 2.5% - 6% or 25,000 ppm - 60,000 ppm



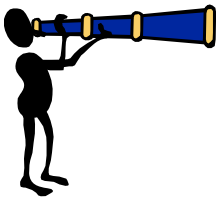
Chemical Hazard Assessment

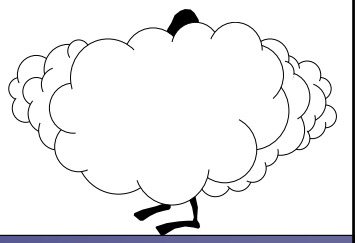
- Five Key Components for Chemical Assessment
  - Identify the Substance or Material(s) & the Source(s)
  - Assess the General Health & Fire Hazards
  - Asses the Physical & Chemical Properties
  - Assess Variables & Modifying Conditions
  - Assess the Behavior and Outcomes



Chemical Hazard Assessment

- Identify the Substance(s) or Material(s) & the Source(s)
  - Proper identification is critical in the success of the operation
  - Many industrial settings have “cocktail blends” of materials
  - In industrial settings the source will tell you what the material(s) is/are.





Chemical Hazard Assessment

- General Health
  - Permissible Exposure Limits (PEL’S)
  - Ceiling Levels (C)
  - Immediately Dangerous to Life & Health (IDLH)
  - First Aid Measures
  - Dermal Exposure

- Fire Hazards
  - Auto Ignition Temperature
  - Flash Point (FP)
  - Lower and Upper Explosive Limits (LEL) & (UEL)

Chemical Hazard Assessment

General Health

- **Permissible Exposure Limits (PEL) - Time Weighted Average concentrations that must not be exceeded during any 8-hour work shift of a 40 hour week.**
- **Immediately Dangerous to Life & Health - (IDLH) – NIOSH values are based on the effects that might occur as a consequence of a 30-minute exposure**

Chemical Hazard Assessment

General Health

- **Immediately Dangerous to Life & Health**
  - **Any condition that poses an immediate or delayed threat to life or that would cause irreversible adverse health effects or that would interfere with an individual's ability to escape unaided from a permit space.**
  - **Note: Some materials -- hydrogen fluoride gas and cadmium vapor, for example -- may produce immediate transient effects that, even if severe, may pass without medical attention, but are followed by sudden, possibly fatal collapse 12-72 hours after exposure. The victim "feels normal" from recovery from transient effects until collapse. Such materials in hazardous quantities are considered to be "immediately" dangerous to life or health. (H2S, CL2, SO2, NH3, etc.)**

Chemical Hazard Assessment

General Health

- First Aid Measures - critical in the care of the victim and for emergency responders. Specific concerns should be focused on emergency procedures for eye and skin contact, inhalation and ingestion of the toxic substance
- Dermal - both the NIOSH "Pocket Guide to Chemical Hazards" (http://www.cdc.gov/niosh/npg/) or Cal-OSHA, Title 8 5155, (http://www.dir.ca.gov/Title8/5155.html) will denote if a substance is hazardous upon contact or if dermal contact is a route of exposure

Chemical Hazard Assessment

Fire Hazards

- Ignition Temperature
  - The minimum temperature at which an external heat source is capable of igniting a flammable fuel / air mixture.
    - Sometimes referred to as auto-ignition temperature
    - Ignition temperature ranges from 800 degrees F to 1000 degrees F for typical hydrocarbons

Chemical Hazard Assessment

Fire Hazards

- Flash Point (FP)
  - The minimum temperature at which a substance produces sufficient flammable vapors to ignite.
  - If the temperature is lower than the FP the material may give off enough vapors to still be toxic.

Chemical Hazard Assessment

Fire Hazards

- Lower Explosive Limit -- LEL
  - A fuel-oxygen mixture below the LEL is considered too lean to ignite. Each fuel source has its own unique LEL depending on its molecular composition.
- Upper Explosive Limit -- UEL
  - A fuel-oxygen mixture above the UEL is considered too rich to ignite. Some fuel sources may have no UEL and will ignite at 100% concentrations.

Chemical Hazard Assessment

Assess Physical and Chemical Properties

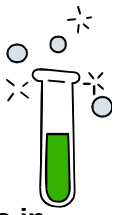
- Physical
  - Liquid / Solid / Gas @ Industrial Hygiene Standard Temperature and Pressure (I.H. STP = 14.7 psia @ 77° F)
- Chemical
  - Vapor Pressure
  - Vapor Density
  - Molecular Weight
  - Specific Gravity
  - Solubility
  - Incompatibilities & Reactivity

Chemical Hazard Assessment

Physical Properties

- What is the current state the substance is in?
- What are the possibilities and probabilities it will change state?
- What are the consequences of the physical change:
  - pressure
  - heat
  - vacuum
  - vapors

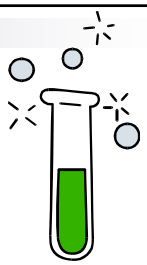
Chemical Hazard Assessment



Chemical Properties

- Vapor Pressure (VP)
  - The pressure exerted by a solid or a liquid when it is in equilibrium with its own vapor.
  - Vapor pressure is usually measured in mm Hg.
    - Normal atmospheric pressure is 760 mm Hg
    - Vapor pressure of substances are given at a specific temp (usually I.H. STP)
    - As temperature increases, the vapor pressure of the liquid or solid also increases.

Chemical Hazard Assessment



Chemical Properties

- Vapor Pressure - Example:

  -effect of temperature on the VP of water

TEMPERATURE	VAPOR PRESSURE
72 F	25 mm Hg
122 F	93 mm Hg
212 F	760 mm Hg

  - At 212 F water boils & will readily evaporate because its VP equals that of the atmosphere

Chemical Hazard Assessment

Chemical Properties

- Molecular Weight
  - A given atom has a specific weight, known as an Atomic Weight
  - The molecular weight of a substance is the total of atomic weights for each of the atoms making up the substance
  - Air Molecular Weight = 29
    - Example: H2S (Hydrogen = 1, Sulfur =32)
      - ☆ MW of H2S is 34.1
      - ☆ VD of H2S is 1.18
        - Is heavier than air
        - 34.1 ÷ 29 = 1.18

Chemical Hazard Assessment

Chemical Properties

- Vapor Density -
  - The density of a gas or vapor compared to the density of ambient air.

    Vapor density of air = 1
    - VD < 1, gas or vapor lighter than air, will tend to rise
    - VD close to 1, gas or vapor will tend to disperse in air
    - VD > 1, gas or vapor heavier than air, will tend to fall

Chemical Hazard Assessment

Chemical Properties

- Specific Gravity
  - The weight of a solid or a liquid compared to an equal volume of water.
  - SG of water = 1
    - If specific gravity < 1 it will float
    - If specific gravity is > than 1 it will sink

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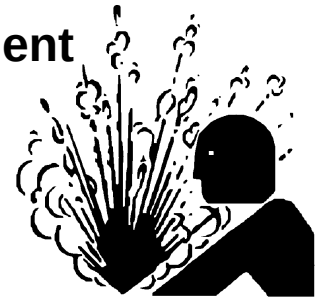
Chemical Hazard Assessment

Chemical Properties



- Solubility
  - Is the material soluble in water?
    - Will it dissolve
    - Will it activate
    - Will it make more of the same?
- Incompatibilities and Reactivity
  - Found in the NIOSH Pock Guide it lists hazardous incompatibilities and reactivities for each substance as applicable.

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Chemical Hazard Assessment

Assess Variables and Modifying Conditions

- When handling or storing chemicals you must take into consideration variables and modifying conditions. These are critical for emergency response and may have an impact during your Product Acceptance Analysis.
- Variables and modifying conditions include:
  - Time of day/day of week/ holiday - Why?
  - Location (city, rural, school) – Why?
  - Weather / time of season – Why?
  - Resource availability – Why?
  - Activity to be performed - Why
  - Simultaneous Operations - Why
  - Drainage and waterway exposure – Why?

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Chemical Hazard Assessment

Assess Variables and Modifying Conditions

- ✓ Using knowledge you have about the chemicals and your work activity and based off real time data you have gained, ***visualize*** the behavior and outcomes that may occur. Ask What If?
- ✓ There have been many HazMat incidents in which tunnel vision on primary hazards resulted in fatalities. Secondary hazards ***kill***. Visualize!!
- ✓ Ask yourself the question "What will make this go catastrophic?" Then mitigate it!

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Safe Work Practices and Regulations

- **Safe Work Practices**
  - **If you are in compliance with the regulatory requirements that govern the handling, storage, use and disposal of chemicals and fully comply with these mandates you will "set up for success".**
  - ***Deviations and non-compliance* of regulations and procedures can cause unsafe conditions and *Lack of Discipline of employees and leadership* to comply with regulations and procedures can cause unsafe acts and conditions. Both set the stage for failure. (Incidents, Citations and Notice of Violations-NOV's, etc.).**

Safe Work Practices and Regulations

- **Safe Work Practice**
  - **Product Acceptance Program**
    - **The Product Acceptance Program, if used properly, should minimize the number of chemicals used in your facilities and projects, facilitate safe handling and waste management procedures and maintains accurate internal chemical inventories and updated business plans.**
      - **Single point control that manages the introduction of a new chemical and ensures other related work process are considered.**
      - **A documented hazards analysis that is designed to be completed in a proactive way that assess the exposures and potential issues as it relates to people and the environment.**

Safe Work Practices and Regulations

Regulations

- §5194. Hazard Communication (https://www.dir.ca.gov/Title8/5194.html)
  - Worker Right to Know – Labels, MSDS, Training, etc.
- §3380. Personal Protective Devices (https://www.dir.ca.gov/Title8/3380.html)
  - Personal Protective Equipment Assessments
  - Heat Illness procedures (to include the micro-environments developed by wearing Chemical Protective Clothing
- §3203. Injury and Illness Prevention Program subsection (2) and (4) (https://www.dir.ca.gov/Title8/3203.html)
  - (2) Include a system for ensuring that employees comply with safe and healthy work practices. Substantial compliance with this provision includes recognition of employees who follow safe and healthful work practices, training and retraining programs, disciplinary actions, or any other such means that ensures employee compliance with safe and healthful work practices.
  - (4) Include procedures for identifying and evaluating work place hazards including scheduled periodic inspections to identify unsafe conditions and work practices. Inspections shall be made to identify and evaluate hazards. (This is your Job Hazards Analysis - JHA, JSA, WSP, SWP, whatever you call it)

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Safe Work Practices and Regulations

- Regulations
  - Group 20. Flammable Liquids, Gases and Vapors; §5145 to §5629 (https://www.dir.ca.gov/Title8/sb7g20.html)
    - Broad spectrum of regulations depending on your specific work activity. Conduct a gaps analysis to ensure alignment.
  - Article 110. Regulated Carcinogens (https://www.dir.ca.gov/Title8/sb7g16a110.html)
    - Narrows down specific chemicals known to be a carcinogen. Very specific regulations.
  - §5192. Hazardous Waste Operations and Emergency Response. (https://www.dir.ca.gov/Title8/5192.html)
    - Depending on your operations you may have to comply with the Hazwoper Regulation. Basically a combination of regulations written with the emergency responder's safety.

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Safe Work Practices and Regulations

- Regulations
  - §3220. Emergency Action Plan (https://www.dir.ca.gov/Title8/3220.html) and 40 CFR, Part 355, Appendix A.
  - CUPA – Hazardous Material Business Plans, California Health and Safety Code (http://www.leginfo.ca.gov/cgi-bin/displaycode?section=hsc&group=25001-26000&file=25500-25520)
    - Basic information on the location, type, quantity, and the health risks of hazardous materials handled, used, stored, or disposed of in the state, which could be accidently released into the environment.
    - Work with your local governing response agency (usually jurisdictional fire department)
    - Also go to the CUPA FAQ document (http://www.calema.ca.gov/HazardousMaterials/Pages/Business-Plan-EPCRA%20312.aspx)
  - California Code of Regulations (CCR), Title 22, Division 4.5 - (http://www.dtsc.ca.gov/LawsRegsPolicies/Title22/index.cfm)
    - Hazardous Waste Management - it is unrealistic to believe you will use all the chemicals and not produce some form of waste stream - be it recyclable or disposable.
    - Prescriptive regulations on times for storage, facilities design and segregation for incompatibilities, disposal and what and how to document both recycle and disposal.

Safe Work Practices and Regulations

Laboratories

- §5191. Occupational Exposure to Hazardous Chemicals in Laboratories (https://www.dir.ca.gov/Title8/5191.html)
  - You must have a Chemical Hygiene Plan (§5191(e))
  - Must be designed and constructed to guidelines for ventilation and fire code.
    - Be careful operator cut labs most of the time meet the requirements of a laboratory

Resources I use Routinely

- NIOSH Pocket Guide to Chemical Hazards, June 1994 (http://www.cdc.gov/niosh/npg/)
- Cal-Osha Title 8, Section 5155 - Airborne Contaminants (http://www.dir.ca.gov/Title8/5155.html)
- Gas Processing Association, Section 23 - Physical Properties (http://gpsa.gpaglobal.org/databook/)
- Rapid Guide to Hazardous Chemical in the Workplace, 4th edition, Richard J. Lewis, SR.(http://www.amazon.com/Rapid-Guide-Hazardous-Chemicals-Workplace/dp/0471355429)
- Quick Selection Guide to Chemical Protective Clothing, Krister Forsberg & S.Z.Mansdolf (http://www.amazon.com/Quick-Selection-Chemical-Protective-Clothing/dp/0470146818)
- A Comprehensive Guide to the Hazardous Properties of Chemical Substances, Pradyot Patnaik (http://www.amazon.com/Comprehensive-Hazardous-Properties-Chemical-Substances/dp/0471714585)
- 2011 TLVs® and BEIs®, *ACGIH®*,Publication #0111 (http://www.acgih.org/store/productdetail.cfm?id=2142)
- Emergency Response Guidebook (Current Edition) (http://www.jjkeller.com/webapp/wcs/stores/servlet/product_2012-Emergency-Response-Guidebook-ERG_10151_-1_10551_99612)

Chemical Safety

- Summery
  - Combination of many regulations and requirements.
  - Not a new hire assignment
  - It not for the weak at heart!
- Questions?