Spring 2015

Environmental Considerations for Treatment of Effluent Waste Solutions and Solid Waste Products

Larry G. Twidwell

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LECTURE 1

The following information was presented to a graduate level class during the Spring semester 2015. The information presented here was prepared for a class that covered metallurgical solutions and solid waste treatment, waste storage, and recycling. The recycling information was presented by Dr. J. Downey and is not presented here.

LECTURE 1

Session 2: Background and Discussion Focused on Solid Waste Disposal and Waste Site Remediation

Presentation Outline

- Drivers for Handling Solid Waste Products
  - Introduction
  - Brief History of EPA
- Acronyms and Definitions

➢ Regulations (more outline)

- CFR (Code of Federal Regulations)
- RCRA (Resource Conservation Recovery Act)
  - Characteristic Waste
    - ♦ Ignitability
    - ♦ Corrosivity
    - ♦ Reactivity
    - ♦ Toxicity
      - TCLP (Toxicity Characterization Leach Procedure)
        - √ Controversy
        - √ Procedure

Regulations (more outline)

- RCRA-BDAT (Best Demonstrated Available Technology)
  - General
  - Listed Waste
    - √ Examples
  - Excluded Waste (Bevill Amendment)
    - √ Short History
    - √ Current List
  - LDR (Land Disposal Restrictions)
    - √ Examples

Regulations(more outline)

- TSCA (Toxic Substances Control Act)
- CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act)
  - SARA (Superfund Amendments and Reauthorization Act) and ARARs (Applicable or Relevant and Appropriate Requirements)
  - NPL (National Priority Listed) Sites, Examples in Region 8
  - Problems with NPL Sites

- Case Studies (more outline)
  - Arsenic Stabilization
    - Ferrihydrite (most used technology throughout the world)
    - Scorodite
    - Arsenic Trisulfide
    - Whitmoyer NPL Site Remediation
    - Sherwin Williams Emeryville Remediation
  - Recycle of Mercury for Chlor-alkali Plants
  - Thallium Remediation at a Heap Leach Gold Operation
  - Copper Smelter Flue Dust Remediation
- Present Day Controversial EPA Practices

➢ Drivers for Handling Solid Waste Products

❖ Introduction

You won’t remember these but you have this ppt for later reference

Intent of this course presentation

- Introduce you to EPA rules and regulations as applied to hazardous solid waste
- **Provide a reference source for your possible future use**
- Give examples of industrial hazardous waste management

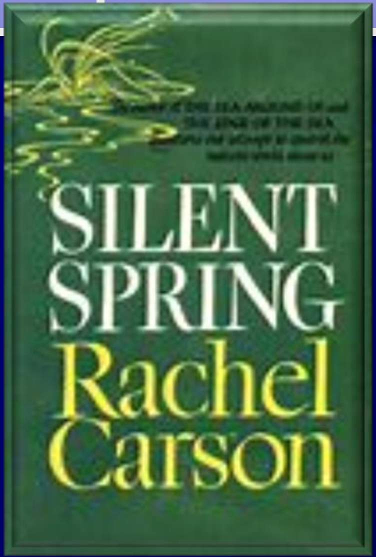
Especially note this site (it is very very helpful to find documents): www.epa.gov/epawaste/hazard/refdocs.htm*

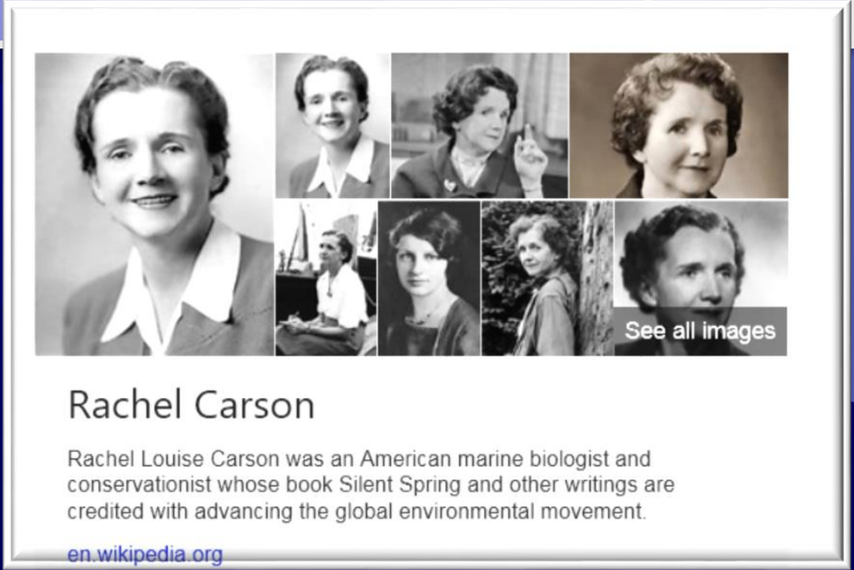
“Hazardous Waste Regulations: User Friendly Reference Documents”

➢ Drivers for Handling Solid Waste Products

❖ Brief History of EPA

EVENT	REASON	YEAR
Family Tree	First step in engaging and focusing people toward protection of our environment was the publication of Rachel Carson's "Silent Spring" because it wound up causing a revolution in public opinion. This publication was a series of articles in the New Yorker about pesticide poisoning and the fact that "the common salad bowl may easily present a combination of organic phosphate insecticides that interact with lethal consequences to the unsuspecting salad muncher‟ (Rachel Carson)	**1962**





Rachel Carson

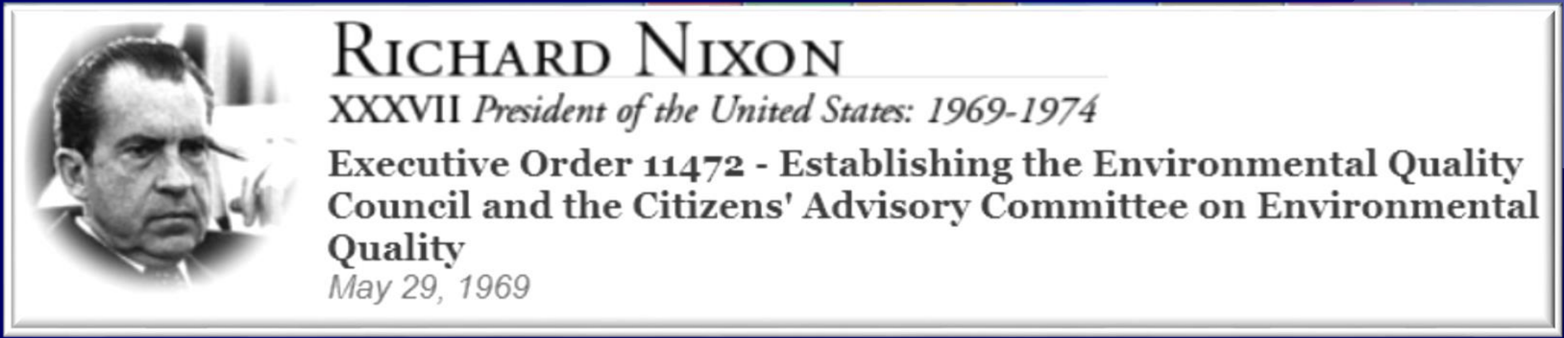
Rachel Louise Carson was an American marine biologist and conservationist whose book Silent Spring and other writings are credited with advancing the global environmental movement.

en.wikipedia.org

➢ Drivers for Handling Solid Waste Products

❖ Brief History of EPA

EVENT	REASON	YEAR
Family Tree	First step in engaging and focusing people toward protection of our environment was the publication of Rachel Carson's "Silent Spring" because it wound up causing a revolution in public opinion. This publication was a series of articles about pesticide poisoning and the fact that "the common salad bowl may easily present a combination of organic phosphate insecticides that interact with lethal consequences to the unsuspecting salad muncher"	**1962**
	Such a great uproar about protection the environment arose that President Nixon set up a Cabinet-level Environmental Quality Council and a Citizen's Advisory Committee on Environmental Quality. The groups were advisory and had almost no real power to change things.	**1969**



RICHARD NIXON

XXXVII *President of the United States: 1969-1974*

Executive Order 11472 - Establishing the Environmental Quality Council and the Citizens' Advisory Committee on Environmental Quality

May 29, 1969

➢ Drivers for Handling Solid Waste Products

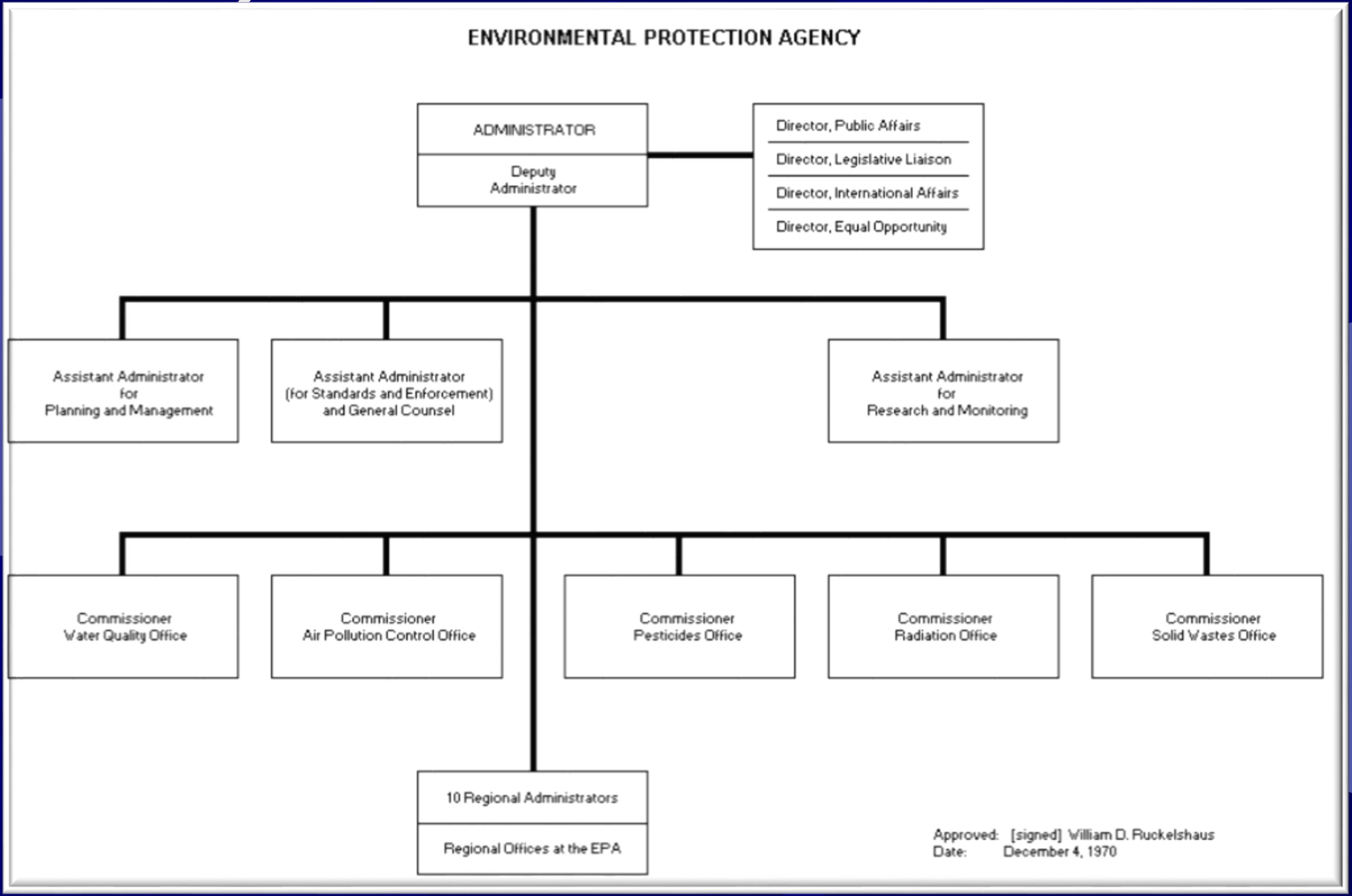
❖ Brief History of EPA

EVENT	REASON	YEAR
Family Tree		
	Such a great uproar about protection the environment arose that President Nixon set up a Cabinet-level Environmental Quality Council and a Citizen's Advisory Committee on Environmental Quality. The groups were advisory and had almost no real power to change things.	**1969**
	Therefore, congress passed the Nat'l Environmental Policy Act. Signed into law by Nixon in Jan 1970. The Act established coordination between government agencies U.S. national policy promoting enhancement of the environment.	**1/1/1970**
	First Earth Day brought 20 million Americans out to demonstrate in favor of Environmental reform.*	**4/22/1970**

Brief History of EPA

Formation	**Birthday of EPA**	
	The Nat'l Environmental Policy Act legislation pulled together several government activities under a common organization (EPA). "A turning point, a year when the quality of life became more than a phase". Agencies collected together included: DOI's water quality and water pollution activities; USDA's insecticide, fungicides and environmental quality branch of the Agricultural Research Service; HEW's Natl Air Pollution Control Adm, Bureau of Water Hygiene, Solid Waste and Radiological Management; AEC gave responsibility of radiation criteria, standards and control of all radioactive materials; and Functions of Council on Environmental Quality.	**12/2/1970**
	5650 employees were pulled together from their previous work to become the EPA work force. William Ruckelshaus was the first EPA administrator (he was dubbed "Mr. Clean" but later was dubbed the "Enforcer"). EPA now has about 15,350 employees.	

❖ Brief History of EPA (First organization chart)



ENVIRONMENTAL PROTECTION AGENCY

ADMINISTRATOR

Deputy Administrator

- Director, Public Affairs
- Director, Legislative Liaison
- Director, International Affairs
- Director, Equal Opportunity

Assistant Administrator for Planning and Management

Assistant Administrator (for Standards and Enforcement) and General Counsel

Assistant Administrator for Research and Monitoring

Commissioner Water Quality Office

Commissioner Air Pollution Control Office

Commissioner Pesticides Office

Commissioner Radiation Office

Commissioner Solid Wastes Office

10 Regional Administrators

Regional Offices at the EPA

Approved: [signed] William D. Ruckelshaus
Date: December 4, 1970

❖ Brief History of EPA

Amendments	**Clean Air Act (CAA) of 1970 directed EPA to set national air standards and national standards for significant new pollution sources and for all facilities emitting hazardous substances. The initial focus was on hydrocarbons, carbon monoxide (automobiles) and sulfur dioxide.**	**1970**
	Clean Water Act (CWA) of 1972 directed EPA to set national water standards; The Great Lakes Water Quality Agreement was historic and resulted in substantial improvement in the water quality of Lakes. Started the discharge permit program.	**1972**
	Mid 1970s enhanced EPAs massive regulatory controls; RCRA of 1976; Reauthorization of the Clean Air Act in 1977.	**1976, 1977**
	RCRA of 1976 was an amendment to the Solid Waste Disposal Act of 1965 that gave strong regulatory powers for handling, transporting, and disposal of solid waste. EPA notes that in 1971 there were 5000 open dumps. They began the process to convert them to sanitary landfills. Gave EPA authority to control hazardous waste from cradle to grave.	
	EPA promulgated the Mineral Mining and Processing effluent guidelines and standards (40 CFR Part 436) in 1975, ad amended the regulation in 1976, 1977, 1978, 1979 and 1995. The regulation covers wastewater discharges from mine drainage, mineral processing operations and storm water runoff.	
	Hazardous and Solid Waste Amendments (HSWA) created in 1984 to RCRA established the Land Ban of hazardous wastes. Final Land Disposal Restrictions (LDR) for Hazardous Wastes completed in 1990. Became effective in May 1992.	**1984, 1990, 1992**
	Standards for air emissions from Hazardous Waste combustors established. Standards established for dioxin, heavy metals, particulate, hydrochloric acid, carbon monoxide, hydrocarbons, and mercury. Standards to be met by 2002.	**1999**

Very important for Metallurgical industries

❖ Brief History of EPA

	Superfund	
Amendments	CERCLA (Comprehensive Environmental Response, Compensation and Liability Act)	**1980**
	Carter proposed legislation to Congress in June 1979 to establish a fund to help clean up Hazardous waste dump sites. There were identified 11,000 industrial sites with hazardous waste problems.	**1979**
	A National Contingency Plan (NCP) was initiated under the Reagan administration in 1980. It set up the process for evaluating the cleanup requirements for a Superfund site.	**1980**
	First 114 top-priority superfund sites announced. 1.6 billion dollar federal cleanup program.	**1981**
	SARA (Superfund Amendments and Reauthorization Act) The Act required EPA to revise the Hazard Ranking System to ensure that it accurately assesses the relative degree of risk to human health and the environment posed by uncontrolled hazardous wastes sites that may be placed on the National Priorities List (NPL)	**1986**

Must have a call for comments period when anyone can submit

Acronyms and Definitions

1985

- **CFR** (Code of Federal Regulations) All federal regulations must be printed in the Federal Register (NARA, Nat’l Archives and Records Adm) asking for comments on proposed and declaring the establishment of new regulations. The CFR for the Protection of the Environment is Title 40 (40-CFR, part 261).
- **SWDA** (Solid Waste Disposal Act) established in 1965

  Established federal control for disposal of all solid waste (mostly aimed at municipal and non-hazardous waste). Authority vested in state regulations.
- **RCRA** (Resource Conservation and Recovery Act) added in 1976 as an amendment to give more federal control of solid waste, especially setup to regulate hazardous waste.

➢ Acronyms and Definitions

- **RCRA-HSWA** (Hazardous and Solid Waste Amendments, 1984 amendment to RCRA)
  - Gave EPA more control to aggressive manage some hazardous waste
  - Restricted (banned) some hazardous waste from disposal without further stabilization. Initiated the Land Disposal Restrictions (**LDR**)
- **TSCA** (Toxic Substance Control Act, 1976)
  - Established federal control for all toxic and hazardous **chemicals**

➢ Acronyms and Definitions

- **CERCLA** (Comprehensive Environmental Response, Compensation, and Liability Act)
  - Established in 1980
  - Gave EPA federal control to determine who should pay for hazardous waste disposal costs.
  - Established the National Priority Listed (NPL) sites to be cleaned up.
- **SARA** (Superfund Amendments and Reauthorization Act)
  - Established in 1986 (amendment to CERCLA)
  - Further defined the goals and requirements of Superfund cleanup regulations

Regulations (Now some more detailed Background Information)

❖ **CFR** (Code of Federal Regulations)

All federal regulations must be printed in the CFR asking for comments on proposed and declaring the establishment of new regulations. The CFR for the Environment is Title 40 (40-CFR).

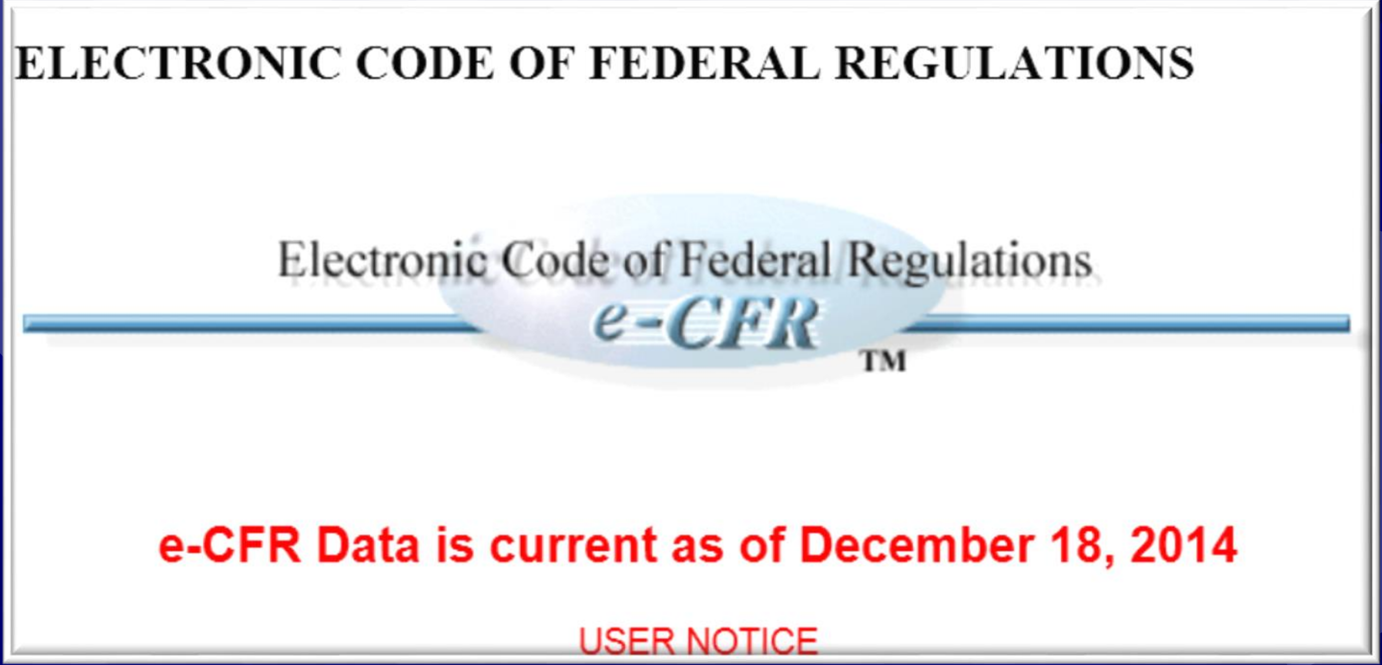
Here is how the CFR is organized:

- ○ There are "50 titles" subject to Federal Regulation
- ○ Each title contains one or more "Volumes"
- ○ Volumes are subdivided into "Chapters"
- ○ Chapters are divided into "Parts"
- ○ Parts are divided into "Paragraphs"
- ○ "Titles" are updated annually on a staggered basis
- ○ "Title" 40 is revised and published July 1

You can locate all these at: **www.ecfr.gov***

➢ Regulations (Background Discussion)

- **Example** (Title 40 and more)
  - ○ www.ECFR.gov*



ELECTRONIC CODE OF FEDERAL REGULATIONS

Electronic Code of Federal Regulations

e-CFR TM

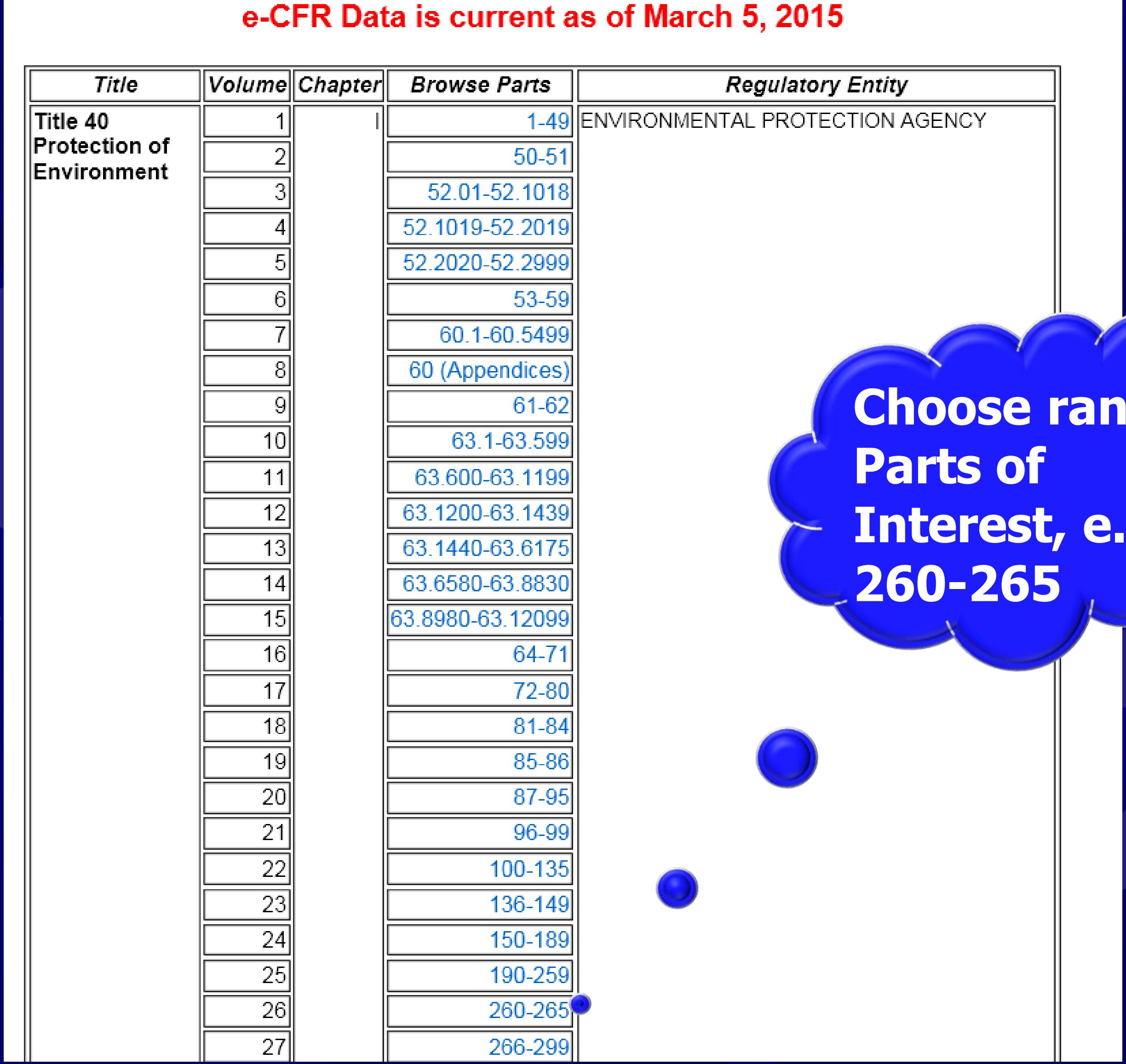
e-CFR Data is current as of December 18, 2014

USER NOTICE

Browse: Select a title from the list below, then press "Go".

Title 40 - Protection of Environment

➢ Regulations (Background Discussion)



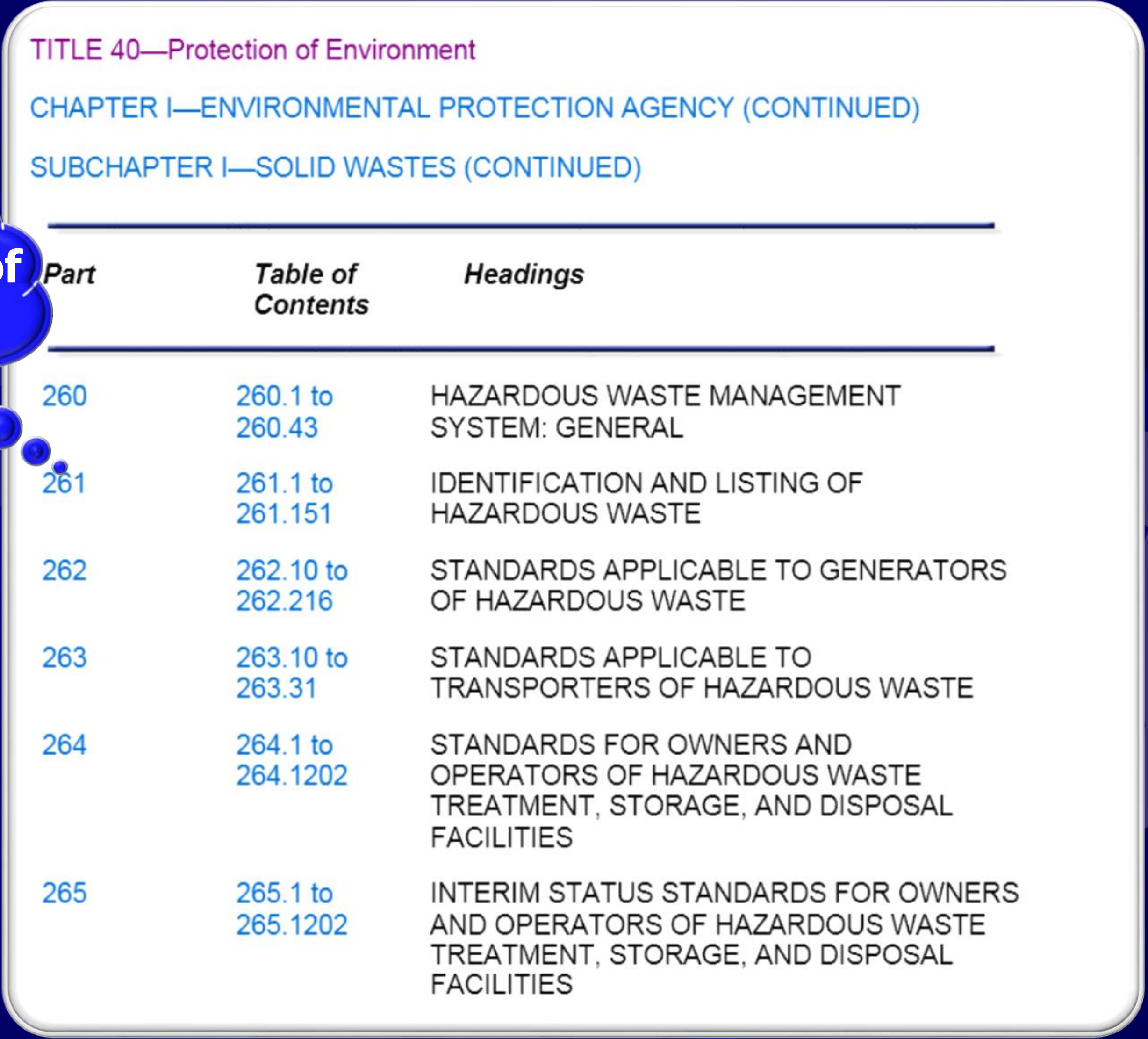
e-CFR Data is current as of March 5, 2015

Title	*Volume*	*Chapter*	*Browse Parts*	*Regulatory Entity*
Title 40 Protection of Environment	1	I	1-49	ENVIRONMENTAL PROTECTION AGENCY
	2		50-51	
	3		52.01-52.1018	
	4		52.1019-52.2019	
	5		52.2020-52.2999	
	6		53-59	
	7		60.1-60.5499	
	8		60 (Appendices)	
	9		61-62	
	10		63.1-63.599	
	11		63.600-63.1199	
	12		63.1200-63.1439	
	13		63.1440-63.6175	
	14		63.6580-63.8830	
	15		63.8980-63.12099	
	16		64-71	
	17		72-80	
	18		81-84	
	19		85-86	
	20		87-95	
	21		96-99	
	22		100-135	
	23		136-149	
	24		150-189	
	25		190-259	
	26		260-265	
	27		266-299	

Choose range Parts of Interest, e.g. 260-265

➢Regulations (Background Discussion)

Choose Part of Interest, e.g. 261



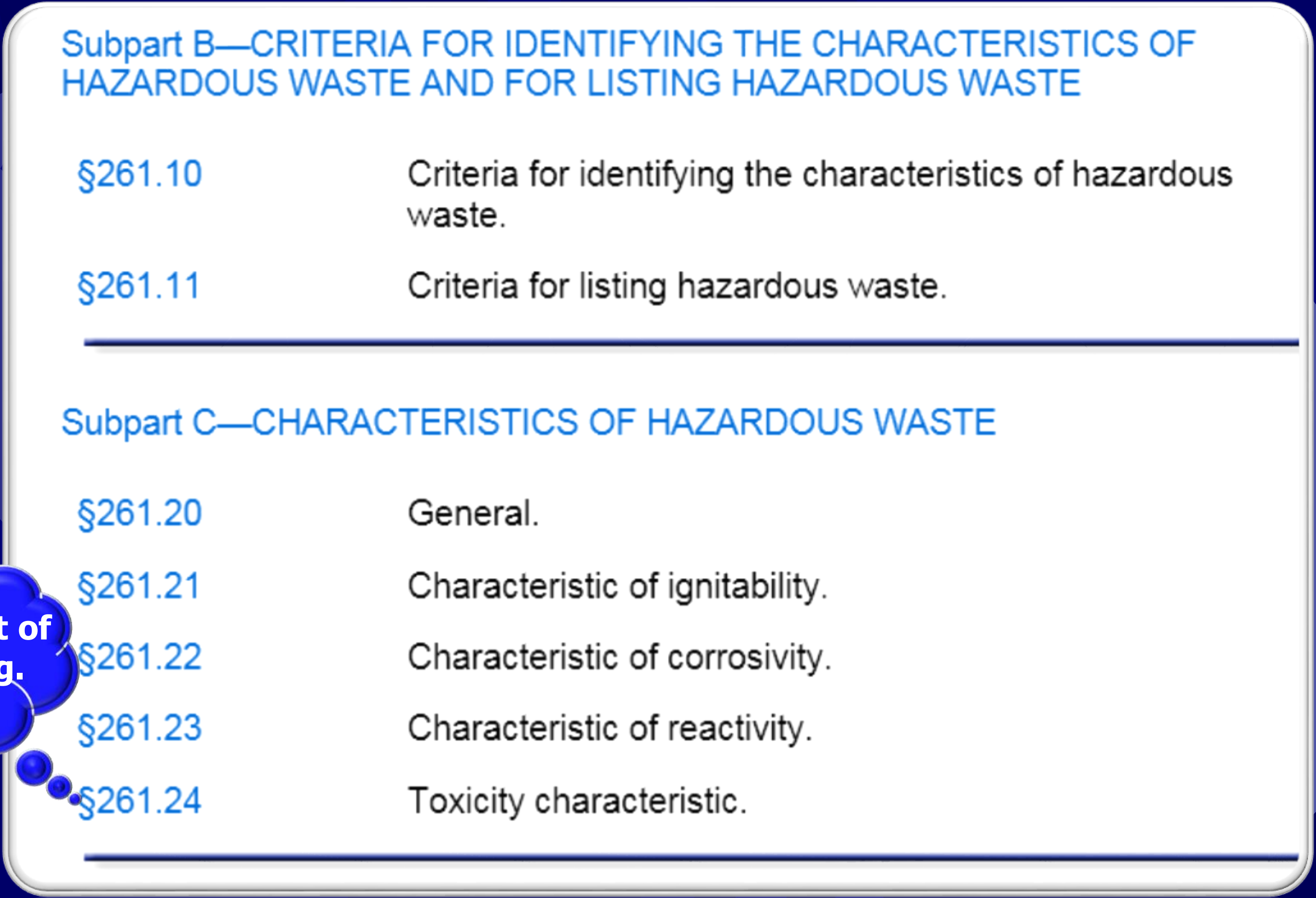
TITLE 40—Protection of Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY (CONTINUED)

SUBCHAPTER I—SOLID WASTES (CONTINUED)

Part	*Table of Contents*	*Headings*
260	260.1 to 260.43	HAZARDOUS WASTE MANAGEMENT SYSTEM: GENERAL
261	261.1 to 261.151	IDENTIFICATION AND LISTING OF HAZARDOUS WASTE
262	262.10 to 262.216	STANDARDS APPLICABLE TO GENERATORS OF HAZARDOUS WASTE
263	263.10 to 263.31	STANDARDS APPLICABLE TO TRANSPORTERS OF HAZARDOUS WASTE
264	264.1 to 264.1202	STANDARDS FOR OWNERS AND OPERATORS OF HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES
265	265.1 to 265.1202	INTERIM STATUS STANDARDS FOR OWNERS AND OPERATORS OF HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES

➢Regulations (Background Discussion)



Subpart B—CRITERIA FOR IDENTIFYING THE CHARACTERISTICS OF HAZARDOUS WASTE AND FOR LISTING HAZARDOUS WASTE

§261.10	Criteria for identifying the characteristics of hazardous waste.
§261.11	Criteria for listing hazardous waste.

Subpart C—CHARACTERISTICS OF HAZARDOUS WASTE

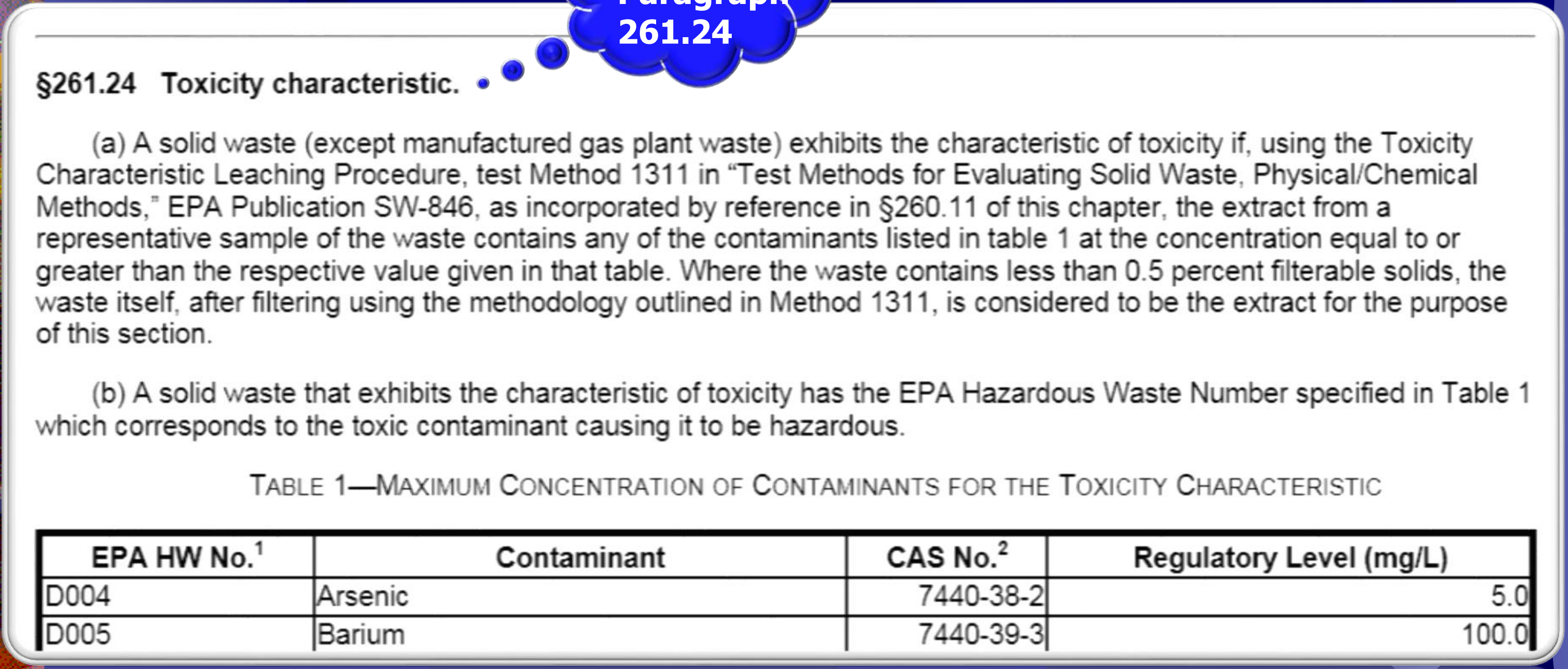
§261.20	General.
§261.21	Characteristic of ignitability.
§261.22	Characteristic of corrosivity.
§261.23	Characteristic of reactivity.
§261.24	Toxicity characteristic.

Choose Part of Interest, e.g. Paragraph 261.24

➢ Regulations (Background Discussion)

- **Example** (Title 40 and more)
  - ○ www.ECFR.gov

Note Paragraph 261.24



§261.24 Toxicity characteristic.

(a) A solid waste (except manufactured gas plant waste) exhibits the characteristic of toxicity if, using the Toxicity Characteristic Leaching Procedure, test Method 1311 in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW-846, as incorporated by reference in §260.11 of this chapter, the extract from a representative sample of the waste contains any of the contaminants listed in table 1 at the concentration equal to or greater than the respective value given in that table. Where the waste contains less than 0.5 percent filterable solids, the waste itself, after filtering using the methodology outlined in Method 1311, is considered to be the extract for the purpose of this section.

(b) A solid waste that exhibits the characteristic of toxicity has the EPA Hazardous Waste Number specified in Table 1 which corresponds to the toxic contaminant causing it to be hazardous.

TABLE 1—MAXIMUM CONCENTRATION OF CONTAMINANTS FOR THE TOXICITY CHARACTERISTIC

EPA HW No.[1]	Contaminant	CAS No.[2]	Regulatory Level (mg/L)
D004	Arsenic	7440-38-2	5.0
D005	Barium	7440-39-3	100.0

➢ Regulations (Background Discussion)

- ❖ RCRA-General

Now you know how to find CFR stuff, let's look at regulation details

  - ○ Defined the different **disposal scenario treatments** required for handling solid, liquids, or mixture wastes, i.e. you must determine if the waste is hazardous or non-hazardous
  - ○ Defined **hazardous and non-hazardous solids**; hazardous wastes are defined as "Characteristic waste or Listed waste"

➢ Regulations (Background Discussion)

- **RCRA**-Characteristic Waste
  - A waste product is defined as a **"Characteristic** hazardous waste" by evaluating whether it shows any or all of four characteristics:
    - Ignitability (D001)
    - Corrosivity (D002)
    - Reactivity (D003)
    - **Toxicity** (D004)

Criteria established in May 1980

Usual concern for us

➢ Regulations (Background Discussion)

❖ RCRA-Characteristic Waste

Quoted from "40 CFR Part 261 Subpart C"

Ignitability (D001) - Ignitable wastes can create fires under certain conditions, are spontaneously combustible, or have a flash point less than 60 °C (140 °F). Examples include waste oils and used solvents. For more details, see **40 CFR §261.21*** .

Test methods that may be used to determine ignitability include the Pensky-Martens Closed-Cup Method for Determining Ignitability (Method 1010A) (PDF) (1 pg, 19K) , the Setaflash Closed-Cup Method for Determining Ignitability (Method 1020B) (PDF) (1 pg, 17K) , and the Ignitability of Solids (Method 1030) (PDF) (13 pp, 116K).

Corrosivity (D002)- Corrosive wastes are acids or bases (pH less than or equal to 2, or greater than or equal to 12.5) that are capable of corroding metal containers, such as storage tanks, drums, and barrels. Battery acid is an example. For more details, see **40 CFR §261.22*** . The **test method** that may be used to determine corrosivity is the Corrosivity Towards Steel (Method 1110A) (PDF) (6 pp, 37K).

➢ Regulations (Background Discussion)

❖ RCRA-Characteristic Waste

Quoted from "40 CFR Part 261 Subpart C

Reactivity **(D003)** - Reactive wastes are unstable under "normal" conditions. They can cause explosions, toxic fumes, gases, or vapors when heated, compressed, or mixed with water. Examples include lithium-sulfur batteries and explosives. For more details, see 40 CFR §261.23* . There are currently no test methods available.

Toxicity **(D004)** - **Toxic** wastes are harmful or fatal when ingested or absorbed (e.g., containing mercury, lead, etc.). When toxic wastes are land disposed, contaminated liquid may leach from the waste and pollute ground water. Toxicity is defined through a laboratory procedure called the Toxicity Characteristic Leaching Procedure (TCLP) (Method 1311) (PDF) (35 pp, 288K). The **TCLP** helps identify wastes likely to leach concentrations of contaminants that may be harmful to human health or the environment. For more details, see 40 CFR §261.24*" .

As an engineer in mineral processing and extractive metallurgy areas you will definitely encounter the TCLP test and its ramifications

TCLP Evaluation to determine if waste is considered a "toxicity characteristic" waste

- The importance of the TCLP leachability test and what is allowable. What is the method for measuring leachability?

EPA **Method 1311**: the TCLP leach test is conducted at either pH 4.93 or 2.88 with pH adjusted using glacial **acetic acid**. Leach conducted for 18 hours. Solution analyzed for 8 characteristic elements.

Method developed based on treating municipal pore and discharge waters

Previous to about 1980 the EPTox test (Method 1310) was Used.

Glacial acetic acid is a Surrogate for Organic constituents

TCLP Evaluation to determine if waste is considered a "toxicity characteristic" waste

EPA Method 1311: The Test Conditions

- Method must be used on any waste solid as generated (not concentrated, not dried, not sized, except must be <10 mm)

- Leach is a buffered acetate solution (acetate chosen as a surrogate for organic acids and because it is a good complexer for heavy metals).

TCLP Evaluation to determine if waste is considered a “toxicity characteristic” waste

EPA Method 1311: The Test Conditions

One of two extraction fluids (EF) must be used.

Pretreatment is: 5 g sample (sized to < 1mm)/500 mL beaker; add 96.5 ml H2O/stir; measure pH; if <5 use EF 1; if >5 add 3.5 ml of 1N HCl, 50 C, 10 min; if pH <5 use EF 1; if pH >5 use EF 2.

- **EF 1** = 5.7 ml glacial acetic acid/500 ml water + 64.3 ml 1N NaOH; dilute to 1 L. pH will be 4.93
- **EF 2** = 5.7 ml glacial acetic acid/1 L water. pH will be 2.88

More acidic EF must be used on the more basic solids

TCLP Evaluation to determine if waste is considered a "toxicity characteristic" waste

EPA Method 1311: The Test Conditions

Run the TCLP leach test

○ Add 100 g spl to extraction vessel

○ Add 20x the sample wt of selected EF

○ Close vessel/rotate at 30 rpm for 16-20 hrs

○ Filter the solids

○ Collect an analytical sample of the filtrate by filtering thorough 0.45 micrometer filter

○ Preserve the spl solution by adding high purity nitric acid (1-5 wt %); store at 4^{o}C until analyzed (but not more than 6 months)

○ Maintain a chain-of-custody for all samples

Solids smaller than this are deemed "solution"*

Example Problem with EPA Method 1311

Table 6.25 Final Arsenic Concentration:
Ferrihydrite Filtration Using Different Pore Sizes and Membranes

Ferrihydrite		
Filter Type	**pH**	**[As, µg/L]**
0.2 µm	4.35	16.9
0.45 µm	4.35	312

Solids smaller than this are deemed "solution"

Shows that some Solids pass the 0.45 filter

J. Hohn, *Modified Ferrihydrite for Enhanced Removal of Arsenic from Mine Wastewater*, Montana Tech MSc Thesis May 2005, 180p

Montana Enviromet	Transfer to Kennecott Utah Division	CHAIN OF CUSTODY	Page 1 of 2
	Managers Names	Project Title: EPA Ferrihydrite	Ship Method: UPS
		Phone No.	Fax

Sample ID	Lab Sample No.	Containers	Matrix				Preserved		Sampling Date	Sampling Time	Elements				
			Soil	Water	Air	Other	Yes	No			As	Fe	Cu	P	Sb
As45pH4	1	3		x			x		12/2/14	8am	x	x	x	x	x

Sample Received Intact: Yes No

Temp received: dry ice No dry ice

Relinq. By sampler (Sign & Print Name)	Date	Time	Received by (Sign & Print Name)
Relinquished by			Received by
Relinquished by			Received by
Relinquished by			Received by Lab Date Time

Excel Example Form*

Chain of Custody must always be Maintained from source to analytical Lab; must have this to be defensible in Court

TCLP Results

TCLP Extract - Analytical Results (ICP or AA)

TCLP* (40 species)

- Eight elements (**mg/L**)-As, Ba, Cd, Cr, Pb, Hg, Se, Ag
- Four pesticides
- Two herbicides
- Twenty six organic compounds

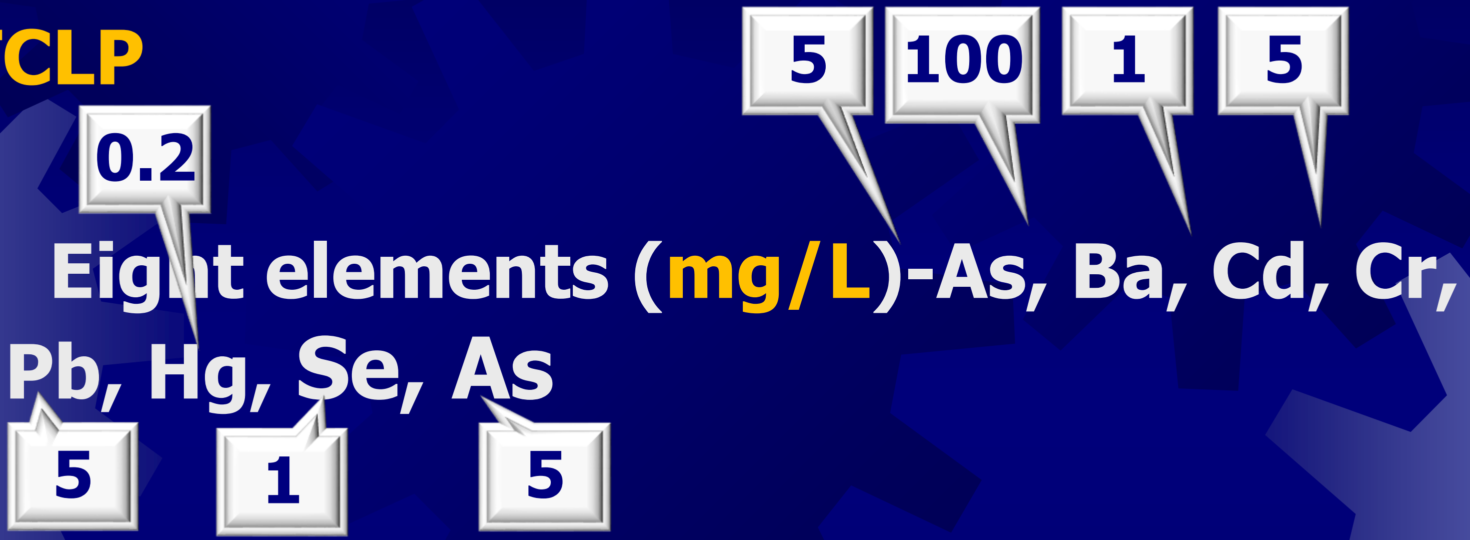
"characteristic elements"

Except for Arsenic*

"The pass or fail values are based on 100x Drinking Water Standard (MCL)"

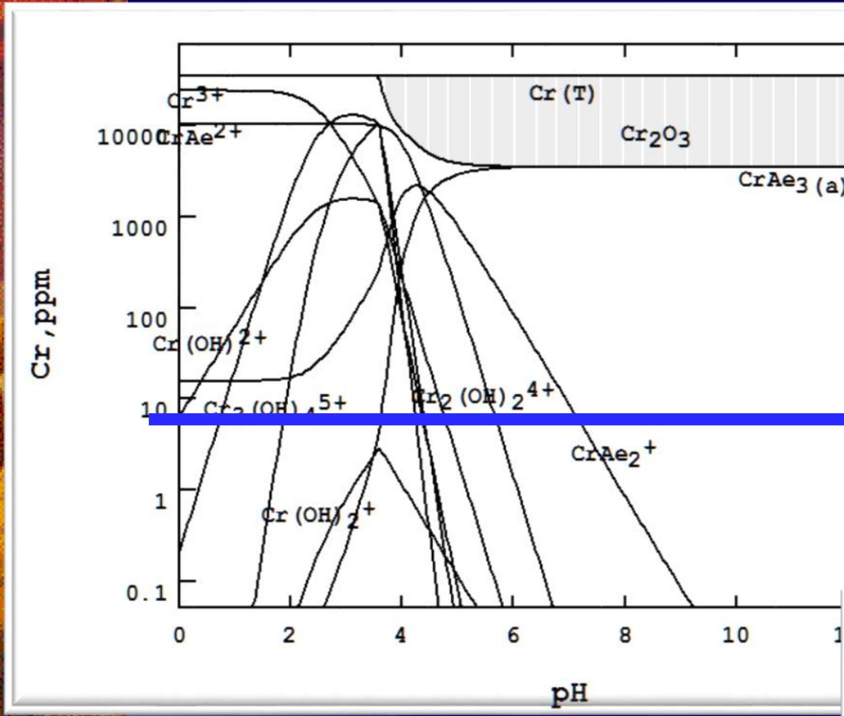
TCLP Extract - Analytical Results (ICP or AA)

TCLP



- Eight elements (**mg/L**)-As, Ba, Cd, Cr, Pb, Hg, Se, As

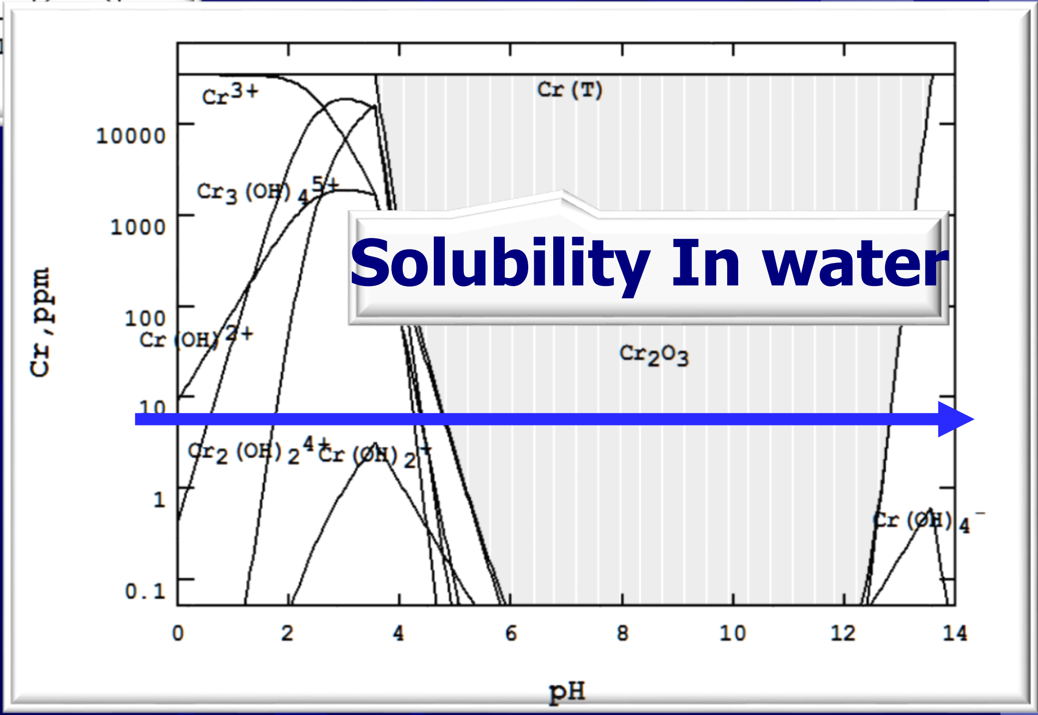
The TCLP test accentuates the dissolution of some of the metals we commonly work with, e.g. Cr (next slides illustrate this).



Stabcal Modeling conditions: 100 g Cr_2O_3 added to 2000 gms H_2O

Cr

Solubility In TCLP



Solubility In water

General Comments

Some States may have more restrictive regulations! Example-California replaced TCLP with **STLC*** (Soluble Threshold Limit Concentration) for the extract in the WET (Waste Extraction Test). It uses Citrate (0.2 M) instead of Acetate as the complexing agent.

TCLP

- Nineteen elements As, Ba, Cd, Cr, Pb, Hg, Se, Ag (they added Sb, Be, Co, Cu, Mo, Ni, Tl, V, Zn)

20

7.0

24

250

15

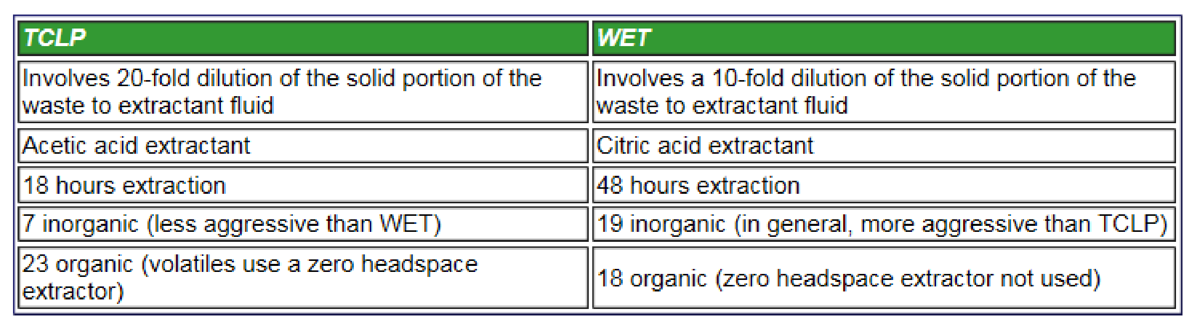
0.075

80

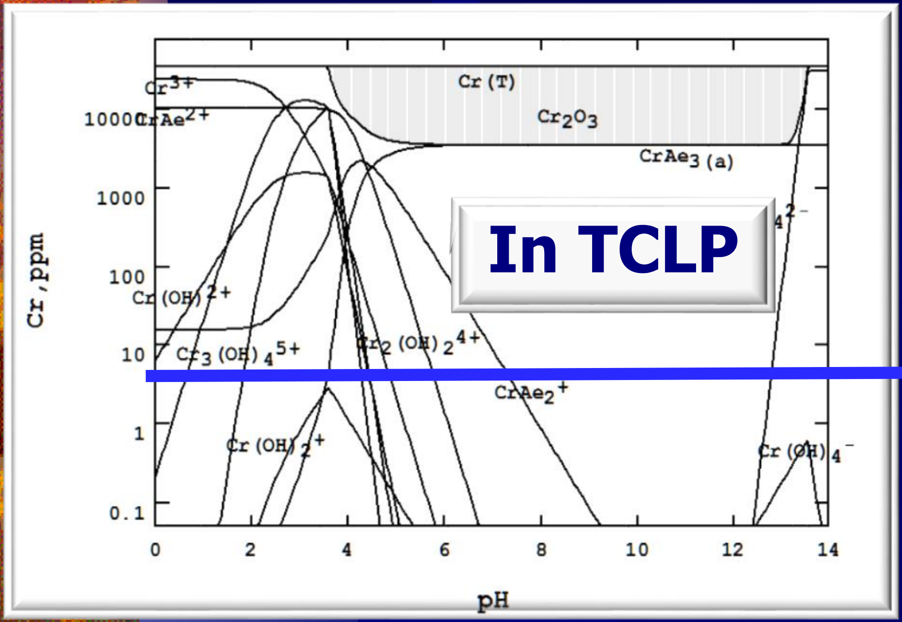
25

350

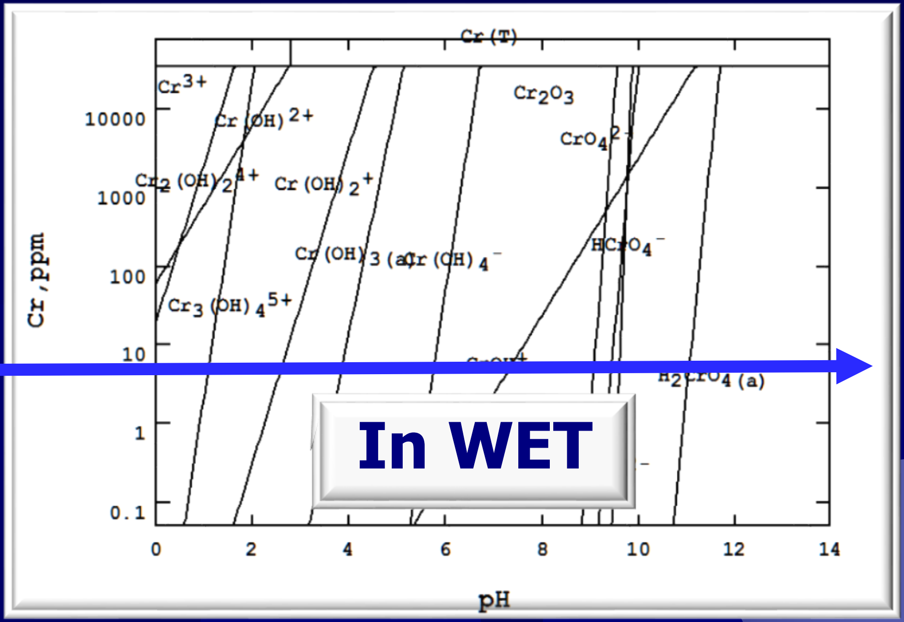
- Ten pesticides and Ten organic compounds



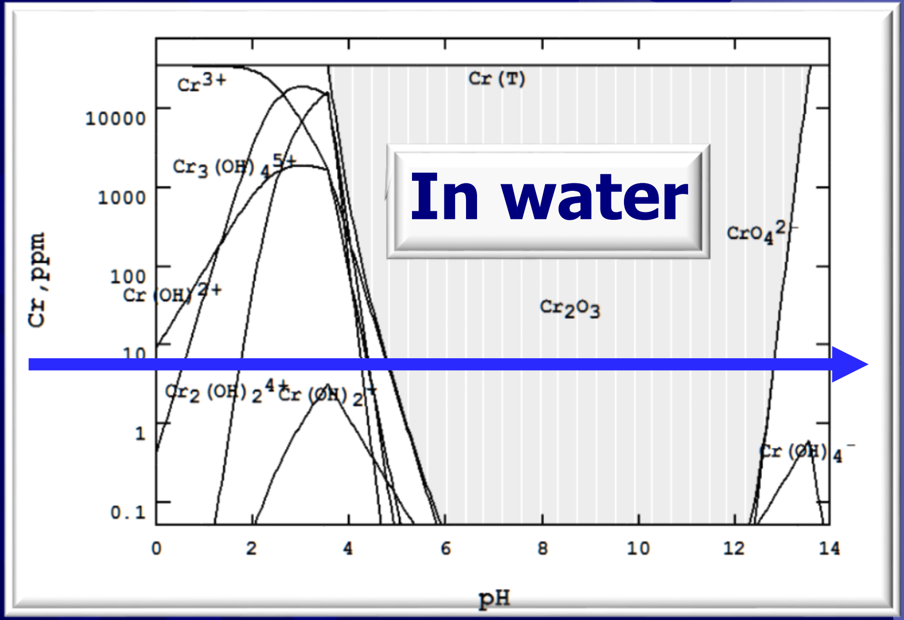
TCLP	WET
Involves 20-fold dilution of the solid portion of the waste to extractant fluid	Involves a 10-fold dilution of the solid portion of the waste to extractant fluid
Acetic acid extractant	Citric acid extractant
18 hours extraction	48 hours extraction
7 inorganic (less aggressive than WET)	19 inorganic (in general, more aggressive than TCLP)
23 organic (volatiles use a zero headspace extractor)	18 organic (zero headspace extractor not used)



In TCLP



In WET



In water

Comparison of Cr_2O_3 solubility

"The WET test more restrictive than TCLP or Water leach

Aside Information

Adopted by
EPA in 1982

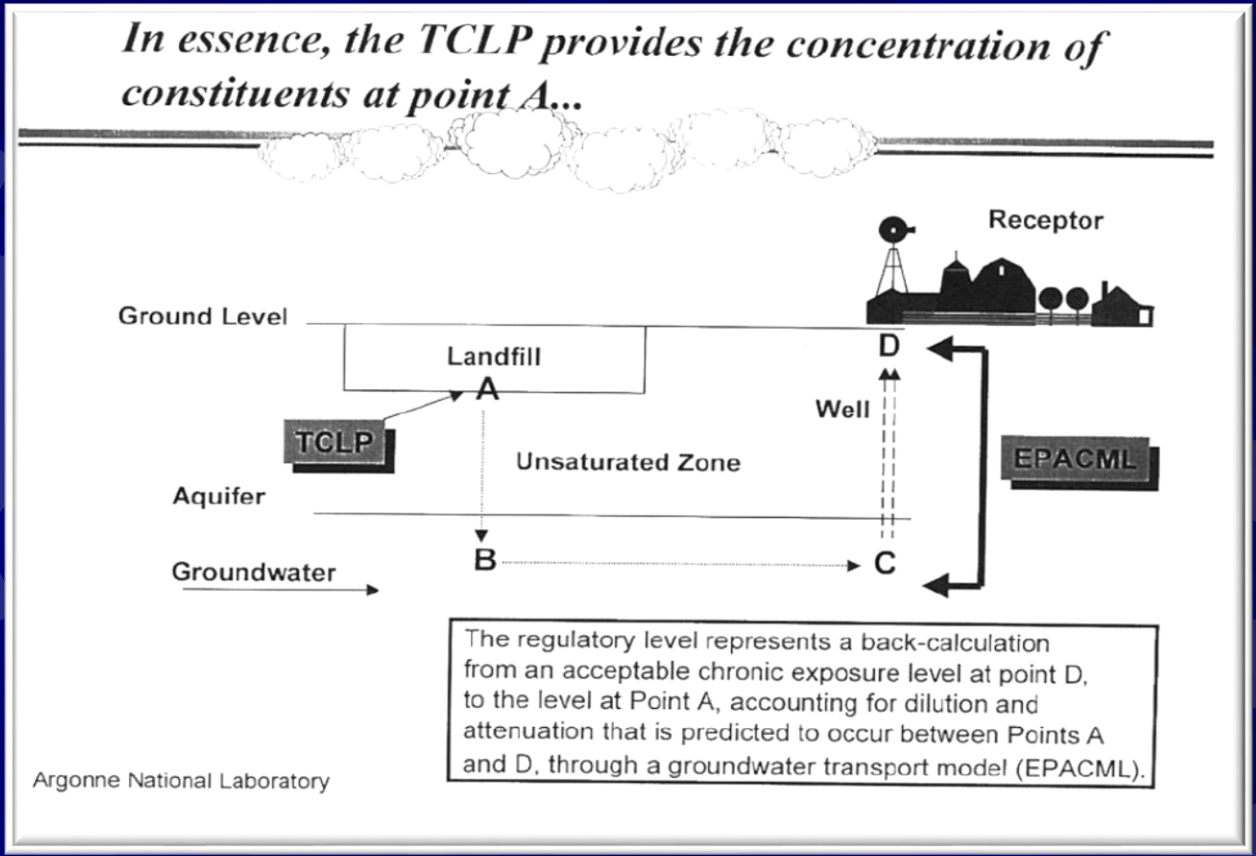
- To be **Defensible** (in lawsuits) analytical data must be collected under Quality Assurance/Quality Control **(QA/QC) Protocols***
- TCLP data can be collected by **ICP or AA** instrumentation. But must be collected using approved Protocols, e.g.

"The EPA publication **SW-846***, **entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*,** is EPA's official compendium of analytical and sampling methods that have been evaluated and approved for use in complying with the RCRA regulations. SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods for the regulated and regulatory communities to use in responding to RCRA-related sampling and analysis requirements."

Controversy for using the TCLP as a method to define whether a waste is hazardous or not!

- The test is conducted under oxidizing conditions at only one pH, one solid/liquid ratio, one temperature, one reaction time; however a real Waste may be stored
  - under reducing conditions
  - under microbiological conditions
  - changing pH conditions
  - changing oxidation/reduction potentials
  - and various temperatures may exist in storage
- The test results are biased by not considering reaction kinetics; size, time and susceptibility to reagent complexation and valence state

Why were the TCLP designated pass/fail concentrations set at 100 times the MCL?



In essence, the TCLP provides the concentration of constituents at point A...

The regulatory level represents a back-calculation from an acceptable chronic exposure level at point D, to the level at Point A, accounting for dilution and attenuation that is predicted to occur between Points A and D, through a groundwater transport model (EPACML).

Argonne National Laboratory

Model developed by soil scientist at Argonne National Laboratory

Technical Evaluation-General Comments

EPA 530-R-02-016*

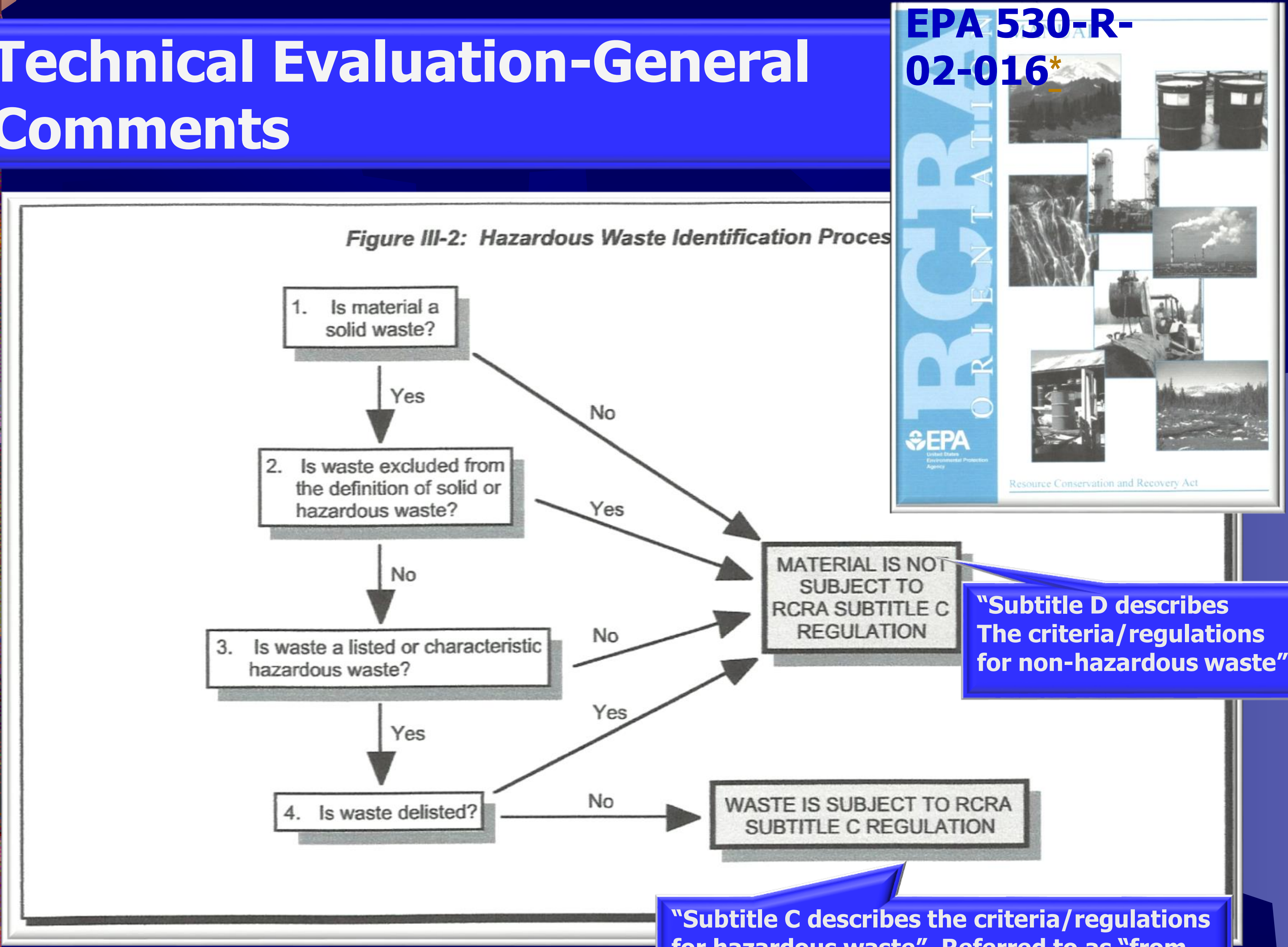


Figure III-2: Hazardous Waste Identification Proces

1. Is material a solid waste?
   - Yes → 2. Is waste excluded from the definition of solid or hazardous waste?
   - No → MATERIAL IS NOT SUBJECT TO RCRA SUBTITLE C REGULATION
2. Is waste excluded from the definition of solid or hazardous waste?
   - Yes → MATERIAL IS NOT SUBJECT TO RCRA SUBTITLE C REGULATION
   - No → 3. Is waste a listed or characteristic hazardous waste?
3. Is waste a listed or characteristic hazardous waste?
   - No → MATERIAL IS NOT SUBJECT TO RCRA SUBTITLE C REGULATION
   - Yes → 4. Is waste delisted?
4. Is waste delisted?
   - Yes → MATERIAL IS NOT SUBJECT TO RCRA SUBTITLE C REGULATION
   - No → WASTE IS SUBJECT TO RCRA SUBTITLE C REGULATION

"Subtitle D describes The criteria/regulations for non-hazardous waste"

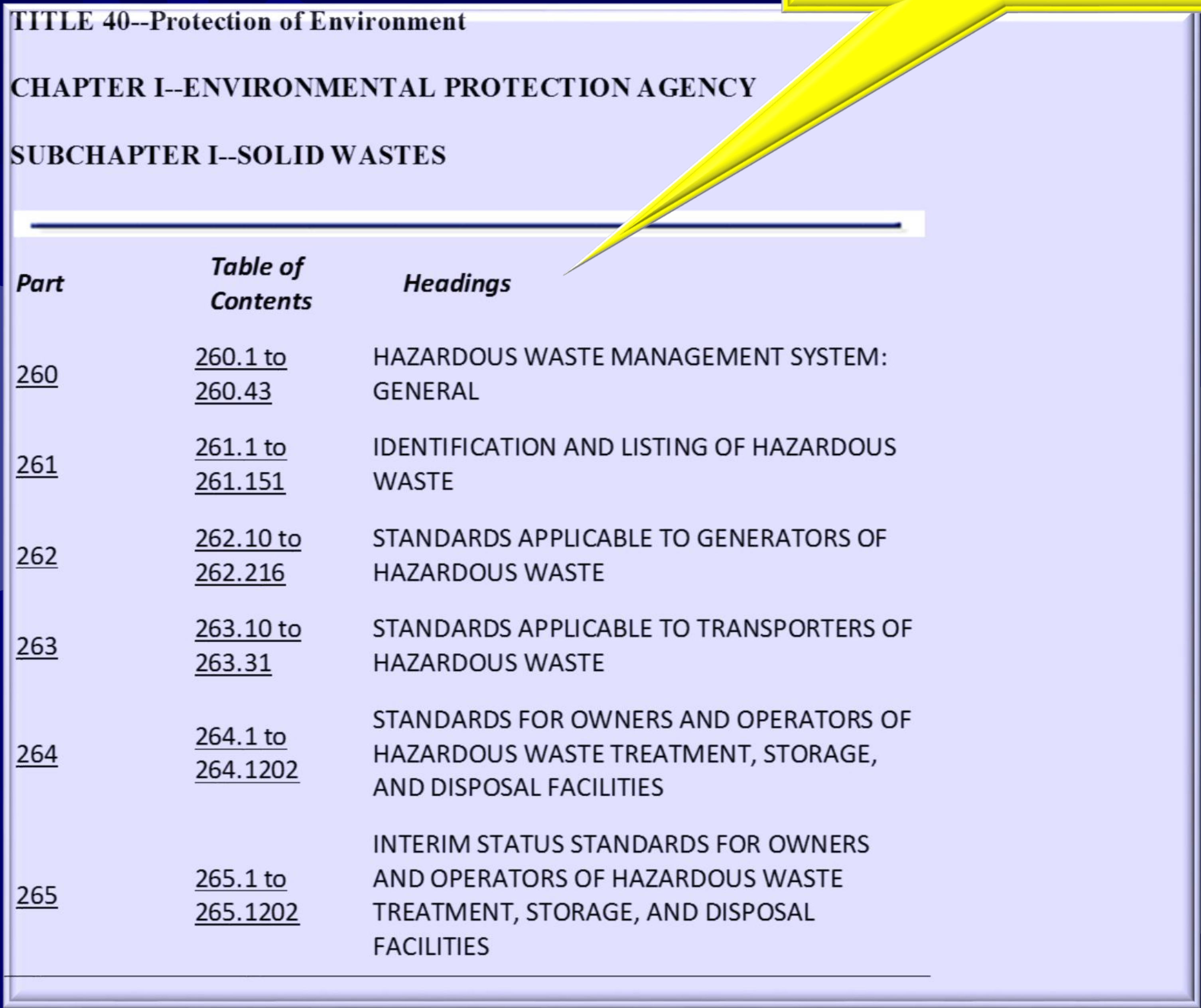
"Subtitle C describes the criteria/regulations for hazardous waste". Referred to as "from cradle to grave"

EPA has Voluminous Requirements!!

Environmental Regulations for Hazardous Waste Solids

“In the US, solid waste generation, handling, transportation, and long-term storage are managed and regulated under the Environmental Protection Agency (EPA). Standards, regulations, and codes for Protection of the Environment are provided under the Code of Federal Register, Title 40 (Sections 260 to 265). A table of contents for the applicable regulations for producing, handling, storage etc is provided”. The web site for the codes can be accessed at http://www.epa.gov/lawsregs/search/40cfr.html

"Where to find info"



TITLE 40--Protection of Environment

CHAPTER I--ENVIRONMENTAL PROTECTION AGENCY

SUBCHAPTER I--SOLID WASTES

Part	*Table of Contents*	*Headings*
260	260.1 to 260.43	HAZARDOUS WASTE MANAGEMENT SYSTEM: GENERAL
261	261.1 to 261.151	IDENTIFICATION AND LISTING OF HAZARDOUS WASTE
262	262.10 to 262.216	STANDARDS APPLICABLE TO GENERATORS OF HAZARDOUS WASTE
263	263.10 to 263.31	STANDARDS APPLICABLE TO TRANSPORTERS OF HAZARDOUS WASTE
264	264.1 to 264.1202	STANDARDS FOR OWNERS AND OPERATORS OF HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES
265	265.1 to 265.1202	INTERIM STATUS STANDARDS FOR OWNERS AND OPERATORS OF HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES

➢ Drivers for Handling Solid Waste Products

❖ **RCRA-Listed Waste (EPA description)**

If your waste is listed you have to abide by the Hazardous waste regulations!!

"**1.The F-list** (non-specific source wastes). This list identifies wastes from common manufacturing and industrial processes, such as solvents that have been used in cleaning or degreasing operations. Because the processes producing these wastes can occur in different sectors of industry, the F-listed wastes are known as wastes from non-specific sources". Wastes included on the F-list can be found in the regulations at **40 CFR §261.31***

The Listed treatment for F006 is "Hydroxide Precipitation"

Example: F006* Wastewater treatment sludge from electroplating operations

➢ Drivers for Handling Solid Waste Products

- **RCRA-Listed Waste (EPA description)**

  "2. The **K-list** (source-specific wastes). This list includes certain wastes from **specific** industries, such as petroleum refining or pesticide manufacturing. Certain sludges and wastewaters from treatment and production processes in these industries are examples of source-specific wastes." Wastes included on the K-list can be found in the regulations at **40 CFR §261.32***

Example: K106* Wastewater treatment sludge (HgS) from mercury cell process in chlorine production

➢ Drivers for Handling Solid Waste Products

❖ **RCRA-Listed Waste** **(EPA description)**

"3. The P-list and the U-list (discarded commercial chemical products). These lists include **specific commercial chemical products** in an unused form. Some pesticides and some pharmaceutical products become hazardous waste when discarded." Wastes included on the P- and U-lists can be found in the regulations at **40 CFR §261.33*** ."

Example: P102 Arsenic Trioxide

➢ Drivers for Handling Solid Waste Products

❖ **RCRA-**Characteristic Elements are also **"Listed" wastes** (by TCLP test) Designation

D009 D010 D004 D005 D006 D007

- Eight elements (mg/L)-As, Ba, Cd, Cr,

D008 Pb, Hg, Se, Ag D011

- Four pesticides
- Two herbicides
- Twenty six organic compounds

You have to analyze for all the elements in your waste; if any one fails then your waste must be treated as hazardous.

See 40 CFR, 261.24* for all 40

NEW TOPIC

➢ Drivers for Handling Solid Waste Products

- ❖ **RCRA-BDAT (Best Demonstrated Available Technology)**
  - ○ EPA was sued by several environmental and industry groups to require that EPA designate formation processes that could meet their "characteristic and listed" regulations. So, EPA developed **BDAT** standards for all waste production processes.
  - ○ The studies began in 1980 and were divided into three efforts, designated first-third, second-third, and third-third.
  - ○ The final third-third was completed and promulgated in 1990.

and recommended treatments

The metallurgical industries are most effected by the third-third processes

There were thousands of pages of publications in the CFR during this time

➢ Drivers for Handling Solid Waste Products

❖ RCRA-BDAT

BDAT waste treatment processes were based on:

- ○ A survey of the Literature and visits to sites using some form of treatment for collection of data to ascertain to what level the hazardous constituent can be lowered (based on, at least, pilot scale processing); and
- ○ Economic viability

➢ Drivers for Handling Solid Waste Products

Like removing
Arsenic from
effluent waters

❖ RCRA-BDAT

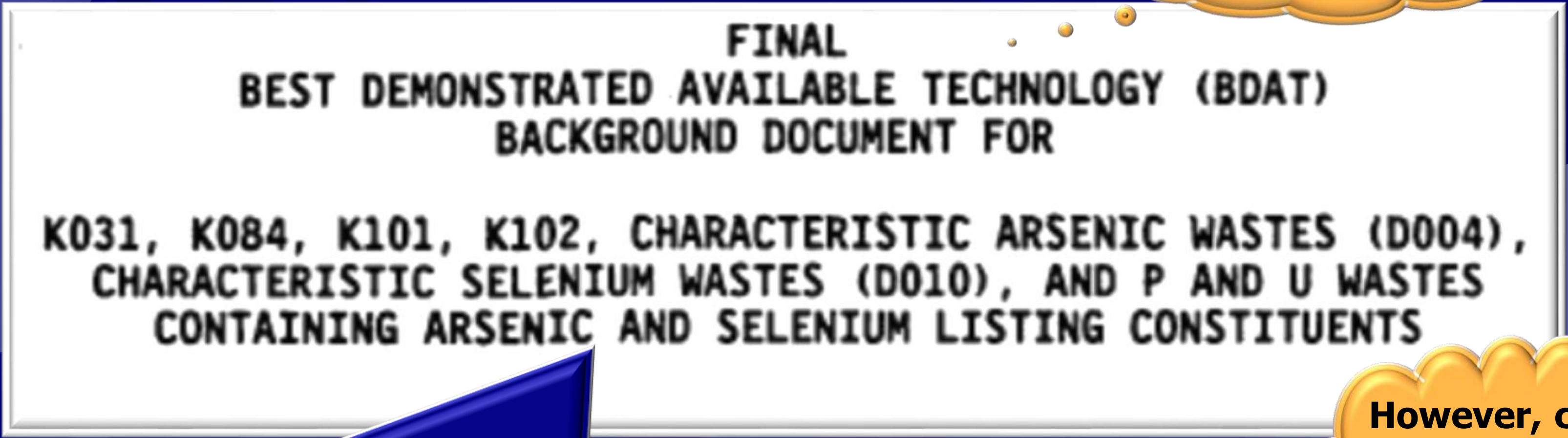
So, here is the evaluation process used by EPA:

- ○ A literature search was conducted to make a list of candidate treatment processes
- ○ Site visits were made to all companies using a treatment process
- ○ Data were compiled for the treatments along with as much economic cost data as possible in a report which was published in the FR for comments
- ○ A selection was made and a treatment process was promulgated and published in the FR

➢ Drivers for Handling Solid Waste Products

- **RCRA-BDAT**- EPA's final report for each "Listed" waste is published in FR

An Example



FINAL
BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT)
BACKGROUND DOCUMENT FOR

K031, K084, K101, K102, CHARACTERISTIC ARSENIC WASTES (D004),
CHARACTERISTIC SELENIUM WASTES (D010), AND P AND U WASTES
CONTAINING ARSENIC AND SELENIUM LISTING CONSTITUENTS

Example: BDAT D004 **Arsenic*** waters treated via Ferrihydrite Adsorption to achieve <5 mg/L in TCLP; BDAT D010 **Selenium*** waters same treatment must achieve <1 mg/L. For Selenium solids the BDAT was vitrification and the required TCLP was 5.7 mg/L

However, can use any process that achieves this level

➢ Drivers for Handling Solid Waste Products

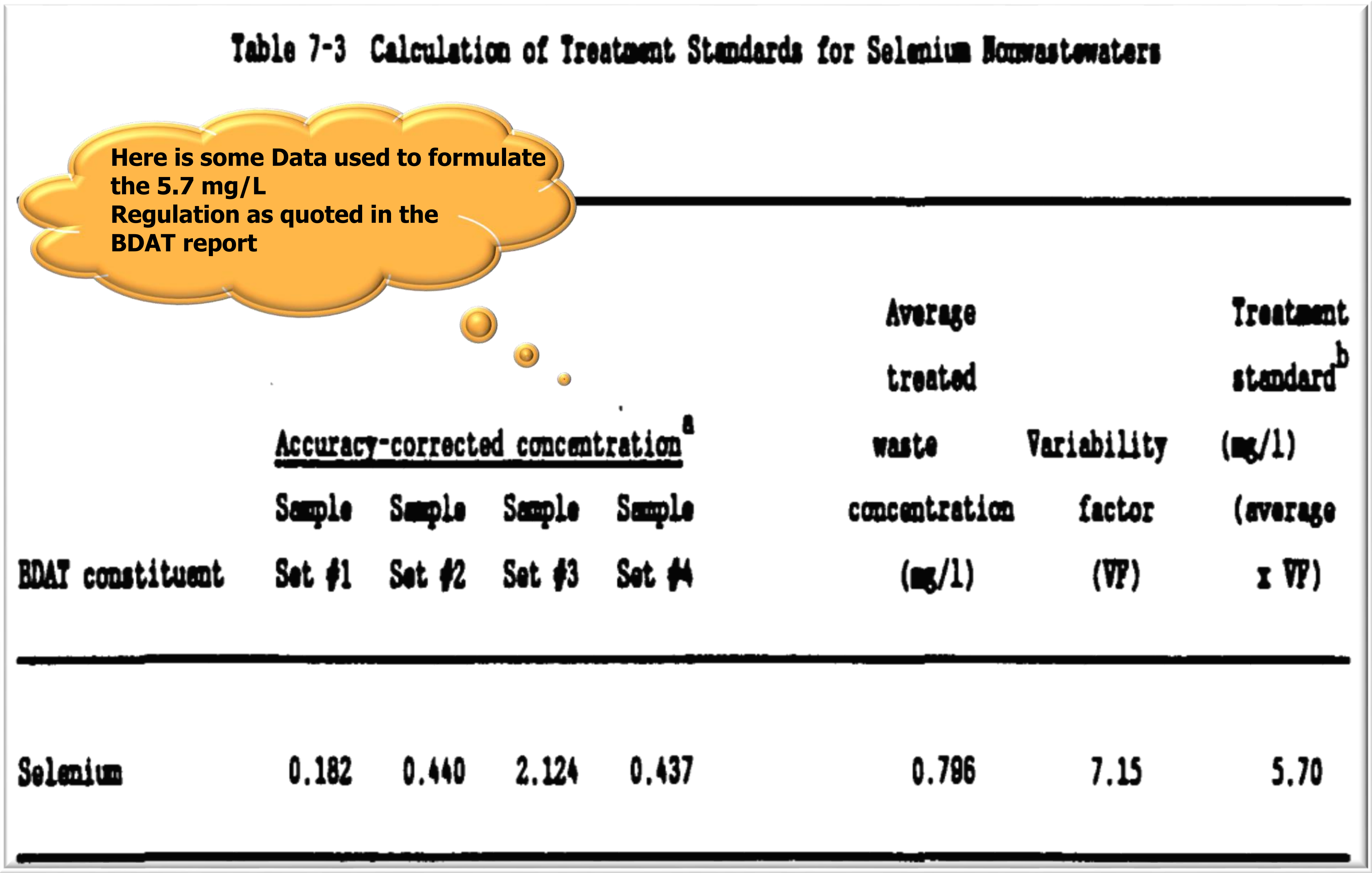


Table 7-3 Calculation of Treatment Standards for Selenium Nonwastewaters

BDAT constituent	Accuracy-corrected concentration[a] Sample Set #1	Sample Set #2	Sample Set #3	Sample Set #4	Average treated waste concentration (mg/l)	Variability factor (VF)	Treatment standard[b] (mg/l) (average x VF)
Selenium	0.182	0.440	2.124	0.437	0.796	7.15	5.70

Here is some Data used to formulate the 5.7 mg/L Regulation as quoted in the BDAT report

➢ Drivers for Handling Solid Waste Products

NEW TOPIC

❖ RCRA-Excluded Waste (Special Waste)

Good references are:
V.R. Housman* in Environmental Law Reporter, 24 ELR 10657 and Linda Luther, CRS Report, R43129*, 2013

Definition of a Special Waste (Excluded from RCRA Subtitle C (hazardous waste) storage/disposal requirements

Amendment was made to RCRA in October 1980 to exclude "solid waste from the **extraction, beneficiation, and mineral processing** of ores and minerals". This extensive exclusion did not hold up based on numerous court law suits by the Environmental Defense Fund (EDF and others) and changes have occurred.

➢ Drivers for Handling Solid Waste Products

NEW TOPIC

❖ RCRA-Excluded Waste (Special Waste)

Definition of a Special Waste (Excluded from RCRA Subtitle C (hazardous waste) storage/disposal requirements

Excluded

EPA defined **extraction and beneficiation** as mining operations that produce low-hazard products; however,

Not Excluded except for 20

mineral processing operations often require chemical and heat intensive operations that drastically change the nature of the mineral and produce low-volume high-hazard wastes. EPA drew a “bright line” between the two operations.

➢ Drivers for Handling Solid Waste Products

❖ RCRA-Excluded Waste (Special Waste)

EPA further defined "**beneficiation activities** as crushing, grinding, washing, dissolution, crystallization, filtration, sorting, sizing, drying, sintering, pelletizing, briquetting, calcining, roasting in preparation for leaching, gravity concentration, magnetic separation, electrostatic separation, **flotation**, ion exchange, solvent extraction, electrowinning, precipitation, amalgamation, and **heap, dump, vat, tank, and in situ leaching**."

So the products (waste) from these activities were all excluded as Hazardous waste in 1980 but that did not stand

➢ Drivers for Handling Solid Waste Products

❖ RCRA-Excluded Waste (Special Waste)

Definition of a Special Waste (Excluded from RCRA Subtitle C (hazardous waste) storage/disposal requirements:

- **Jan 1990 EPA defined exclusion* only for "High Volume/low toxicity" mineral processing wastes (>45,000 metric tons/yr/waste stream/facility and must pass the Method 1312 toxicity test). These can be placed in Subtitle D repositories.**

This is a water leach at pH 4.2 SPLP* (Synthetic Precipitation Leach Procedure)

- **EPA promulgated a final ruling in 1991 stating that only 20 mineral processing wastes were to remain excluded. The basis for the decision was that "RCRA Subtitle C was inappropriate for these wastes because of extremely high costs to the industry and the technical infeasibility of managing them under the Subtitle C requirements".**

➢ Drivers for Handling Solid Waste Products

❖ RCRA-Excluded Waste (Special Waste*)

"Taken from EPA 40 CFR §261.4b Exclusions (Solid Wastes Which Are Not Hazardous Waste)

- §261.4(b)(1) Household Hazardous Waste
- §261.4(b)(2) Agricultural Waste
- **§261.4(b)(3) Mining Overburden**
- **§261.4(b)(4) Fossil Fuel Combustion Waste (Bevill)**
- §261.4(b)(5) Oil, Gas, and Geothermal Wastes (Bentsen Amendment)
- §261.4(b)(6) Trivalent Chromium Wastes
- **§261.4(b)(7) Mining and Mineral Processing Wastes (Bevill)**
- **§261.4(b)(8) Cement Kiln Dust (Bevill)**
- **§261.4(b)(9) Arsenically Treated Wood**
- §261.4(b)(10) Petroleum Contaminated Media & Debris from Underground Storage Tanks
- §261.4(b)(11) Injected Groundwater
- §261.4(b)(12) Spent Chloroflurocarbon Refrigerants
- §261.4(b)(13) Used Oil Filters
- §261.4(b)(14) Used Oil Distillation Bottoms
- §261.4(b)(15) Landfill Leachate or Gas Condensate Derived from Certain Listed Wastes
- §261.4(b)(17) §261.4(b)(18) Project XL Pilot Project Exclusions"

RCRA-Excluded Waste (Bevill)

"§261.4(b)(7) **Mining and Mineral Processing Wastes (Bevill)**

20 Wastes Covered by the Mining Waste Exclusion

Metallurgical waste are highlighted

- **Slag from primary copper processing**
- **Slag from primary lead processing**
- Red and brown muds from bauxite refining
- Phosphogypsum from phosphoric acid production
- Slag from elemental phosphorous production
- Gasifier ash from coal gasification
- Process wastewater from coal gasification
- **Calcium sulfate wastewater treatment plant sludge from primary copper processing**
- **Slag tailings from primary copper processing**
- Flurogypsum from hydrofluoric acid production
- Process wastewater from hydrofluoric acid production
- Air pollution control dust/sludge from iron blast furnaces
- Iron blast furnace slag
- Treated residue from roasting/leaching of chrome ore
- Process wastewater from primary magnesium processing by the anhydrous process
- Process wastewater from phosphoric acid production
- Basic oxygen furnace and open hearth furnace air pollution control dust/sludge from carbon steel production
- Basic oxygen furnace and open hearth furnace slag from carbon steel production
- Chloride process waste solids from titanium tetrachloride production
- **Slag from primary zinc processing"**

See FR Vol 63, No. 100, May 26, 1998, Pp 28556-28753 for latest revisions to LDR for metals UTS*. See also the User Friendly document in 2009*.

➢ Drivers for Handling Solid Waste Products

❖ RCRA-Mineral Processing Excluded Waste

Last promulgated changes for Mineral Processing Excluded Waste was made in 1998. Important things to the mineral processing and extractive metallurgica industries included:

- Restated that the 20 mineral processing and **Bevill waste are still excluded** and are not "listed" hazardous solids
- Emphasized that Mineral Processing solids that are subjected to **recycling** are not defined as solid wastes and are therefore not hazardous waste.
- Hazardous mineral processing wastes can be "co-processed with normal raw materials in beneficiation operations which generate Bevill exempt wastes, **without changing the exempt status** of the resulting Bevill waste"

These are very important to the Extractive industries

Legislative and Regulatory Timeline* Summary

October 2, 1985 —EPA proposes in the Federal Register (50 FR 40292) to **reinterpret the scope of the mining waste exclusion as it applies to mineral and ore processing wastes, leaving only large-volume processing wastes excluded**. Only the large-volume processing wastes still covered by the exclusion would be studied for the Report to Congress.

August 1984 —EPA **is sued for failing** to submit the Report to Congress and make the required regulatory determination by the statutory deadline (Concerned Citizens of Adamstown v. EPA No. 84-3041, D.D.C., August 21, 1985). EPA responds to the lawsuit explaining that it plans to propose a narrower interpretation of the scope of the Mining Waste Exclusion so that it would encompass fewer wastes. EPA also proposes two schedules for completing the Mining Waste Report to Congress—one for completing the report on extraction and beneficiation wastes and one for promulgating a reinterpretation for mineral processing waste.

October 31, 1983 —EPA **misses the statutory deadline** for submitting its mining waste Report to Congress.

November 19, 1980 —EPA promulgates interim final amendments to hazardous waste regulations in the Federal Register (45 FR 76618) This FR notice includes an **exclusion for mining waste from the definition of hazardous** (§261.4(b)(7)).

October 12, 1980 —Congress enacts the Solid Waste Disposal Act Amendments of 1980 (Public Law 96-482) which amends RCRA. Among the amendments, Section 3001(b)(3)(A)(i-iii)—frequently referred to as the Bevill Amendment—temporarily **exempts three special wastes from hazardous waste regulation** until further study can be completed. Section(b)(3)(A)(ii) specifically exempts "**solid waste from the extraction, beneficiation, and processing of ores and mineral, including phosphate rock and overburden from the mining of uranium ore.** EPA is required to complete the report by October 1983 and to evaluate the adverse effects on human health and the environment, if any, from the disposal and utilization of these wastes. EPA is further required to make a regulatory determination (within six months of the completing the Report to Congress) as to whether mining wastes warrant regulation under RCRA Subtitle C or some other set of regulations.

December 18, 1978 —EPA publishes the first set of proposed hazardous waste management standards in the Federal Register (43 FR 58946). This FR notice includes a proposal to **exempt six categories of "special wastes" from the RCRA Subtitle C regulations until further study can be completed. Mining waste; phosphate rock mining, beneficiation, and processing waste; and uranium waste are three of the six special wastes identified.**

October 21, 1976 —Congress passes the (RCRA) (Public Law 94-580) which requires EPA to **develop regulations governing the identification and management of hazardous waste.**

Legislative and Regulatory Timeline* Summary

May 26, 1998 —EPA publishes Land Disposal Restrictions Phase IV: Final Rule Promulgating Treatment Standards for Metal Wastes and Mineral Processing Wastes; Mineral Processing Secondary Materials and Bevill Exclusion Issues; Treatment Standards for Hazardous Soils, and Exclusion of Recycled Wood Preserving Wastewaters; Final Rule (63 FR 28555). LDR Phase IV establishes treatment standards for metal-bearing wastes including Toxicity Characteristic (TC) waste (those with high levels of metal constituents) and waste generated in mineral processing operations.

June 13, 1991 —EPA publishes Special Wastes from Mineral Processing (Mining Waste Exclusion); Final Regulatory Determination and Final Rule (56 FR 27300). This final regulatory determination and rule determines that regulation of the 20 mineral processing wastes studied in the Report to Congress and identified in previous final rules as hazardous waste under RCRA Subtitle C is not warranted. These **20 specified mineral processing wastes continue to be excluded** from the definition of hazardous waste.

July 31, 1990 —EPA submits a Report to Congress on Special Wastes from Mineral Processing (EPA530-SW-90-070A-C) which addresses the "large-volume, low hazard" mineral processing waste meeting the Court narrowed criteria.

September 1, 1989 and January 23, 1990 —EPA publishes in the Federal Register (54 FR 36592; September 1, 1989 and 55 FR 2322; January 23, 1990) the **final boundaries of the Mining Waste Exclusion for mineral processing wastes, limiting the exclusion to 20 specific mineral processing wastes generated by 91 facilities located in 29 states, representing 12 mineral commodity sectors.**

July 1988 —EPA **is sued for withdrawing its October 2, 1985 proposal to reinterpret the mining waste exclusion in regards to mineral processing waste** (51 FR 36233; October 9, 1986. The **Court orders EPA to reinterpret the scope of the exclusion for mineral processing waste according to a new schedule. EPA also is directed to restrict the scope of the exclusion to include only "large-volume, low hazard" wastes.**

July 3, 1986 —EPA publishes the Final Regulatory Determination for Extraction and Beneficiation Waste (51 FR 24496) which determines that **regulation of these wastes under RCRA Subtitle C is not warranted**. These wastes continue to be excluded from the definition of hazardous waste.
December 31, 1985 —EPA submits a Report to Congress on Wastes from the Extraction and Beneficiation of Metallic Ores, Phosphate Rock, Asbestos, Overburden from Uranium Mining, and Oil Shale (EPA530-SW-85-033).

➢ Drivers for Handling Solid Waste Products

So does exclusion mean no regulation??

Highlighting added by
Current author

Quoted from Luther's* Congressional Research Service (CRS 2013)

"Exemption from Subtitle C ***does not mean the waste is unregulated****. As noted above, the waste is* ***subject to other state or federal regulatory requirements****. Those "other" requirements would include any established by individual states, including requirements established under their solid waste management programs.* ***Potentially applicable federal regulatory requirements include those established under the Clean Water Act (CWA) and Safe Drinking Water Act (SDWA).*** *Commonly implemented by authorized states, both CWA and SDWA requirements apply to the management of some Bevill-Bentsen waste. For example, CWA requires that discharges of pollutants to surface waters (e.g., wastewater discharges to a river, bay, or ocean) must be authorized by a permit issued under the National Pollutant Discharge Elimination System (NPDES *) program. Wastewater discharges to publicly owned treatment works (POTWs) are also subject to NPDES permitting requirements. Also, the SDWA regulates subsurface injection of fluids, including wastewater, pursuant to regulations established under the Underground Injection Control (UIC) program."*

NEW TOPIC

See EPA530-R-01-007*and 2005* update

➢ Drivers for Handling Solid Waste Products

❖ RCRA-Land Disposal Restrictions (LDR)

The LDR resulted because many municipal and industrial sites leached contaminates and were creating New superfund sites

Also see FR Vol 63, No. 100, May 26, 1998 pp 28558-753 for latest revisions to LDR for metals UTS*

"The LDR program consists of three main components:

Disposal Prohibition — Requires that waste-specific treatment standards must be met before a waste can be land disposed.

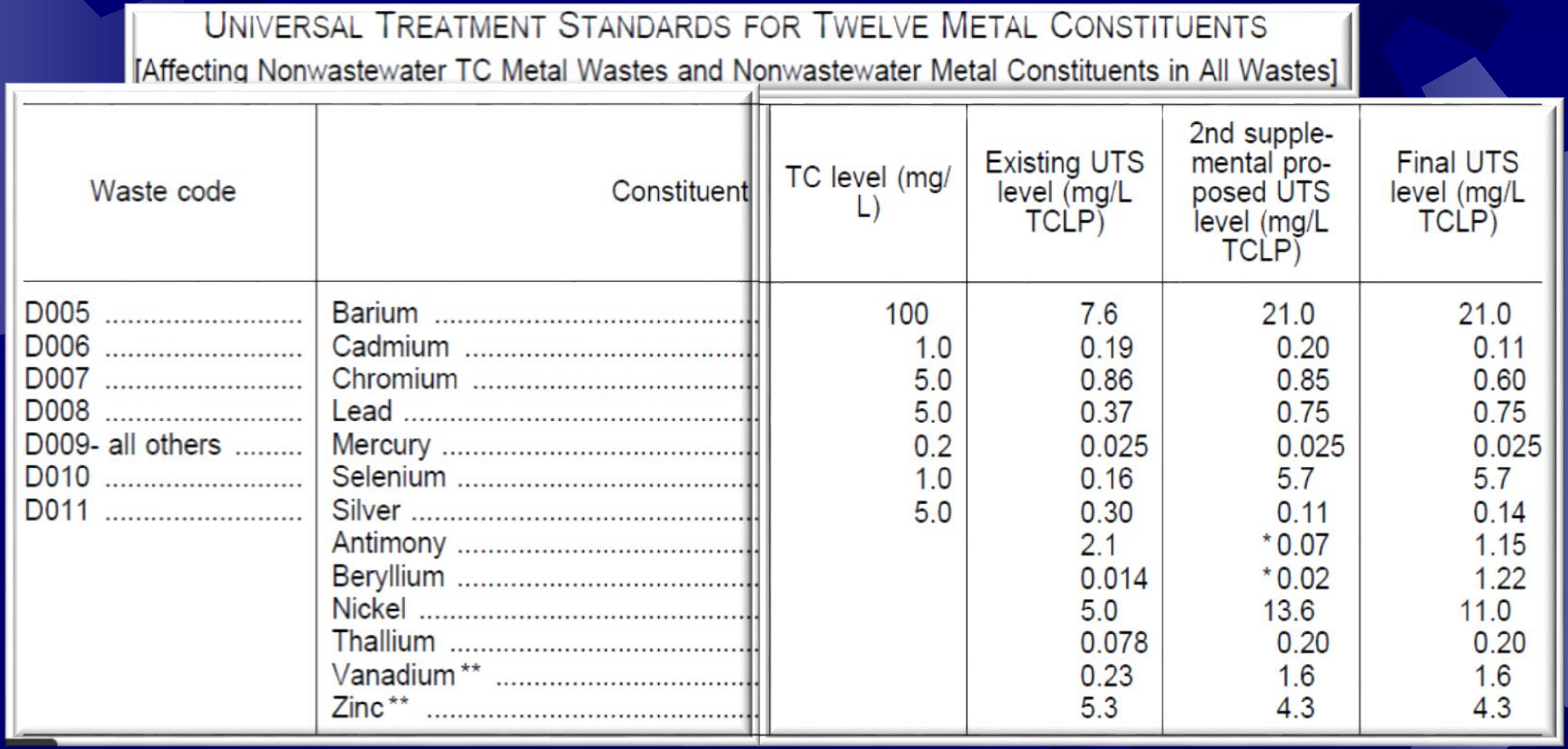
Dilution Prohibition — Ensures that wastes are properly treated and not simply diluted to mask the concentration of hazardous constituents.

Storage Prohibition — Prevents the indefinite storage of hazardous wastes instead of treating the waste promptly.

Together these prohibitions protect human health and the environment by providing for the proper treatment and management of hazardous waste prior to land disposal."

➢ Drivers for Handling Solid Waste Products

- **RCRA-LDR UTS* (Universal Treatment Standards) for Toxicity Characteristic solids promulgated in 1998 based on BDATs** (see comments on next slide)



UNIVERSAL TREATMENT STANDARDS FOR TWELVE METAL CONSTITUENTS

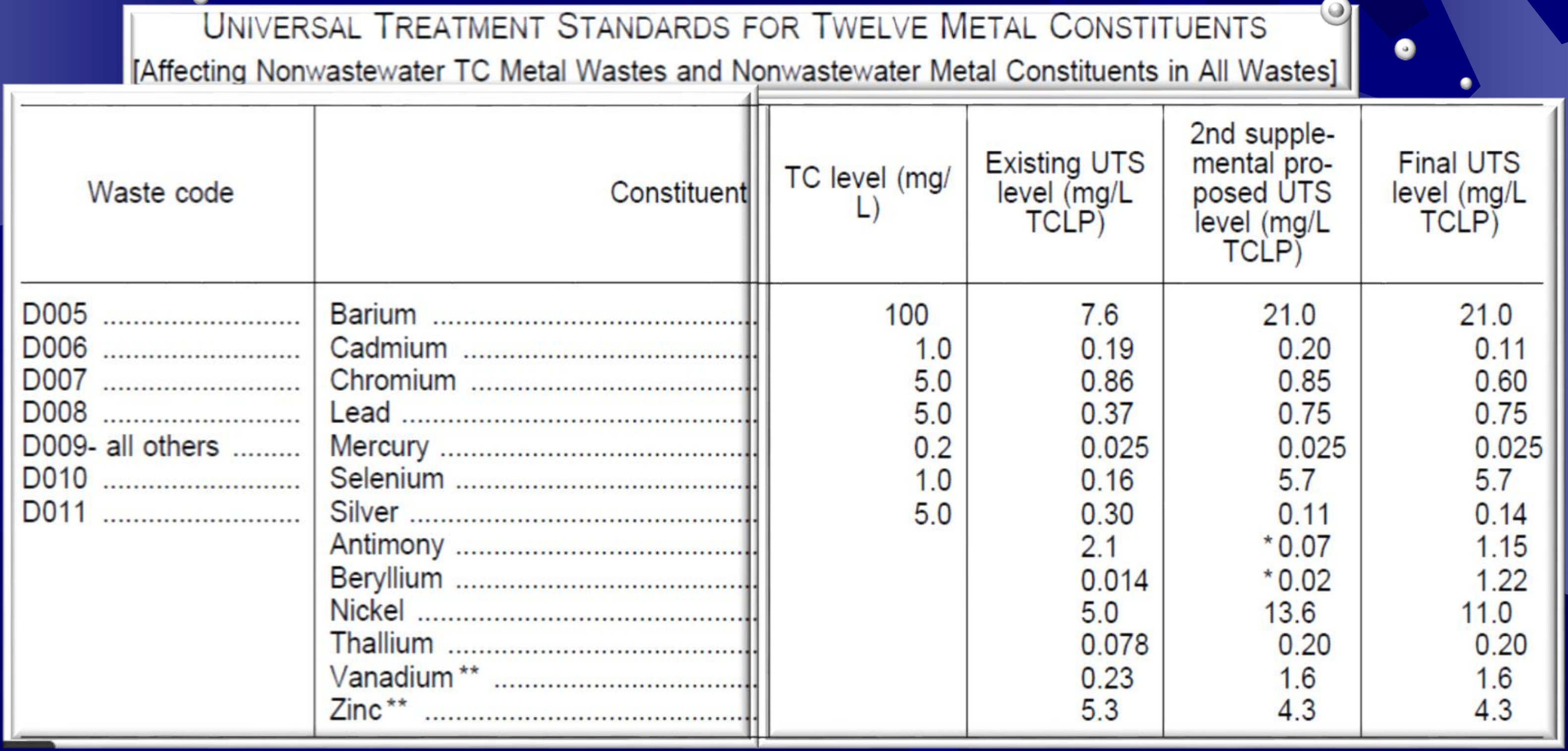
[Affecting Nonwastewater TC Metal Wastes and Nonwastewater Metal Constituents in All Wastes]

Waste code	Constituent	TC level (mg/L)	Existing UTS level (mg/L TCLP)	2nd supplemental proposed UTS level (mg/L TCLP)	Final UTS level (mg/L TCLP)
D005	Barium	100	7.6	21.0	21.0
D006	Cadmium	1.0	0.19	0.20	0.11
D007	Chromium	5.0	0.86	0.85	0.60
D008	Lead	5.0	0.37	0.75	0.75
D009- all others	Mercury	0.2	0.025	0.025	0.025
D010	Selenium	1.0	0.16	5.7	5.7
D011	Silver	5.0	0.30	0.11	0.14
	Antimony		2.1	* 0.07	1.15
	Beryllium		0.014	* 0.02	1.22
	Nickel		5.0	13.6	11.0
	Thallium		0.078	0.20	0.20
	Vanadium **		0.23	1.6	1.6
	Zinc **		5.3	4.3	4.3

➢ Drivers for Handling Solid Waste Products

Note the UTS values are less than the TCLP toxicity requirement levels (except for Se). Also the levels for the last six metals regulated in CA are less but recall the CA leach is in citrate.

So even though a waste solid passes the characteristic element requirement it also must pass the established UTS requirement.



Universal Treatment Standards for Twelve Metal Constituents

[Affecting Nonwastewater TC Metal Wastes and Nonwastewater Metal Constituents in All Wastes]

Waste code	Constituent	TC level (mg/L)	Existing UTS level (mg/L TCLP)	2nd supplemental proposed UTS level (mg/L TCLP)	Final UTS level (mg/L TCLP)
D005	Barium	100	7.6	21.0	21.0
D006	Cadmium	1.0	0.19	0.20	0.11
D007	Chromium	5.0	0.86	0.85	0.60
D008	Lead	5.0	0.37	0.75	0.75
D009- all others	Mercury	0.2	0.025	0.025	0.025
D010	Selenium	1.0	0.16	5.7	5.7
D011	Silver	5.0	0.30	0.11	0.14
	Antimony		2.1	*0.07	1.15
	Beryllium		0.014	*0.02	1.22
	Nickel		5.0	13.6	11.0
	Thallium		0.078	0.20	0.20
	Vanadium **		0.23	1.6	1.6
	Zinc **		5.3	4.3	4.3

NEW TOPIC

Technical Evaluation-General Comments

Example: Selenium solid waste (Se BDAT is vitrification) required by RCRA and LDR

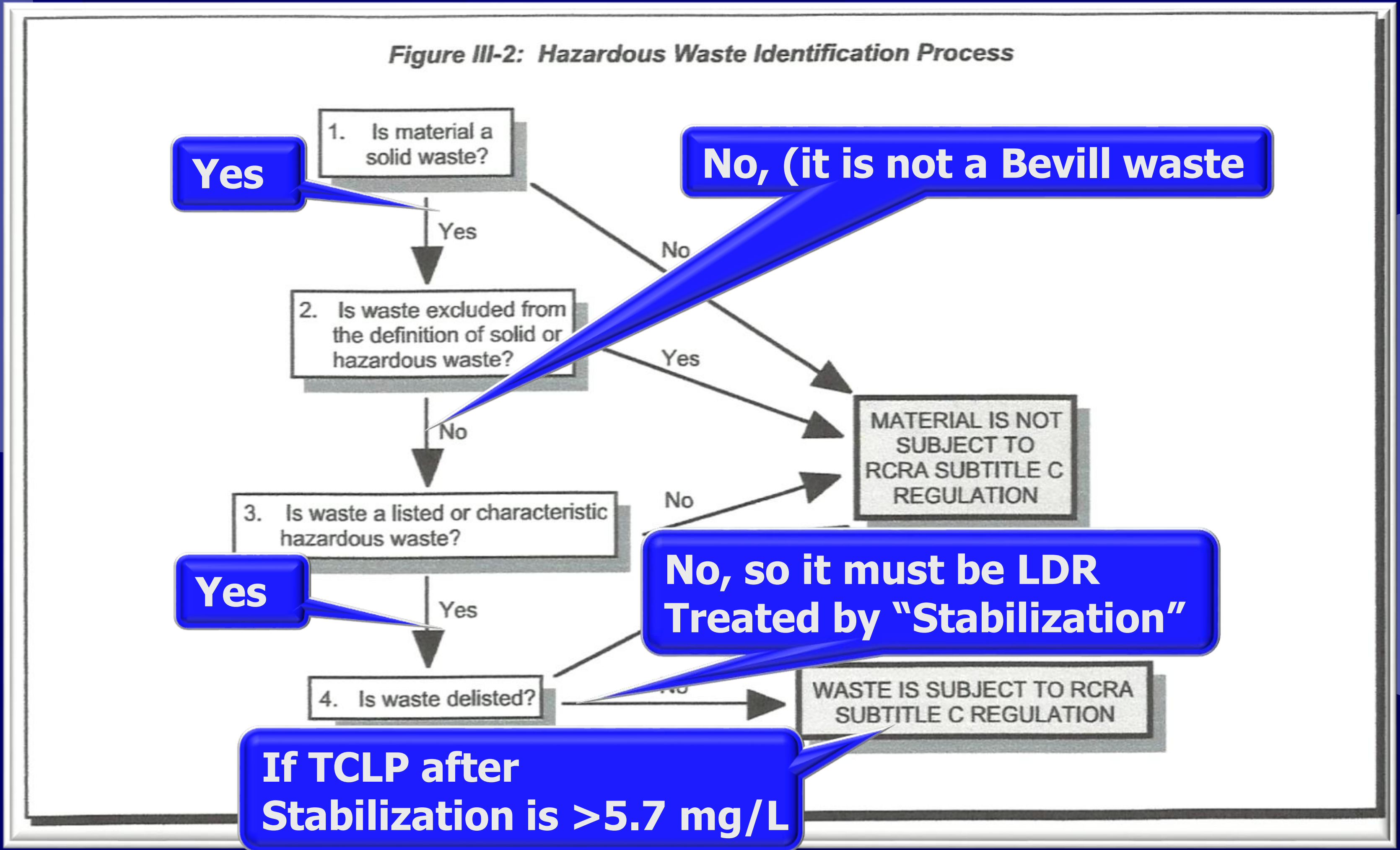


Figure III-2: Hazardous Waste Identification Process

Yes

No, (it is not a Bevill waste

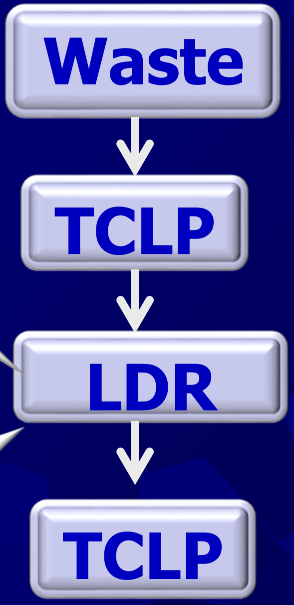
Yes

No, so it must be LDR Treated by "Stabilization"

If TCLP after Stabilization is >5.7 mg/L

Technical Evaluation-General Comments

Example: Selenium solid waste testing required by RCRA and LDR



It has to be Stabilized before disposal. Vitrification is the LDR specification

If>1mg/L it is a "Characteristic" waste

It is considered hazardous

The LDR for selenium is "stabilization"

It can be treated on site or at a permitted TSDF Repository

LDR-UTS requires TCLP of <0.16 mg/L after stabilization treatment. This was Challenged and EPA set the Universal Treatment Standard (UTS) to be 5.7 mg/L for Se waste solids

Variances are possible, e.g. Next slide

Example: Selenium solid waste testing required by RCRA and LDR

Land Disposal Restrictions: Site-Specific Treatment Variance for Hazardous Selenium-Bearing Waste Treated by U.S. Ecology Nevada in Beatty, NV

A Rule by the Environmental Protection Agency on 08/22/2012

ACTION Final Rule.

SUMMARY EPA (or the Agency) is granting a site-specific treatment variance, under the Land Disposal Restrictions program, to U.S. Ecology Nevada in Beatty, Nevada for the treatment of a hazardous selenium-bearing waste generated by the Owens-Brockway Glass Container Company in Vernon, California. The Agency has determined that the chemical properties of the waste generated by the Owens-Brockway Glass Container Corporation differ significantly from the waste used in developing the Land Disposal Restrictions treatment standard for selenium-bearing wastes, and as such cannot be treated to the specified treatment level of 5.7 mg/L for selenium, as measured by the Toxicity Characteristic Leaching Procedure (TCLP). The site-specific treatment variance provides an alternative treatment standard of 59 mg/L TCLP for selenium, with the condition that the waste-to-reagent ratio not exceed 1:0.45.

Publication Date:
Wednesday, August 22, 2012

Agency:
Environmental Protection Agency

Dates:
This final rule will be effective August 22, 2012.

Effective Date:
08/22/2012

Entry Type:

Variances*
Are possible

Variances*
second
reference

LDR-UTS requires TCLP of <0.16 mg/L after stabilization treatment. This was Challenged and EPA set the Universal Treatment Standard (UTS) to be 5.7 mg/L for Se waste solids

EPA United States Environmental Protection Agency

Guest Lecture

by

This presentation
is available by
Contacted Mr. Coleman

Charles Coleman
Remedial Project Manager
EPA Region 8, Montana
Coleman.Charles@epa.gov

Case Study #1
NPL Site in Anaconda Montana

LECTURE 5

Summary of RC rements

NEW TOPIC

Subtitle C (hazar ous waste) Repositories

Hazardous "Characteristic" or "Listed"

These facilities must be Certified, Permitted, and Regulated by EPA

Or in some cases by states.

Treatment Storage Disposal Facilities (TSDF*)

Solid wastes may be:

- ✓ Disposed of in **Subtitle C** landfill; or
- ✓ Treated and disposed of in **Subtitle C** landfill; or
- ✓ Treated and disposed of in **Subtitle D** landfill

If it doesn't pass LDR

If it passes LDR-UTS

Summary of RCRA Requirements

Subtitle C (hazardous waste) Repositories

Treatment Storage Disposal Facilities (TSDF)

What if the waste can't achieve the requirement of LDR-UTS?? Can it be landfilled??

Very Important: "The U.S. EPA LDRs state that **"no-migration"** can be considered a proper LDR land disposal technology **(EPA 530-K-05-013, p12)**:

"Waste handlers can land dispose hazardous wastes subject to LDR in a land-based unit **without meeting treatment standards**, if a petitioner can demonstrate that there will be **no migration** of hazardous constituents from the unit for as long as the waste remains hazardous (§268.6). EPA interprets "no migration" to mean that constituents will not leave the unit boundary at concentrations above Agency-approved health-based levels. EPA may grant a **no-migration variance for up to 10 years**, but may not extend the variance beyond the term of the particular disposal unit's RCRA permit."

Subtitle C (hazardous waste) Repositories

Treatment Storage Disposal Facilities (TSDF)

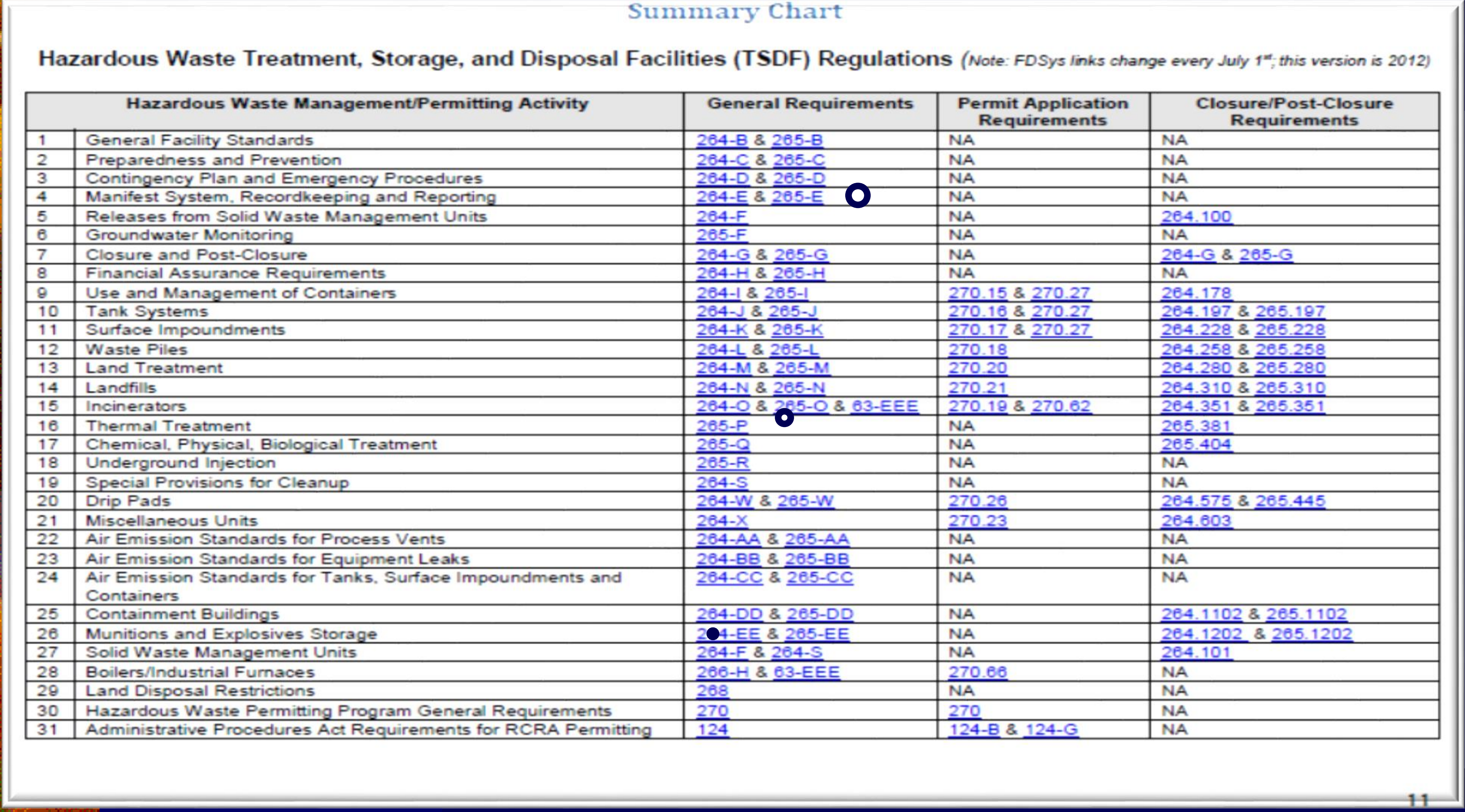
Solid hazardous wastes can be accepted:

- **As a “characteristic” or “listed” waste which is treated by the TSD facility to pass the LDR, or**
- **Treated by your company to pass the LDR**

An extensive U.S. EPA document tool that provides guidance to documentation of the rules for the generation and regulation of hazardous waste in the U.S. is available and is **highly recommended**, i.e. ***Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) Regulations: A User-Friendly Reference Document for RCRA, Subtitle C Permit Writers and Permittees, October 2014 (EPA 530-R-11-006*, Version 4)***.

Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) Regulations: A User-Friendly Reference Document for RCRA, Subtitle C Permit Writers and Permittees, October 2014 (EPA 530-R-11-006, Version 4).

When you get this EPA Document downloaded the sections are Hyperlinked to the descriptive document



Summary Chart

Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) Regulations *(Note: FDSys links change every July 1st; this version is 2012)*

	Hazardous Waste Management/Permitting Activity	General Requirements	Permit Application Requirements	Closure/Post-Closure Requirements
1	General Facility Standards	264-B & 265-B	NA	NA
2	Preparedness and Prevention	264-C & 265-C	NA	NA
3	Contingency Plan and Emergency Procedures	264-D & 265-D	NA	NA
4	Manifest System, Recordkeeping and Reporting	264-E & 265-E	NA	NA
5	Releases from Solid Waste Management Units	264-F	NA	264.100
6	Groundwater Monitoring	265-F	NA	NA
7	Closure and Post-Closure	264-G & 265-G	NA	264-G & 265-G
8	Financial Assurance Requirements	264-H & 265-H	NA	NA
9	Use and Management of Containers	264-I & 265-I	270.15 & 270.27	264.178
10	Tank Systems	264-J & 265-J	270.16 & 270.27	264.197 & 265.197
11	Surface Impoundments	264-K & 265-K	270.17 & 270.27	264.228 & 265.228
12	Waste Piles	264-L & 265-L	270.18	264.258 & 265.258
13	Land Treatment	264-M & 265-M	270.20	264.280 & 265.280
14	Landfills	264-N & 265-N	270.21	264.310 & 265.310
15	Incinerators	264-O & 265-O & 63-EEE	270.19 & 270.62	264.351 & 265.351
16	Thermal Treatment	265-P	NA	265.381
17	Chemical, Physical, Biological Treatment	265-Q	NA	265.404
18	Underground Injection	265-R	NA	NA
19	Special Provisions for Cleanup	264-S	NA	NA
20	Drip Pads	264-W & 265-W	270.26	264.575 & 265.445
21	Miscellaneous Units	264-X	270.23	264.603
22	Air Emission Standards for Process Vents	264-AA & 265-AA	NA	NA
23	Air Emission Standards for Equipment Leaks	264-BB & 265-BB	NA	NA
24	Air Emission Standards for Tanks, Surface Impoundments and Containers	264-CC & 265-CC	NA	NA
25	Containment Buildings	264-DD & 265-DD	NA	264.1102 & 265.1102
26	Munitions and Explosives Storage	264-EE & 265-EE	NA	264.1202 & 265.1202
27	Solid Waste Management Units	264-F & 264-S	NA	264.101
28	Boilers/Industrial Furnaces	266-H & 63-EEE	270.66	NA
29	Land Disposal Restrictions	268	NA	NA
30	Hazardous Waste Permitting Program General Requirements	270	270	NA
31	Administrative Procedures Act Requirements for RCRA Permitting	124	124-B & 124-G	NA

Treatment Storage Disposal Facility (TSDF)

"The Federal Definition of a TSD Facility, according to 40 CFR 260.10, is a facility that performs one or more of the following functions:

Treatment -- Any method, technique, or process, including neutralization, designed to change the physical, chemical, or biological character or composition of any hazardous waste so as to neutralize such waste, or so as to recover energy or material resources from the waste, or so as to render such waste non-hazardous, or less hazardous; safer to transport, store, or dispose of; or amenable for recovery, amenable for storage, or reduced in volume.

Storage -- The holding of hazardous waste for a temporary period, at the end of which the hazardous waste is treated, disposed of, or stored elsewhere.

Disposal -- The discharge, deposit, injection, dumping, spilling, leaking, or placing of any solid waste or hazardous waste into or on any land or water so that such solid waste or hazardous waste or any constituent thereof may enter the environment or be emitted into the air or discharged into any waters, including ground waters."

Example Commercial TDS Facilities (Clear Harbor)

TSDF sites:

- AZ
- CA (2)
- FL
- IL
- KS
- LA
- MA
- MD
- NC
- OH
- TX

Ultimate and Fail-Safe Waste Disposal

Clean Harbors thoroughly audits and routinely inspects all sites to ensure that final disposal is conducted in full compliance with all applicable regulations. Sites are state-of-the-art and fully engineered with sophisticated liner and leachate collection systems. Continuous monitoring, as well as strong financial mechanisms, protects Clean Harbors and our customers from future liabilities. An extensive waste history for each site is maintained by Clean Harbors.

Example Commercial TDS Facility Cost Rate Sheet (Clear Harbor)

Part A: GENERAL HAZARDOUS WASTE DISPOSAL SERVICE PRICE

SERVICE ITEM K PRICE SHEET (Added September 2, 2010)
CHEMICAL WASTE MANAGEMENT/ARLINGTON

No.	Description	Units	Shipping	Disposal Fee
	Sub C Landfill			
1	**RCRA Hazardous Solids** - Direct Landfill, F-listed waste codes	Ton	$5.43 /mi.	**$166** ✸
3	**Non-Hazardous Solids** - Direct Landfill, Waste Treated prior to arrival at CWM so the waste no longer exhibits the hazardous characteristic (D004 - D011)	Ton	$5.43 /mi.	**$91** ✸
7	**RCRA Stabilization** - Bulk Solid, Liquid, Sludge-Sub C Disposal, Metals Waste for Stabilization Treatment (RCRA D004-D011 Codes) requiring Sub C disposal.	Ton	$5.43 /mi.	**$194** ✸
8	**Bioremediation** – Bulk Solid, listed codes only, spill clean-up/remediation.	Ton	$5.43 /mi.	**$456** ✸
9	**Macroencapsulation**, Material requiring Macro Encapsulation.	Cubic yard	$5.43 /mi.	**$267**
10	**Microencapsulation**, Material requiring Micro Encapsulation.	Cubic yard	$5.43 /mi.	**$209**

Class C Hazardous Waste Repository Requirements

The following conditions must be established in the storage system:

a. Chemical and physical isolation from the surrounding environment, migration of toxic constituents cannot be allowed

b. Protection of the waste from contacting water sources, surface and groundwater, storm events

c. Institutional controls so that limitations are placed on access to the site by people and animals

d. Monitoring to ensure that migration of toxic constituents can be detected if release does occur

e. Have a manifest and recordkeeping plan

f. Emergency contingency plans are in place in case an unexpected migration does occur

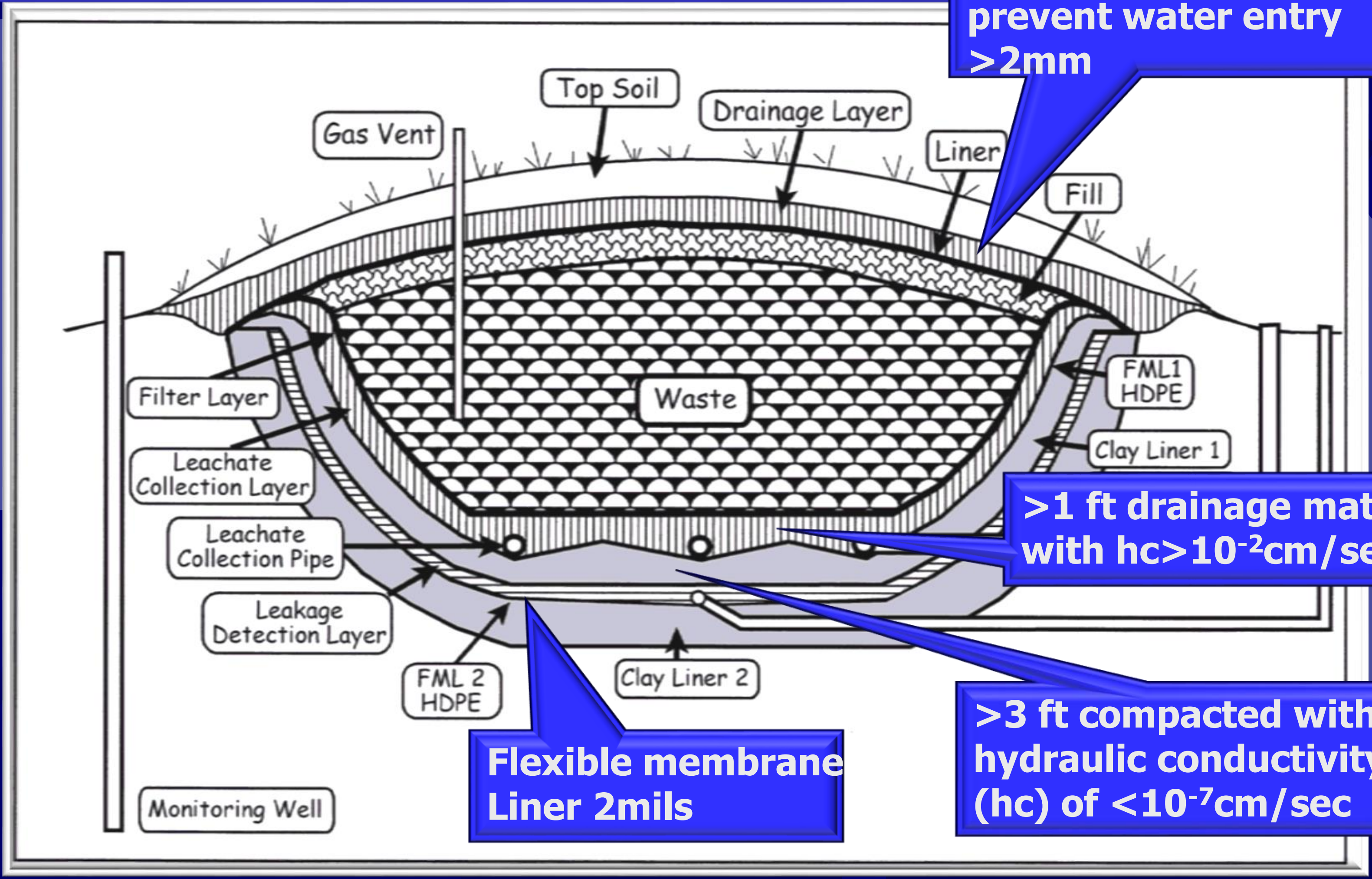
g. Personnel training programs for preparedness to minimize and prevent emergency situations

h. Personnel health and safety plan

i. Local authority notification plan in case of emergency situations

Class C Hazardous Waste Repository Requirements (What does a storage cell look like?)

40 CFR 264.301



Geotechnical layer to prevent water entry >2mm

>1 ft drainage material with hc>10^{-2}cm/sec

Flexible membrane Liner 2mils

>3 ft compacted with hydraulic conductivity (hc) of <10^{-7}cm/sec

Class D Non-hazardous Waste (Montana Local Example)

"**Flue Dust Operable Unit, Montana** - EMC^2 staff developed the design and provided construction quality assurance oversight for treatment and impoundment of 500,000 cubic yards of hazardous copper smelting waste at this site. The waste was treated using cement/lime stabilization prior to placement ina modified **RCRA Subtitle D repository**. Design work included repository siting investigations; stabilization mix determination; repository slope stability, settlement and infiltration evaluations; surface water drainage and erosion control; groundwater monitoring; and material suitability/quantity determinations. EMC^2 staff subsequently provided construction quality assurance oversight during construction of the waste repository including liner inspection and testing, field geotechnical testing and construction documentation."

"**OU 11 Flue Dust (EPA 5 Year Monitoring Review*, 2010)**
The remedy for the Flue Dust OU currently protects human health and the environment because there is no current direct exposure to treated waste materials. Flue dust, a principal threat waste at the site, was treated to below TCLP standards for arsenic cadmium and lead and placed in an engineered repository. Active monitoring and maintenance of the site is currently conducted and site access is controlled by fencing, gates and security. However, unexpected leachate continues to be collected from the repository. In order for the remedy to remain protective in the long-term, the repository must meet the performance requirements. It is recommend that additional action be taken to determine if the repository liner and cap are functioning as designed and determine if additional remedial action is necessary."

NEW TOPIC

- **CERCLA** (Comprehensive Environmental Response, Compensation and Liability Act 1980); **Superfund Act**

An act passed in 1980 to address the need to clean up toxic constituent releases from TSD industrial sites and leaking Municipal sites

Administered by EPA's Office of Solid Waste and Emergency Response

➢ CERCLA (Comprehensive Environmental Response, Compensation and Liability Act 1980); Superfund Act

Enabling Legislation:
SARA (Superfund Amendments and Reauthorization Act, 1996); sets remedial requirements using ARARs* (Applicable or Relevant and Appropriate Requirements)

What's the difference??

Applicable: "an applicable requirement is one with which a private party would have to comply by law if the same action was being undertaken apart from CERCLA authority. All jurisdictional prerequisites of the requirement must be met in order for the requirement to be applicable"

This is what happened at the Anaconda Flue Dust Operable Unit, e.g. The flue dust was a characteristic waste, it was stabilized with cement/lime, passed the LDR so was deemed non-hazardous and it could have been disposed of in a Class D repository.

Applicable: "an applicable requirement is one with which a private party would have to comply by law if the same action was being undertaken apart from CERCLA authority. All jurisdictional prerequisites of the requirement must be met in order for the requirement to be applicable"

Relevant and Appropriate:
"A requirement that is relevant and appropriate may "miss" on one or more jurisdictional prerequisites for applicability but still make sense at the site, given the circumstances of the site and release."

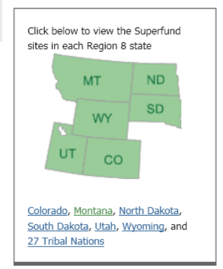
However the ARAR requirements were deemed appropriate because of it high As and Cd content so the stabilized product was required to be disposed of in a "modified" Class D repository that essentially had all the features of a Class C hazardous requirements.

(see EPA/ROD/R08-91-053*, Sept 1991, page 21)

➢ **CERCLA** (Comprehensive Environmental Response, Compensation and Liability Act 1980); Superfund* Act

Implemented within 10 regions

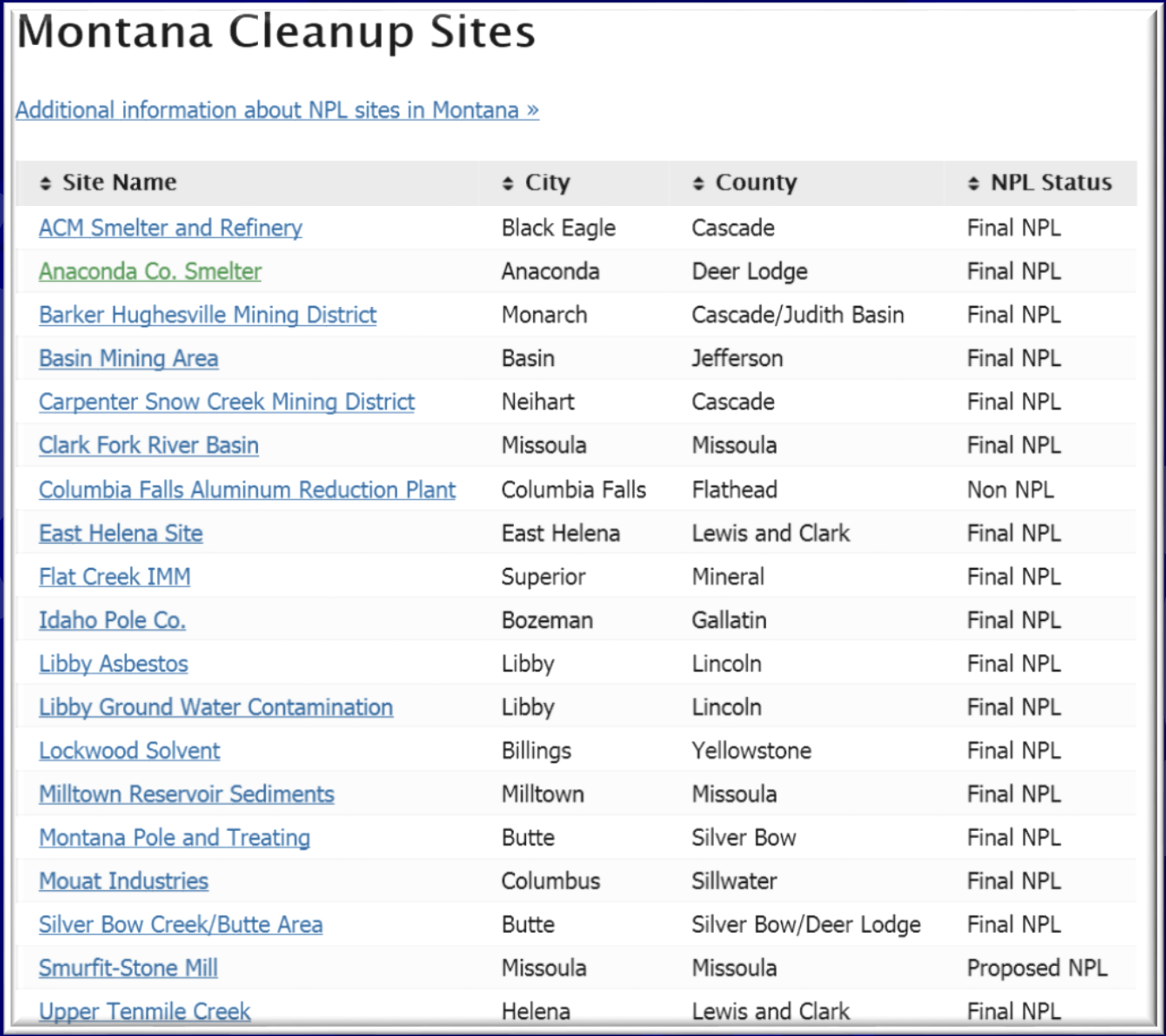
Region 1--ME NH VT MA RI CT
Region 2--NY NJ PR VI
Region 3--PA DE DC MD VA WV
Region 4--KY TN NC SC MS AL GA FL
Region 5--MN WI IL MI IN OH
Region 6--NM TX OK AR LA
Region 7--NE KS IA MO
Region 8--MT ND WY SD UT CO
Region 9--CA NV AZ HI
Region 10--WA OR ID AK


Click below to view the Superfund sites in each Region 8 state

Colorado, Montana, North Dakota, South Dakota, Utah, Wyoming, and 27 Tribal Nations

Headquarters In Denver

Example of Montana NPL sites



Montana Cleanup Sites

Additional information about NPL sites in Montana »

⬍ Site Name	⬍ City	⬍ County	⬍ NPL Status
ACM Smelter and Refinery	Black Eagle	Cascade	Final NPL
Anaconda Co. Smelter	Anaconda	Deer Lodge	Final NPL
Barker Hughesville Mining District	Monarch	Cascade/Judith Basin	Final NPL
Basin Mining Area	Basin	Jefferson	Final NPL
Carpenter Snow Creek Mining District	Neihart	Cascade	Final NPL
Clark Fork River Basin	Missoula	Missoula	Final NPL
Columbia Falls Aluminum Reduction Plant	Columbia Falls	Flathead	Non NPL
East Helena Site	East Helena	Lewis and Clark	Final NPL
Flat Creek IMM	Superior	Mineral	Final NPL
Idaho Pole Co.	Bozeman	Gallatin	Final NPL
Libby Asbestos	Libby	Lincoln	Final NPL
Libby Ground Water Contamination	Libby	Lincoln	Final NPL
Lockwood Solvent	Billings	Yellowstone	Final NPL
Milltown Reservoir Sediments	Milltown	Missoula	Final NPL
Montana Pole and Treating	Butte	Silver Bow	Final NPL
Mouat Industries	Columbus	Sillwater	Final NPL
Silver Bow Creek/Butte Area	Butte	Silver Bow/Deer Lodge	Final NPL
Smurfit-Stone Mill	Missoula	Missoula	Proposed NPL
Upper Tenmile Creek	Helena	Lewis and Clark	Final NPL

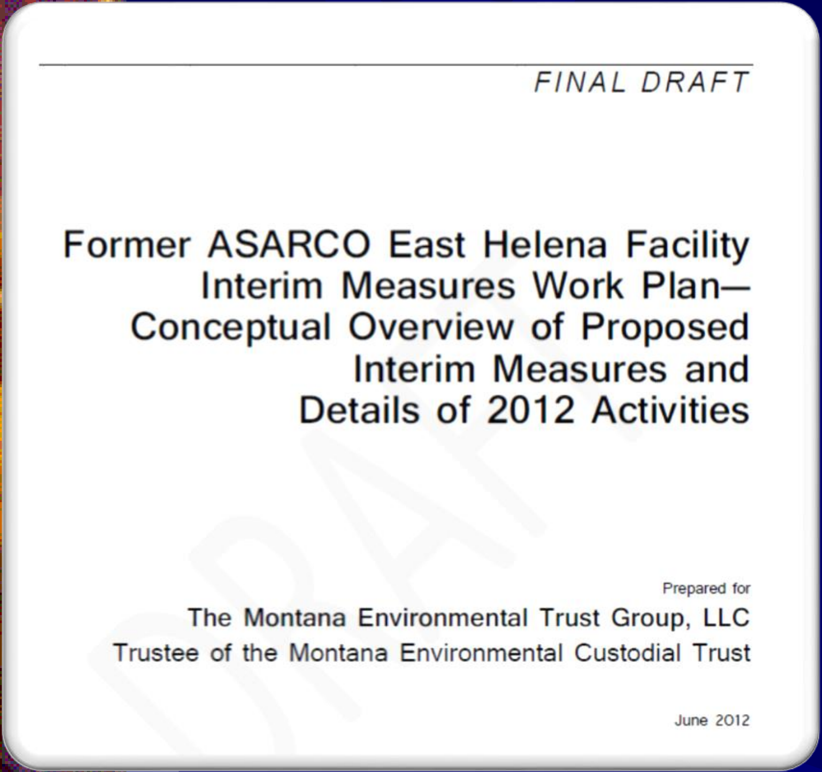
NPL (National Priority List)

As of 2013 1,389 sites now have exposure under control and 1091 sites have contaminated groundwater migration under control; 69% of all identified NPL sites have been remediated.

The following table shows the number of Federal and general sites for each status and milestone as of December 03, 2014:

Status	Non-Federal (General)	Federal	Total
Proposed Sites	**45**	4	49
Final Sites	1164	157	1321
Deleted Sites	368	17	385

EXAMPLE NPL SITE (ASARCO East Helena Site)

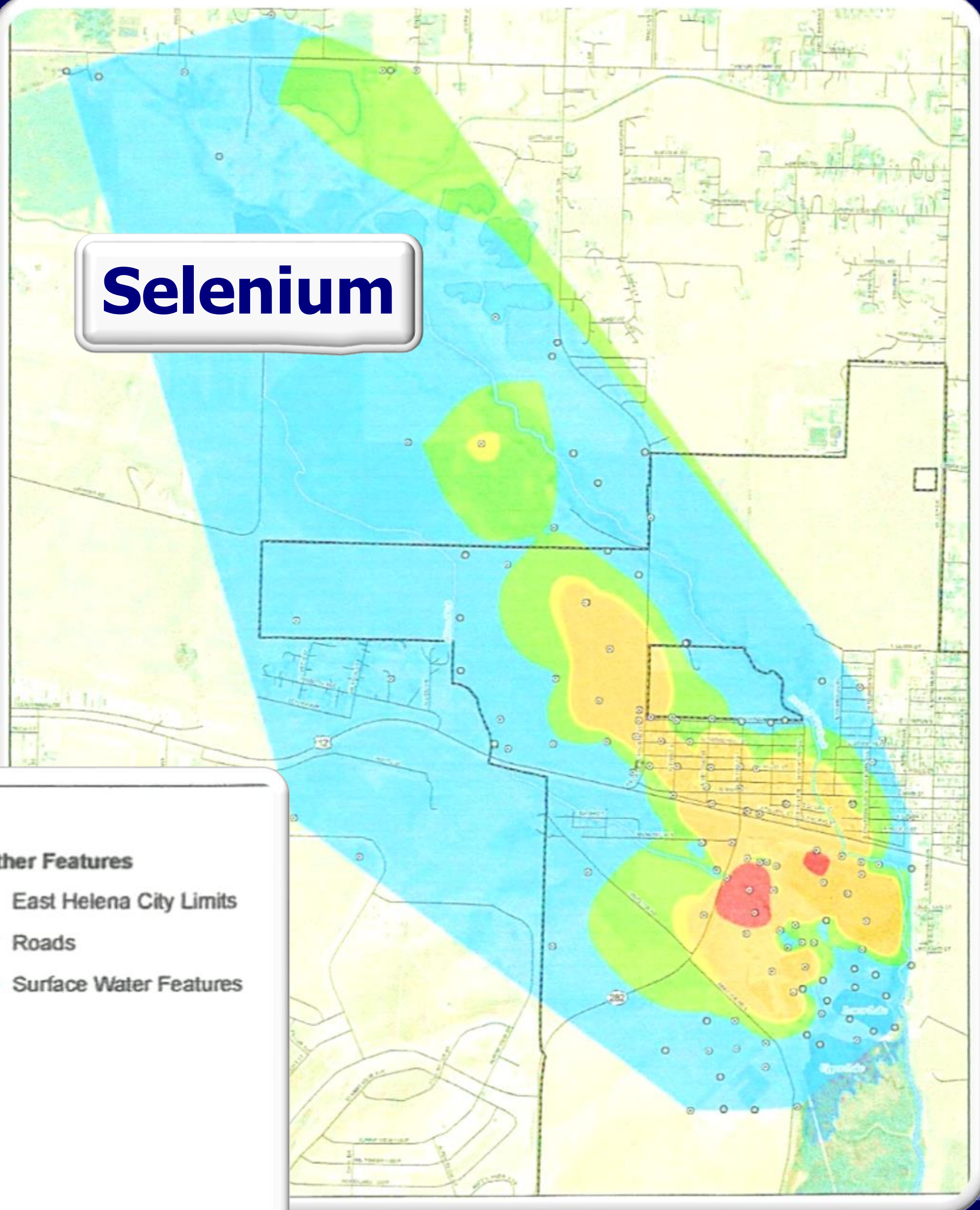


FINAL DRAFT

Former ASARCO East Helena Facility
Interim Measures Work Plan—
Conceptual Overview of Proposed
Interim Measures and
Details of 2012 Activities

Prepared for
The Montana Environmental Trust Group, LLC
Trustee of the Montana Environmental Custodial Trust

June 2012



Selenium

LEGEND

Selenium Concentrations (mg/L)

- 🟪 >6
- 🟥 >0.6 - 6
- 🟧 >0.06 - 0.6
- 🟨 >0.05 - 0.06
- 🟩 >0.012 - 0.05
- 🟦 >0.0006 - 0.012
- 🟦 <0.0006

Groundwater Monitoring Locations

- ⊙ Detect
- ○ Non-Detect

Regional Groundwater Background Concentration for Selenium is 0.006

All Other Features

- East Helena City Limits
- Roads
- Surface Water Features

MAP NOTES:
Date: April 26, 2011
Data Sources: Hydrometrics, USGS, Lewis and Clark County GIS

Arsenic

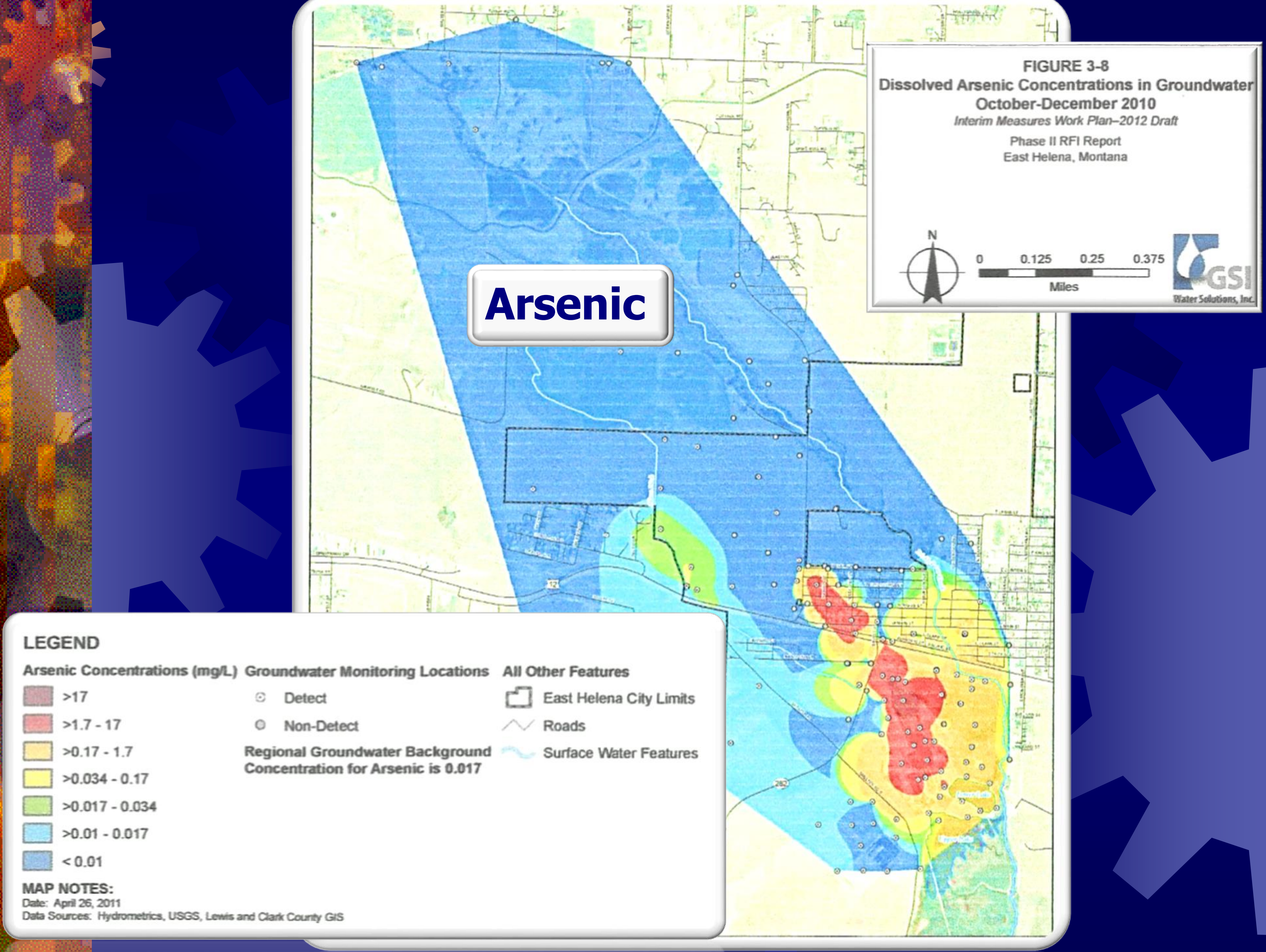


FIGURE 3-8
Dissolved Arsenic Concentrations in Groundwater
October-December 2010
Interim Measures Work Plan–2012 Draft
Phase II RFI Report
East Helena, Montana

LEGEND

Arsenic Concentrations (mg/L)
- 🟥 >17
- 🟥 >1.7 - 17
- 🟧 >0.17 - 1.7
- 🟨 >0.034 - 0.17
- 🟩 >0.017 - 0.034
- 🟦 >0.01 - 0.017
- 🟦 < 0.01

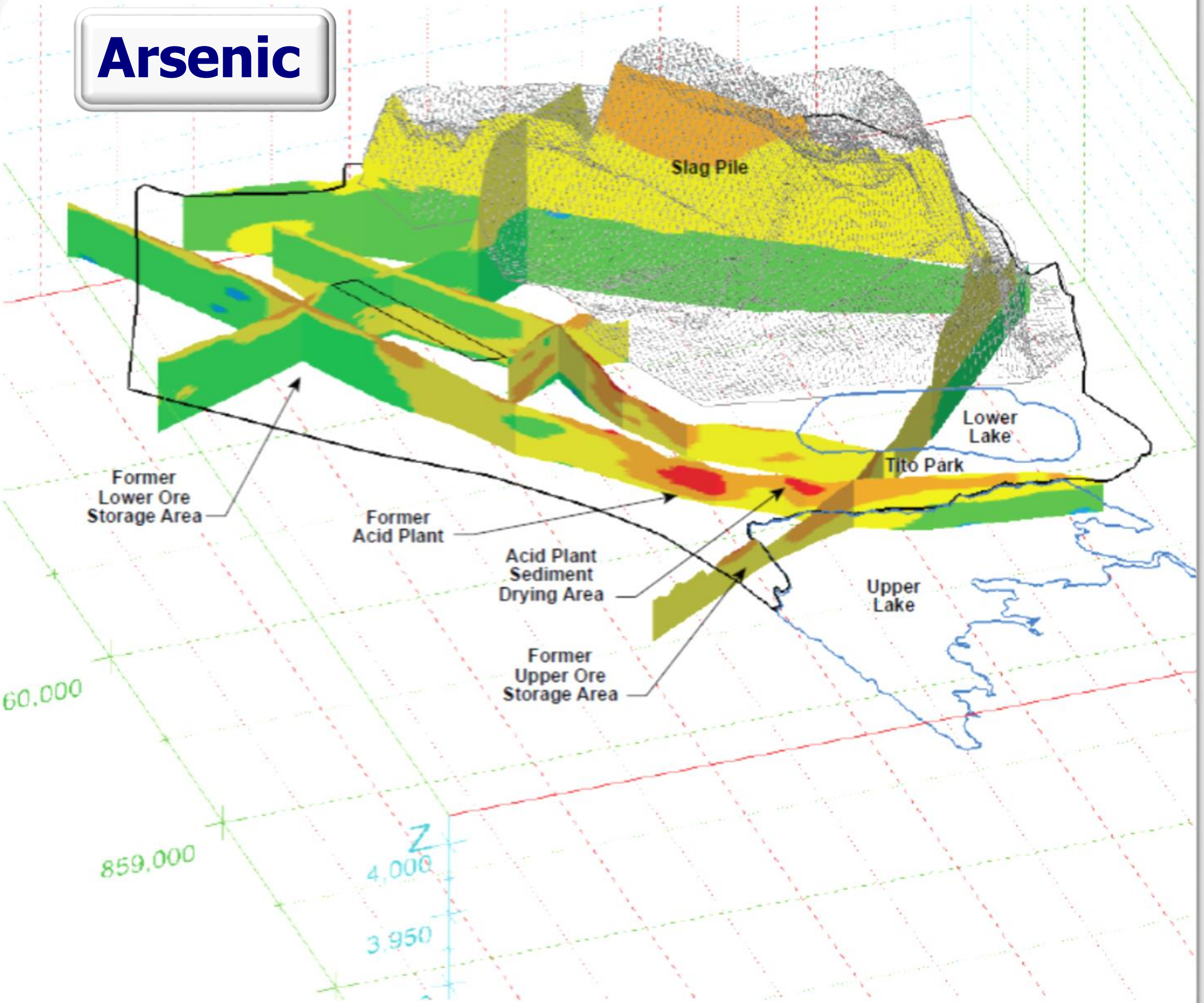
Groundwater Monitoring Locations
- ⊙ Detect
- ● Non-Detect

Regional Groundwater Background Concentration for Arsenic is 0.017

All Other Features
- ☐ East Helena City Limits
- Roads
- Surface Water Features

MAP NOTES:
Date: April 26, 2011
Data Sources: Hydrometrics, USGS, Lewis and Clark County GIS

Arsenic



LEGEND

Arsenic Concentrations

- 🟦 Dark Blue: <0.29 mg/kg
- 🟦 Light Blue: 0.29 - 2.9 mg/kg
- 🟩 Green: 2.9 - 40 mg/kg
- 🟨 Yellow: 40 - 290 mg/kg
- 🟧 Orange: 290 - 2,900 mg/kg
- 🟥 Red: >2,900 mg/kg

Abbreviation:
mg/kg = milligrams per kilogram

FIGURE 3-4
Arsenic Contamination in Soil – Surface to Top of Tertiary Ash/Clay Layer
Interim Measures Work Plan–2014
East Helena, Montana

NEW TOPIC

Identifies who is/are responsible and who must pay, i.e. PRPs (Principal Responsible Parties)

NPL* Site Listing Process

Six Staged Process used to identify and clean-up sites

1. PA/SI-Preliminary Assessment/Site Inspection
   Investigations of site conditions. If the release of hazardous substances requires immediate or short-term response actions, these are addressed under the Emergency Response program of Superfund.

   HRS (Hazardous Ranking System, 1990) of Superfund.
   - Anyone or group can petition for the addition of a Problem site. If selected then the PA/SI Preliminary Process is initiated.
   - Risk is determined based on:
     - Potential for release of hazardous substances
     - Characteristics of the waste (toxicity, quantity)
     - People affected by the release

NPL Process

Evaluates a list of possible Alternative treatments with respect to technical success and treatment costs

2. RI/FS*-Remedial Investigation/Feasibility Study

Determines the nature and extent of contamination. Assesses the treatability of site contamination and evaluates the potential performance and cost of treatment technologies.

Often requires extensive Analytical characterization

Many companies contract to do these investigations

NPL Process

The ROD is a legal document
Stating who will perform and,
in some cases, to pay
for the cleanup

3. ROD-Records of Decision
Explains which **cleanup alternatives** will be used at the site or sites. When remedies exceed 25 million, they are reviewed by the National Remedy Review Board.

4. RD/RA-Remedial Design/Remedial Action
Preparation and implementation of plans and specifications for applying site remedies. The bulk of the cleanup usually **occurs during this phase**. All new fund-financed remedies are reviewed by the National Priorities Panel.

5. Construction Completion
Identifies completion of physical cleanup construction, although this does not necessarily indicate whether final cleanup levels have been achieved.

NPL Process

Extensive!

Extensive!

Extensive!

6. Post Construction Completion

Ensures that Superfund response actions provide for the long-term protection of human health and the environment. Included here are Long-Term Response Actions (LTRA), Operation and Maintenance, Institutional Controls, Five-Year Reviews, Remedy Optimization.

7. NPL Delete-National Priorities List Deletion

Removes a site from the NPL once all response actions are complete and all cleanup goals have been achieved.

NEW TOPIC

LECTURE7

➢Case Studies (to be considered)

As

- Arsenic Stabilization
  1) Ferrihydrite (most used technology throughout the world)
  2) Scorodite (best for high concentrations of arsenic)
  3) Arsenic Trisulfide
  4) Whitmoyer NPL Site Remediation
  5) Sherwin Williams Emeryville Remediation
- Recycle of Mercury for alkali Plants

Hg

- Case Studies

As

- Arsenic Stabilization

1. Ferrihydrite (most used technology throughout the world)

Background

As

Dr. Arsenic

R.G. Robins
Emeritus Prof.

Lime Precipitation

- Widely used for metal cations removal but don’t use for arsenic removal!!

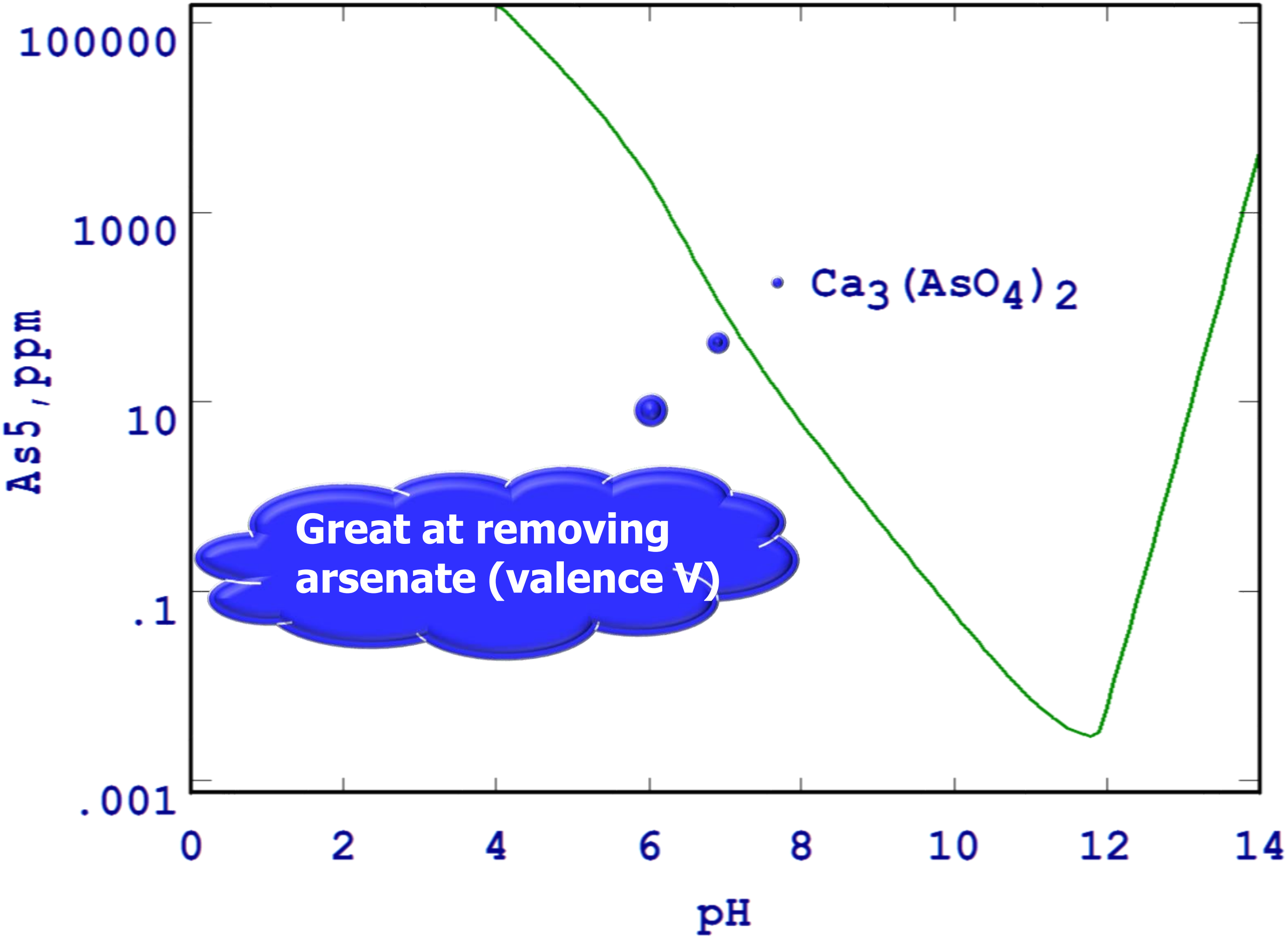
Arsenic Compounds formed are not stable in outdoor storage ponds. The compounds react with carbon dioxide in air to form calcium carbonate.

$$CO_{2(\text{in air})} + H_2O = CO_3^{-2} + 2H^+$$

$$Ca_3(AsO_4)_2 + 3CO_3^{-2} = 3CaCO_3 + 2AsO_4^{-3}$$

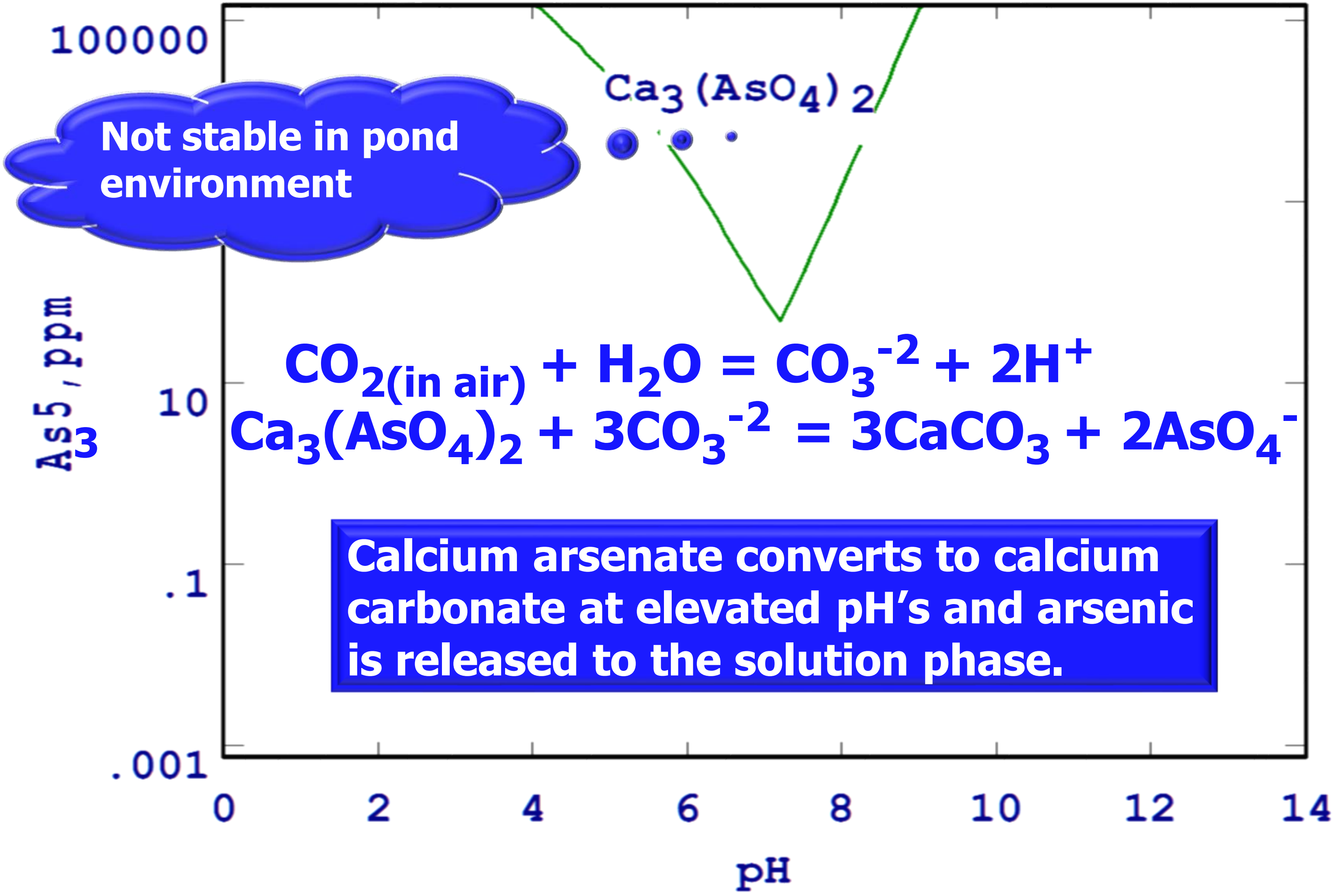
pH>8.2

CALCIUM ARSENATE SOLUBILITY



Great at removing arsenate (valence V)

CALCIUM ARSENATE INSTABILITY IN AIR



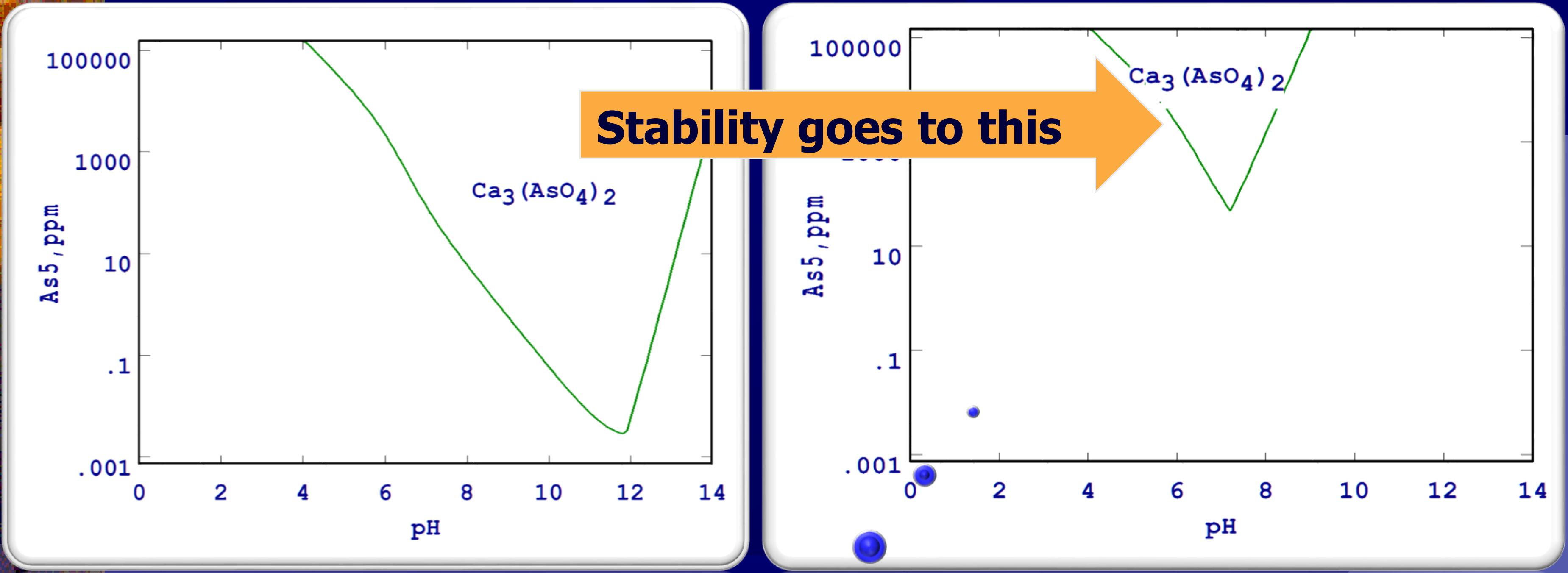
Not stable in pond environment

$$CO_{2(in\ air)} + H_2O = CO_3^{-2} + 2H^+$$

$$Ca_3(AsO_4)_2 + 3CO_3^{-2} = 3CaCO_3 + 2AsO_4^-$$

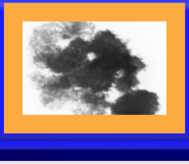
Calcium arsenate converts to calcium carbonate at elevated pH's and arsenic is released to the solution phase.

CALCIUM ARSENATE INSTABILITY IN AIR



Stability goes to this

Therefore, not used anymore. Ferrihydrite process has
Replaced lime precipitation as the best approach.



Introduction

Arsenic adsorption on ferrihydrite is EPA's designated Best Demonstrated Available Technology (BDAT) for removing arsenic from process and wastewater.

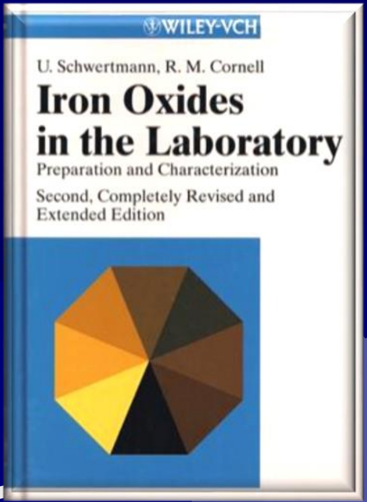
It is also designated by EPA as one of the Best Available Technologies (BAT) for treating arsenic bearing drinking water.

It is the **most** widely used arsenic removal technology in the world.

Ferrihydrite Literature

Ferrihydrite

Important reviews detailing conditions for formation and the stability of ferrihydrite are presented by Jambor and Dutrizac [1998], Schwertmann and Cornell [1996, 2000] and Cornell and Schwertmann [2003].

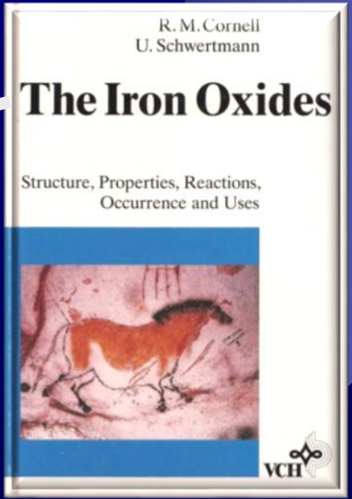

WILEY-VCH

U. Schwertmann, R. M. Cornell

Iron Oxides in the Laboratory

Preparation and Characterization

Second, Completely Revised and Extended Edition


R. M. Cornell
U. Schwertmann

The Iron Oxides

Structure, Properties, Reactions, Occurrence and Uses

VCH

Ferrihydrite Literature

What is Ferrihydrite?

Often referred to as ferric oxyhydroxide, amorphous ferric oxide, hydrated ferric oxide (HFO) or simply as ferric hydroxide.

Paktunc, Dutrizac, V. Gertsmann, et al. [2008] suggest the formula $5Fe_2O_3{:}9H_2O$.

Hydrated hematite

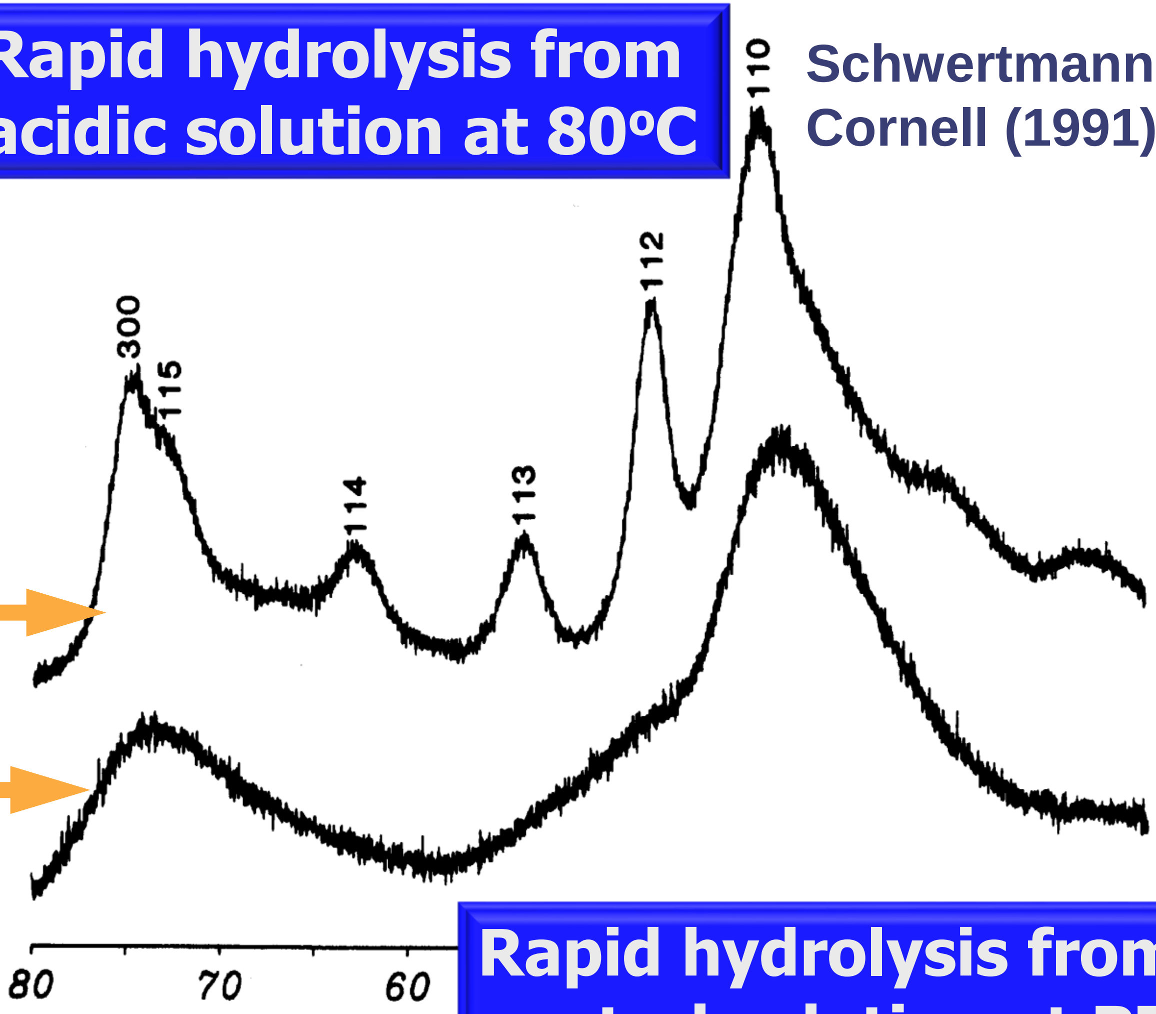
Ferrihydrite Literature

What is Ferrihydrite?

It is a large surface area, solid phase precursor to goethite (FeOOH) and/or hematite Fe2O3). It is a nanocrystalline material. Crystallite sizes have been reported to be 1-4 nm and 5-6 nm for 2-line and 6-line ferrihydrite, respectively.

Our study by Hohn showed a 1-2 nm particle size

XRD patterns



Schwertmann & Cornell (1991)

Rapid hydrolysis from acidic solution at 80ºC

6-line

2-line

Rapid hydrolysis from neutral solution at RT

Ferrihydrite Literature

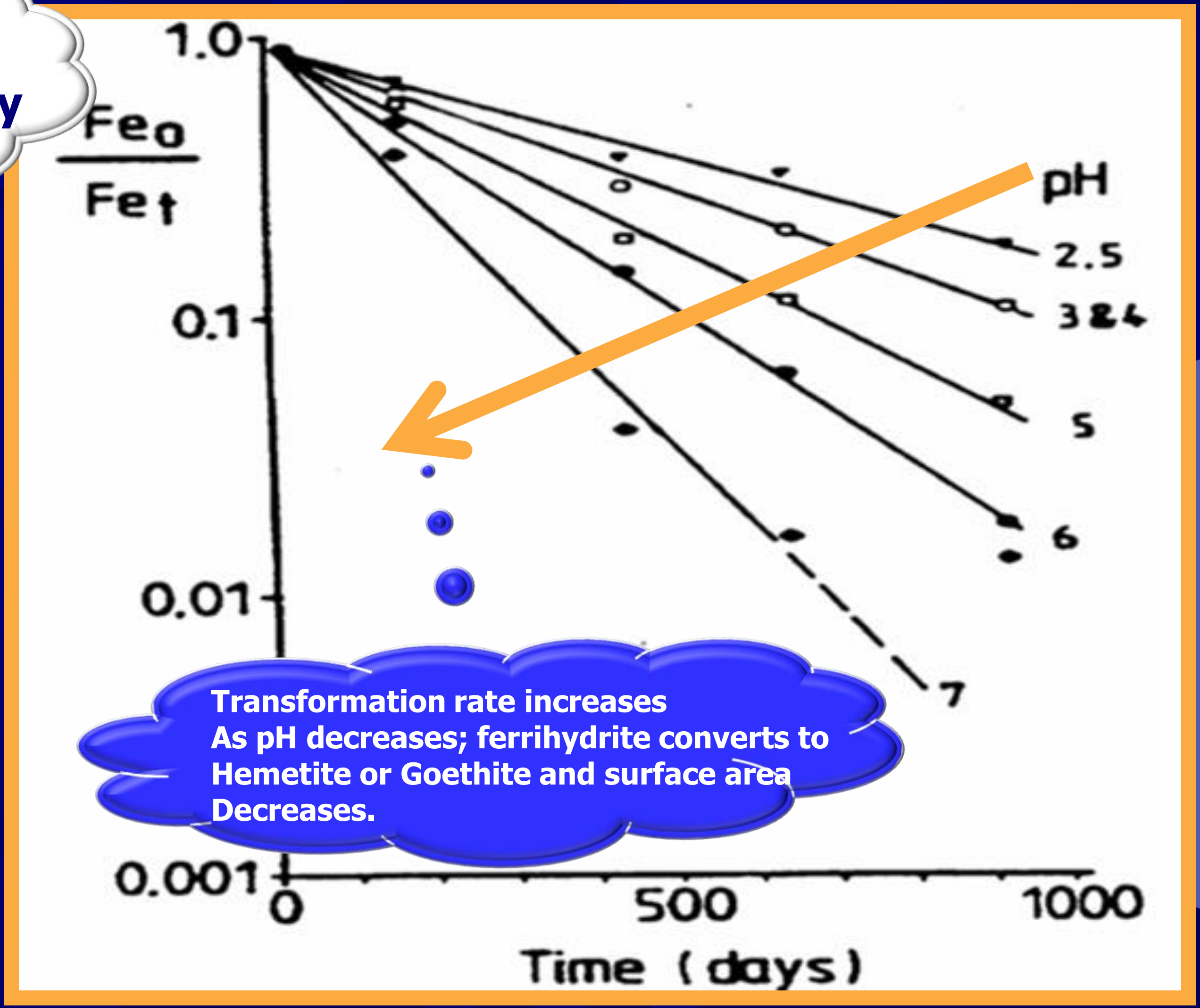
Surface area of 2-line ferrihydrite is 200-420 m^2/gm.

Rate of transformation of ferrihydrite to hematite or goethite is a function of time, temperature and pH.

Ferrihydrite Literature

God of iron hydrometallurgy

(Schwertmann & Murad, 1983)



Transformation rate increases
As pH decreases; ferrihydrite converts to
Hemetite or Goethite and surface area
Decreases.

Fe_0=Ferrihydrite

Fe_t=Total Iron

T=25°C

Ferrihydrite Literature

A significant decrease in surface area may hold important negative consequences for long term outdoor storage stability for adsorbed arsenic.

FH 200-400 m^2/g
goethite 50 m^2/g

Ferrihydrite Literature

The ferrihydrite conversion rate may be mitigated (changed from days to perhaps years) by the presence of other species and solution conditions.

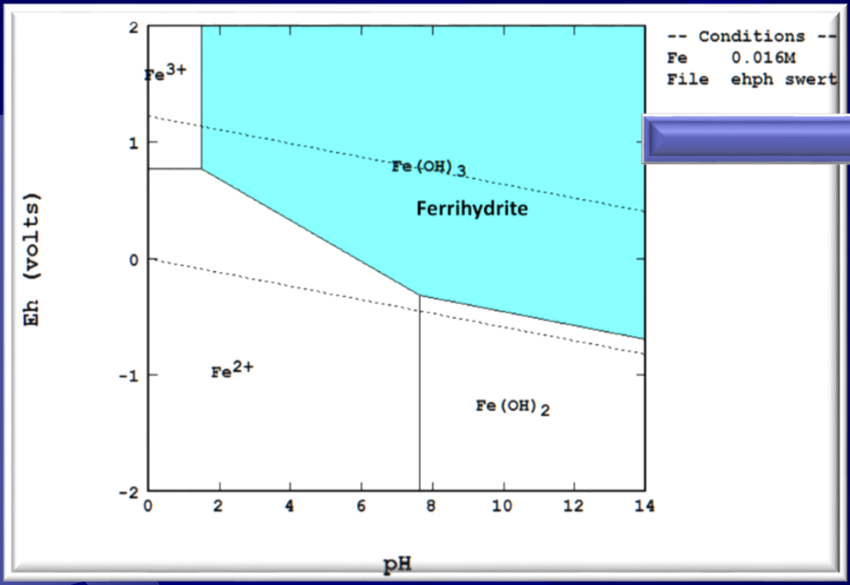
General factors that **decrease** the rate include: lower pH, lower temperatures, presence of silicate, aluminum, arsenic, manganese, metals, and organics.

Ferrihydrite 101

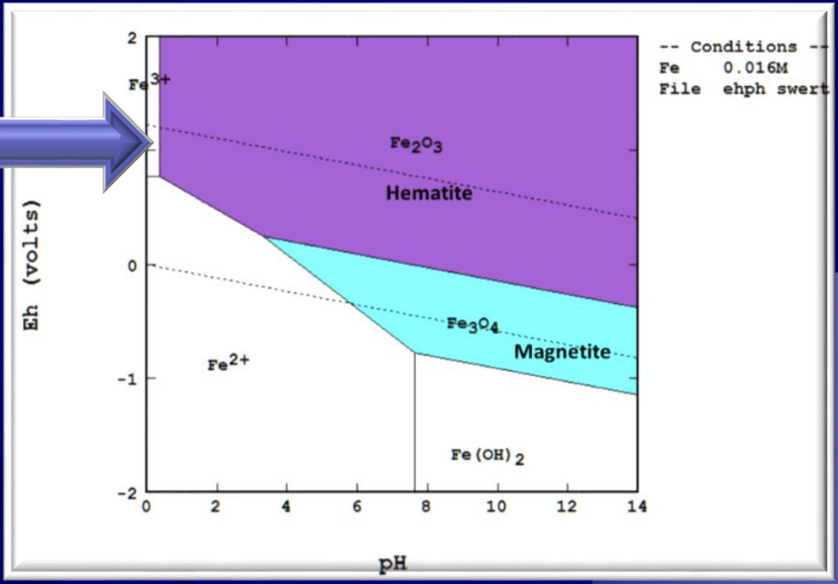
Long-Term Storage Stability

Will the arsenic loaded ferrihydrite remain stable in a pond environment?

Thermodynamics



Solution potential/pH (Eh/pH) diagram illustrating the **metastable FH** phase regions in the iron/water system. Metastable FH forms from chloride, nitrate and low concentration sulfate solutions under oxidizing conditions (shaded region) but transforms hematite or magnetite as show Figure 5.



Solution potential/pH diagram illustrating the **equilibrium phases** formed in the iron/water system. Metastable FH transforms to the equilibrium stable phases of Hematite or Magnetite.

Low Sulfate

Thermodynamics

Schwertmannite forms in Berkeley Pit

High Sulfate

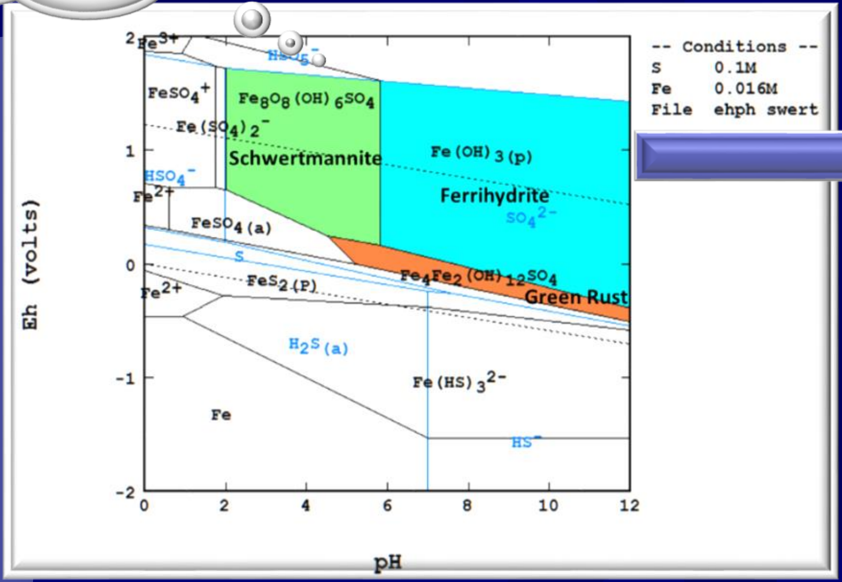


Figure 7. Solution potential/pH diagram illustrating the **metastable Schw, FH, and GR phases** formed in the iron/sulfur/water system. Metastable Schw and FH form when precipitated from sulfate bearing solutions under oxidizing conditions. Metastable Green Rust (GR) forms under slightly reducing conditions. Schw forms in preference to FH in the noted pH range. The boundaries for each stability region, of course, varies as a function of sulfate and iron concentrations.

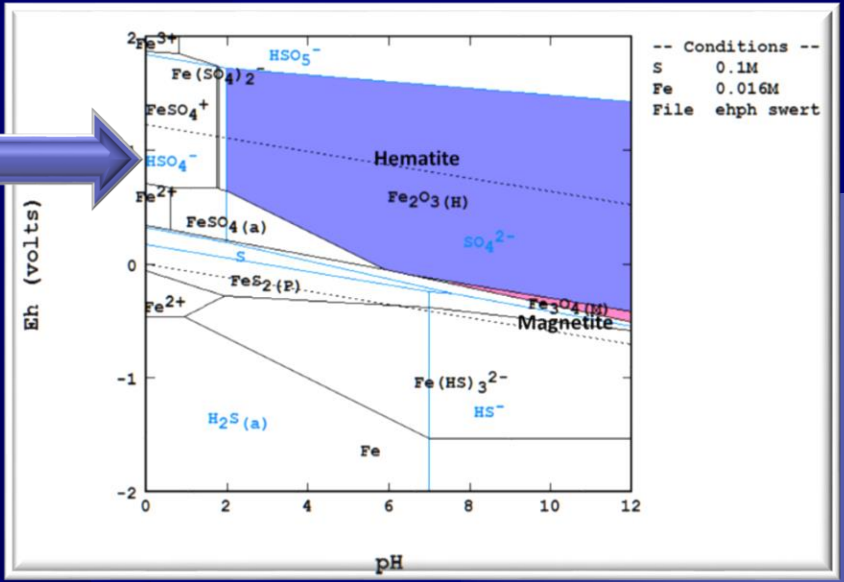


Figure 8. Solution potential/pH diagram illustrating the final stable equilibrium phases formed in the iron/sulfur/water system. See note in Figure 6. Jarosite forms at pH<approximately 2-3 (not shown on diagram).

Long-Term FH/As Stability

Concerns

- Conversion to hematite or goethite with loss of adsorbed arsenic back to aqueous phase
- Release of arsenic after precipitation during storage by desorption

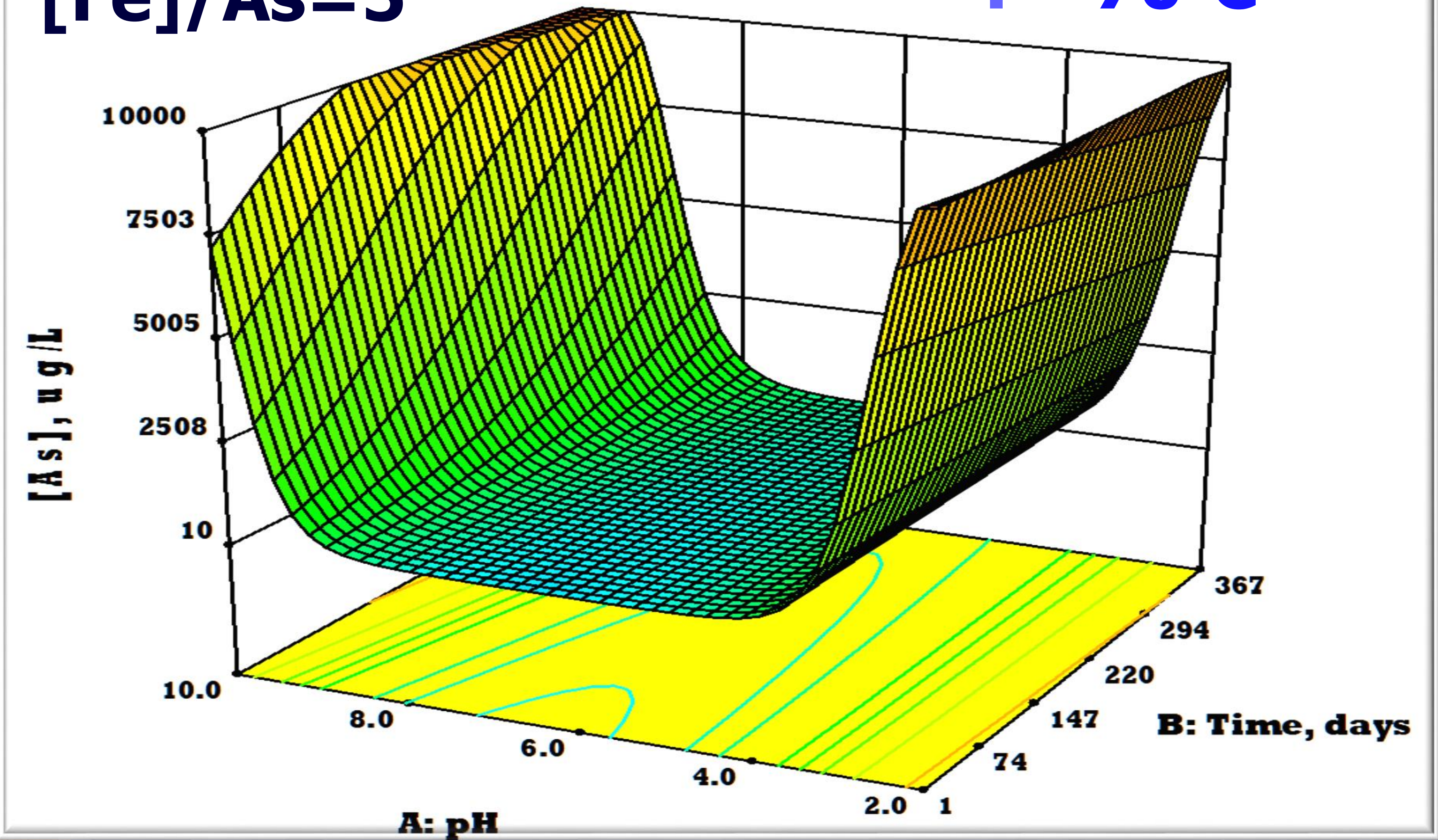
Usually aging studies are conducted at 70°C to accelerate the aging rate.

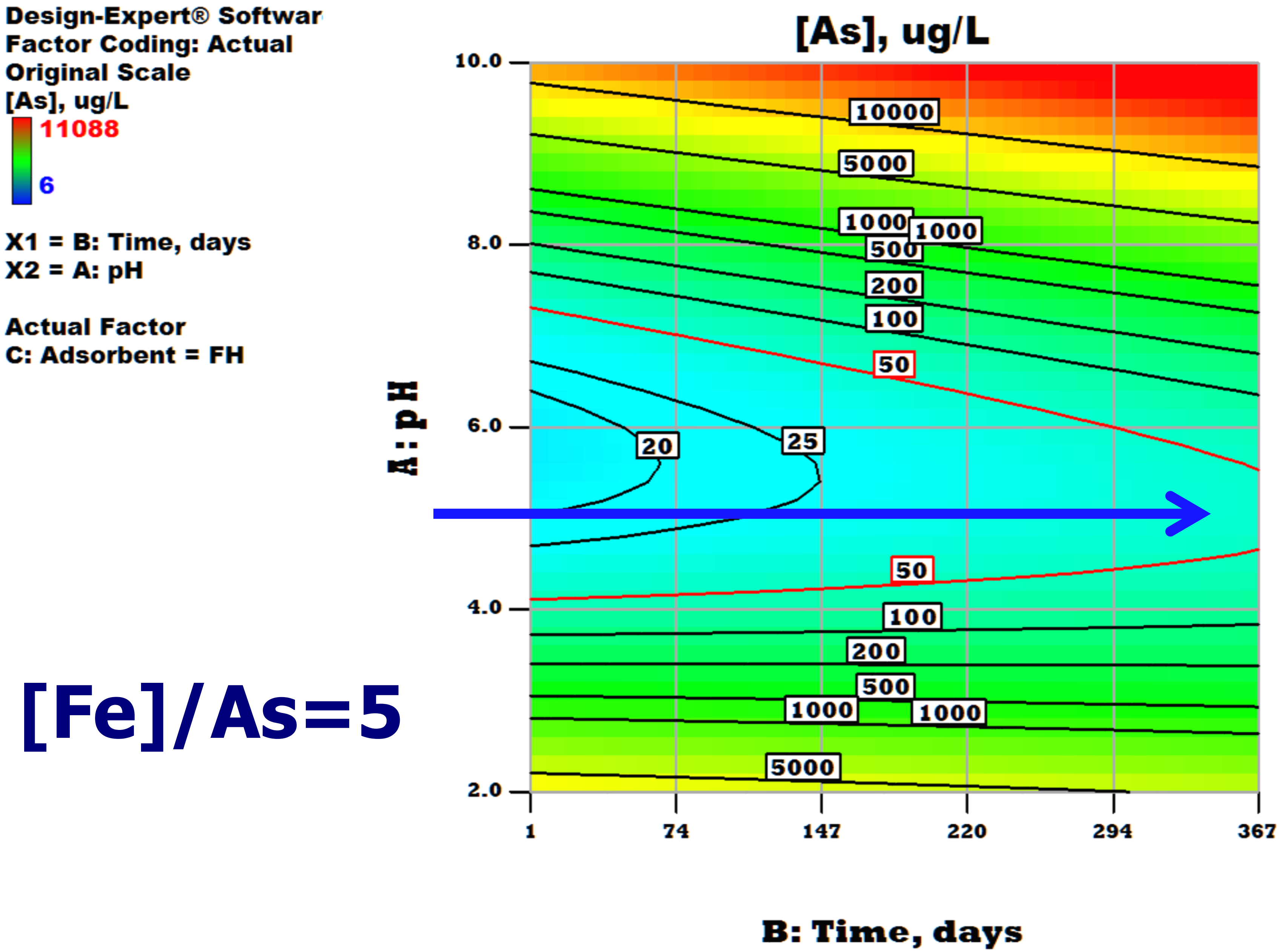
Ford (2002) states that conducting aging at 70°C is equal to 25 times the rate at ambient; so aging for one year at 70 is equivalent to about 25 years at ambient temperature

Long-Term Fe/As Stability

[Fe]/As=5

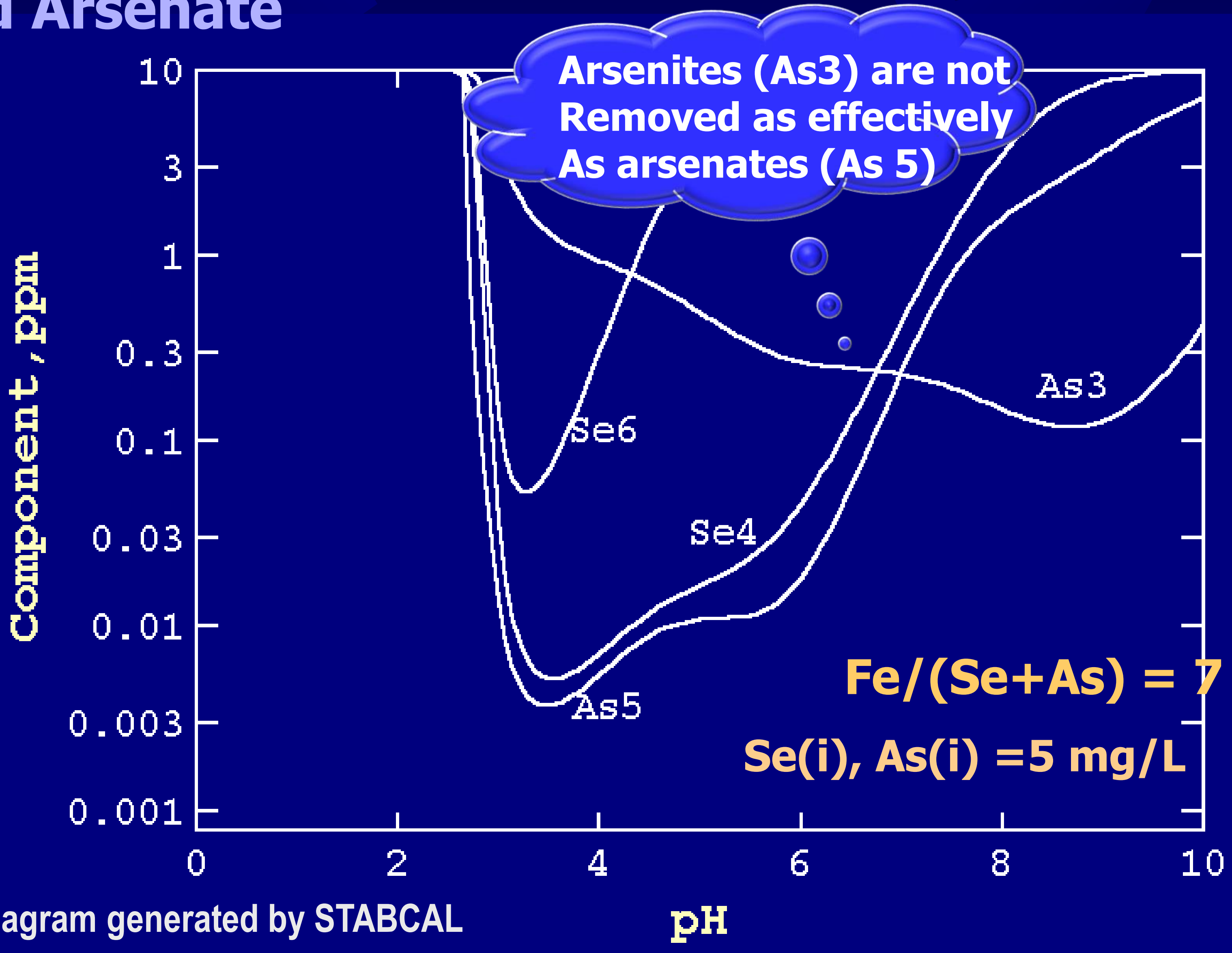
T =70ºC




Design-Expert® Softwar
Factor Coding: Actual
Original Scale
[As], ug/L
11088
6
X1 = B: Time, days
X2 = A: pH
Actual Factor
C: Adsorbent = FH
[As], ug/L
10000
5000
1000
1000
500
200
100
50
25
20
50
100
200
500
1000
1000
5000
10.0
8.0
6.0
4.0
2.0
A: pH
1
74
147
220
294
367
B: Time, days

[Fe]/As=5

Comparison of Ferrihydrite Adsorption of Arsenite and Arsenate



Arsenites (As3) are not Removed as effectively As arsenates (As 5)

Fe/(Se+As) = 7

Se(i), As(i) =5 mg/L

Diagram generated by STABCAL

Ferrihydrite Adsorption: Best Conditions

- As^{+5} preferred (oxidizing conditions best)
- Fe/As mole ratio >4-6 (Lab)
  >10 (Plant)
- pH = 4-6 (Lab)
  = 6-8 (Plant)
- Fe^{+2} added, then oxidized or Fe^{+3} added (both used industrially, Fe^{+2} preferred)

Summary Thoughts

Pros for use of FH

- Used for generations
- EPA has designated FH formation as the BDAT
- Relatively inexpensive treatment
- Ambient temperature formation process
- Usually passes TCLP test
- Stability of stored product enhanced by using elevated Fe/As mole ratios

Summary Thoughts

Cons for use of FH

- Storage conditions must be considered
  - pH must not be too high
  - Oxidizing conditions necessary
  - Must know microbial environment
  - High As solutions produce lots of sludge; increased expense, limited to <1 g/L solutions

Summary Thoughts

Examples of industrial use

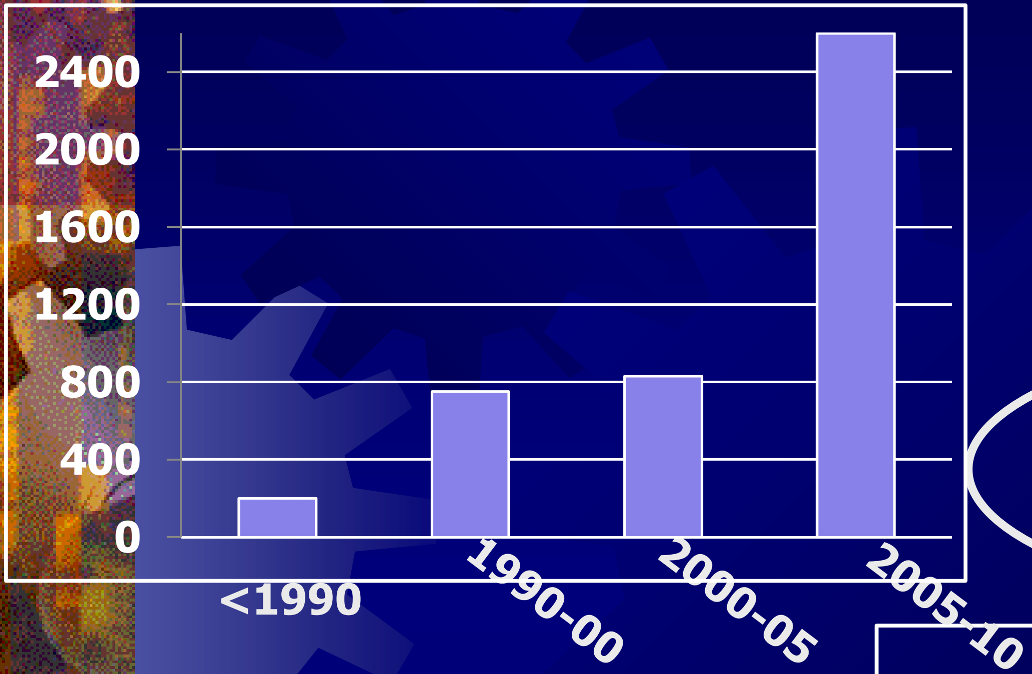
- Inco's CRED plant in Sudbury has been operating for close to forty years, with no sign of ferrihydrite breakdown, or of arsenic release.
- Kennecott Utah smelter
- Noranda Horne smelter
- Barrick's Gold mining in Nevada
- EPA "operations applying it correctly (molar Fe(III)/As(V) ratio>4) have not reported any contamination of local groundwater"

Summary Thoughts

New Research

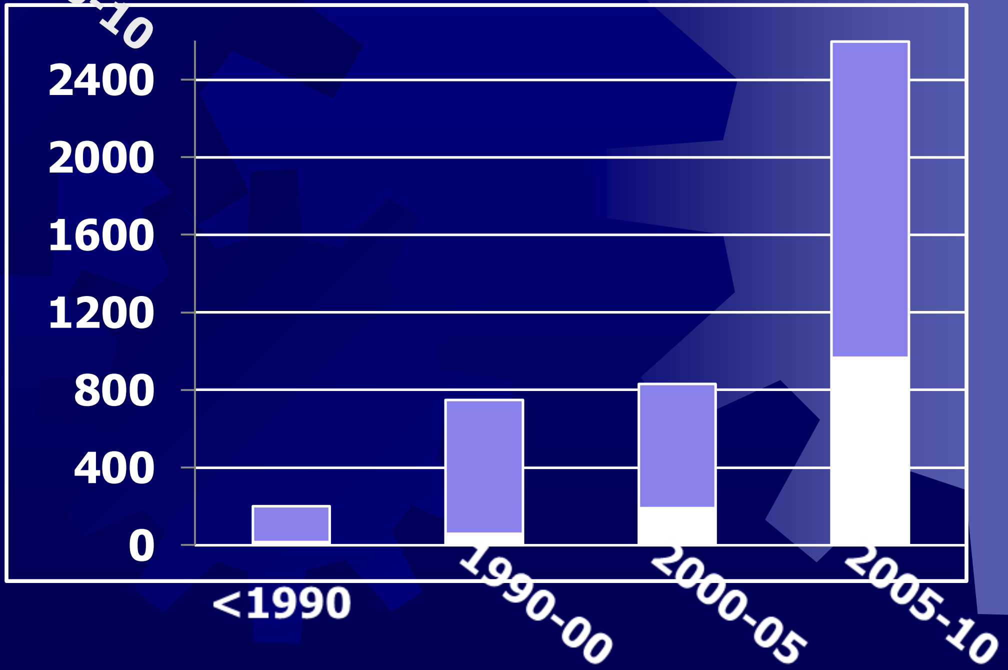
A great deal of research has been and is currently being directed toward the use of ferrihydrite for arsenic removal from effluents and drinking waters

Ferrihydrite Publications



Journal articles only, does not pick up proceedings or theses

Ferrihydrite/Arsenic Publications



Science Direct Search Engine

2010-2014: Fe 3000, Fe/As 1200
2015: Fe 351, Fe/As 148

Summary Thoughts

New Research . . .

More needs to be Done.

- Stability in microbacterial environments
- Stability in reductive environments
- Stability as precipitates formed from acid mine waters
- Development of Better coagulants
  - Fe/Al precipitates
  - Fe/Al/Ca precipitates

LECTURE 8

Scorodite Discussion

As

New Topic

❖ Case Studies

- Arsenic Stabilization
  2) Scorodite

The **other major way** to remove and store arsenic is as Scorodite

www.Wikipedia.org/wiki/scorodite

$FeAsO4:2H2O$ "Scorodite is a common hydrated iron arsenate mineral, with the chemical formula $FeAsO4 \cdot 2H2O$. Scorodite was discovered in the Schwarzenberg, Saxony district, Erzgebirge, Saxony, Germany. Named from the Greek *Scorodion*, "garlicky". When heated it smells of garlic, which gives it the name."

Rule of thumb: if the [As] is >1 gm/L, then scorodite is preferred; if <1 gm/L FH is preferred

Scorodite Discussion

As

References listed at end of these lectures

Ways to produce Scorodite

"There are **several technologies** that can be used **to form scorodite** (example of each approach is presented in a publication by **Twidwell* 2014**):

Industrial application uses this at present

1) **Autoclave hydrothermal precipitation of scorodite** from acidic solutions (pH ~1, ~150°C) containing Fe(III) and As(V) (**Gomez et al. 2011a**, and **many others**)
2) **Elevated temperature ambient pressure precipitation** from acidic solutions (pH ~1, 90-95°C) containing Fe(III) and As(V) or As (III) (**Demopoulos 2008**, **2005, many others**)

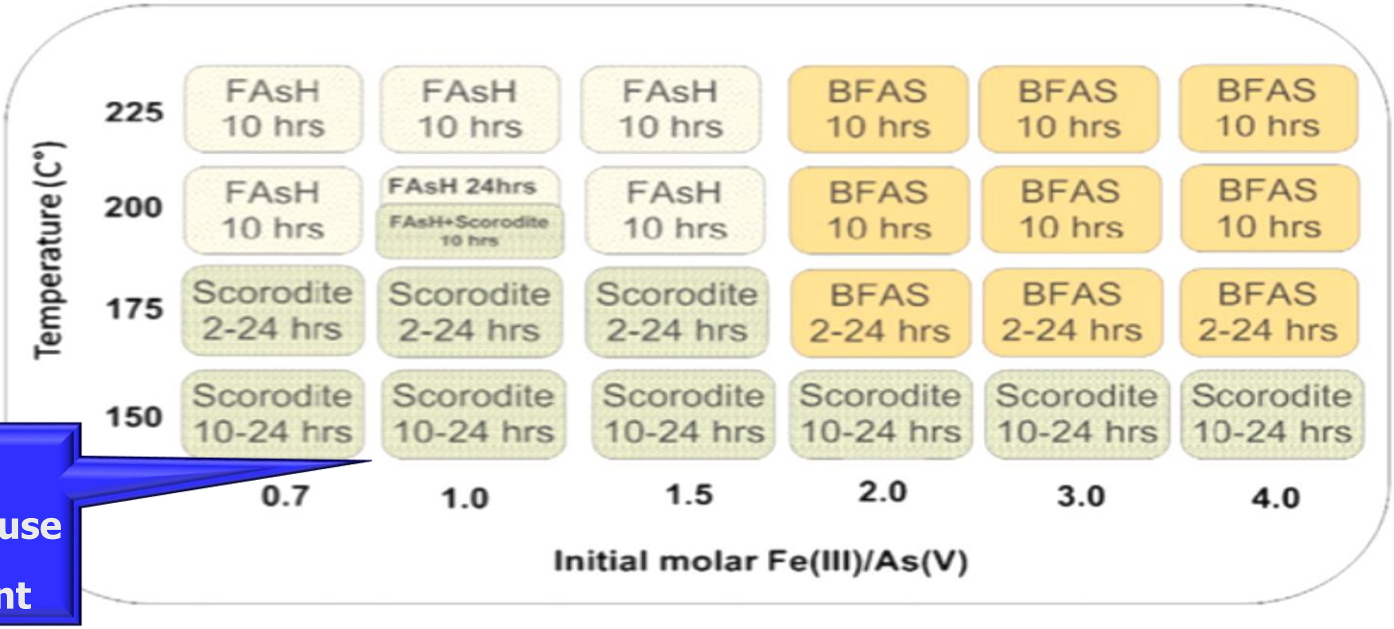
Ways to produce Scorodite

3) Intermediate temperature **ambient pressure precipitation by insitu oxidation of Fe(II)** in the presence of As(V) from acidic solutions (pH ~1, ~70°C, 95°C) (**Fujita et al. 2012, many others**)

4) Intermediate temperature **ambient pressure precipitation by biogenic insitu oxidation of Fe(II)** in the presence of As(V) from acidic solutions (pH ~1, ~70°C) (**Okibe et al. 2013, 2014**)”

Ways to produce Scorodite

- Gomez*, et al. (2014) Summary for Autoclave hydrothermal precipitation of scorodite



Temperature (C°)	0.7	1.0	1.5	2.0	3.0	4.0
225	FAsH 10 hrs	FAsH 10 hrs	FAsH 10 hrs	BFAS 10 hrs	BFAS 10 hrs	BFAS 10 hrs
200	FAsH 10 hrs	FAsH 24hrs FAsH+Scorodite 10 hrs	FAsH 10 hrs	BFAS 10 hrs	BFAS 10 hrs	BFAS 10 hrs
175	Scorodite 2-24 hrs	Scorodite 2-24 hrs	Scorodite 2-24 hrs	BFAS 2-24 hrs	BFAS 2-24 hrs	BFAS 2-24 hrs
150	Scorodite 10-24 hrs	Scorodite 10-24 hrs	Scorodite 10-24 hrs	Scorodite 10-24 hrs	Scorodite 10-24 hrs	Scorodite 10-24 hrs

Initial molar Fe(III)/As(V)

Fig. 2. The Gomez–Becze–Demopoulos ("GBD") Precipitation Diagram of the arsenate phases found in the Fe (III)–AsO_4–SO_4 system.

Industrial applications use this at present

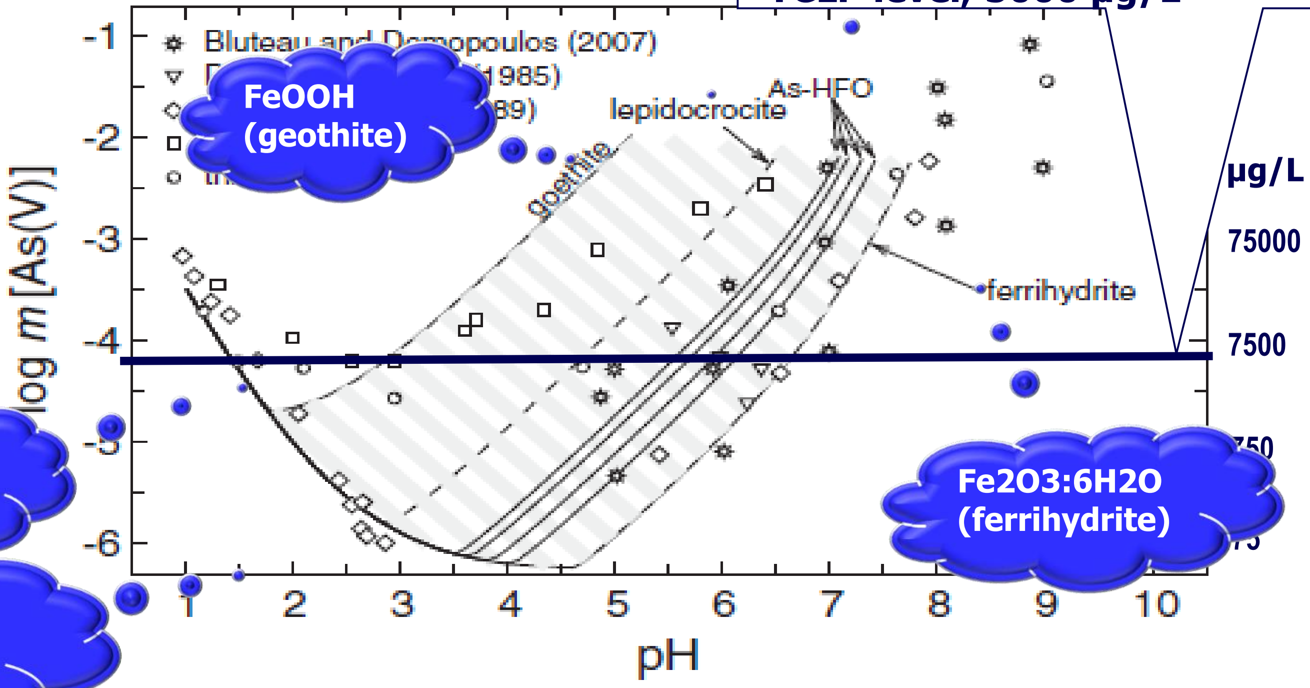
- Is it stable in outdoor storage areas??

Scorodite Discussion

As (Thermo)

Fe2O3 (hematite)

TCLP level, 5000 µg/L



FeOOH (geothite)

Fe2O3:6H2O (ferrihydrite)

$FeAsO_4$ (scorodite)

$FeAsO_4$ Thermodynamically un stable above pH 1.7

Fig. 8. Solubility of scorodite in aqueous media. Symbols show the solubility results reported by Dove and Rimstidt (1985), Krause and Ettel (1989), Robins (1990), Bluteau and Demopoulos (2007), and from this work. The solid curves are models in which scorodite dissolves and an Fe^{3+}-phase precipitates. For each curve, the Fe^{3+}-phase is specified in the figure. Thermodynamic data for the Fe^{3+}-phases were taken from Majzlan (2011) and references therein. The large hatched field shows the possible aqueous As concentrations in situations in which scorodite dissolves and Fe^{3+}-phase(s) precipitate. For details, see text.

Majzlan* et al. 2012

Summary Thoughts

Pros for use of Scorodite

- Used since the 1980's
- Fe/As mole ratio is one; small amount of product to be stored
- Useful for [As] concentrations > 1 gm/L
- Low Fe dosing required
- Usually passes TCLP test
- Stability of stored product well demonstrated

Summary Thoughts

Cons for use of Scorodite

- Relative expensive because it is an autoclave process
- Low pH, high pressure process
- Oxidizing conditions necessary: oxygen

  reagent required
- Must know conditions of the storage environment
  - Microbial
  - Oxidizing or reducing

Summary Thoughts

New Research

- Fujita (primary at Dowa Mining Japan)- Better ways to form Scorodite, ambient pressure and <boiling temperature processes
- Okibe (primary at Kyushu University Japan)- Formation of Scorodite in Biogenic reactors at ambient pressure and temperature
- Demopoulos (primary at McGill University Canada)-
  - Encapsulation of Scorodite with phosphate or silicate coatings
  - Formation of Yutonite $Ca_2Fe_3(AsO_4)_4(OH)\cdot 12H_2O$

LECTURE 9

- Case Studies
  - Arsenic Stabilization
    - 3) Arsenic Trisulfide

As

New Topic

As

Another way to remove arsenic is as Orpiment (Arsenic Trisulfide)

Orpiment (As_2S_3) can effectively be produced in biochemical reactors.

As

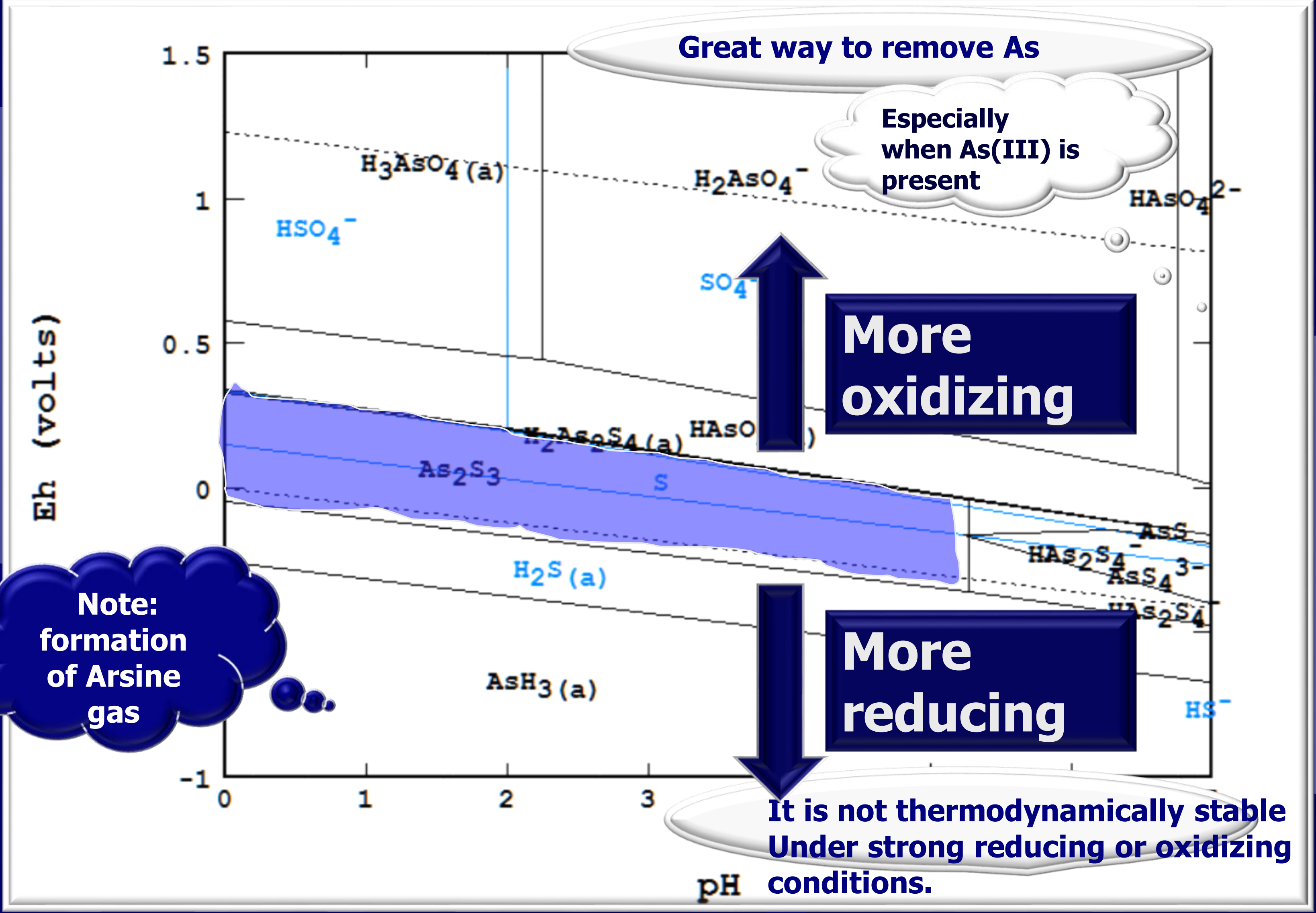
Here is a comparison between FH, Scorodite, Orpiment

Process	Formula	Fe/As mole ratio	pH	Form of As	Conditions to Form
FH	$5Fe_2O_3{:}9H_2O$	~4	3-4 best	$As(V)O_4^{-3}$	Oxidizing
Scorodite	$FeAsO_4$	1	<1	$As(V)O_4^{-3}$	Oxidizing
Orpiment	As_2S_3	0	<3.5 (<1.5 best)	$As(III)O_3^{-3}$	Biological Reducing

Process	Grams of Product Formed for 1 g As/Liter
FH	85.9
Scorodite	2.6
Orpiment	1.6

Orpiment Discussion

As (thermodynamics)



Great way to remove As

Especially when As(III) is present

More oxidizing

More reducing

Note: formation of Arsine gas

It is not thermodynamically stable Under strong reducing or oxidizing conditions.

Sahinkaya et al. (2014); good reference for biochem reactor

Biochemical Reactions

Sulfate Reducing Bacteria (SRB) which survive in reducing conditions

$$C_2H_4O_2+SO_4^{-2}+SRB=H_2S_{(Aq)}+2HCO_3^{-1}$$

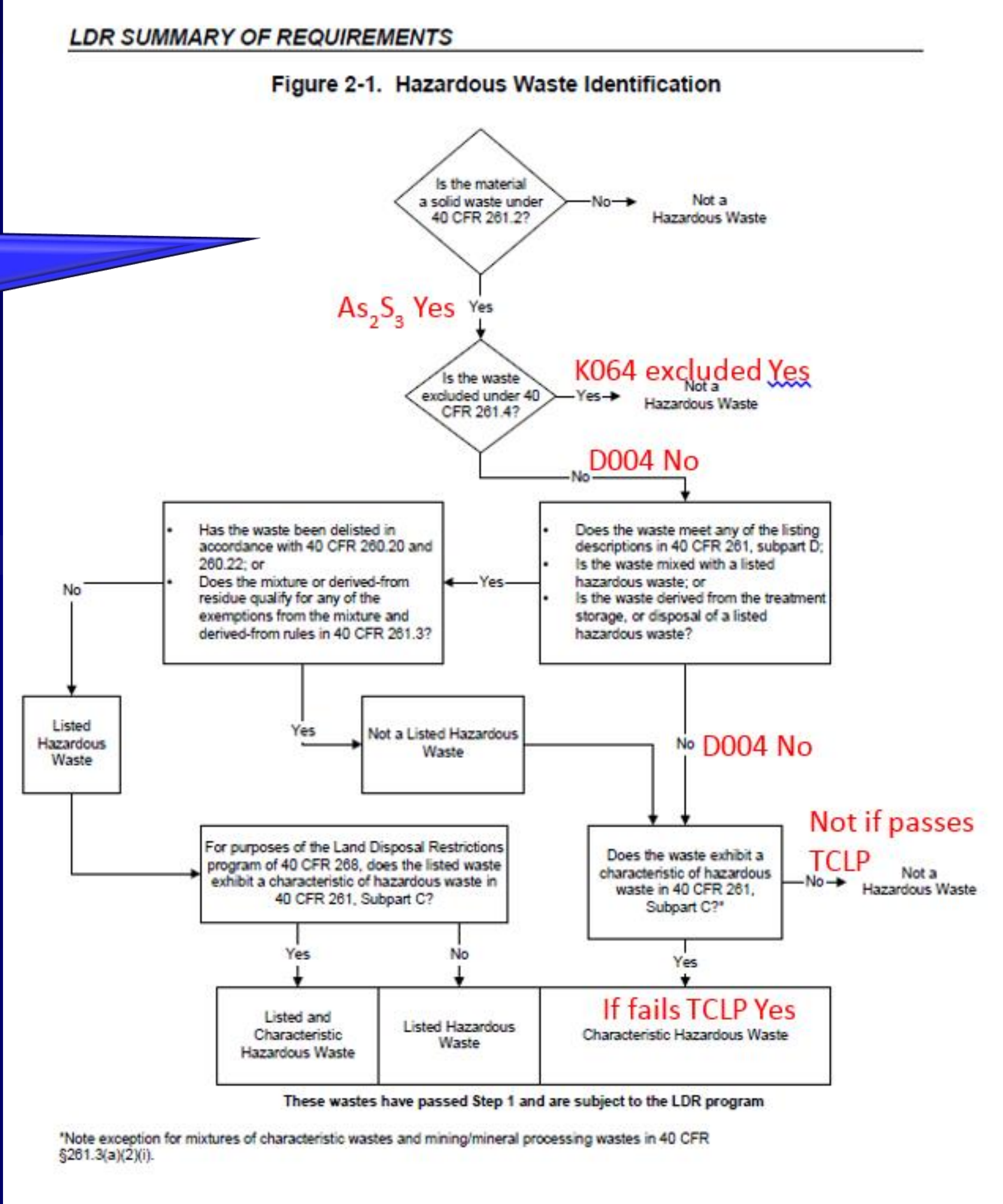
Carbon source and electron donor

+6 Sulfur Reduction -2

$$H_2S_{(Aq)} = H^+ + HS^{-1}$$

$$2HAsO_3^{-2} + 3HS^{-1} + 7H^+ = As_2S_{3(solid)} + 6H_2O$$

Example of LDR disposal considerations for orpiment



LDR SUMMARY OF REQUIREMENTS

Figure 2-1. Hazardous Waste Identification

These wastes have passed Step 1 and are subject to the LDR program

*Note exception for mixtures of characteristic wastes and mining/mineral processing wastes in 40 CFR §261.3(a)(2)(i).

Orpiment Discussion

As

Great way to remove As,
However, how do you
Store it??

It is not thermodynamically stable under oxidizing conditions. How about depending on kinetic rate??

The oxidation rate equations for As_2S_3 (amorphous), according to Lengke et al (2009), follow:

$$R\ (\text{mol } As_2S_3/m^2/sec) = 10^{-10.89}[H+]^{-0.17}$$

(N_2/ anoxic conditions)

$$R\ (\text{mol } As_2S_3/m^2/sec) = 10^{-17.76}[H+]^{-1.18}$$

(oxic conditions)

Orpiment Discussion

As

It is not thermodynamically stable
Under oxidizing conditions. How about
Depending on kinetic rate??

The Lengke et al (2009) study demonstrated that the oxidation of amorphous As_2S_3 would be extremely slow. For example, the oxidation of As_2S_3 in one year at pH 2.5 would only be $1.8*10^{-4}$ mg As_2S_3 oxidized/gm residue/year (assuming a surface area = 3.68 m^2/gm, value from Lengke et al 2001).

Lengke and Tempel (2005) reported the results of their oxidation study by geochemical modeling arsenic sulfide oxidation kinetics in a mining environment. Their conclusions for amorphous As_2S_3 are that the rate of oxidation at a pH of 2.3 would be $1.11X10^{-11}$ (mol/m_2/sec) and at circumneutral pH (8) the rate would be $5.93X10^{-9}$ (mol/m_2/sec). Therefore, they concluded that the release of arsenic could exceed the U.S. National Drinking Water Standard of 50 ppb (value in 2005, now the value is 10 ppb) in 200-300 days.

As

The result of the author’s study was that great care would have to be exercised with respect to how the waste was stored. The company chose not to try to get a “no migration” variance to the Chilean version of the RCRA LDR regulations. They chose to use the scorodite process for treating acid blow down effluents for the removal and storage of arsenic.

As

- Case Studies
  - Arsenic Stabilization
    - 4) Whitmoyer (NPL) Site **Remediation**

New Topic

As

➢ Whitmoyer Laboratories **NPL*** Site (PAD003005014)

What had to be cleaned: waste from chemical production of arsenic pharmaceuticals, fungicides, contaminated ground water, miscellaneous solids and sludge.

NPL Site Listing Process (example stages shown in next slides) Six Staged Process used to identify and clean-up sites

[Eleven PRP's identified in July 1987 (they shared cleanup costs); cost 50 million dollars]

1. PA/SI-Preliminary Assessment/Site Inspection

Investigations of site conditions. If the release of hazardous substances requires immediate or short-term response actions, these are addressed under the Emergency Response program of Superfund.

[Author's treatability work completed May 1989], described later

2. RI/FS-Remedial Investigation/Feasibility Study

Determines the nature and extent of contamination. Assesses the treatability of site contamination and evaluates the potential performance and cost of treatment technologies.

[Selection of treatment alternative and ROD signed 1989, 1990]

3. ROD-Records of Decision

Explains which **cleanup alternatives** will be used at the site or sites. When remedies exceed 25 million, they are reviewed by the National Remedy Review Board.

However, RODs can be Modified Using ESDs (Explanation of Significant Difference) procedure and 4 have been used at this site

[Initiation and application 1992]

4. RD/RA-Remedial Design/Remedial Action

Preparation and implementation of plans and specifications for applying site remedies. The bulk of the cleanup usually **occurs during this phase**. All new fund-financed remedies are reviewed by the National Priorities Panel.

5. Construction Completion

Identifies completion of physical cleanup construction, although this does not necessarily indicate whether final cleanup levels have been achieved.

[2002 celebrated end of clean up Construction]

[2004-05 most land purchased for
local development; long-term water treatment
continues; fourth 5-year review completed in 2010]

6. Post Construction Completion

Ensures that Superfund response actions provide for the long-term protection of human health and the environment. Included here are Long-Term Response Actions (LTRA), Operation and Maintenance, Institutional Controls, Five-Year Reviews, Remedy Optimization.

7. NPL Delete-National Priorities List Deletion

Removes a site from the NPL once all response actions are complete and all cleanup goals have been achieved.

[not deleted from NPL regulations because
Water discharge must meet new arsenic
MCL of 10 µg/L]

Treatment Alternatives Selected

- 17 buildings demolished and residues and materials incinerated or encapsulated (515 tons) off-site repositories
- 785 tons of metal debris decontaminated and recycle
- 1290 tons of non-hazardous waste placed in off-site landfills and 227,000 gallons of wastewater treated on-site.
- 3230 tons of vault (calcium arsenate) material and 1,415 tons of soils excavated and sent to off-site repositories.
- 150,000 gallons/day of contaminated groundwater pumped and treated on-site (since 1998). Plume still exists. Produces 15 tons/month of arsenic bearing products (ferrihydrite) which are disposed of off-site in TSDF facilities. ESD 4 required the discharge water to meet the MCL (50 µg/L in 2002). Now that has been changed to 10 µg/L in 2012
- 18,000 lagoon waste containing 1 million pounds of arsenic transported and treated at off-site repositories. Off-site stabilization of sludge and solids by cement encapsulation (author’s work)

Author’s (Twidwell and Chapwin) Treatability Study

- 3 major arsenic contaminated materials investigated
  - Vault material (calcium arsenate, 17.9% As)
  - Lagoon material (ferrihydrite/arsenic, 1.1% As)
  - Lagoon and Soil material (ferrihydrite/arsenic, 2.2%)

- Variables studied:
  - Waste/cement or waste/cement+lime weight ratio: 1 to 0.3
  - Time: curing time 4-24 hrs; roasting 15 minutes to 1 hr
  - Temperature: RT to 1000C

- Response:

  Cast (3/8-inch cubes) materials subjected to TCLP test; response was arsenic released to Extraction Fluid

Author's (Twidwell and Chapwin) Treatability Study

Results:

- Project stated goal: <1 mg/L [As] in TCLP test
- Best conditions for all materials:
  - Waste/Cement weight ratio=0.3
  - Roasting required at 600C, 0.5 hr
- Arsenic concentration <0.4 mg/L
- Selected alternative: Varied as described previously but roasting option too expensive; decided to transport to off-site TSDF repository for stabilization there; used cement as the stabilizing additive; placed in secure cells

Site Cleanup Result

Land Revitalization Program
Breathing New Life into Old Waste Sites
Summer 2005

Former Laboratory Site Now Recreational Area

Whitmoyer Laboratories, Jackson Township, Lebanon County, PA

The Whitmoyer Laboratories site was the home to a veterinary and pharmaceutical manufacturing plant from 1934 to 1987 (left). The site was cleaned up under Superfund and is in the process of becoming a recreational area for the township (right).

Location
The site occupies 22 acres along S. Fairlane Ave. in Jackson Township, Lebanon County, PA.

Current Status
All cleanup construction activities have been completed and the site is ready for redevelopment. Groundwater is still being treated.

Current Owner
Jackson Township purchased the property from Whitmoyer Laboratories, Inc. in April 2005.

Potential Future Uses
Plans are underway by Jackson Township to redevelop the site into a recreational area to include three soccer fields, a baseball field, a playground, a walking/jogging trail and a picnic area. The redevelopment is limited only to projects that will not disturb the site's protective cap.

Past Use
Former veterinary and pharmaceutical manufacturing plant which opened in 1934. In the 1950s arsenic was used to produce feed additives. The plant ceased manufacturing in 1987.

Contamination
Arsenic was found in area drinking wells. Concentrated liquids were abandoned on site in tanks and other vessels. Buildings, soils, sediments, lagoons and groundwater were contaminated. Drums were buried.

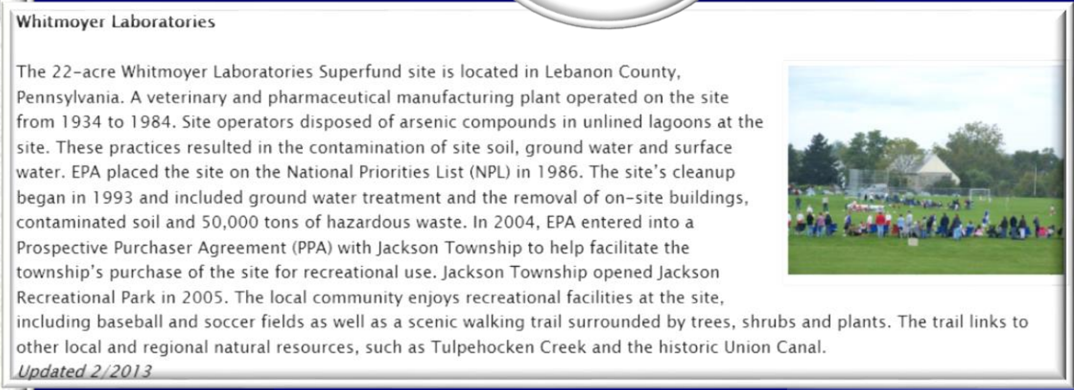
Cleanup History
The site was placed on Superfund's National Priorities List in 1987 and a preliminary close-out report was issued in 2002. The groundwater is still being treated.

Contacts for More Information

For more information about the cleanup, contact Bhupi Khona, EPA Remedial Project Manager, (215) 814-3213 or khona.bhupi@epa.gov.

For more information about the recreational area, contact the Jackson Township Supervisor Dean Moyer at (717) 866-4771.

For more information about EPA's Land Revitalization Program go to: http://www.epa.gov/region03/revitalization/



Whitmoyer Laboratories

The 22-acre Whitmoyer Laboratories Superfund site is located in Lebanon County, Pennsylvania. A veterinary and pharmaceutical manufacturing plant operated on the site from 1934 to 1984. Site operators disposed of arsenic compounds in unlined lagoons at the site. These practices resulted in the contamination of site soil, ground water and surface water. EPA placed the site on the National Priorities List (NPL) in 1986. The site's cleanup began in 1993 and included ground water treatment and the removal of on-site buildings, contaminated soil and 50,000 tons of hazardous waste. In 2004, EPA entered into a Prospective Purchaser Agreement (PPA) with Jackson Township to help facilitate the township's purchase of the site for recreational use. Jackson Township opened Jackson Recreational Park in 2005. The local community enjoys recreational facilities at the site, including baseball and soccer fields as well as a scenic walking trail surrounded by trees, shrubs and plants. The trail links to other local and regional natural resources, such as Tulpehocken Creek and the historic Union Canal.

Updated 2/2013

- **Case Studies** → As
  - **Arsenic Stabilization**

5) Sherwin Williams Site

Remediation*

LECTURE 11

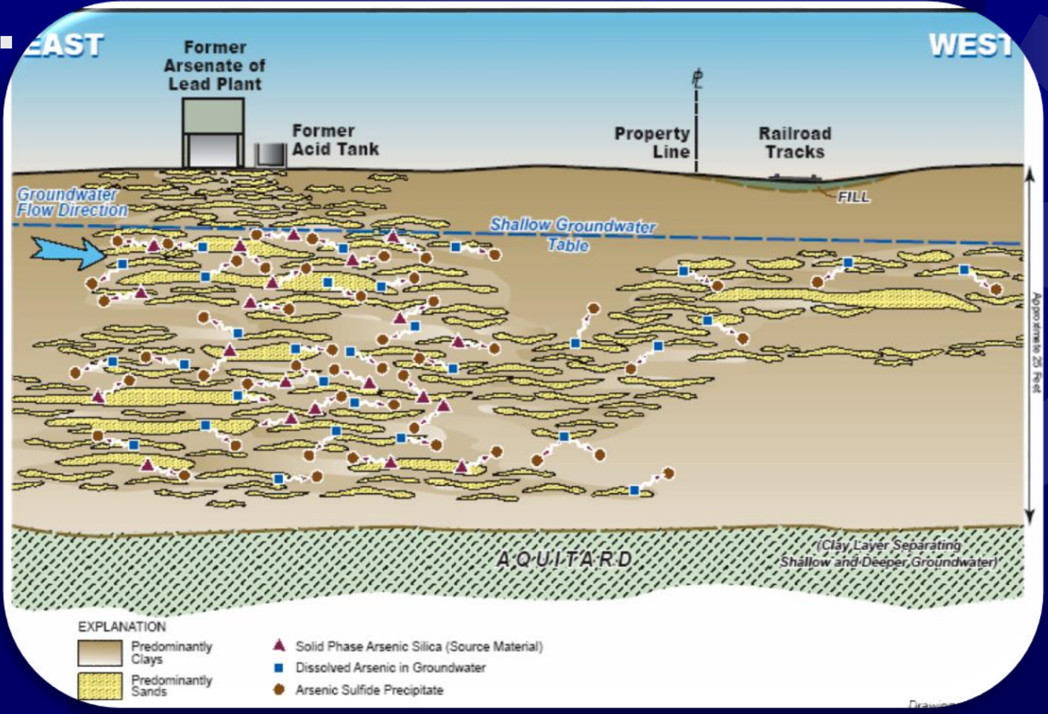
New Topic

❖Case Studies

As

- **Arsenic Stabilization at Sherwin Williams facility in Emeryville, CA**

What had to be cleaned: waste from chemical production of Lead Arsenate, contaminated ground water, miscellaneous solids and sludge.



❖Case Studies

As

- **The goal of process**
  - **Removal of As (100 ppm) from pumped water (30 gpm) to <25 ppb**
- **Development of the process**
  - **Montana Envirometal (Twidwell and Jay McCloskey developed process)**
  - **Jay McCloskey now at Montana Emergent Technologies (Butte, MT)**
- **Installation of treatment process by MSE (Butte, MT) at Emeryville site to treat up to 100 gpm in a pump and treat system**

❖ Case Studies

As

♦ Arsenic Stabilization

- Development of the process
  - Pilot scale demonstration
    - Three treatment alternatives considered
      - Copper Arsenate precipitation for resale
      - Fe cementation
      - Arsenate precipitation/ferrihydrite polishing

Problem-not pure copper arsenate, resale value poor

Problem- must be done in an inert atmosphere (N2)

Chosen

❖Case Studies

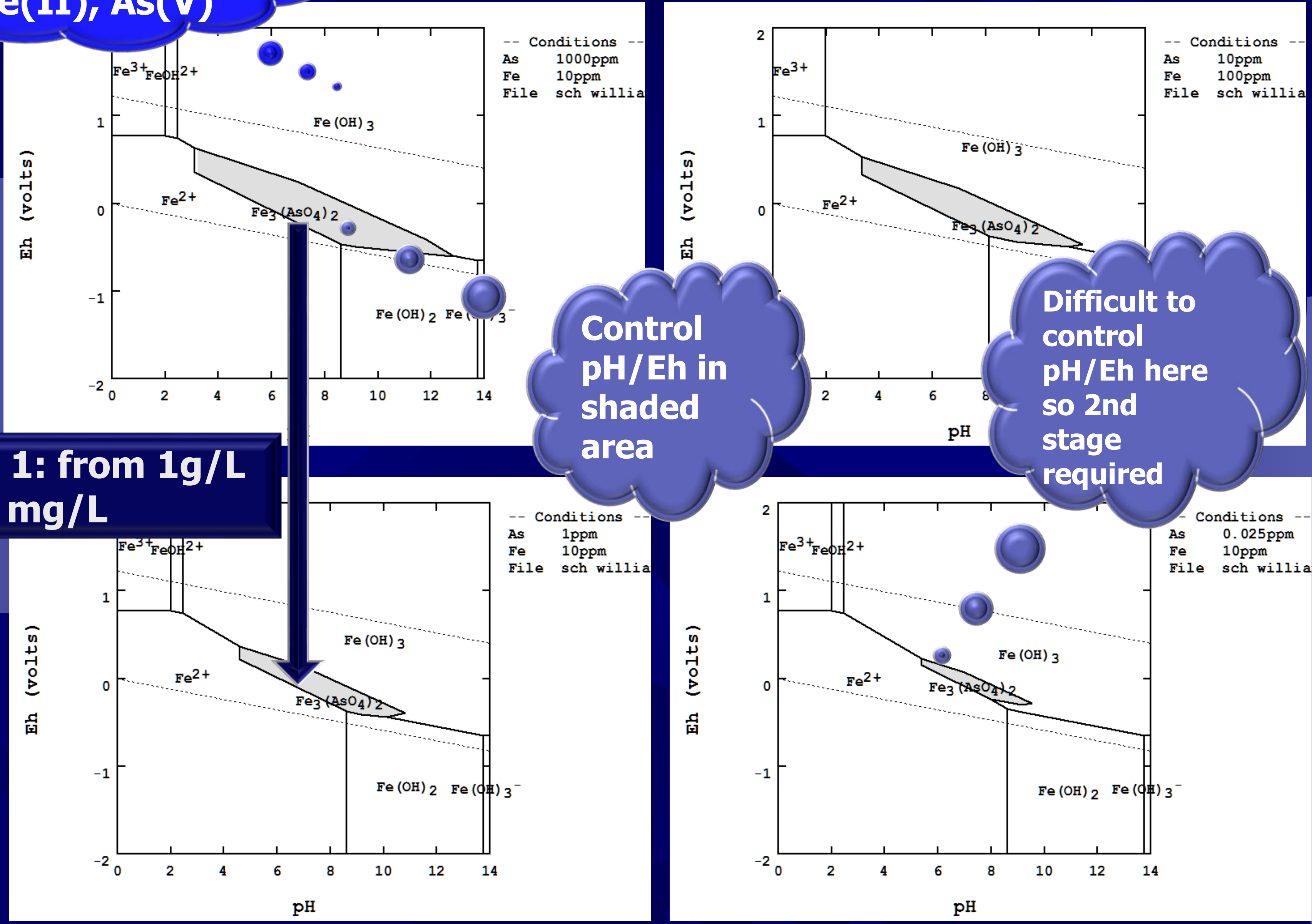
As

♦Arsenic Stabilization

- Development of the process
  - Two stage treatment
    - Novel application of ferrous arsenate precipitation followed by ferrihydrite polishing
    - See next slides

Our Treatability Study: Stage 1

Must be Fe(II), As(V)



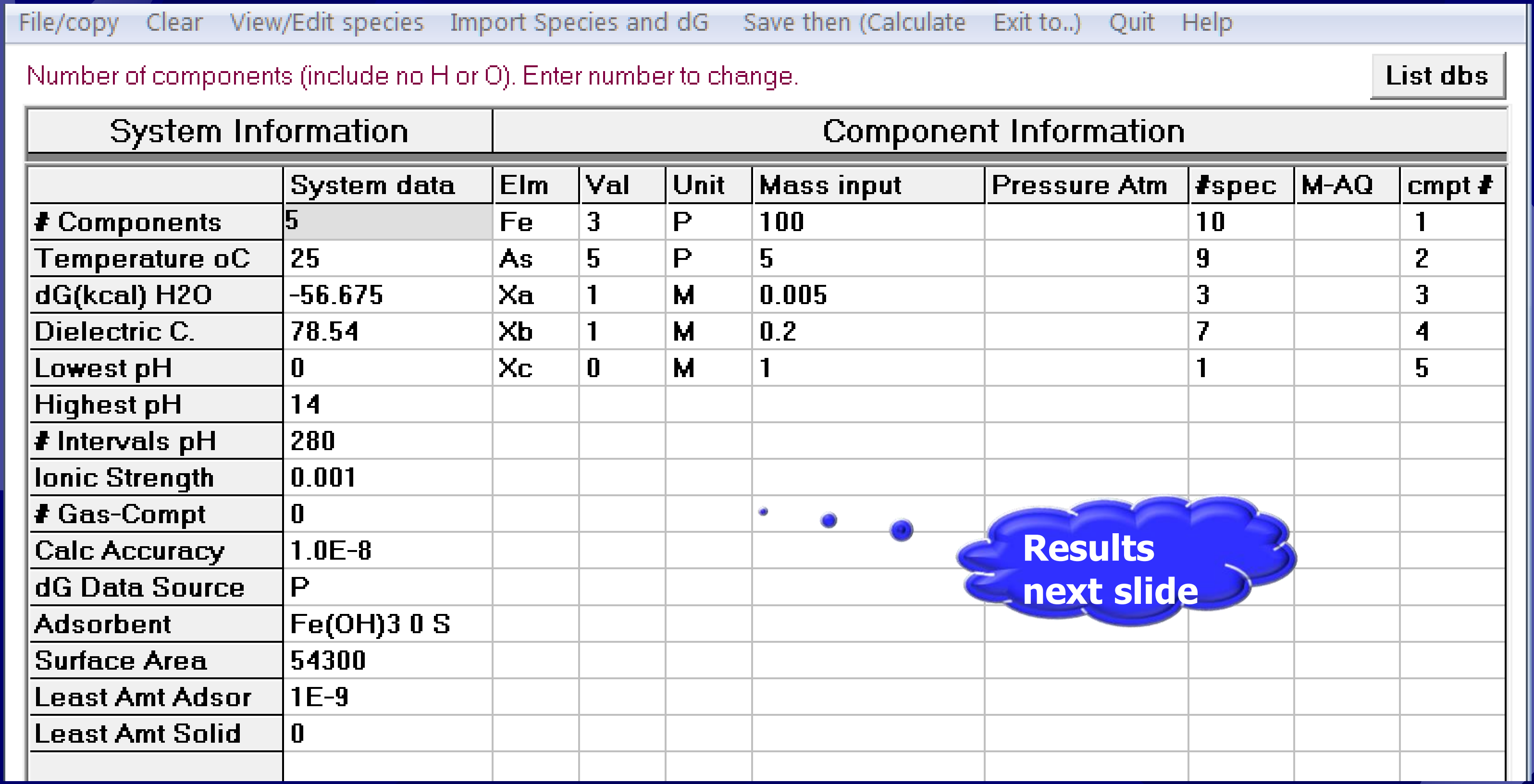
Control pH/Eh in shaded area

Difficult to control pH/Eh here so 2nd stage required

Stage 1: from 1g/L to <5 mg/L

Stage 2: Arsenic adsorption on Ferrihydrite

You can model adsorption using STABCAL (H.H. Huang, Montana Tech)



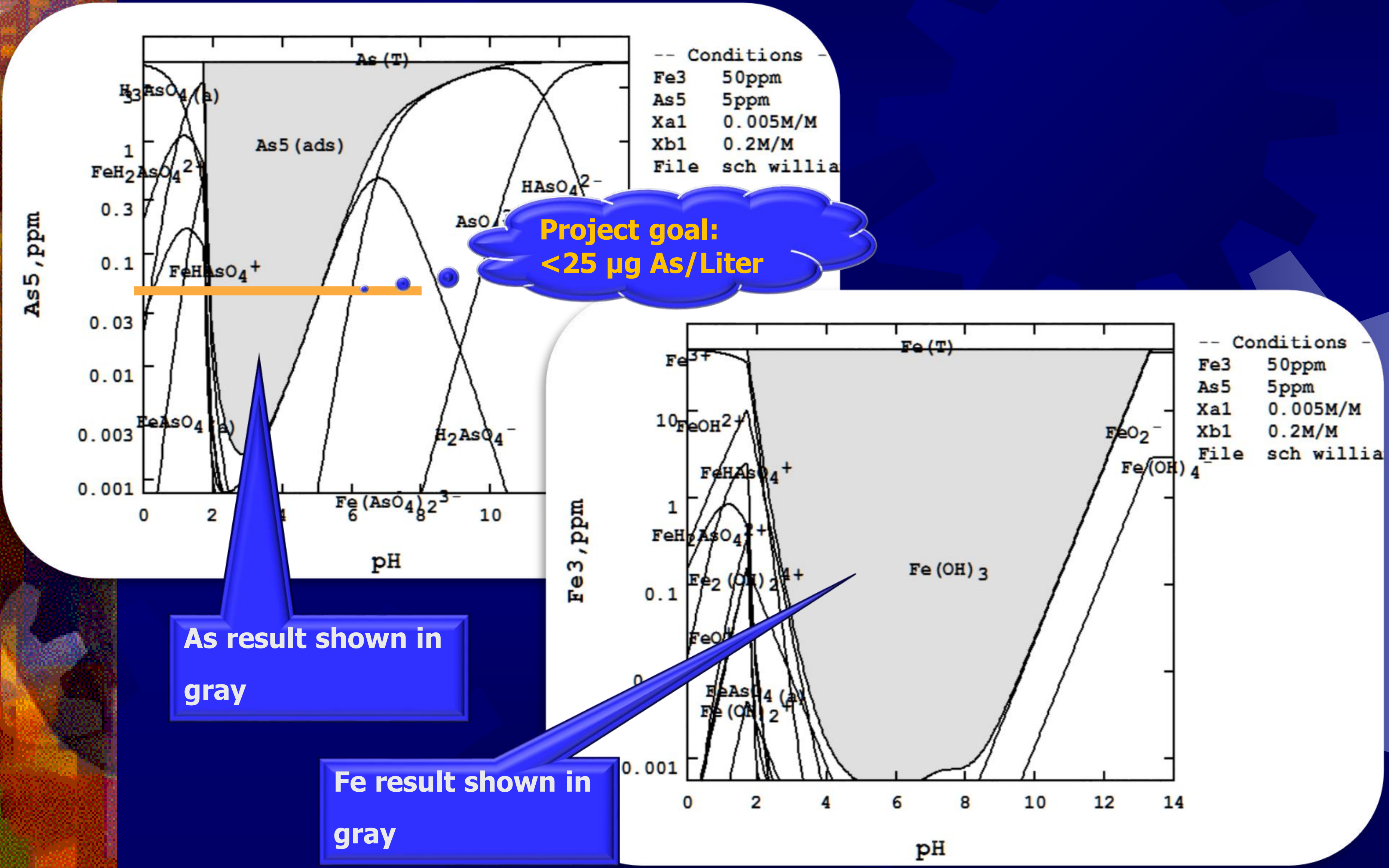
Number of components (include no H or O). Enter number to change.

System Information		Component Information							
	System data	Elm	Val	Unit	Mass input	Pressure Atm	#spec	M-AQ	cmpt #
# Components	5	Fe	3	P	100		10		1
Temperature oC	25	As	5	P	5		9		2
dG(kcal) H2O	-56.675	Xa	1	M	0.005		3		3
Dielectric C.	78.54	Xb	1	M	0.2		7		4
Lowest pH	0	Xc	0	M	1		1		5
Highest pH	14								
# Intervals pH	280								
Ionic Strength	0.001								
# Gas-Compt	0								
Calc Accuracy	1.0E-8								
dG Data Source	P								
Adsorbent	Fe(OH)3 0 S								
Surface Area	54300								
Least Amt Adsor	1E-9								
Least Amt Solid	0								

Results next slide

Stage 2: Arsenic adsorption on Ferrihydrite (Stage 1 lowered As to < 5 mg/L)

Stage 2: Requires addition of Fe(II) which is oxidized to Fe(III) using H2O2

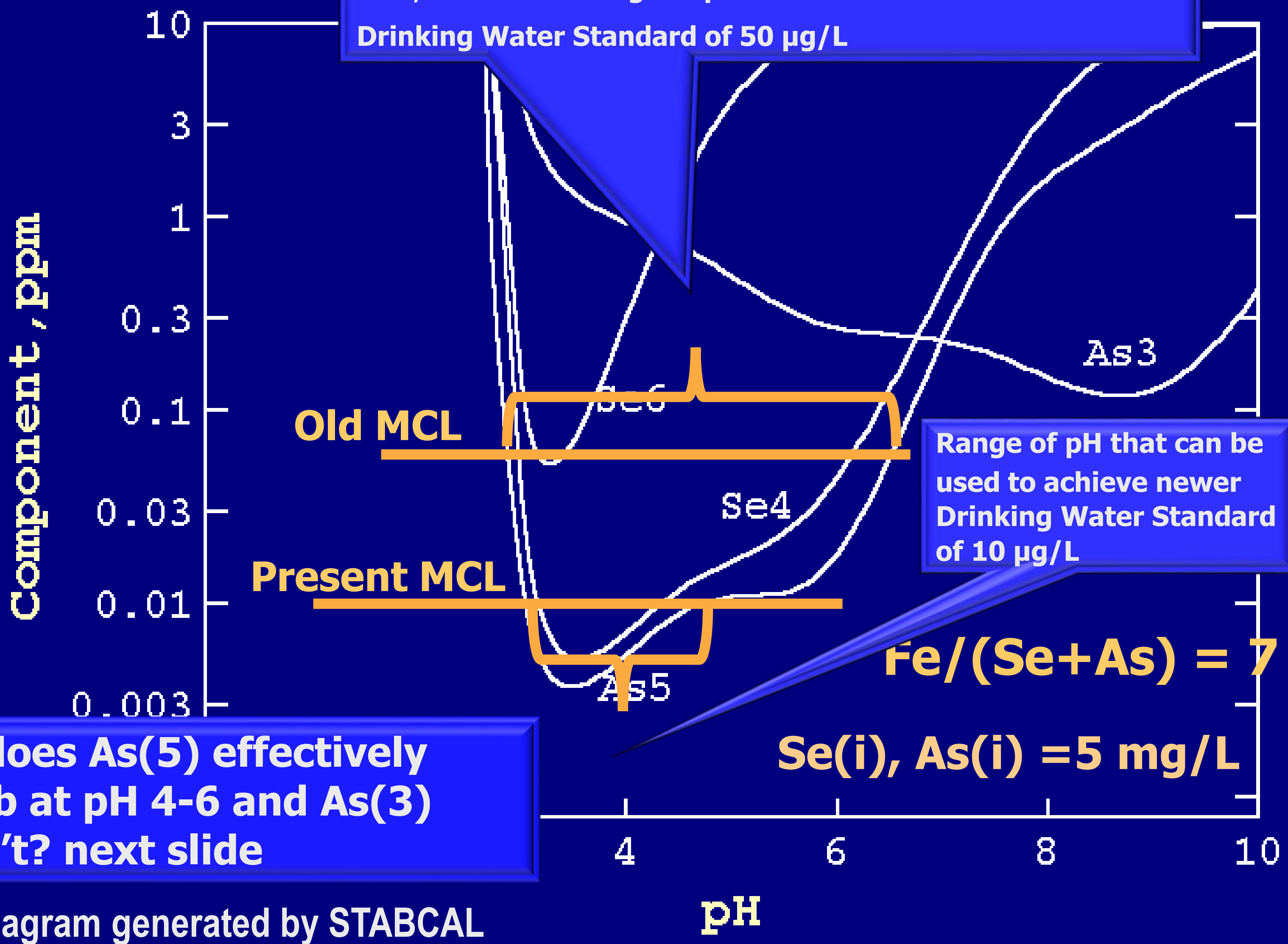


Project goal: <25 µg As/Liter

As result shown in gray

Fe result shown in gray

Comparison of Ferrihydrite Adsorption of Arsenite and Arsenate



Here is the reason that As must be present as As(V) valence. Also, this shows range of pH that can be used to achieve old Drinking Water Standard of 50 µg/L

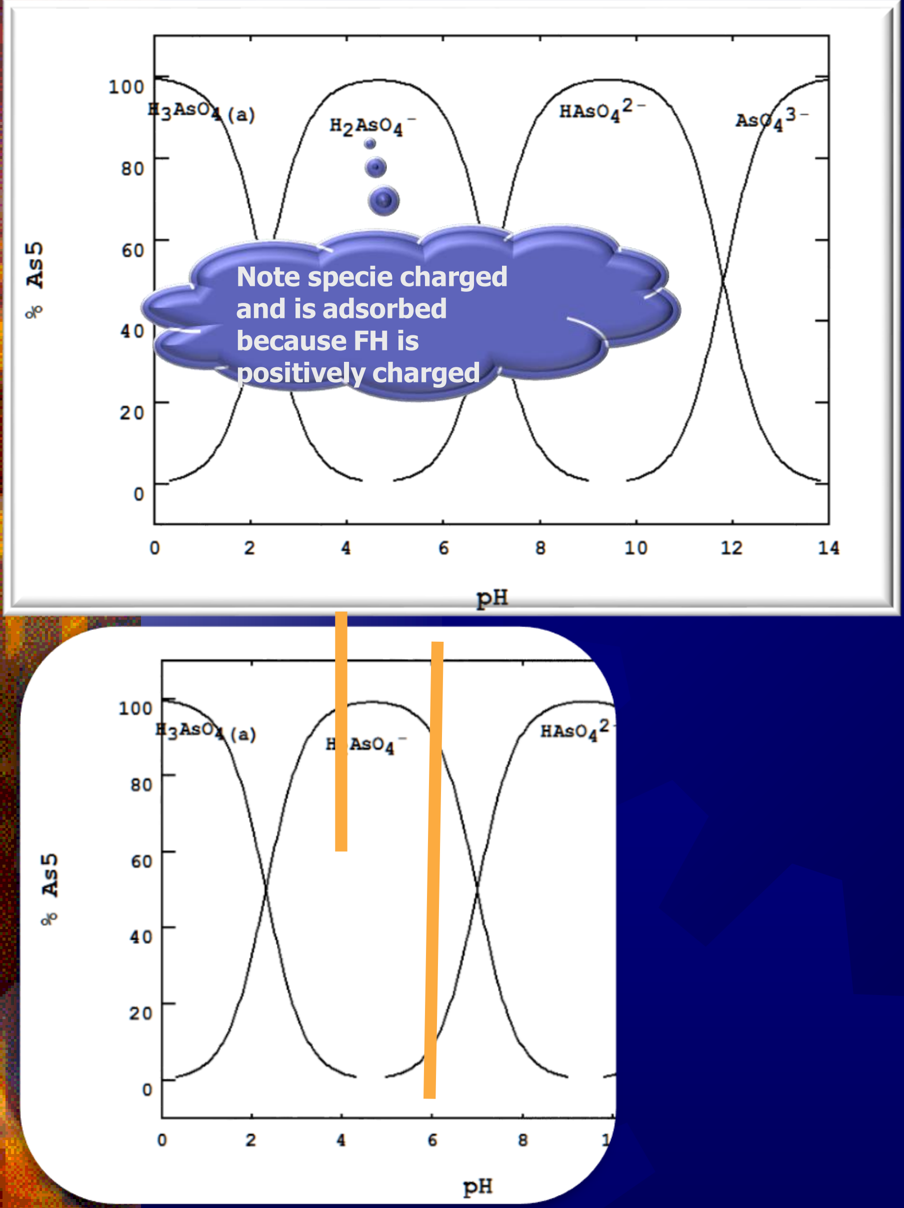
Range of pH that can be used to achieve newer Drinking Water Standard of 10 µg/L

Why does As(5) effectively adsorb at pH 4-6 and As(3) doesn’t? next slide

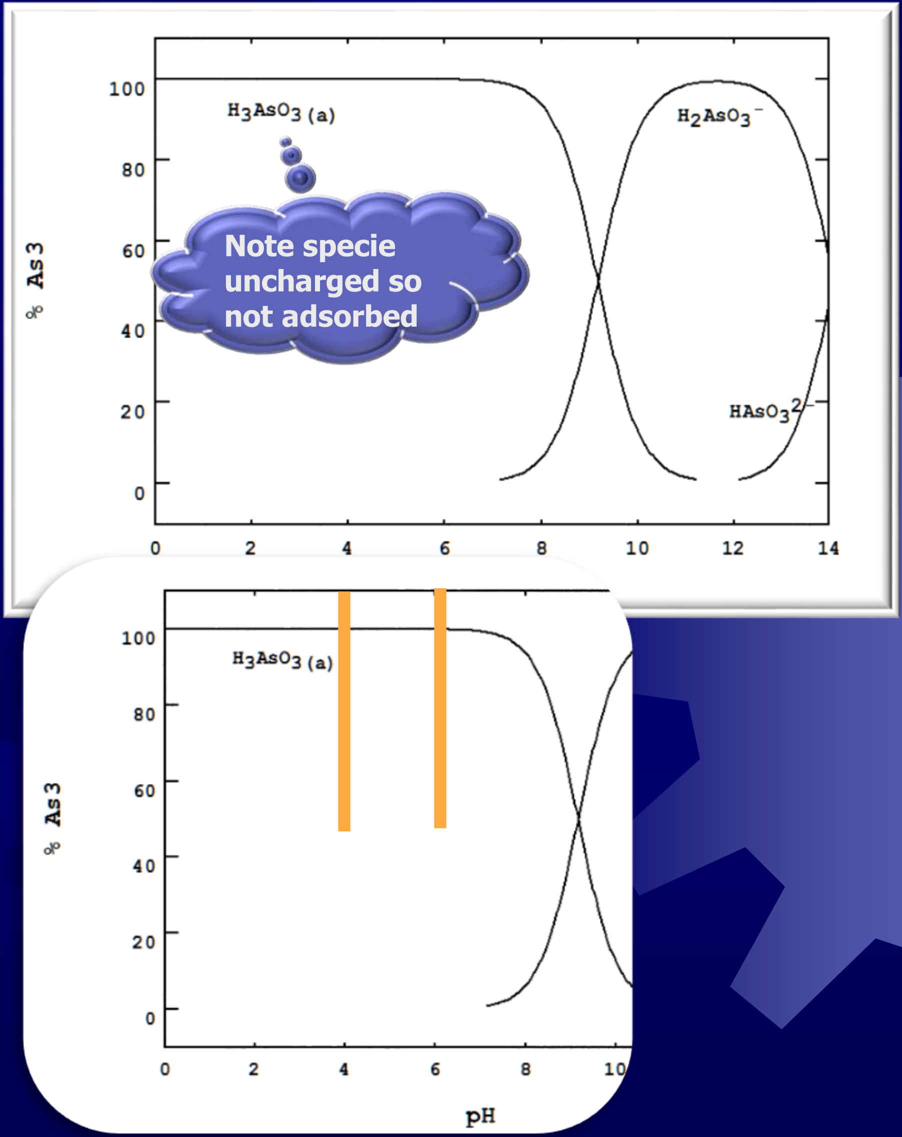
Diagram generated by STABCAL

Distribution of aqueous arsenic species as a function of pH

Diagrams generated by STABCAL



Note specie charged and is adsorbed because FH is positively charged



Note specie uncharged so not adsorbed

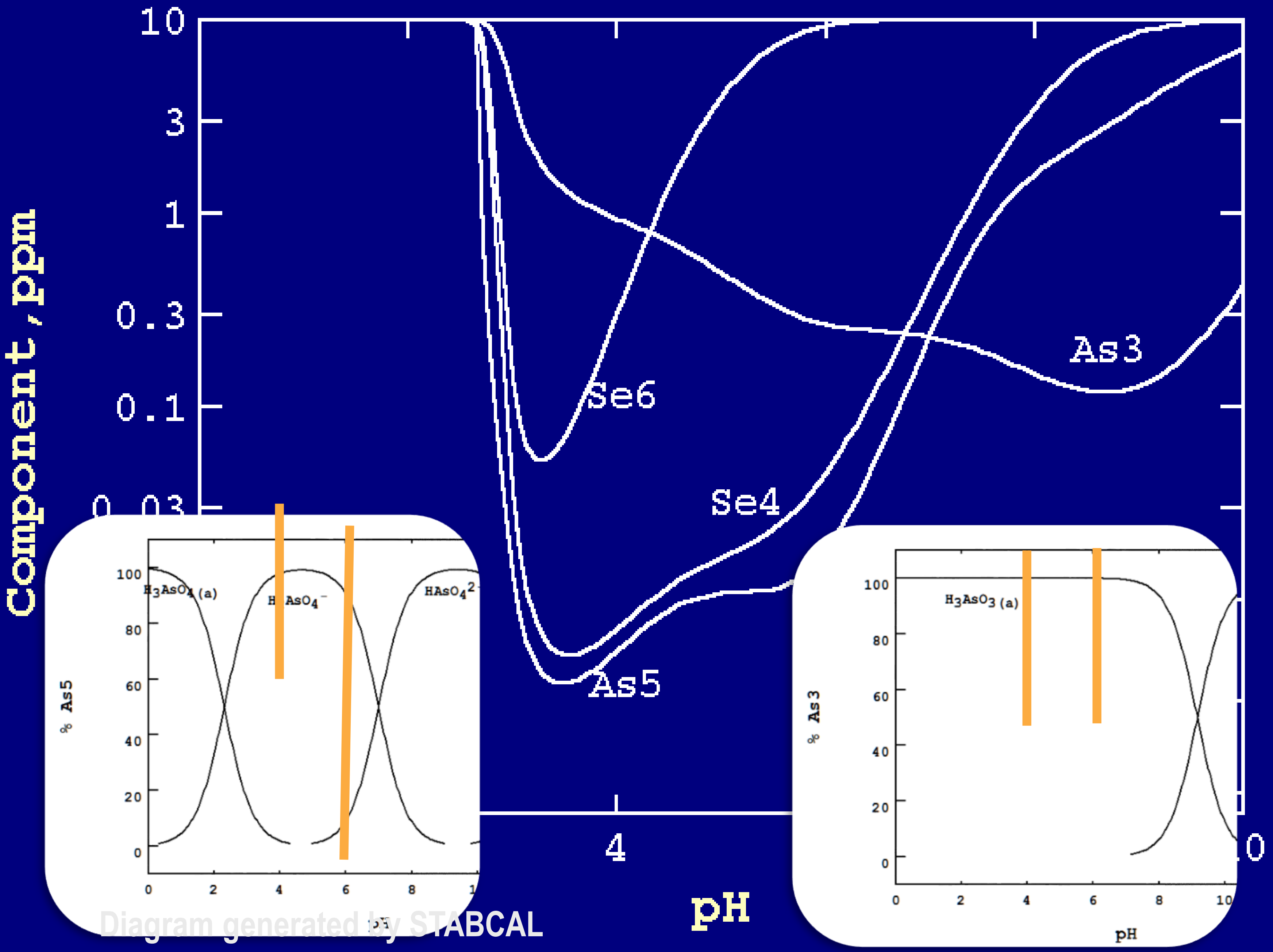
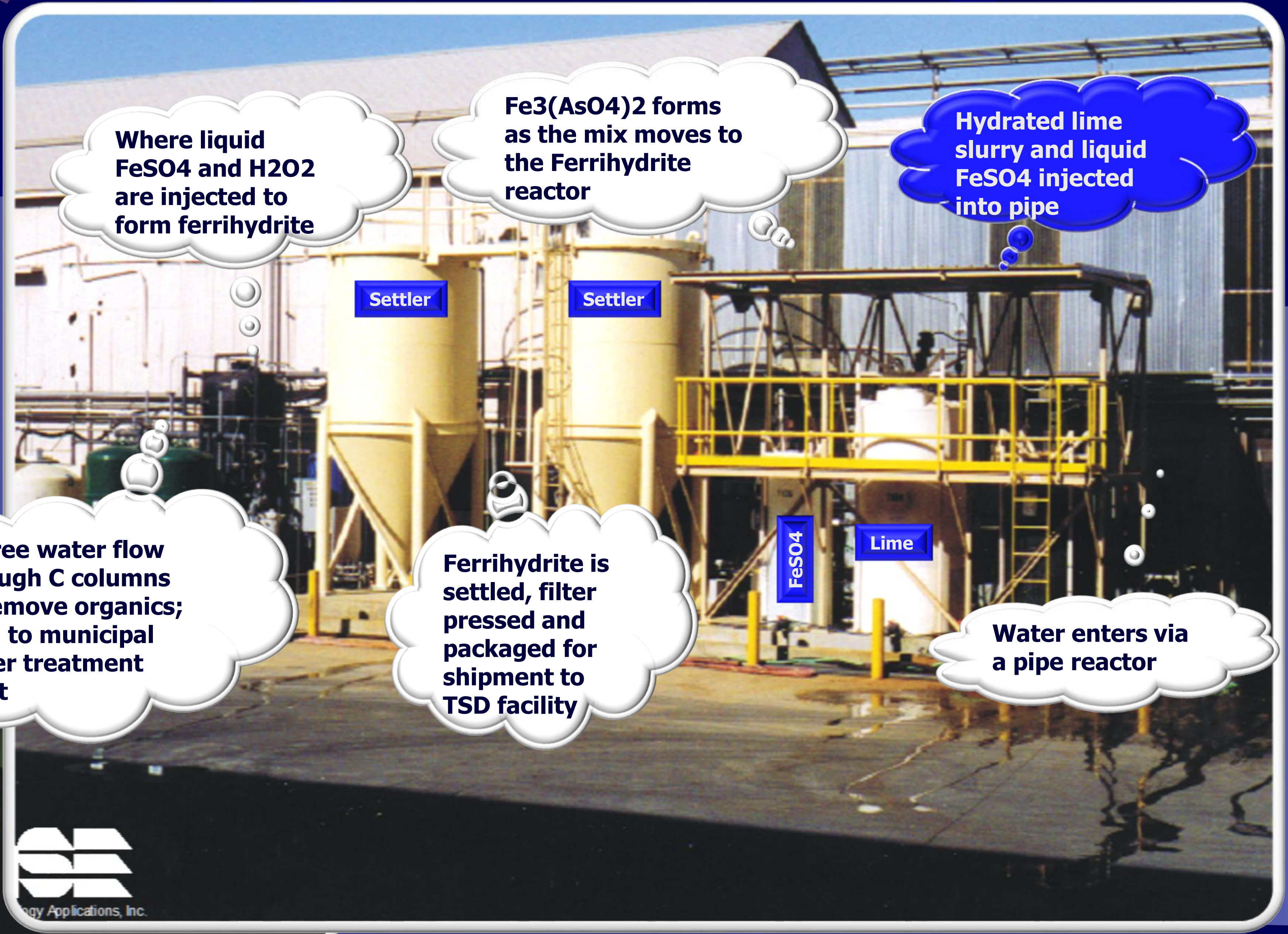


Diagram generated by STABCAL

Operating Process



Where liquid FeSO4 and H2O2 are injected to form ferrihydrite

Fe3(AsO4)2 forms as the mix moves to the Ferrihydrite reactor

Hydrated lime slurry and liquid FeSO4 injected into pipe

As free water flow through C columns to remove organics; then to municipal water treatment plant

Ferrihydrite is settled, filter pressed and packaged for shipment to TSD facility

Water enters via a pipe reactor

GROUNDWATER TREATMENT PLANT
NPDES Permit Requirements for discharge to municipal water treatment plant

(<25 ppb for 30 gpm; <100 ppb for 100 gpm)

Constituents	Influent, ppb	NPDES Limit, ppb
TPH-extractables (diesel)	58,000	50
TPH-purgeable (gasoline)	5,400	50
Benzene	8.7	1
Toluene	690	5
M,P-xylenes	1,600	5 (total xylenes)
O-xylenes	520	5 (total xylenes)
Arsenic	50,000 – 100,000	25

LECTURE 12

Case Studies

Hg

- Mercury Recycle

New Topic

- Chlor-alkali RCRA Listed Waste K106 **Treatment and Recycle**

LECTURE 12

❖ Case Studies

Hg

♦ Mercury* Recycle

THE RECOVERY AND RECYCLE OF MERCURY FROM CHLOR-ALKALI PLANT WASTEWATER SLUDGE

L.G. Twidwell and R.J. Thompson

ABSTRACT

Universal Dynamics, Innochem Engineering and Montana Tech of the University of Montana have developed a hydrometallurgical process for the recovery and recycle of mercury from chlor-alkali plant wastewater sludge materials (EPA hazardous waste classification K106). The hydrometallurgical process is also applicable for the treatment of mercury contaminated soils (EPA hazardous waste classification D009) and other mercury bearing waste materials. The process is capable of lowering the mercury content in the K106 solids from 10% to <50 mg/kg Hg. The treated solids pass the U.S. EPA Toxicity Characteristic Leach Procedure for Hg of <25 mg/liter. The process has been commercialized and utilized at three U.S. Chlor-Alkali plants.

This paper describes the fundamental chemistry of the process, the flowsheet being used industrially (2-stage hypochlorite leach with subsequent recovery of mercury by iron cementation or electrowinning), and operating plant case histories.

❖Case Studies

Hg


Federal Register / Vol. 64, No. 184 / Thursday, September 23, 1999 / Notices


ACTION: Notice of intent to grant petition.

SUMMARY: The United States Environmental Protection Agency is announcing our intent to grant the petition of Pioneer Chlor-Alkali, Inc. in St. Gabriel, Louisiana for a site-specific determination of equivalent treatment (DET). This DET would address Pioneer's Remerc process for treating K106 mercury wastes under the Resource Conservation and Recovery Act (RCRA).

The proposed DET would recognize Remerc, a hydrometallurgical process, as an equivalent technology to roasting or retorting with recovery of mercury for reuse, our current land disposal restrictions (LDR) hazardous waste treatment standard for high mercury K106 waste (wastewater treatment sludge from the mercury cell process

This hydrometallurgical process has been accepted by the EPA as an alternative BDAT*. Universal Dynamics has commercialized the process under the name REMERC. The REMERC hydrometallurgical process has been installed at three U.S. Chlor-Alkali plants (Georgia-Pacific, Bellingham, Washington; Westlake C&D Corporation, Calvert City, Kentucky; and Pioneer Chlor-Alkali, St. Gabriel, Louisiana).

Comparative Requirements

Table II. United States Environmental Requirements for Mercury Bearing Nonwastewaters

Category[1]	Total Hg in original sludge, ppm	TCLP Hg on treated waste, ppb[2]	BDAT applied to original sludge[3]
K106	>260	<200	Thermal Recovery (Retort/Roast)
K106	<260	<25	Acid Leach/Oxidize/Dewater
K071	Not specified	<200	Thermal Recovery
K071	Not specified	<25	Acid Leach/Oxidize/Dewater
D009	>260	<200	Thermal Recovery
D009	<260	<25	Acid Leach/Oxidize/Dewater

1 K106 is sludge produced by sulfide precipitation from mercury cell chlor-alkali wastewater; K071 is mercury cell chlor-alkali brine purification muds; D009 is mercury bearing sludge from generic sources.

2 TCLP is the maximum leachable mercury allowed by EPA for sludge treated for land disposal.

3 The EPA required treatment technology.

Industry Results

Table I. K106 Waste Generation by Chlor-Alkali Plants in the United States that Utilize the REMERC Technology.

Facility	Waste Generation, tons/yr	Mercury Content, %
Georgia-Pacific, Bellingham, Washington	110	3-4
Westlake Chemicals, Calvert City, Kentucky	180	8-10
Pioneer Chlor-Alkali, St. Gabriel, Louisiana	180	5-6

These waste materials cannot be disposed in U.S. landfills without prior pretreatment (EPA requirement since May 1994).

- The Process
  - LEACH

    Hypochlorite Leach to dissolve the mercury from mercury sulfide
  - RECOVERY

    Iron Cementation to recover elemental mercury
  - RECYCLE

    Recycled to the chlorine gas production electrolysis cells

The Process

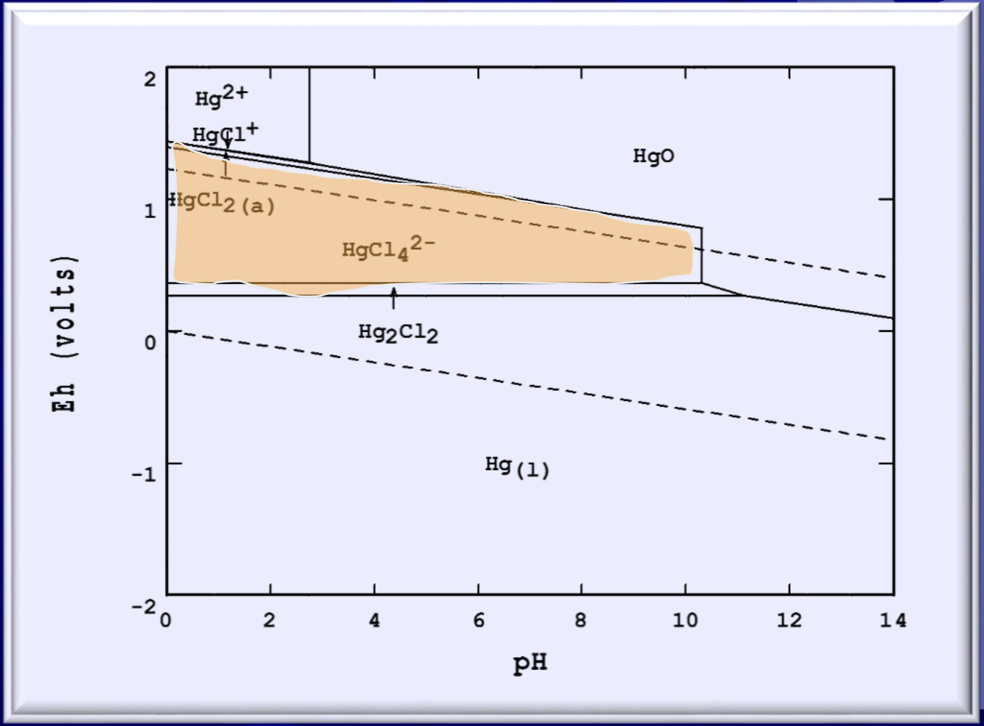
LEACH

Hypochlorite Leach to dissolve the mercury from mercury sulfide

Oxidizing Chloride leach required to dissolve HgS

For mercury sulfide,

$$HgS + 4\ NaOCl + 2\ Cl^{-1} = HgCl_4^{-2} + Na_2SO_4 + 2\ NaCl$$



◆The Process

$HgS + 4\ NaOCl + 2\ Cl^{-1} = HgCl_4^{-2} + Na_2SO_4 + 2\ NaCl$

Leach solution: 5-27% NaCl, 20-100 C, Eh 1100 mv, stage 1-1 hr, stage 2-15 min

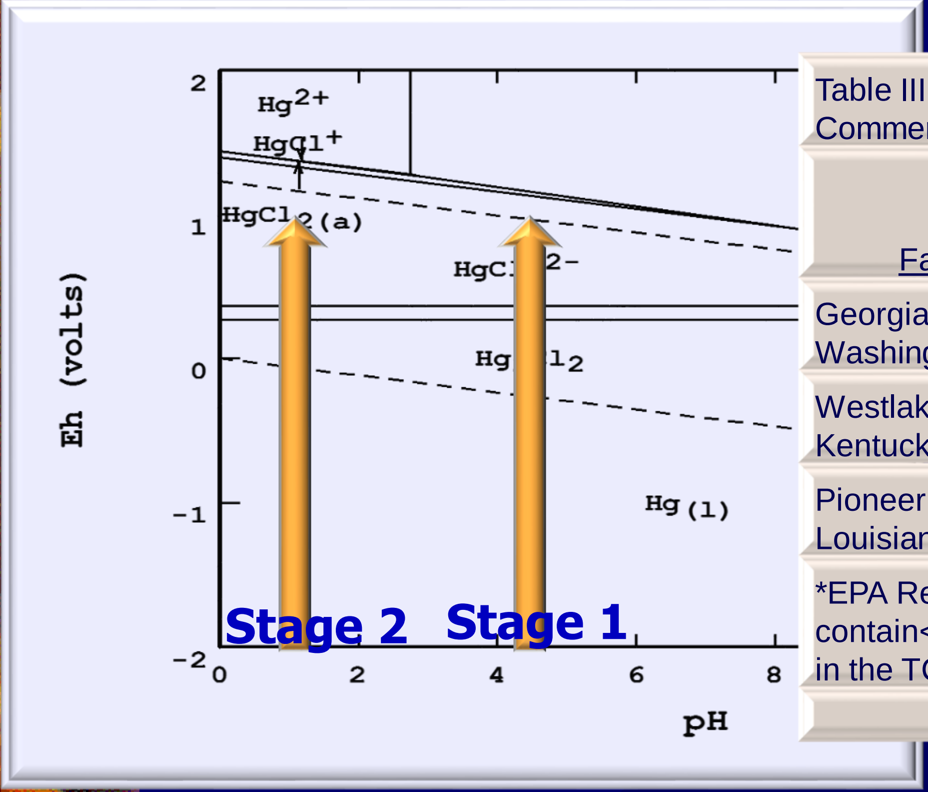


Table III. Typical Mercury Recovery Leach Results Achieved by Commercial Facilities

Facility/Location/Date Adopted	Initial Hg, ppm	Residual Hg, ppm*
Georgia-Pacific/Bellingham, Washington/1993	60,000	150
Westlake Chemicals/Calvert City, Kentucky/1994	110,000	220
Pioneer Chlor-Alkali/St. Gabriel, Louisiana/1996	55,000	50

*EPA Regulatory Requirement: the hypochlorite leach residue must contain<260 ppm mercury and the treated product must leach mercury in the TCLP test to < 25 ppb.

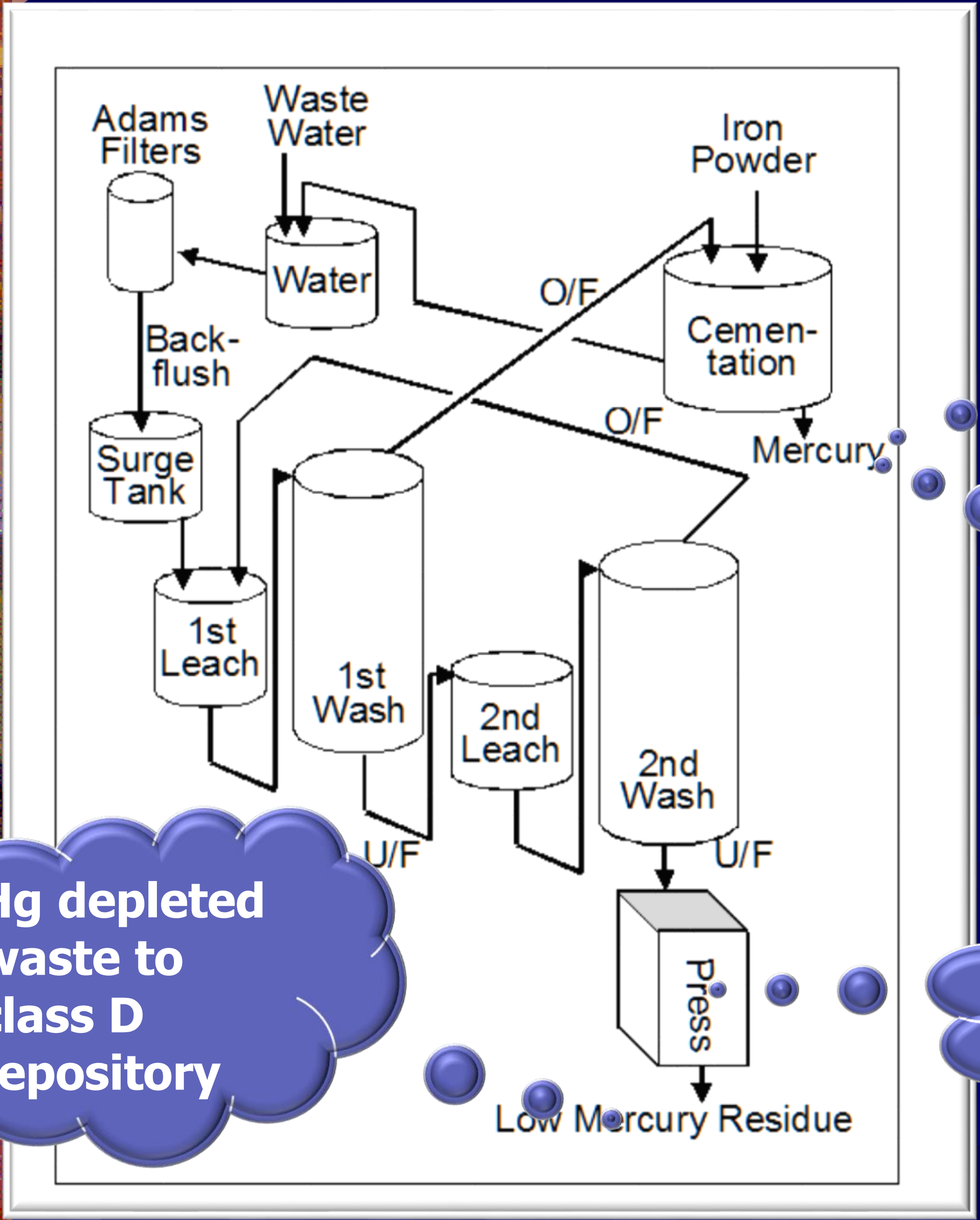
- The Process
  - RECOVERY of Mercury from Solution

    Iron Cementation to recover elemental mercury

Primary Reaction

$$HgCl_4^{-2} + Fe^{o} = Hg^{o} + FeCl_2 + 2\ Cl^{-1}$$

Elemental Mercury forms in receiving chamber



Equivalent to triply distilled Hg

Recycled to electrolytic cells

Depleted solution back to electrolytic cells

Hg depleted waste to class D repository

❖Case Studies

Tl

Thallium Remediation at a Heap Leach Gold Operation in Montana

New Topic

LECTURE 13

LECTURE 13

❖Case Studies

Tl

Thallium Remediation at a Heap Leach Gold Operation in Montana

Environmental Standards

Source	Standard, µg/L
U.S. EPA MCL	2
U.S. EPA RCRA BDAT	140
Montana Water Quality Board Human Health	1.7
Montana Non-Degradation Trigger	0.3

Thallium Occurrence

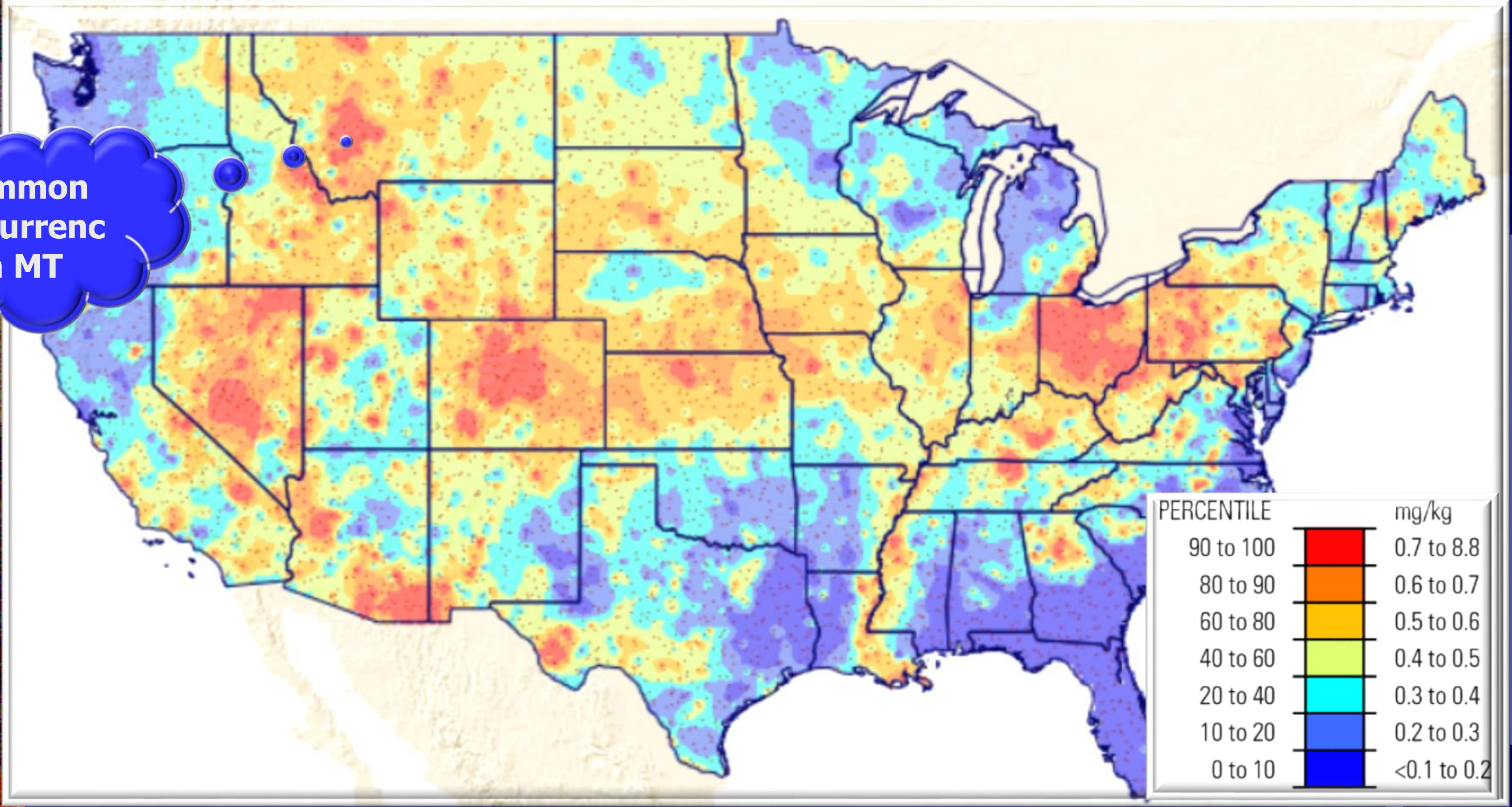
- The major sources of thallium are the base metal sulfides and precious metal bearing sulfides, especially gold bearing pyrites and copper sulfide
- Therefore, thallium is often a contaminant in waters emanating from heavy metal deposits, e.g., sulfide bearing deposits.

Thallium Sources-Wastewater

Source	Water, $\mu g/L$
Mining	
Hg/Tl Ores	400-27,000
Hg/As Ores	100-13,000
Coal Mines	50-10,000
Smelters	
Pb	480-18,000
Cu	0-1,600
Pb/Zn Process Solution	1,000,000

Thallium Distribution (mrdata.USGS.gov/ds-801/map.html)

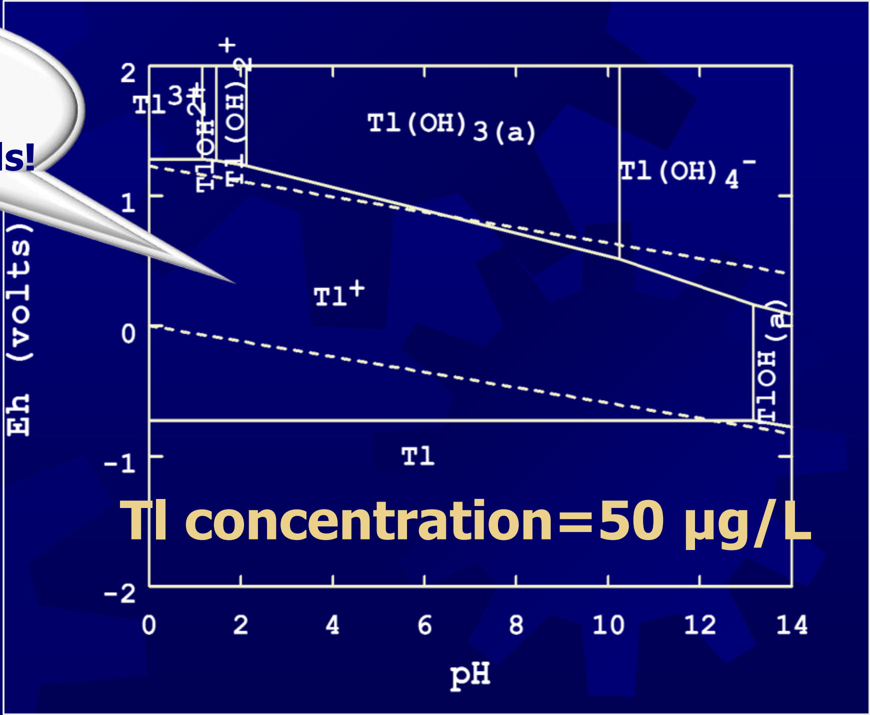
Common occurrence in MT



Thallium Chemistry

- Thallium chemistry resembles potassium
- Compounds of thallium are relatively soluble, at least, compounds do not form that have solubilities <2µg/L
- Thallium with a +1 valence predominates in natural waters (see following figure)

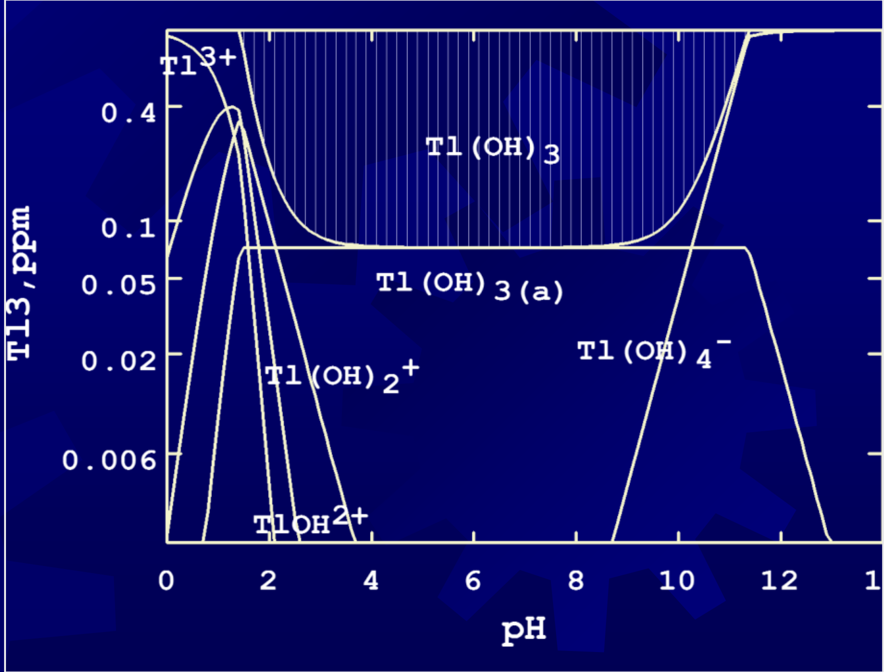
No solids form within water stability potentials!



Tl concentration=50 µg/L

Thallium Precipitation

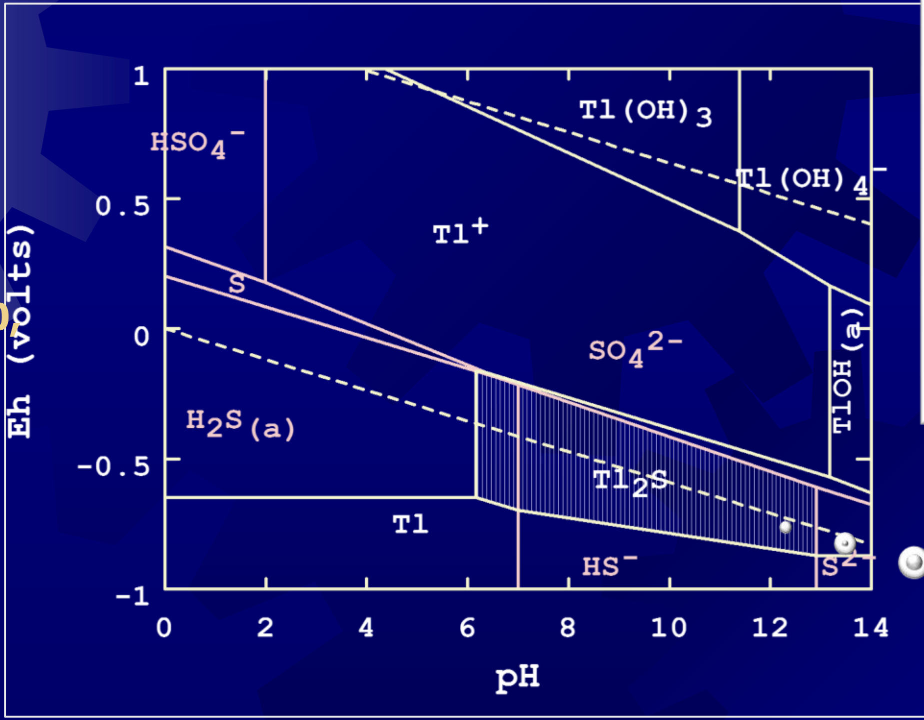
- Hydroxide
  - EPA BDAT-precipitation of $Tl(OH)_3$ under very aggressive oxidizing conditions
  - However, the BDAT is only capable of achieving removals to >75 µg/L

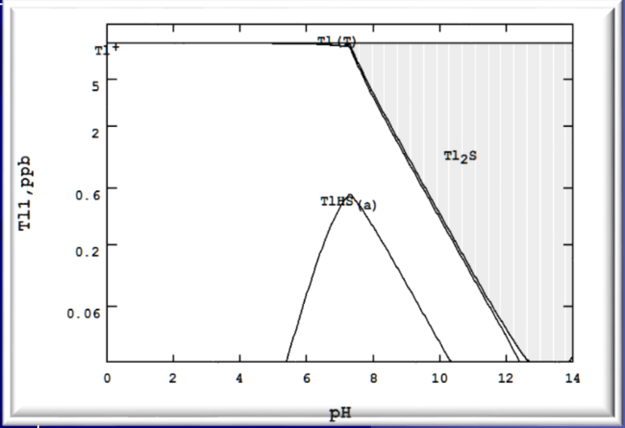


Thallium Precipitation

- ○ **Sulfide Precipitation** (used at some smelters)
  - Requires high sulfide/Tl concentrations, low solution potentials, and neutral to basic pHs
  - Has been used at some smelter sites (but not at the example remediation site)

S/Tl=100,
Tl=1
mg/L





Note: requires reducing conditions

Thallium Adsorption

Another approach

- Manganese Dioxide

Catherin Williams-Beam Montana Tech M.Sc. Degree

EPA Mine Waste Technology Program (MWTP)

  Demonstrated conditions for removal of Tl (+1) to MCL levels using MnO2

Great absorber for Tl and dissolved metals

Thallium Adsorption

Manganese Dioxide Adsorbent

○ **Short Summary** (Williams-Beam)

Two level factorial design results:

Final Tl (μ/L) = 82.85 + 0.80*Initial pH + 1.40*MnO2 (g/L) - 0.12*Initial Tl (μg/L) – 9.87*Time (hrs) - 0.87*Initial pH*MnO2 (g/L) + 0.024*Initial pH*Initial Tl (μ/L).

Thallium Adsorption

Manganese Dioxide Adsorbent

- ○ **Short Summary** (Williams-Beam)
  - To achieve <5 µg/L
    - pH 5-8
    - Amount of MnO_2: >0.5 g/L
    - Time >30 minutes; Passes TCLP

Thallium* Remediation (Successful Example)

CR KENDALL MINE CLOSURE PLAN WATER MANAGEMENT

Background

- MDEQ lead agency
- Non-operating open pit Gold mines (closed 1995)
  - CN gold heap leach process
  - Near Lewistown, MT
  - Heap capping approved 2011 to prevent egress of water
  - Remediation projected to be completed in 10-40 years

Thallium* Remediation

CR KENDALL MINE CLOSURE PLAN

- Thallium major element of concern

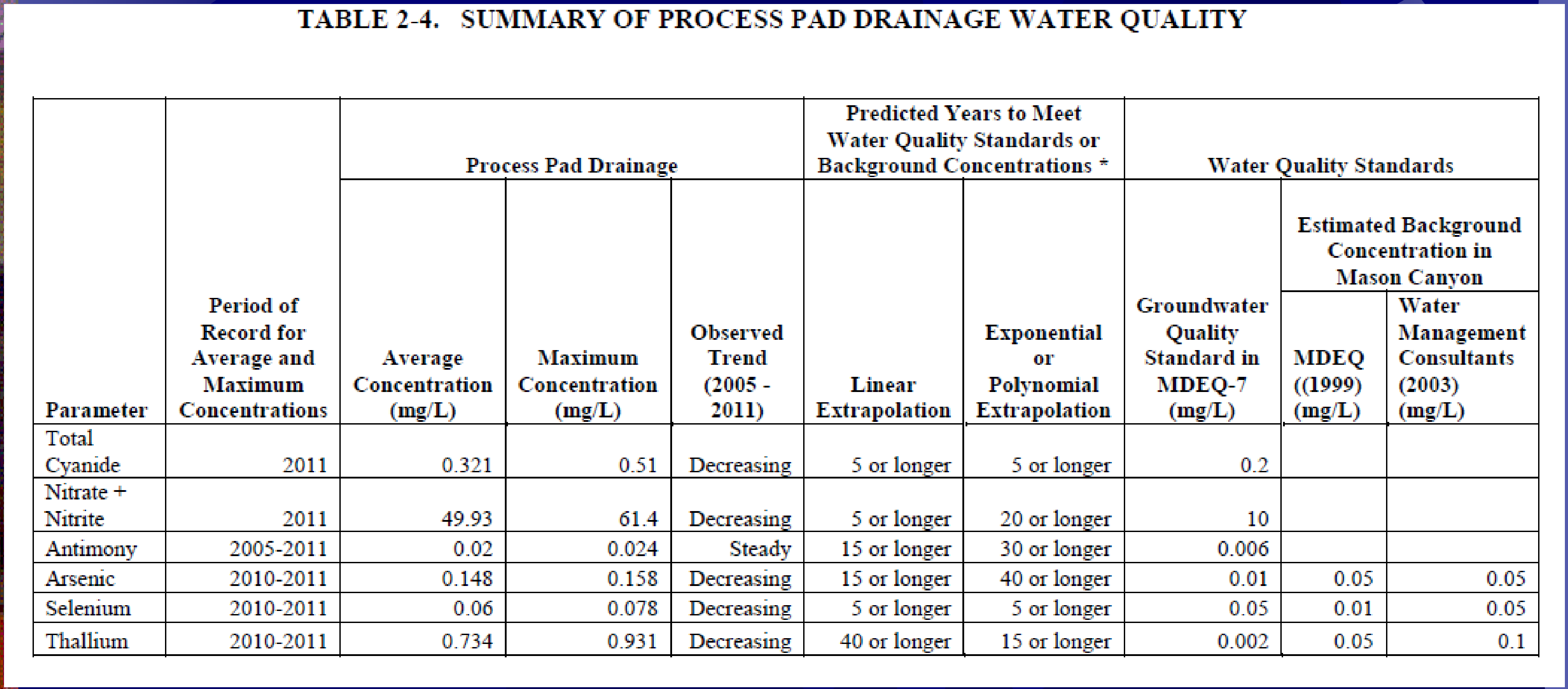


TABLE 2-4. SUMMARY OF PROCESS PAD DRAINAGE WATER QUALITY

		Process Pad Drainage			Predicted Years to Meet Water Quality Standards or Background Concentrations *		Water Quality Standards		
								Estimated Background Concentration in Mason Canyon	
Parameter	Period of Record for Average and Maximum Concentrations	Average Concentration (mg/L)	Maximum Concentration (mg/L)	Observed Trend (2005 - 2011)	Linear Extrapolation	Exponential or Polynomial Extrapolation	Groundwater Quality Standard in MDEQ-7 (mg/L)	MDEQ ((1999) (mg/L)	Water Management Consultants (2003) (mg/L)
Total Cyanide	2011	0.321	0.51	Decreasing	5 or longer	5 or longer	0.2		
Nitrate + Nitrite	2011	49.93	61.4	Decreasing	5 or longer	20 or longer	10		
Antimony	2005-2011	0.02	0.024	Steady	15 or longer	30 or longer	0.006		
Arsenic	2010-2011	0.148	0.158	Decreasing	15 or longer	40 or longer	0.01	0.05	0.05
Selenium	2010-2011	0.06	0.078	Decreasing	5 or longer	5 or longer	0.05	0.01	0.05
Thallium	2010-2011	0.734	0.931	Decreasing	40 or longer	15 or longer	0.002	0.05	0.1

Thallium* Remediation

CR KENDALL MINE CLOSURE PLAN

- ○ Alternatives Investigated
  - ○ RO-good for nitrate and CN, not for Tl
  - ○ Biological (SRB)-good for Tl and metals, but produced ammonia, H2S, and organic carbon
  - ○ Sulfide precipitation-good for Tl and most metals but "how do you store the product?"

Possible treatment technologies

Chosen

Zeolite adsorption proven in lab and pilot demonstrations. Good for Tl and metals. Passed TCLP and SPLP tests

Thallium* Remediation

CR KENDALL MINE CLOSURE PLAN

- ○ Zeolite adsorption proven in lab and pilot demonstrations. Passed TCLP and SPLP tests

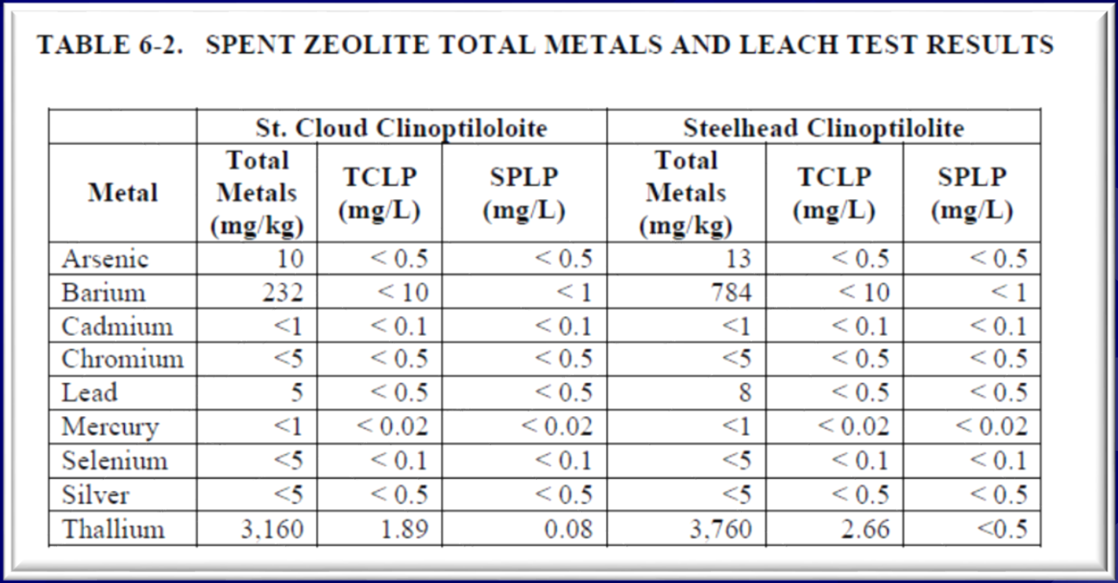


TABLE 6-2. SPENT ZEOLITE TOTAL METALS AND LEACH TEST RESULTS

	St. Cloud Clinoptiloloite			Steelhead Clinoptilolite		
Metal	Total Metals (mg/kg)	TCLP (mg/L)	SPLP (mg/L)	Total Metals (mg/kg)	TCLP (mg/L)	SPLP (mg/L)
Arsenic	10	< 0.5	< 0.5	13	< 0.5	< 0.5
Barium	232	< 10	< 1	784	< 10	< 1
Cadmium	<1	< 0.1	< 0.1	<1	< 0.1	< 0.1
Chromium	<5	< 0.5	< 0.5	<5	< 0.5	< 0.5
Lead	5	< 0.5	< 0.5	8	< 0.5	< 0.5
Mercury	<1	< 0.02	< 0.02	<1	< 0.02	< 0.02
Selenium	<5	< 0.1	< 0.1	<5	< 0.1	< 0.1
Silver	<5	< 0.5	< 0.5	<5	< 0.5	< 0.5
Thallium	3,160	1.89	0.08	3,760	2.66	<0.5

- ○ Loaded Zeolite (0.3%Tl) disposed of in a dry open impoundment, rainwater not a problem because it passes SPLP test

Thallium* Remediation

CR KENDALL MINE CLOSURE PLAN

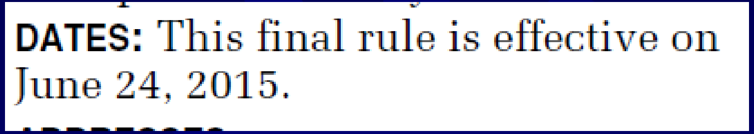
- Final Tl in treated water <0.2 µg/L; this is the columns controlled break through value, if the break through exceeds this value the zeolite is replaced
- Loaded Zeolite (0.3%Tl) disposed of in a dry open impoundment, rainwater not a problem because it passes SPLP test

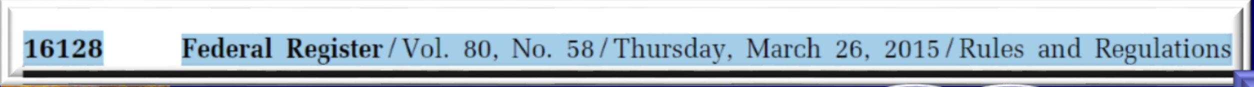
- Present Day Controversial EPA Practices

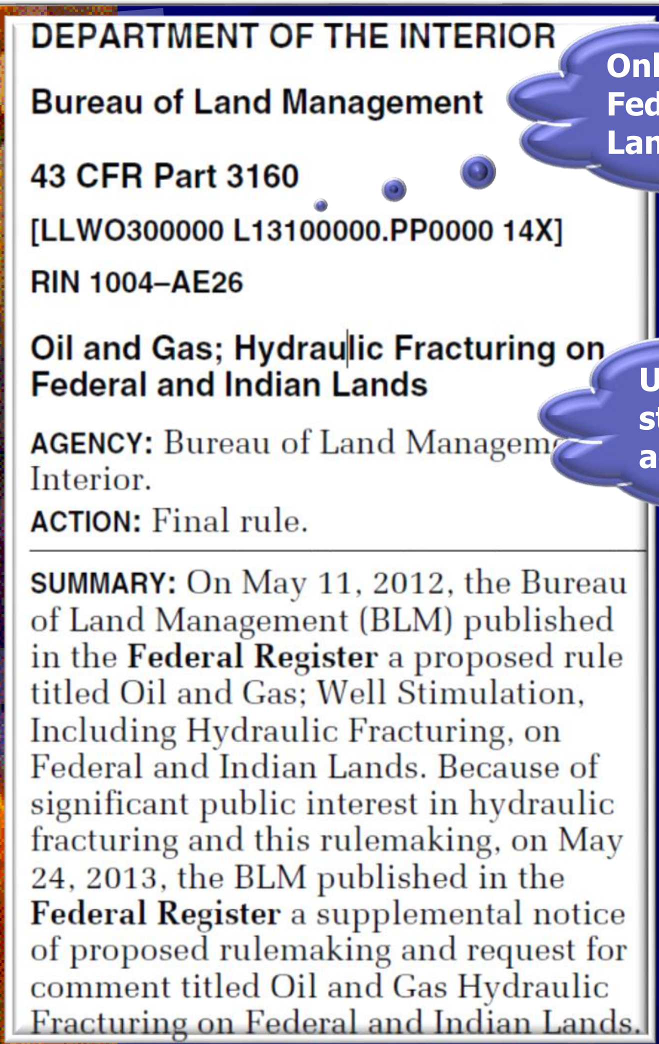
New Topic

➢ Present Day Controversial EPA Practices

○ Example: Fracting*


DATES: This final rule is effective on June 24, 2015.


16128 **Federal Register** / Vol. 80, No. 58 / Thursday, March 26, 2015 / Rules and Regulations


DEPARTMENT OF THE INTERIOR

Bureau of Land Management

43 CFR Part 3160

[LLWO300000 L13100000.PP0000 14X]

RIN 1004–AE26

Oil and Gas; Hydraulic Fracturing on Federal and Indian Lands

AGENCY: Bureau of Land Managem Interior.

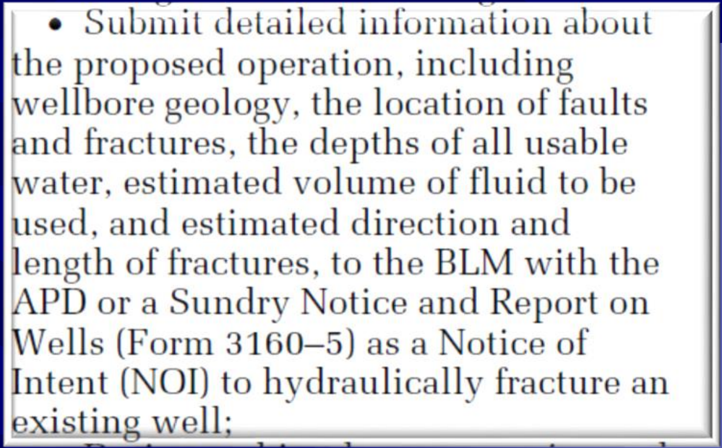
ACTION: Final rule.

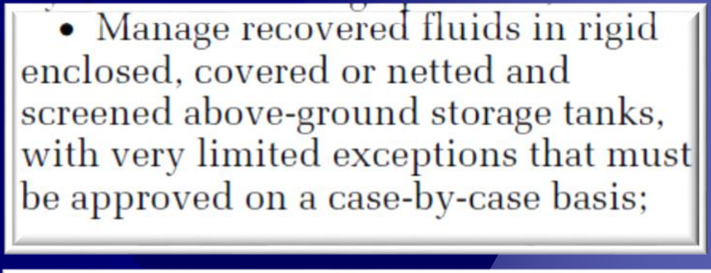
SUMMARY: On May 11, 2012, the Bureau of Land Management (BLM) published in the **Federal Register** a proposed rule titled Oil and Gas; Well Stimulation, Including Hydraulic Fracturing, on Federal and Indian Lands. Because of significant public interest in hydraulic fracturing and this rulemaking, on May 24, 2013, the BLM published in the **Federal Register** a supplemental notice of proposed rulemaking and request for comment titled Oil and Gas Hydraulic Fracturing on Federal and Indian Lands.

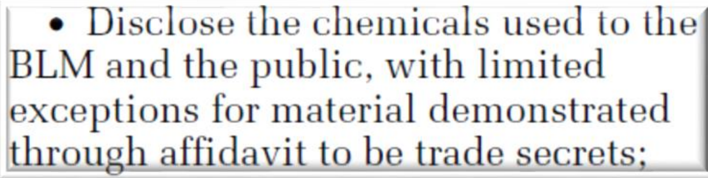
Only applies to Federal and Indian Lands

Unless individual states choose to adopt

Controversial Changes:


- Submit detailed information about the proposed operation, including wellbore geology, the location of faults and fractures, the depths of all usable water, estimated volume of fluid to be used, and estimated direction and length of fractures, to the BLM with the APD or a Sundry Notice and Report on Wells (Form 3160–5) as a Notice of Intent (NOI) to hydraulically fracture an existing well;


- Manage recovered fluids in rigid enclosed, covered or netted and screened above-ground storage tanks, with very limited exceptions that must be approved on a case-by-case basis;


- Disclose the chemicals used to the BLM and the public, with limited exceptions for material demonstrated through affidavit to be trade secrets;

➢ Present Day Controversial EPA Practices

NEWS » NATIONAL

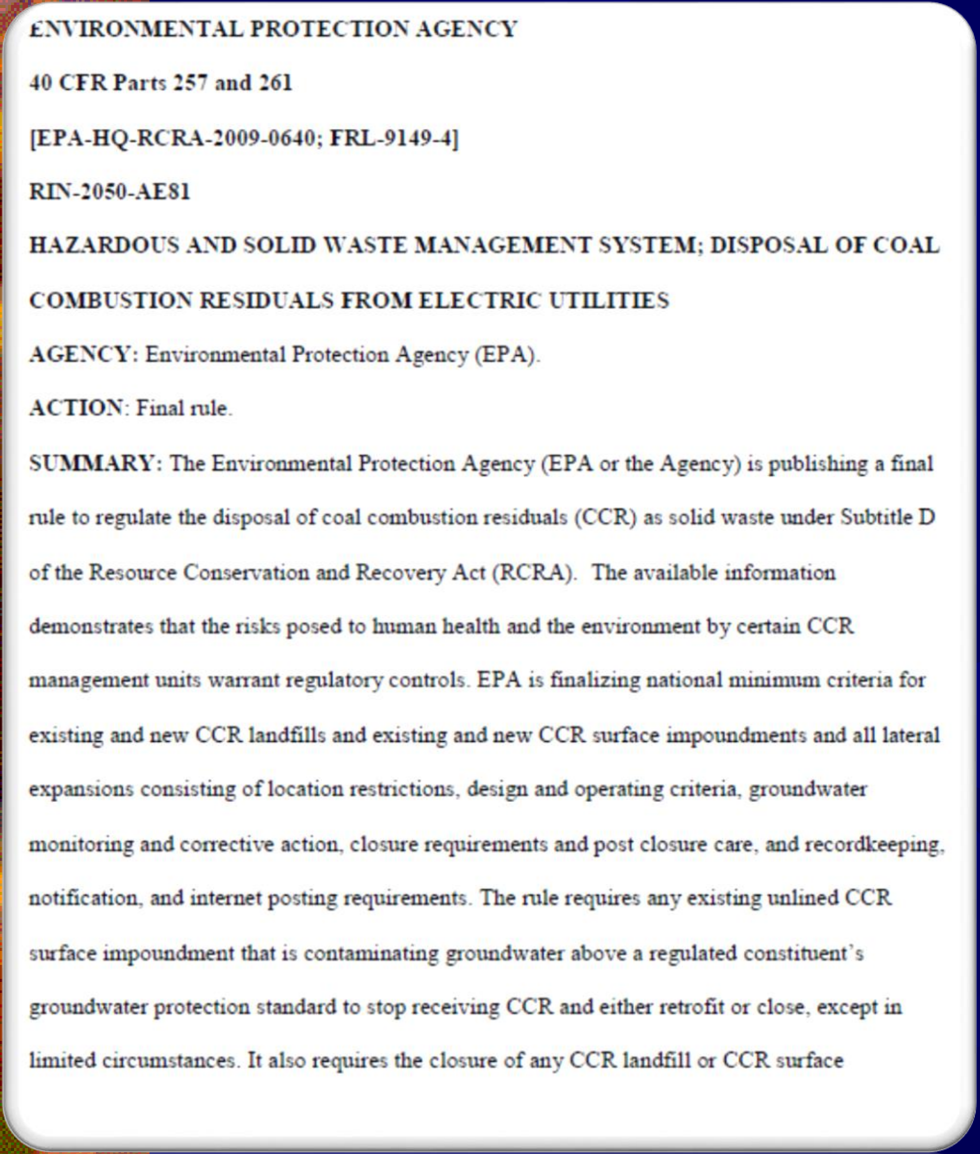
MARCH 20, 2015

U.S. Sets First Major Fracking Rules on Federal Lands

Although only about 10 percent of fracking occurs on federal lands, the Obama administration is hoping the new rules will become a model for industry standards elsewhere, especially in states that do not have fracking rules.

➢ Present Day Controversial EPA Practices

➢ Example: Coal Combustion Residuals (CCR*)



ENVIRONMENTAL PROTECTION AGENCY

40 CFR Parts 257 and 261

[EPA-HQ-RCRA-2009-0640; FRL-9149-4]

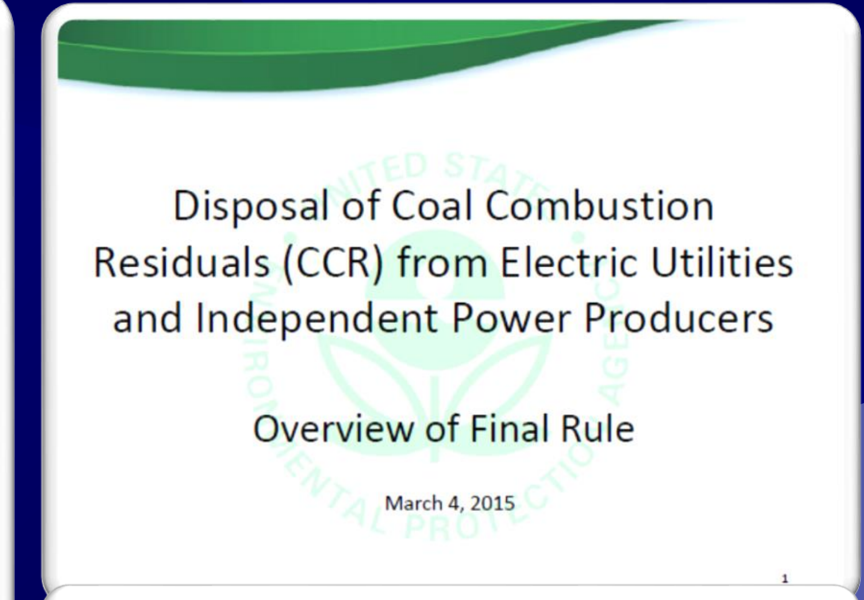
RIN-2050-AE81

HAZARDOUS AND SOLID WASTE MANAGEMENT SYSTEM; DISPOSAL OF COAL COMBUSTION RESIDUALS FROM ELECTRIC UTILITIES

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: The Environmental Protection Agency (EPA or the Agency) is publishing a final rule to regulate the disposal of coal combustion residuals (CCR) as solid waste under Subtitle D of the Resource Conservation and Recovery Act (RCRA). The available information demonstrates that the risks posed to human health and the environment by certain CCR management units warrant regulatory controls. EPA is finalizing national minimum criteria for existing and new CCR landfills and existing and new CCR surface impoundments and all lateral expansions consisting of location restrictions, design and operating criteria, groundwater monitoring and corrective action, closure requirements and post closure care, and recordkeeping, notification, and internet posting requirements. The rule requires any existing unlined CCR surface impoundment that is contaminating groundwater above a regulated constituent's groundwater protection standard to stop receiving CCR and either retrofit or close, except in limited circumstances. It also requires the closure of any CCR landfill or CCR surface



Disposal of Coal Combustion Residuals (CCR) from Electric Utilities and Independent Power Producers

Overview of Final Rule

March 4, 2015

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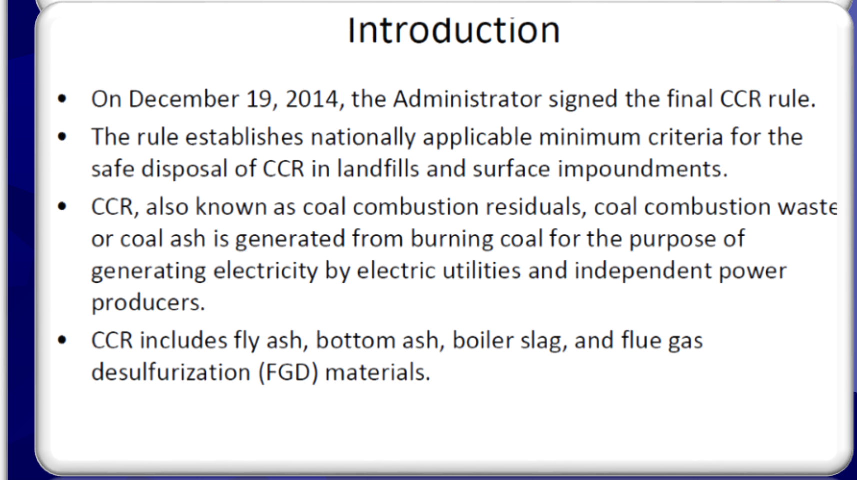
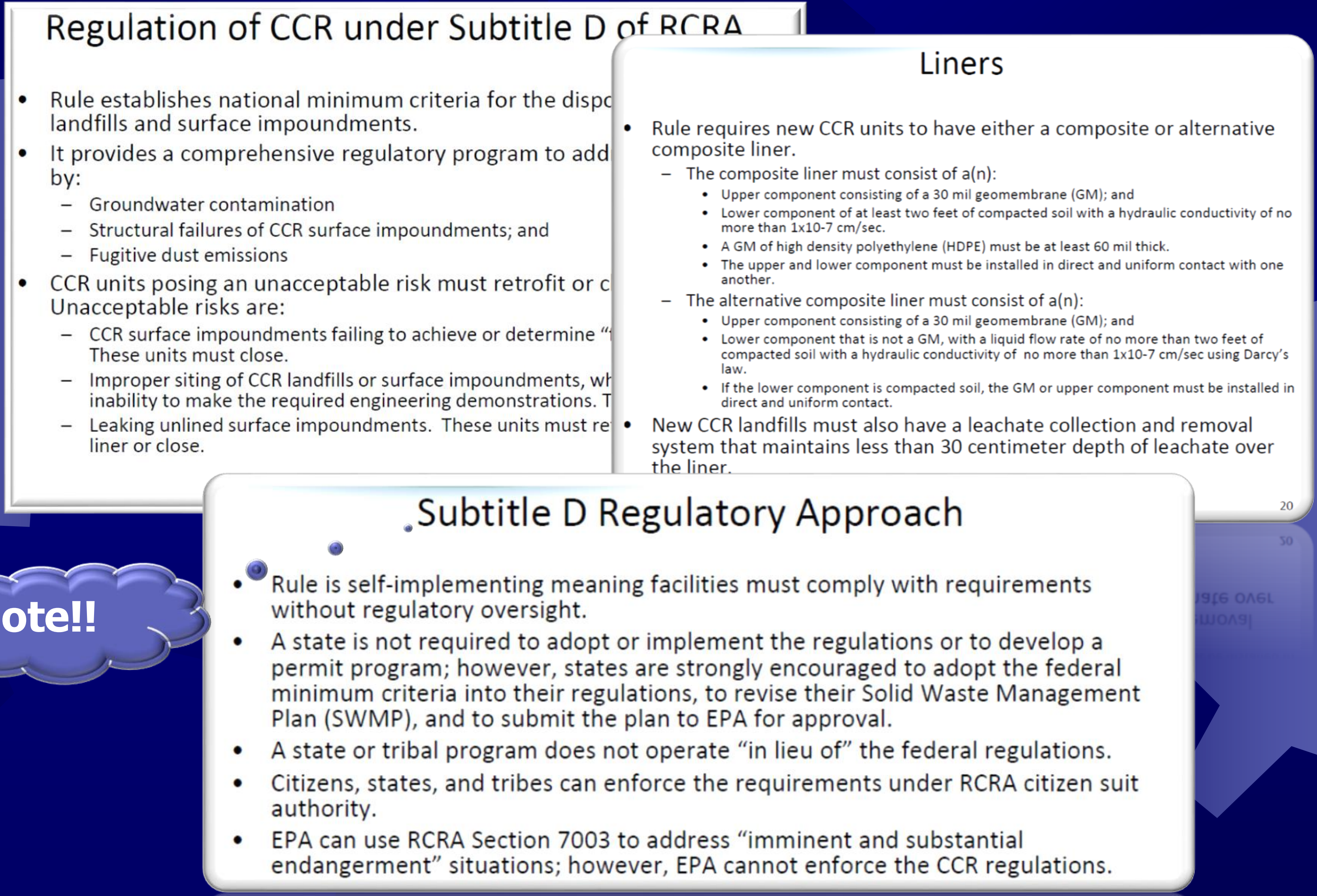


Introduction

- On December 19, 2014, the Administrator signed the final CCR rule.
- The rule establishes nationally applicable minimum criteria for the safe disposal of CCR in landfills and surface impoundments.
- CCR, also known as coal combustion residuals, coal combustion waste or coal ash is generated from burning coal for the purpose of generating electricity by electric utilities and independent power producers.
- CCR includes fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) materials.

➢ Present Day Controversial EPA Practices

○ Example: Coal Combustion Residuals (CCR*)



Regulation of CCR under Subtitle D of RCRA

- Rule establishes national minimum criteria for the dispo landfills and surface impoundments.
- It provides a comprehensive regulatory program to add by:
  - Groundwater contamination
  - Structural failures of CCR surface impoundments; and
  - Fugitive dust emissions
- CCR units posing an unacceptable risk must retrofit or c Unacceptable risks are:
  - CCR surface impoundments failing to achieve or determine " These units must close.
  - Improper siting of CCR landfills or surface impoundments, wh inability to make the required engineering demonstrations. T
  - Leaking unlined surface impoundments. These units must re liner or close.

Liners

- Rule requires new CCR units to have either a composite or alternative composite liner.
  - The composite liner must consist of a(n):
    - Upper component consisting of a 30 mil geomembrane (GM); and
    - Lower component of at least two feet of compacted soil with a hydraulic conductivity of no more than 1x10-7 cm/sec.
    - A GM of high density polyethylene (HDPE) must be at least 60 mil thick.
    - The upper and lower component must be installed in direct and uniform contact with one another.
  - The alternative composite liner must consist of a(n):
    - Upper component consisting of a 30 mil geomembrane (GM); and
    - Lower component that is not a GM, with a liquid flow rate of no more than two feet of compacted soil with a hydraulic conductivity of no more than 1x10-7 cm/sec using Darcy's law.
    - If the lower component is compacted soil, the GM or upper component must be installed in direct and uniform contact.
- New CCR landfills must also have a leachate collection and removal system that maintains less than 30 centimeter depth of leachate over the liner.

Subtitle D Regulatory Approach

- Rule is self-implementing meaning facilities must comply with requirements without regulatory oversight.
- A state is not required to adopt or implement the regulations or to develop a permit program; however, states are strongly encouraged to adopt the federal minimum criteria into their regulations, to revise their Solid Waste Management Plan (SWMP), and to submit the plan to EPA for approval.
- A state or tribal program does not operate "in lieu of" the federal regulations.
- Citizens, states, and tribes can enforce the requirements under RCRA citizen suit authority.
- EPA can use RCRA Section 7003 to address "imminent and substantial endangerment" situations; however, EPA cannot enforce the CCR regulations.

Note!!

➢ Present Day Controversial EPA Practices

○ Example: Uranium* Mining

WATER POLLUTION:

EPA proposes expanded oversight of uranium mining

Manuel Quiñones, E&E reporter

Greenwire: Wednesday, January 14, 2015

U.S. EPA is proposing new water protection and monitoring regulations for a controversial form of uranium mining, according to a copy obtained by *Greenwire*.

Administrator Gina McCarthy [illegible] the proposed rule Dec. 31, and the agency is scheduled to make it public in the near future. The proposal comes under EPA's effort to address concerns surrounding in-situ recovery uranium extraction sites.

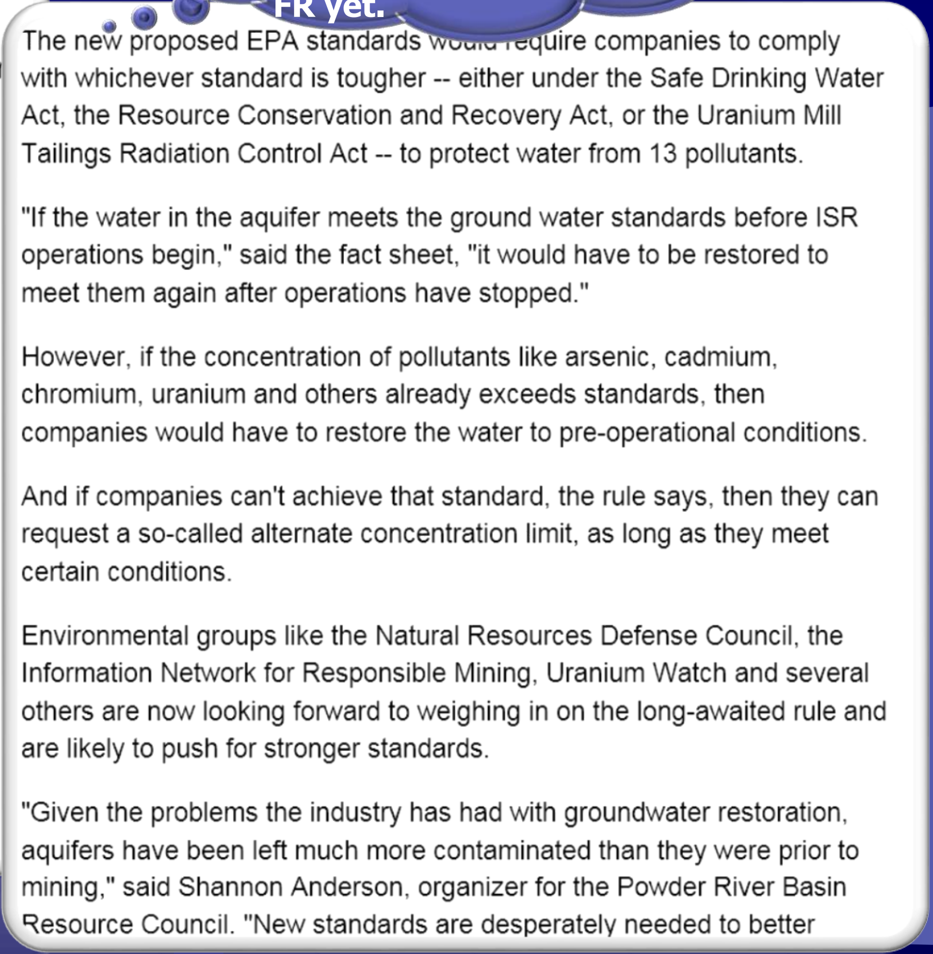
Not yet

In-situ recovery, also known as in-situ leach, involves injecting fluids underground to free uranium deposits, which are then pumped out. It is now, where geologically possible, the preferred method for uranium mining.

The proposed rule, according to an agency fact sheet, sets standards for companies to study existing water resources prior to the mining process.

While environmentalists complain the practice jeopardizes drinking water resources, the industry maintains it only touches already-polluted water (*Greenwire*, Dec. 23, 2011). Companies generally have to obtain an aquifer protection exemption from EPA.

Comment period 90 days from publication in FR. Not published in FR yet.



The new proposed EPA standards would require companies to comply with whichever standard is tougher -- either under the Safe Drinking Water Act, the Resource Conservation and Recovery Act, or the Uranium Mill Tailings Radiation Control Act -- to protect water from 13 pollutants.

"If the water in the aquifer meets the ground water standards before ISR operations begin," said the fact sheet, "it would have to be restored to meet them again after operations have stopped."

However, if the concentration of pollutants like arsenic, cadmium, chromium, uranium and others already exceeds standards, then companies would have to restore the water to pre-operational conditions.

And if companies can't achieve that standard, the rule says, then they can request a so-called alternate concentration limit, as long as they meet certain conditions.

Environmental groups like the Natural Resources Defense Council, the Information Network for Responsible Mining, Uranium Watch and several others are now looking forward to weighing in on the long-awaited rule and are likely to push for stronger standards.

"Given the problems the industry has had with groundwater restoration, aquifers have been left much more contaminated than they were prior to mining," said Shannon Anderson, organizer for the Powder River Basin Resource Council. "New standards are desperately needed to better

- Present Day Controversial EPA Regulations
  - Example: Selenium from coal mining
    - EPA’s* Case

THE PLANET

SIERRA CLUB STORIES FROM THE FRONT LINES

« Urban Girls Explore, Enjoy, and Protect | Main | Connecting the 9 in New Orleans »

pril 16, 2014

elenium: Mountaintop Removal Coal Mining's Toxic Legacy

ountaintop removal mining in West Virginia. Photo by Vivian Stockman, courtesy of the Ohio Valley Environmental Coalition.

Peter Morgan, Staff Attorney, Sierra Club Environmental Law Program

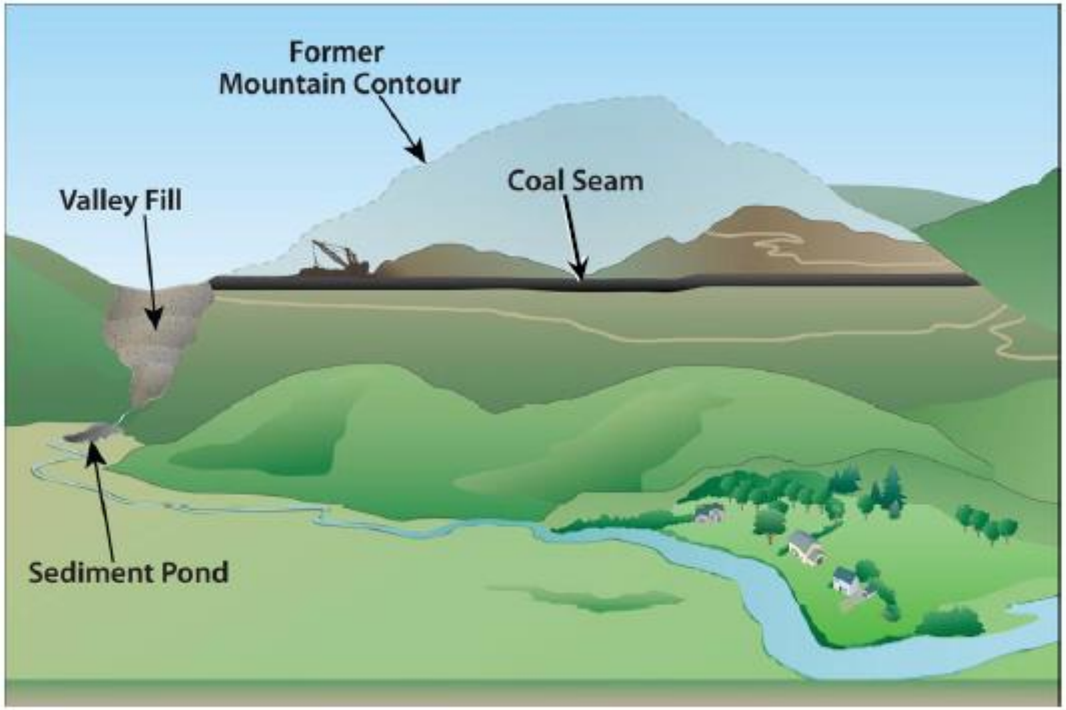
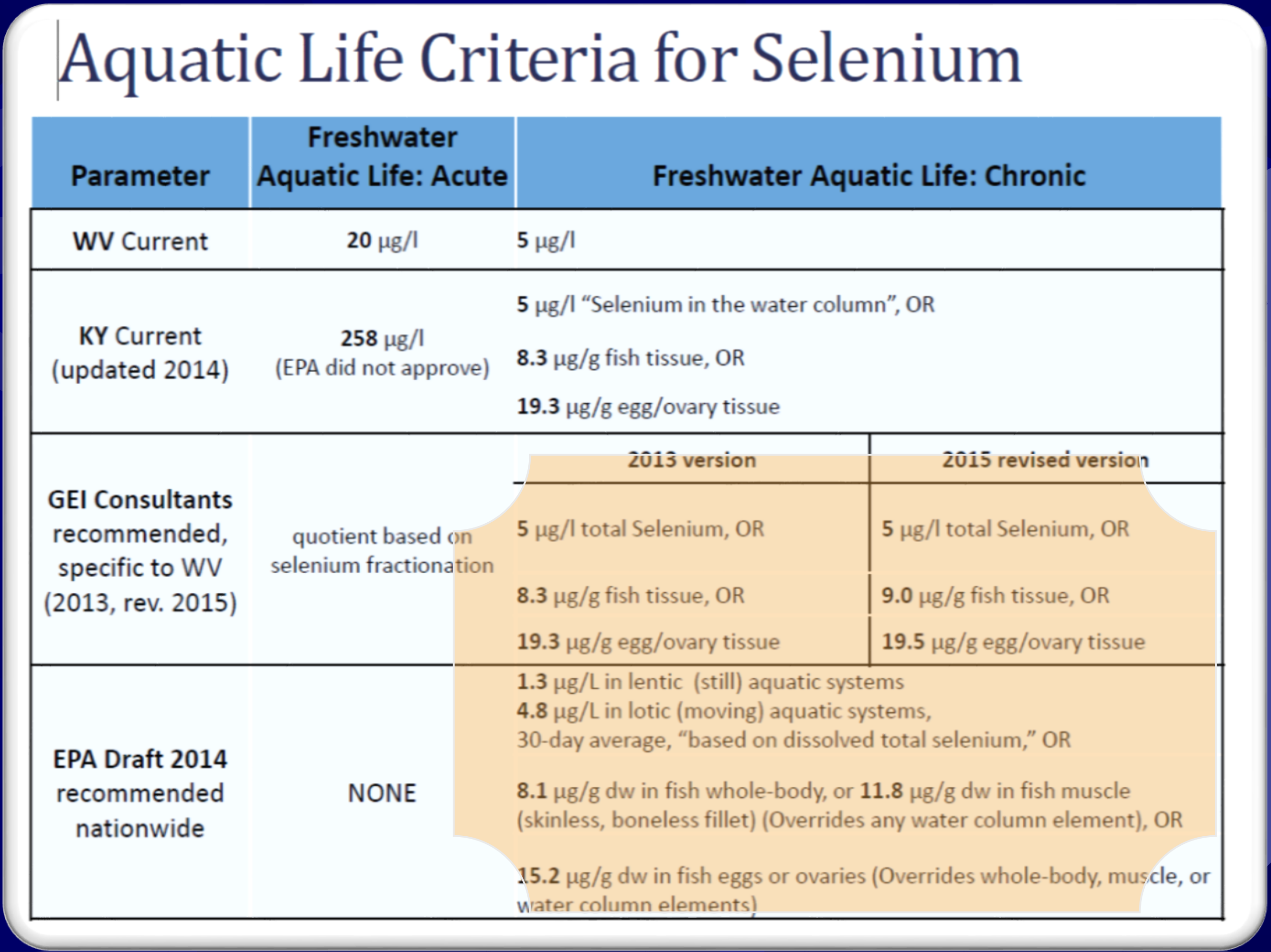


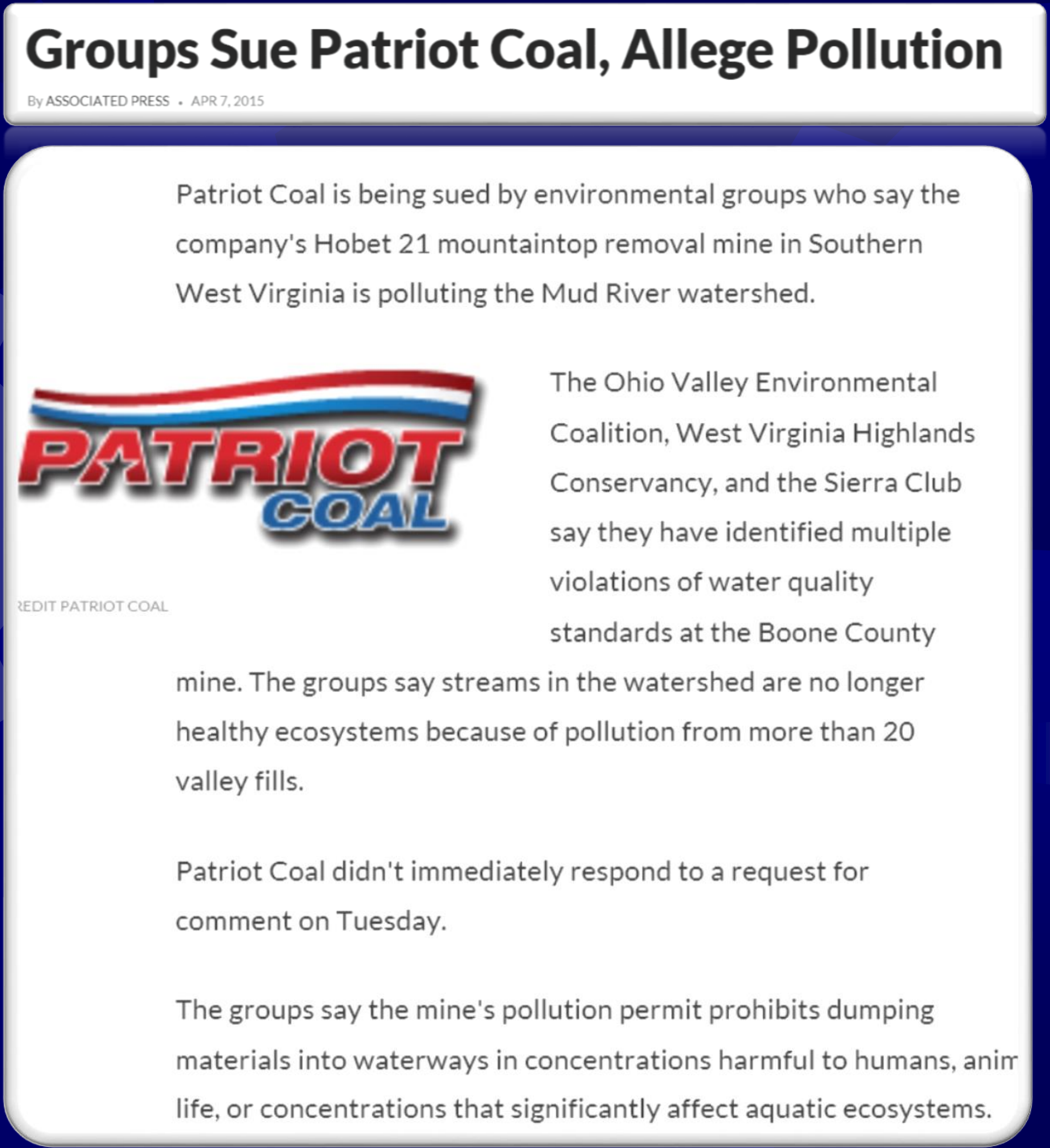
Figure 2. A watershed view of a mountaintop mine and valley fill (no consistent scale).

- Present Day Controversial EPA Regulations
  - Example: Selenium from coal mining
    - EPA's* Case



Aquatic Life Criteria for Selenium

Parameter	Freshwater Aquatic Life: Acute	Freshwater Aquatic Life: Chronic	
WV Current	**20** µg/l	**5** µg/l	
KY Current (updated 2014)	**258** µg/l (EPA did not approve)	**5** µg/l "Selenium in the water column", OR **8.3** µg/g fish tissue, OR **19.3** µg/g egg/ovary tissue	
GEI Consultants recommended, specific to WV (2013, rev. 2015)	quotient based on selenium fractionation	**2013 version**	**2015 revised version**
		5 µg/l total Selenium, OR **8.3** µg/g fish tissue, OR **19.3** µg/g egg/ovary tissue	**5** µg/l total Selenium, OR **9.0** µg/g fish tissue, OR **19.5** µg/g egg/ovary tissue
EPA Draft 2014 recommended nationwide	NONE	**1.3** µg/L in lentic (still) aquatic systems **4.8** µg/L in lotic (moving) aquatic systems, 30-day average, "based on dissolved total selenium," OR **8.1** µg/g dw in fish whole-body, or **11.8** µg/g dw in fish muscle (skinless, boneless fillet) (Overrides any water column element), OR **15.2** µg/g dw in fish eggs or ovaries (Overrides whole-body, muscle, or water column elements)	



Groups Sue Patriot Coal, Allege Pollution

By ASSOCIATED PRESS • APR 7, 2015

Patriot Coal is being sued by environmental groups who say the company's Hobet 21 mountaintop removal mine in Southern West Virginia is polluting the Mud River watershed.

REDIT PATRIOT COAL

The Ohio Valley Environmental Coalition, West Virginia Highlands Conservancy, and the Sierra Club say they have identified multiple violations of water quality standards at the Boone County mine. The groups say streams in the watershed are no longer healthy ecosystems because of pollution from more than 20 valley fills.

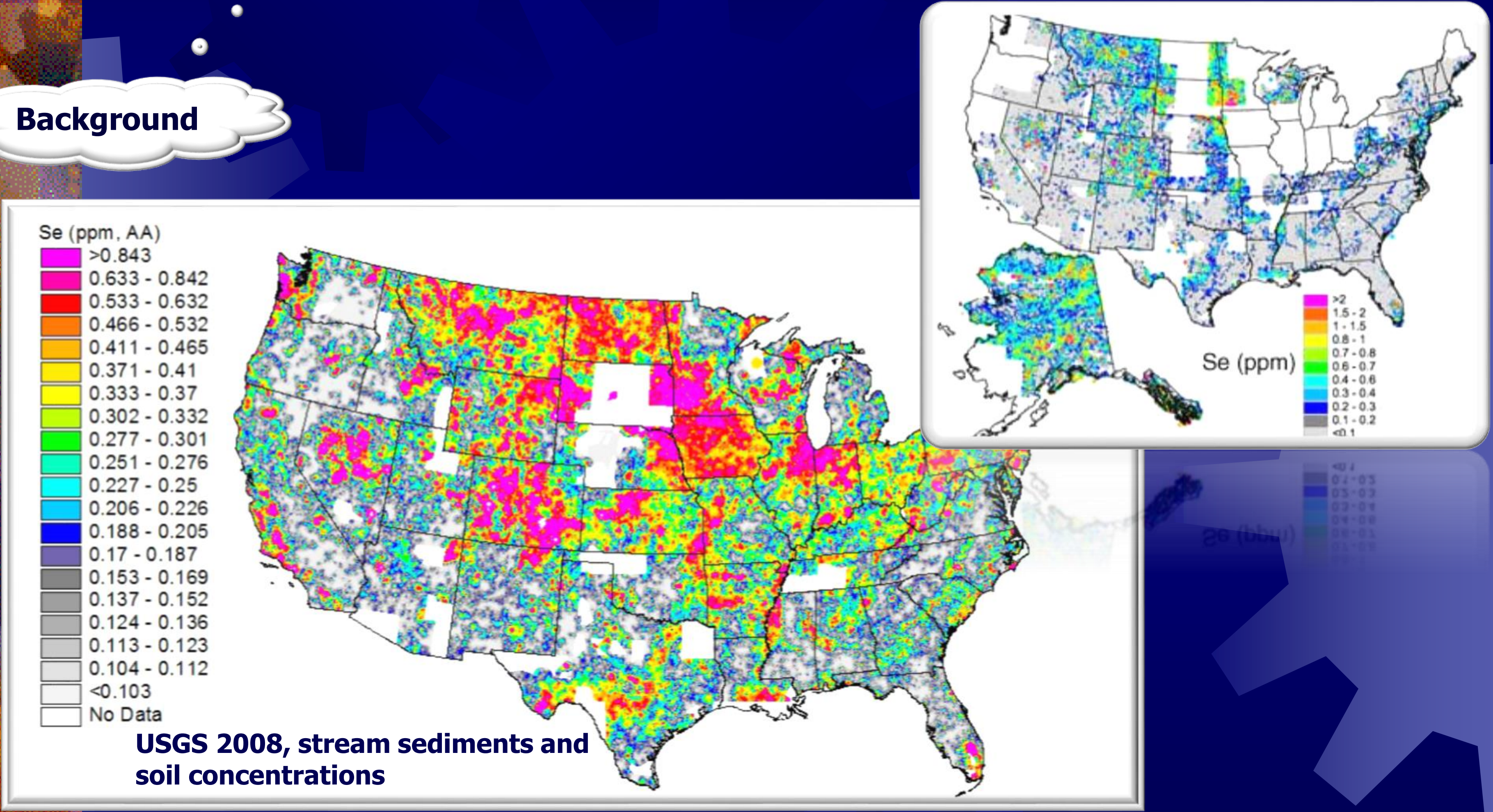
Patriot Coal didn't immediately respond to a request for comment on Tuesday.

The groups say the mine's pollution permit prohibits dumping materials into waterways in concentrations harmful to humans, anim life, or concentrations that significantly affect aquatic ecosystems.

Selenium Background

- Selenium distribution in US (USGS)

Background



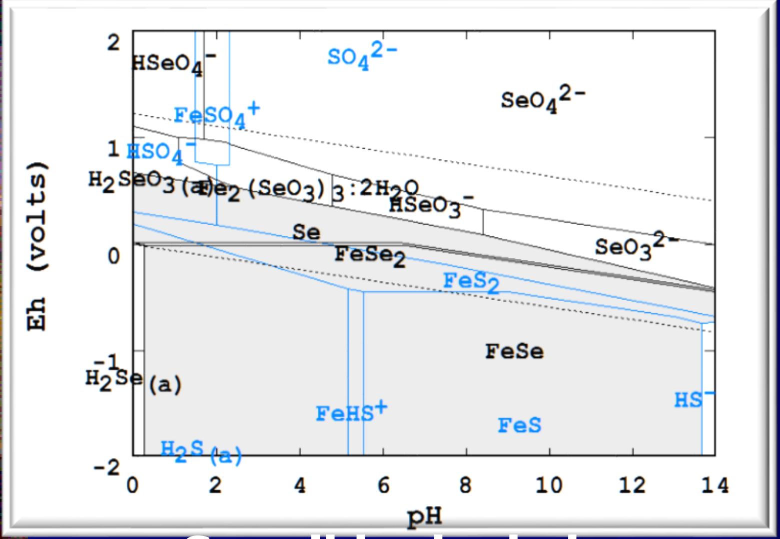
USGS 2008, stream sediments and soil concentrations

Selenium Background

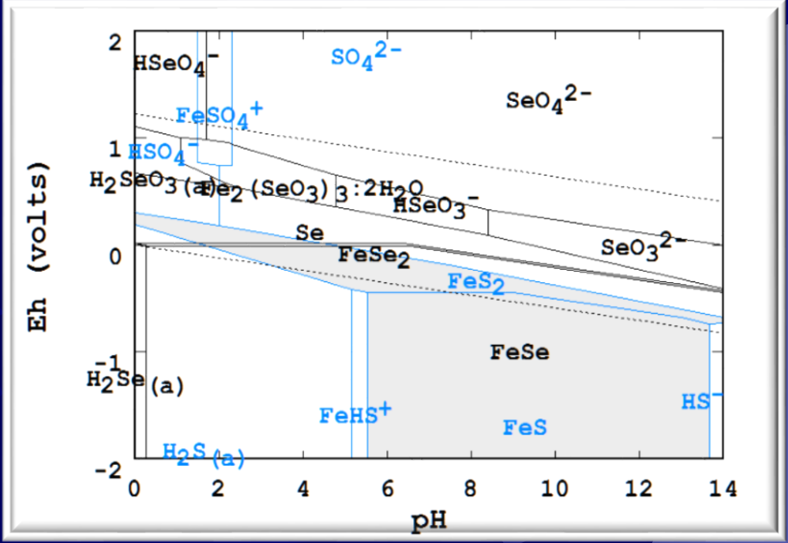
- Selenium distribution in US (where does it occur?)

Background

Selenium often associated with sulfide mineralization as adsorbed selenite/selenate and as FeSe, $FeSe_2$, and selenium substituted for S in pyrite



Se solids shaded

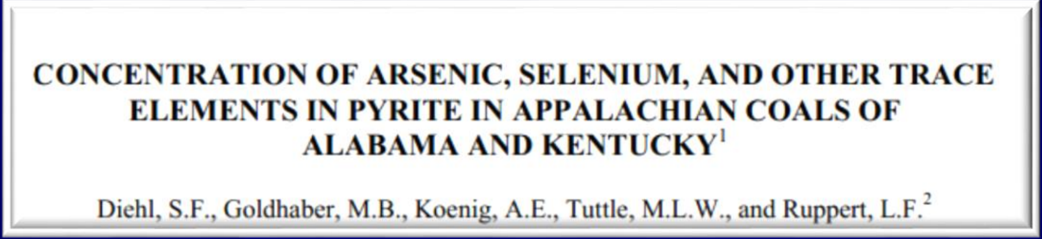


Fe sulfide solids shaded

Note similar phase stability for selenide and sulfide minerals

Hardrock and Coal Selenium Occurrence

Background



CONCENTRATION OF ARSENIC, SELENIUM, AND OTHER TRACE ELEMENTS IN PYRITE IN APPALACHIAN COALS OF ALABAMA AND KENTUCKY[1]

Diehl, S.F., Goldhaber, M.B., Koenig, A.E., Tuttle, M.L.W., and Ruppert, L.F.[2]

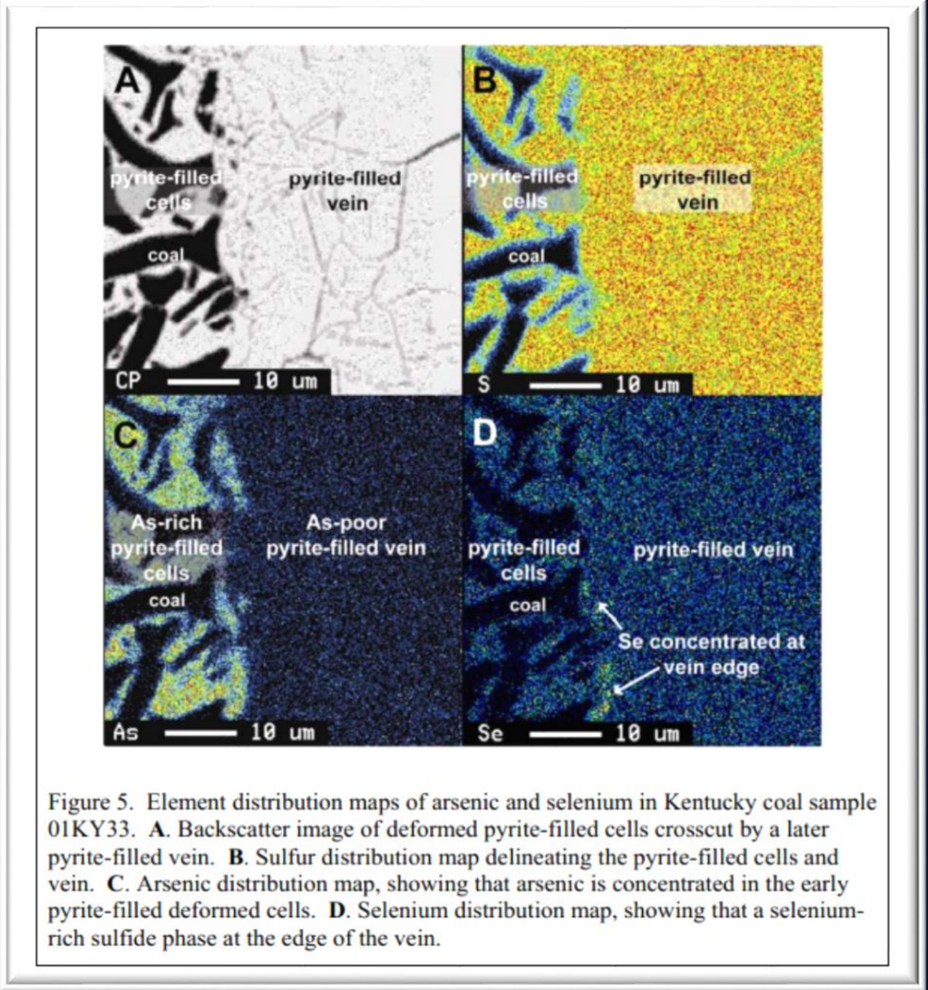
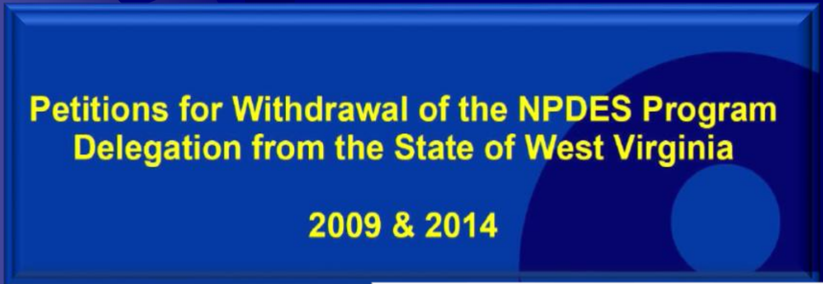


Figure 5. Element distribution maps of arsenic and selenium in Kentucky coal sample 01KY33. **A**. Backscatter image of deformed pyrite-filled cells crosscut by a later pyrite-filled vein. **B**. Sulfur distribution map delineating the pyrite-filled cells and vein. **C**. Arsenic distribution map, showing that arsenic is concentrated in the early pyrite-filled deformed cells. **D**. Selenium distribution map, showing that a selenium-rich sulfide phase at the edge of the vein.

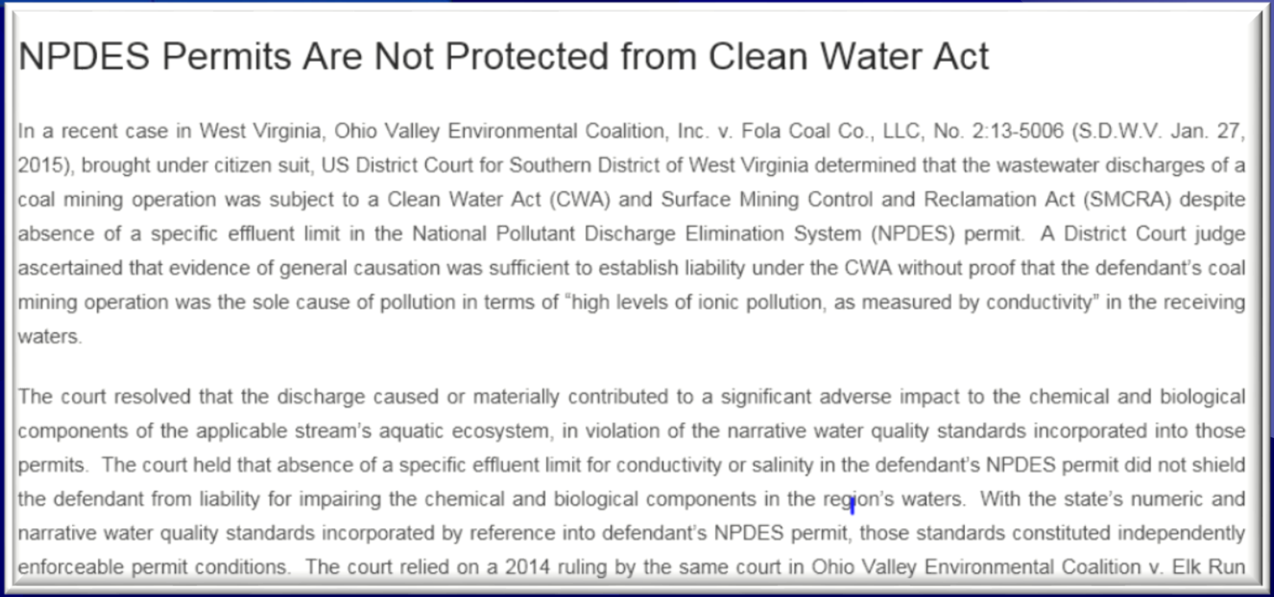
Selenium

- ○ Regulation control is a mixed bag
- ○ See hyperlinked file* (Example W. Virginia escapades)



Petitions for Withdrawal of the NPDES Program Delegation from the State of West Virginia

2009 & 2014



NPDES Permits Are Not Protected from Clean Water Act

In a recent case in West Virginia, Ohio Valley Environmental Coalition, Inc. v. Fola Coal Co., LLC, No. 2:13-5006 (S.D.W.V. Jan. 27, 2015), brought under citizen suit, US District Court for Southern District of West Virginia determined that the wastewater discharges of a coal mining operation was subject to a Clean Water Act (CWA) and Surface Mining Control and Reclamation Act (SMCRA) despite absence of a specific effluent limit in the National Pollutant Discharge Elimination System (NPDES) permit. A District Court judge ascertained that evidence of general causation was sufficient to establish liability under the CWA without proof that the defendant's coal mining operation was the sole cause of pollution in terms of "high levels of ionic pollution, as measured by conductivity" in the receiving waters.

The court resolved that the discharge caused or materially contributed to a significant adverse impact to the chemical and biological components of the applicable stream's aquatic ecosystem, in violation of the narrative water quality standards incorporated into those permits. The court held that absence of a specific effluent limit for conductivity or salinity in the defendant's NPDES permit did not shield the defendant from liability for impairing the chemical and biological components in the region's waters. With the state's numeric and narrative water quality standards incorporated by reference into defendant's NPDES permit, those standards constituted independently enforceable permit conditions. The court relied on a 2014 ruling by the same court in Ohio Valley Environmental Coalition v. Elk Run

References in this presentation

All of the quotations and general references in the fourteen lectures (that are shown with an asterisk) are available by contacting Dr. Larry Twidwell. The original course material references were hyperlinked to the respective documents.

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Stop! Stop!

Thanks class!! I hope this presentation will be helpful to your careers in the future.