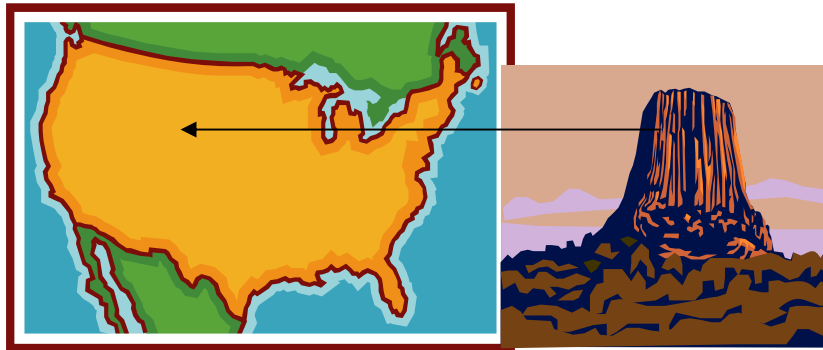
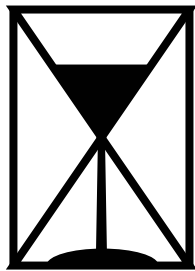


Selenium Story
IMnI EPD China Conference
Guilin (Guangxi Province)
March 30, 2007

Karen Hagelstein, Ph.D., CIH
TIMES Limited
Sheridan, WY USA
aircaredoc@aol.com

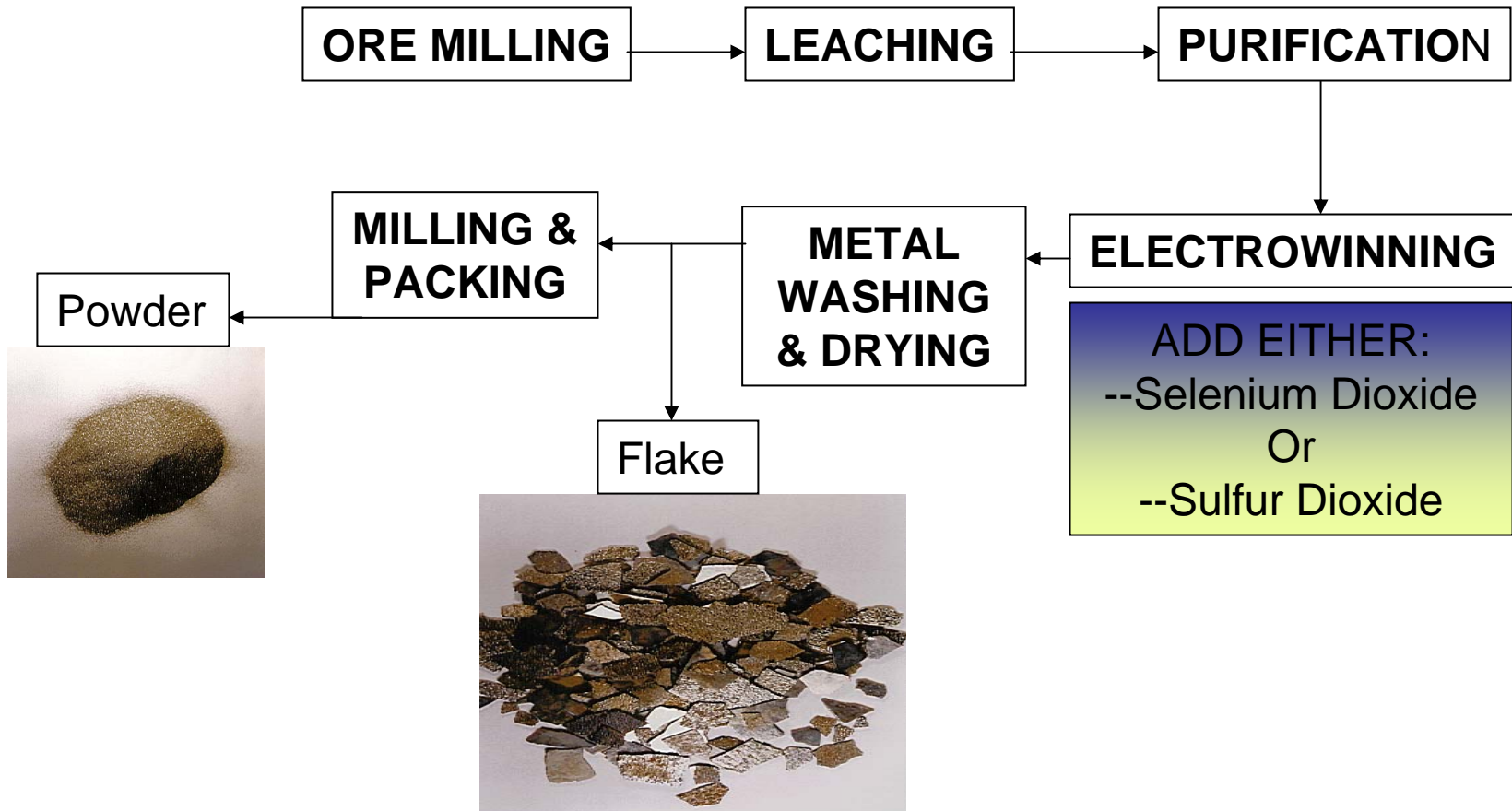


Selenium Story Objectives

- Manganese Metal Processing
- Selenium Health Characteristics
- Environmental Impacts
- Pollution Controls
- Worker Exposures
- Biological Monitoring
- Chinese EMM Industry Studies
- Environmental Management



Electrolytic Manganese Metal Production Processes



Characteristics of Selenium



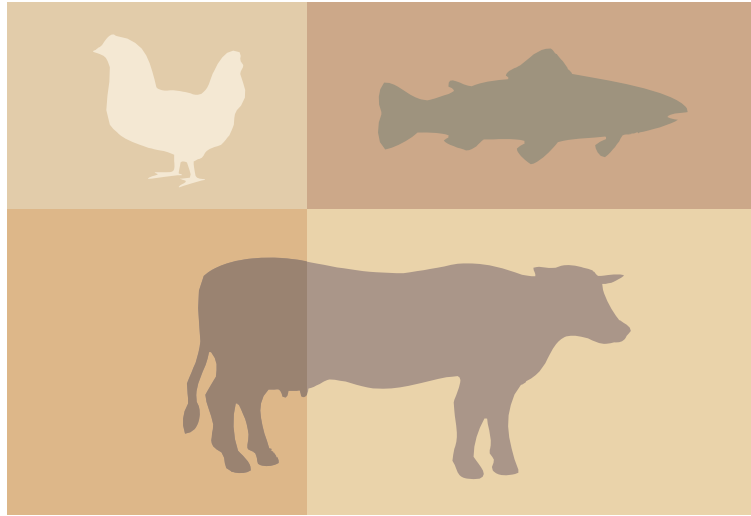
67th Most Abundant Element

- Minerals Containing Sulfides of Copper, Zinc, and Lead
- Naturally Occurring Volatile Methyl Selenide Compounds
- By-product in Copper Slimes

Estimated Global Production~3500 tpy

- Electronics/Light Meters
- Glass Industry
- Animal Feed/Supplements

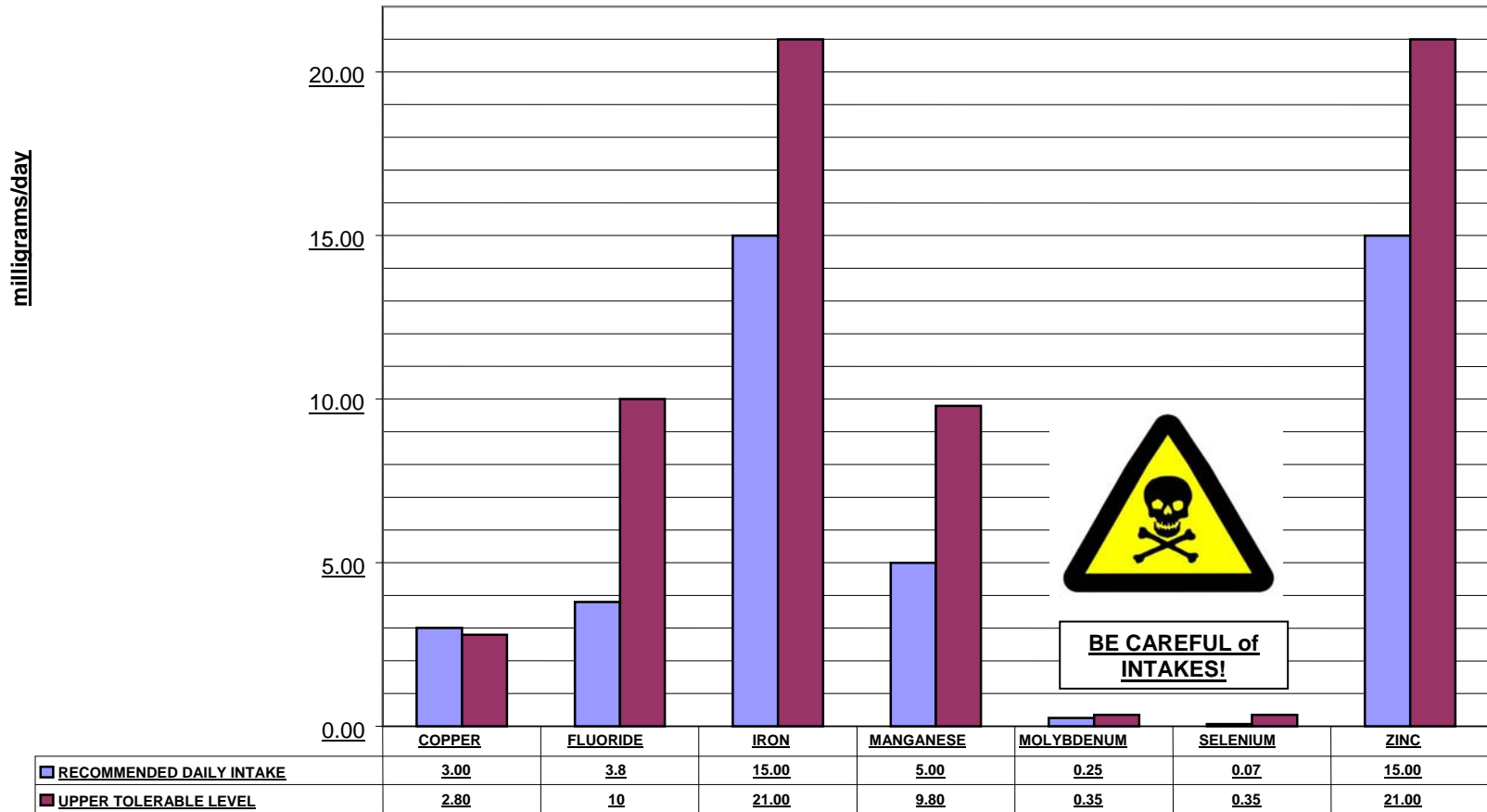
Dietary Sources of Selenium



- One Serving of Turkey (4 ounces) **or**
- Four Fish Servings (4 ounces each) **or**
- Brazil Nuts (1/2 ounce) =

Upper Tolerable Daily Selenium Oral Intake = ~0.35 mg/day

Trace Elements: Recommended Intake & Toxicity



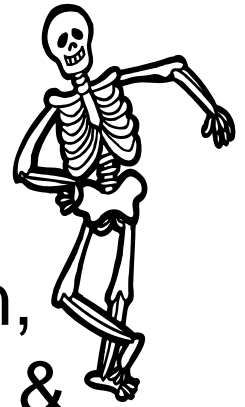
Recommended Daily Allowance RDA = 0.07 mg Se/day (blue)

Chronic Oral Upper Tolerable Reference Dose RfD = 0.35 mg Se/day

Based on Chinese Dietary Intake Studies = 0.91 mg Se/day

Mammalian Selenosis

- Chinese Studies—Skin & tooth discoloration, bone & nail deformities, loss of hair, cardiac & nervous system disorders
- U.S. Studies—Sheep kill & blind staggers in cattle due to selenium in forage
- Selenium Sulfide—Probable Carcinogen



TOXICITY of Selenium = DOSE X TIME

Intake of Vitamins (B,C, & E) & Minerals (Cu, Mn)

Selenium Industrial Wastes & Impacts

Coal Fired Power Plants Fly Ash

- Spine Deformities in Fish & Tadpoles
- Decreased Hatching Success & Craniofacial Abnormalities in Toad Embryos

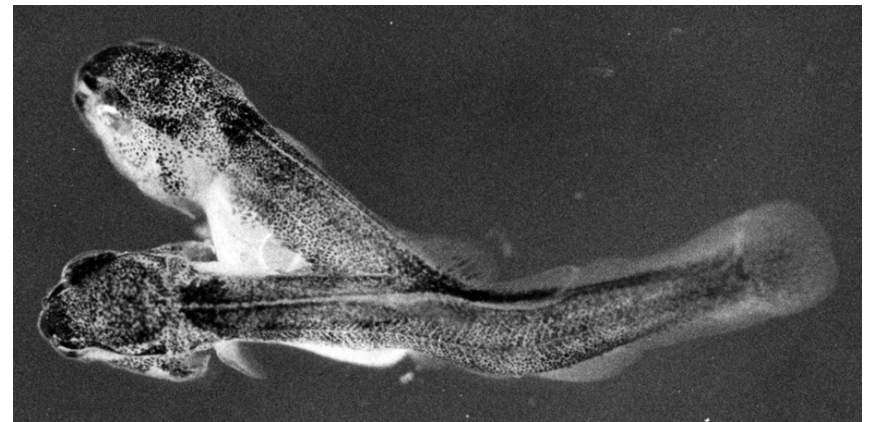
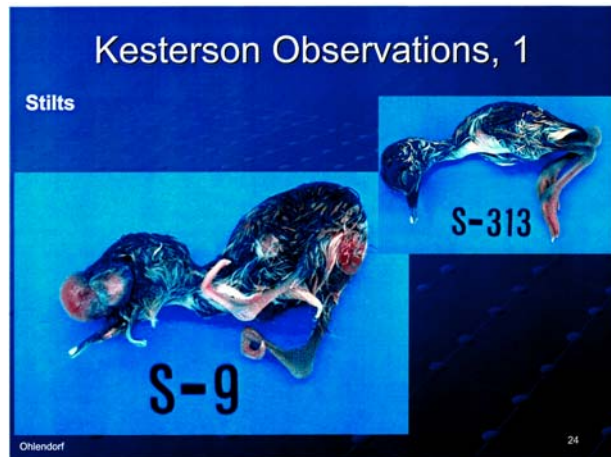


Refinery Wastewaters

- Wetlands Restored
- Dimethyl Selenide Volatilized



Selenium in Coal Fly Ash & Surface Waters—Skeletal Deformities



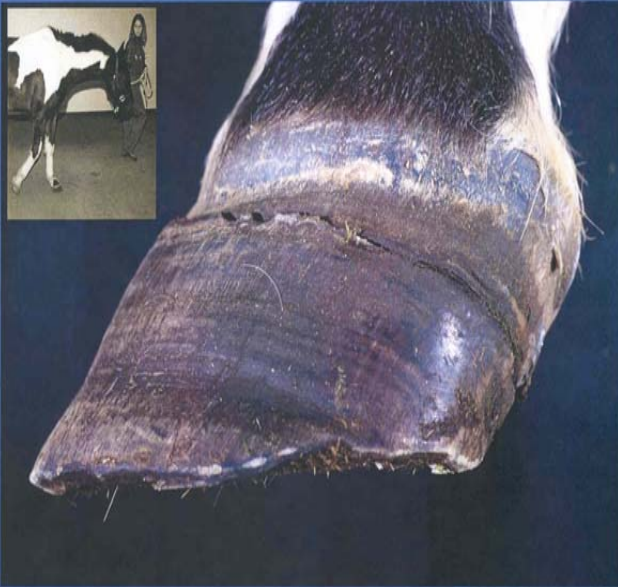
Phosphate Industry Selenium Impacts

- Idaho 17 Mining Sites Remediation Needed
- Selenium in Waste Shales Oxidized/Solubilized
- Surface Water Contaminated
- Foragers Impacted
- Native Trout Populations Threatened



Mammalian Impacts of Selenium

Chronic Selenosis



44

Idaho Sheep Kill, July 2001



80

ECOSYSTEM EFFECTS OF SELENIUM

Aquatic Life Criteria

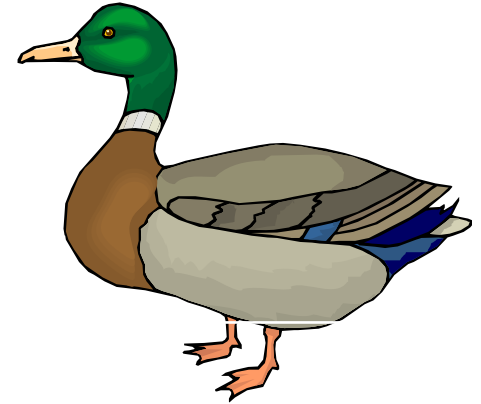
- Based on about 1300 References
- Toxic Effects: Feeding Behavior, Immobilization, Deformities, Reduced Reproduction
- Dietary EC10 = 5 mg Se/kg Dry Weight Fish Tissue
- Fish Flesh Standard Proposed U.S. EPA

Bioconcentration

- Organic & Reduced Inorganic Forms
- Skeletal & Egg Deformities
- Lentic Systems Bioaccumulation > Lotic Waters



Background Concentrations



USA WATERS

<0.01 mg Se/L

SEDIMENT

0.20 to 2.0 mg Se/kg dry weight

INVERTEBRATES

0.10 to 2.0 mg Se/kg dry weight

WATERFOWL EGGS

0.50 to 4.0 mg Se/kg dry weight

FISH

1.0 to 4.0 mg Se/kg dry weight

BIOCONCENTRATION

UP TO 1000 TIMES



U.S. Environmental Regulations (12+) & Selenium Compounds

	CHEMICALS REGULATED	LISTs	Al Cpds	Mn Cpds	Se Cpds
OSHA, 1999	Occupational Safety and Health Act (1970)				
29 CFR Parts 1900-1910	Occupational Exposures Limits for Air Contaminants/Subpart Z Time Weighted Averages (TWAs, 8 Hr) Short Term Exposure Levels (15 minutes) Not to be Exceeded Levels (Ceiling) Immediately Dangerous to Life or Health (IDLH) Carcinogen (NTP, IARC, or OSHA) Skin Designation/Target Organ Odor Threshold	677			
			15 mg/m3 Total Dust 5 mg/m3 Resp. Dust	5 mg/m3 Ceiling 500 mg/m3 IDLH	0.2 mg/m3 TWA 1.0 mg/m3 IDLH
			Yes		Se Sulfide Yes 0.3 ppm Hydrogen Selenide
29 CFR Part 1910.119	Process Safety Management of Highly Hazardous Chemicals (1992)				
	List of Highly Hazardous Chemicals, Toxics and Reactives: Threshold Quantity (TQ) in Pounds	137	No	No	No
29 CFR Part 1910.1200	Hazard Communication Standard (1983) Limits for Air Contaminants/Subpart Z	677	Yes	Yes	Yes
EPA, 2000	Environmental Protection Agency				
40 CFR Part 50	Clean Air Act (CAA of 1970) Criteria Air Pollutants	7			
40 CFR Part 63	Hazardous Air Pollutants (HAPS) National Emission Standards for HAPS (NESHAP) Major Sources: 10 tons/yr/HAP or 25 tons/yr/all HAPS	188	No	Yes	Yes
40 CFR Part 68	Risk Management Plans/LEPCs				
40 CFR Part 131	Clean Water Act (CWA of 1972 and 1977) Priority (120) Non-priority Pollutants (45) Organoleptic (Taste/Odor) Effects (23)		Non Priority	Non Priority	Priority
40 CFR Part 131 Section 304 CWA	Water Quality Criteria for Priority Toxic Pollutants Acute (CMC) Aquatic Freshwater Standards Chronic (CCC) Freshwater Standards Acute Saltwater Standards Chronic Saltwater Standards Human Health: Freshwater + Organism Consumption Organism Consumption Only State, Local, and Site or Industry Specific Standards	157			0.020 mg/L 0.005 mg/L 0.290 mg/L 0.710 mg/L 0.170 mg/L 11.0 mg/L
40 CFR Part 141	Safe Drinking Water Act (1974) Maximum Contaminant Levels (MCLs) Primary: Microbes (7), Disinfectants/Products (7), Inorganics (16), Organics (53), Radionuclides (4) Secondary: Chemicals/Characteristics	102	Secondary	Secondary Taste/Odor	Primary Health
		87	0.05-0.2 mg/L	0.05 mg/L	0.05 mg/L
40 CFR Parts 260-	Hazardous Wastes (RCRA, 1976, TSCA, 1976, CERCLA, 1980 and SARA, 1986)	400			
40 CFR Part 261	Listed: Hazardous Wastes and Waste Streams Characteristics: Reactive, Ignitable, Corrosive, Toxic (TCLPs = 40) Appendices VII, VIII Lists Hazardous Constituents of Waste Streams		No	No	1.0 mg/L TCLP

	CHEMICALS REGULATED	LISTs	Al Cpds	Mn Cpds	Se Cpds
40 CFR Part 263	Standards for Transporters of Hazardous Wastes				
40 CFR Part 264	Design & Operating Specifications for Treatment, Storage, and Disposal Facilities (TSDF) Maximum Contaminant Concentrations for Protection of Groundwater	14	No	No	0.01 mg/L
40 CFR Part 266	Standards for Specific Hazardous Wastes and TSDF				
40 CFR Part 268	Land Disposal Restrictions: Universal Treatment Standards for Hazardous Wastes (UTS)				
	Regulated Hazardous Constituent Wastewater Nonwastewater		No	No	0.82 mg/L 5.7 mg/L
40 CFR Part 302	List of Hazardous Substances and Reportable Quantities (Section 311 of SARA and CWA, CAA, RCRA) RCRA Waste Number Reportable Quantities (RQ)	717	Yes	Yes	Yes D010
40 CFR Part 355	List of Extremely Hazardous Substances (Section 304 of SARA) Reportable Quantities in Pounds (RQ) Threshold Planning Quantities (TPQ)	406			NaSelenate Na Selenite 100 pounds
40 CFR Part 372	Specific Toxic Chemical Listings (TRI) (Section 313 of SARA) Manufacture, Import, or Process Chemicals over 25,000 pounds/yr Use over 10,000 pounds/yr of Toxic Chemical/Category De Minimus Conc. (% of Mixtures: 1.0% Not Carcinogen 0.1% for Carcinogens	646	Yes Since 1987 CAS No. 7429-90-5	Yes Since 1987 CAS No. 7439-96-5	Yes Since 1987 CAS No. 7782-49-2
			1%	1%	1%
40 CFR Part 400	Effluent Guidelines and Standards National Pollutant Discharge Elimination System (NPDES)/Best Available Control Technology Economically Achievable (BAT)				
40 CFR Part 401	Toxic Pollutants Conventional Pollutants	65 5			
40 CFR Part 503	Standards for the Use or Disposal of Sewage Sludge Loading Rate—Ceiling Concentration				100 mg/kg
EPA Region III	Risk-Based Concentration (RBC) Table (10/9/02) Source: EPA Risk Assessment Guidance for Superfund Assumptions: 70 kg Body Wt., 20 m3/day Carcinogenic Lifetime Cancer Risk of 1E-6 Non-carcinogenic Hazard Quotient = 1	400-500			
	Oral Reference Dose (RID)—mg/kg/day Oral Cancer Slope Factor (CSF)—1/mg/kg/day Inhalation Reference Dose—mg/kg/day Inhalation Cancer Slope Factor—1/mg/kg/day		1.0	0.02	0.005
	Tap Water—ug/liter Ambient Air—ug/m3 Fish—mg/kg Soil Industrial—mg/kg Soil Residential—mg/kg Forage—mg/kg		37,000 3.7 1,400 2E+6 78,000	730 0.52 27 41,000 1,600	180 18 6.8 10,000 390 5
DOT, 2000	Department of Transportation (1996) (Section 101 of CERCLA)				
49 CFR Part 172.101	List of Hazardous Substances and Waste Streams Reportable Quantities in Pounds EPA Characteristic Wastes/Waste Streams	1000	No	No	100 pounds

Selenium Environmental Standards

- Water Quality Standards MCL = 0.05 mg/L
- Aquatic Life Standards CCC = 0.005 mg/L
- Groundwater Protection Se < 0.01 mg/L
- Industry Treatment Standards
 - Wastewaters = 0.82 mg/L
 - Nonwastewaters = 5.7 mg/L
- U.S. EPA Toxic Release Inventory if
 - >10,000 lbs/year
 - >1.0% Se in mixtures

Metals Toxicity Ranking

Hazardous Waste
Toxicity Characteristic

Leaching Procedure

Mercury = 0.2 mg/L

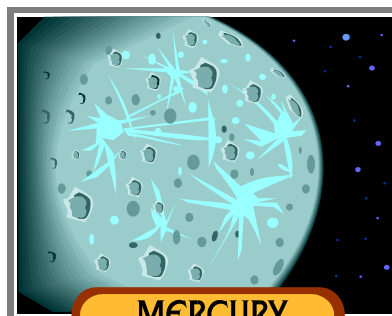
Selenium = 1.0 mg/L

Cadmium = 1.0 mg/L

Lead = 5.0 mg/L

Chromium = 5.0 mg/L

Arsenic = 5.0 mg/L





Controlling Particulate Metals-Additive

- Cyclone/Scrubber
- Fabric Filters
- Electrostatic Precipitation
- Wet Flue Gas Desulfurization

WATER TREATMENT DIFFICULT

- Chemical Treatment
 - Iron Salts at Acidic pH
 - Sludge Management
- Physical Treatment
 - Reverse Osmosis
- Biological Treatment
 - Anaerobic Systems

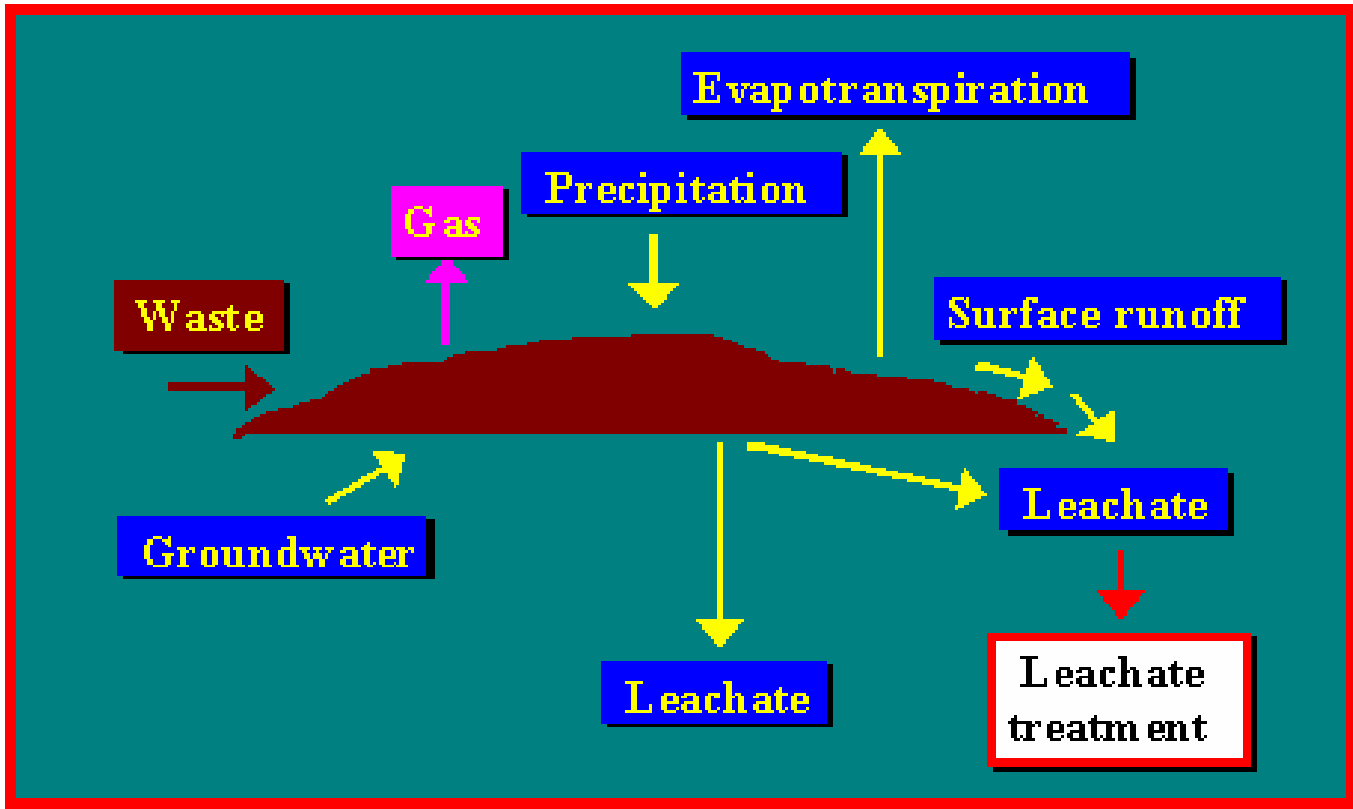


WASTE DISPOSAL DIFFICULT

- Chemical Producer Violates Clean Water Act
12/2006 Conspiracy Charges & Fines For
Concealing Waste Discharges (Se)
Salt Lake City, Utah
- EPA Landfill Disposal Variances
 - 1999 Selenium Wastes, Kettleman City, CA
Waste Treatment TCLP Limit Increased
 - 2004 Selenium Hazardous Waste from Glass
Manufacturing, Model City, NY
Site Specific Treatment Required

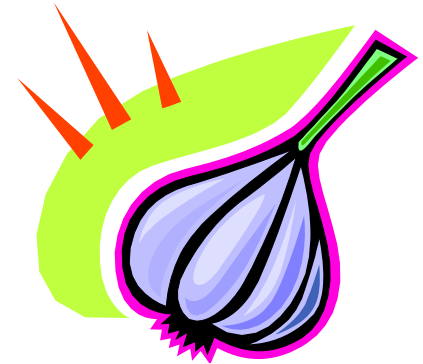
Hazardous Waste Treatment

The landfill as a flow system



Worker Exposures to Selenium

- **INHALATION---Particulates/Metals**
OSHA PEL (0.2 mg/m³ Se) LESS THAN
Odor Threshold (0.3 mg/m³ H₂Se)



- **POOR WARNING PROPERTIES**
- **TARGET ORGANS—Skin, Respiratory System, Eyes, Liver, Kidneys, Blood, Spleen**
Symptoms of Metal Fume Fever

- **RESPIRATORY PROTECTION**
Dust/Mist/Fume Filter until
IDLH (1.0 mg/m³)



Biological Monitoring

- Taiwan Steel Workers 2002
Urinary Concentrations:
Selenium, Arsenic, Beryllium
Exceeded Controls
- Selenium Blood Levels Correlate with
Hair/Nail Concentrations
- Dermal Contact Causes Burns
- Topical 10% Thiosulfate Cream



Worker Monitoring— Particulate Metals

Worst Case Exposures

- Respirable Particulates
- Pumps/Cassettes/Filter Metals—ICAP-AES, XRD
- Real Time Particulate Optical Sensors
- Colorimetric Detector Tubes for Gases
- Area/Breathing Zones



Risk Characteristics of Selenium



- NARROW Margin of Human Health Safety
- WATER TREATMENT Difficult
- HAZARDOUS Solid Waste
- ACCUMULATIVE Pollutant
- WORKER ODOR Warning Inadequate
- EXPOSURE CONTROLS Adequate

Recent Chinese EMM Studies

- Xiangxi Mn Industry Association:1996-2006
Material Consumption Rates Decreased
- China's Mn Industry, National Committee on Mn Industry & Technology 2006.3
Waste Water, Residues Chemistry<Standards
- **Site Specific Environmental Assessments**
Selenium Drinking & Surface Water Hazards

Chinese Selenium Releases ~1000 tons SeO_2 at 2006 Estimated EMM Output ~700 000 tons

**M
O
N
I
T
O
R
I
N
G**

AIR EXPOSURES

Control Manual Operations
Air Pollution Controls
Worker Protection
Training

SITE SPECIFIC
WASTEWATER
TREATMENT

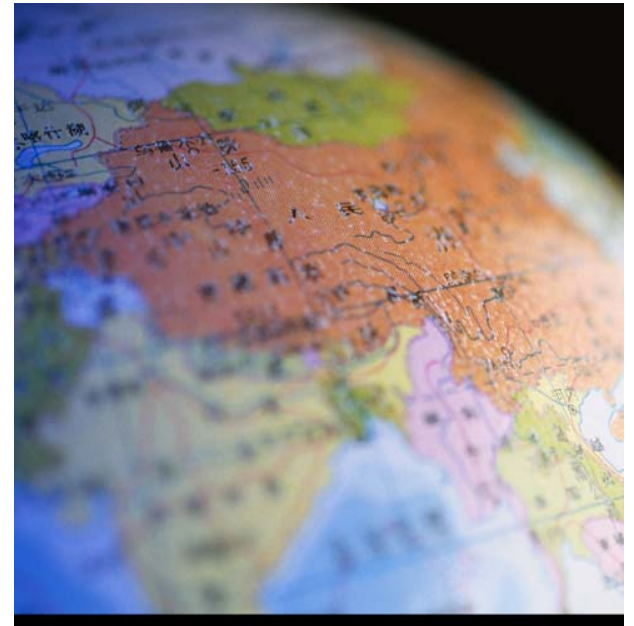
HAZARDOUS SOLID WASTES

Lined Landfill Disposal
Cementation

PREVENT SURFACE &
GROUNDWATER EXPOSURES

Selenium Site Specific Guidance Levels Recommended

- Waste Effluent Standards
- Sewage Sludge Treatment
- Landfill Disposal Loadings
- Forage Quality & Livestock
- Fish Protection Standards
- Ambient Air Quality Levels
- Chronic Oral Exposures



EMM Industry Environmental Management Recommendations

- Hazard Communication—Worker/Public
- Worker Training—Task Specific
- Pollution Releases—Ongoing Monitoring
- Regulations—Protective if Enforced
- Pollution Controls—Effective if Maintained
- Environmental Audits—
Document Progress



**THANK YOU
FOR YOUR
TIME**

