Economic recovery of zinc from Mining Influenced Water (MIW)

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Project Goals

- EPA Resource Conservation: “Reduce, reuse, **recycle**”

- Current paradigm for MIW: **disposal**

  But…heavy metals are a resource.

- In order to recycle effectively, we must know what is economically viable:
  - Chemical forms, assays, supply chains
  - **Zinc** as a case study for this paradigm shift

Presentation Outline

1. Current Practices in MIW Treatment
2. Opportunities for Recycling:
    a. **Smelting**
        - Industry Overview
        - Specifications
    b. **Micronutrient Fertilizers**
        - Industry Overview
        - Supply chain
        - Specifications
3. Expanding Recycling Opportunities

Context:
Mining Influenced Water


Sosbluewaters.org : Rio Tinto River

- Mining influenced water in EPA Region 8
  - 51,700 abandoned mine land (AML) sites
  - 22,000 are located in Colorado
  - Heavy metal loading
- Water Treatment Plants
  - Wellington Oro, Argo Tunnel
- Diversity of influent and effluent quality
  - pH, metal concentrations
- TCLP Tests: Hazardous or non-hazardous?

Metal	**TCLP Limit (mg/L)**
Arsenic	5.0
Barium	100
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

Typical Methods of Treatment

- **Hydroxide Precipitation**

  Most common for large scale application

  High water content sludge

  Product: $Zn(OH)_2$ typically mixed with other metals

- **Sulfide precipitation**

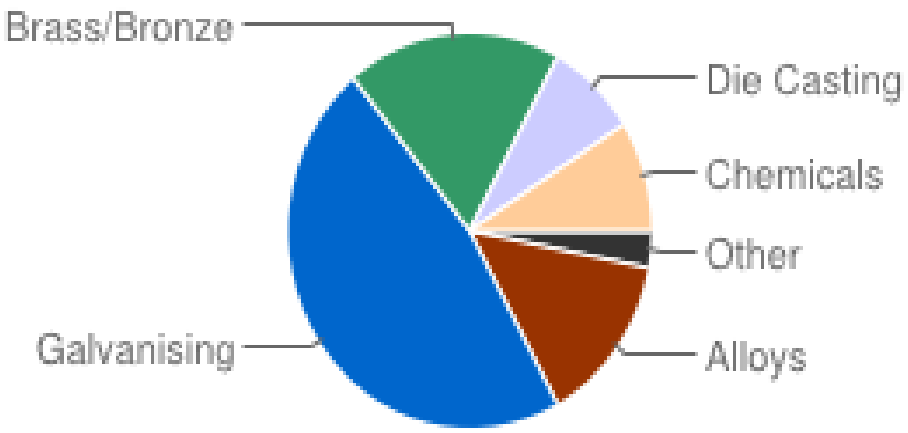
  Typically used for higher metal loading

  Low water content sludge

  Product: ZnS may be selectively precipitated

Zinc End Uses

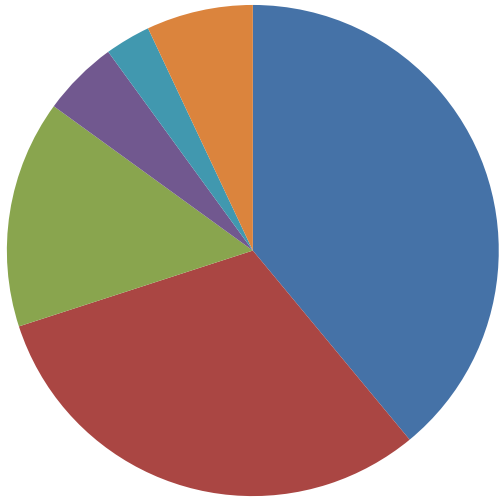
Zinc Use by Industry



INDUSTRY	%
Galvanising	47
Brass/Bronze	19
Alloys	14
Chemicals	9
Die Casting	8
Other	3
Total	100

Source: LME Zinc Industries

Secondary Zinc Forms Produced



	%
Brass and Bronze	39
Zinc metal	31
Zinc Oxide	15
Zinc dust and powder	5
Zinc Sulfate	3
Misc	7

Source: USGS 1998

Zinc Pricing

- The London Metals Exchange (LME) Sets zinc price for sources
- Hovering at around 95 cents/lb zinc
- Secondary sources are priced at a percentage of LME, usually 40%

Opportunities for Recycling

- **Smelting**
  - Product: Zinc metal
  - High grades desired
- **Micronutrient Fertilizers**
  - Product: various Zinc compounds
  - Solubility and limited co-contaminants desired

Regulatory Exemptions

Federal: RCRA Reuse Exemption: 40 CFR 261.4

Spent materials recovered from mining water, if not accumulated speculatively

Hazardous waste for zinc micronutrient fertilizers, given some storage and transportation regulations

Colorado: CHWR 261.4(a)
(lists exemptions from hazardous waste)

Secondary materials used in zinc fertilizers

Zinc fertilizers made from hazardous waste

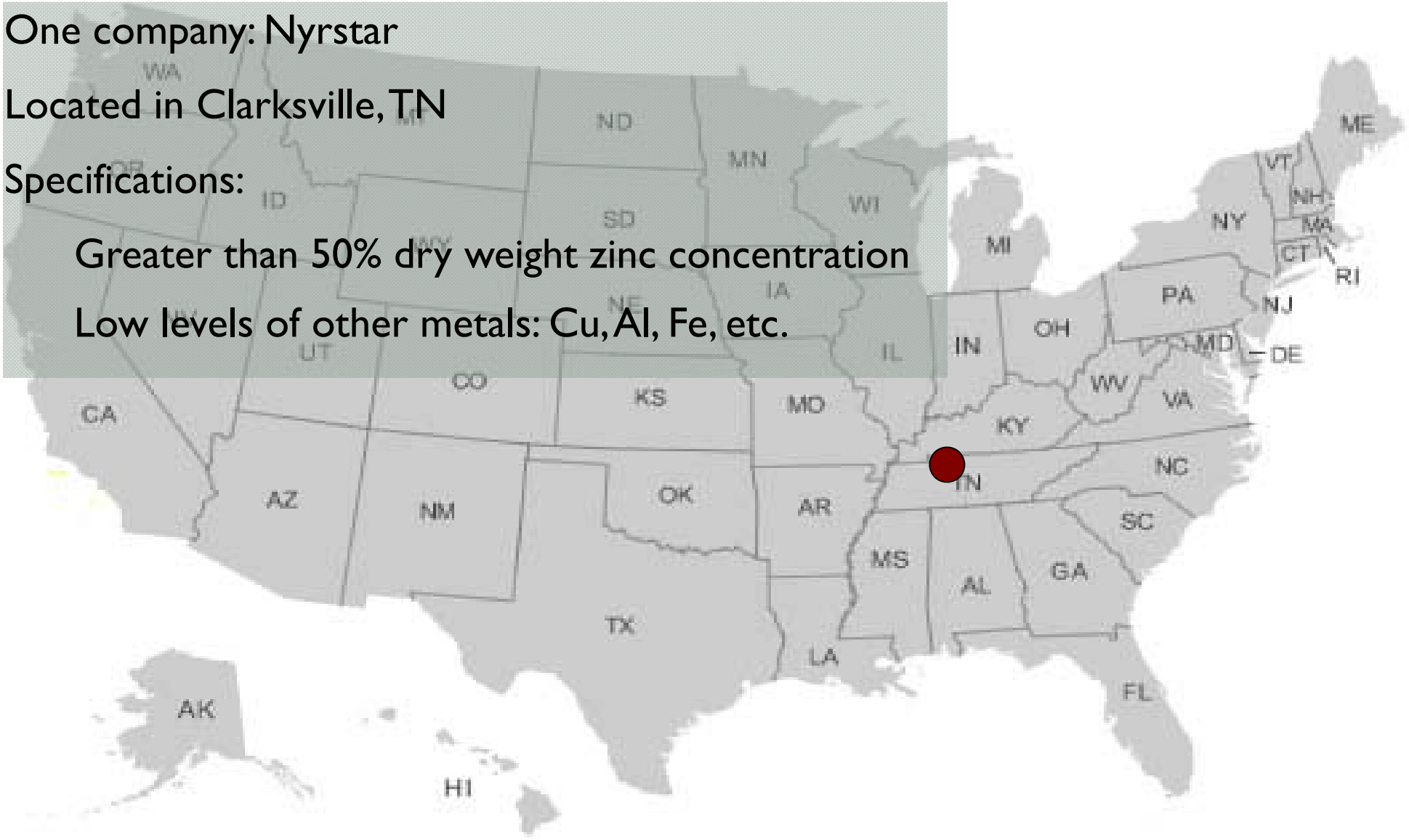
Zinc Smelting Industry

One company: Nyrstar

Located in Clarksville, TN

Specifications:

- Greater than 50% dry weight zinc concentration
- Low levels of other metals: Cu, Al, Fe, etc.



Specifications for Zinc Smelter feed

Wellington Oro Zinc Sludge Composition

Constituent	**Percent** [1]
Moisture	18%
Zinc	57%
Sulfur	38%
Other	5%

[1] *Solids percentages are based on dry weights*

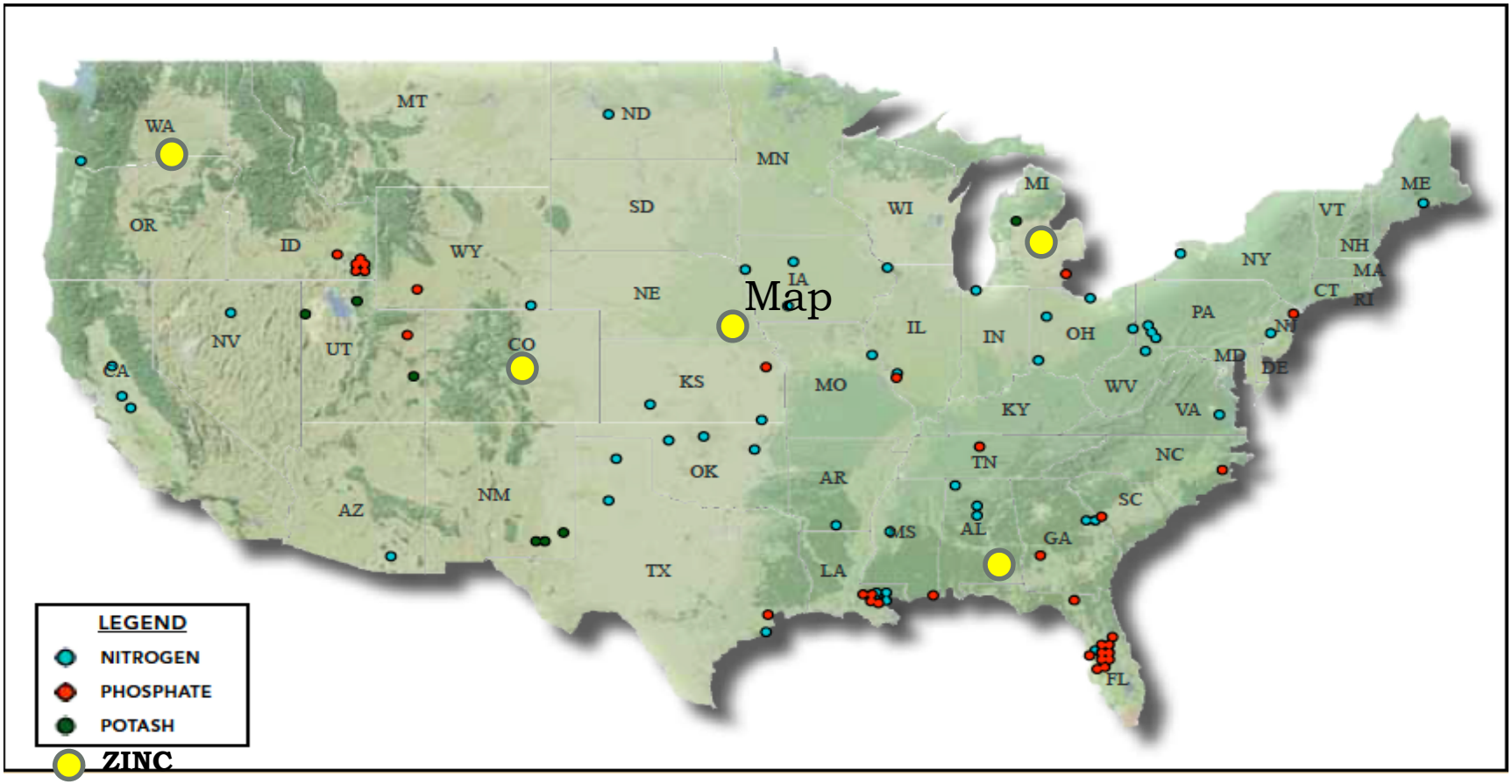
Source: Nyrstar Smelter, Material Acceptance Profile

2009 Operating Results
100,000 m^3 of water treatment
28,000 lbs of Zn recovered

2010 Operating Results
73,000 m^3 of water treatment
25,000 lbs of Zn recovered

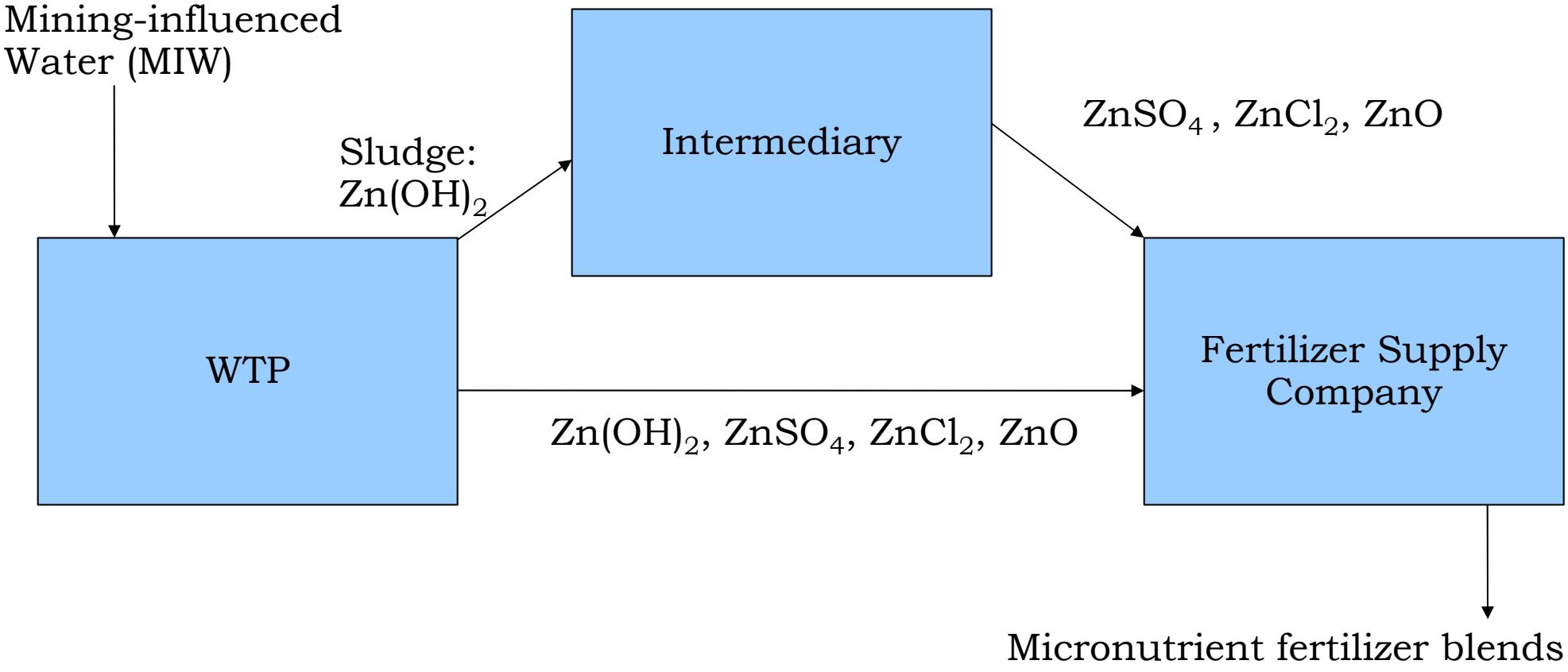
Source: BioTeq Environmental Technologies Inc.

Micronutrient Fertilizer Industry



Map of NPK Fertilizer Production Facilities, The Fertilizer Institute

Proposed Zinc Micronutrient Fertilizer Supply Chain:



Forms of zinc in fertilizer

Inorganic Compounds	Formula	% Zn
Zinc Sulphate Monohydrate	$ZnSO_4$, H_2O	36-37
Zinc Sulphate Heptahydrate	$ZnSO_4$, 7 H_2O	22-23
Zinc Oxysulfate	$xZnSO_4$, $xZnO$	20-50
Basic Zinc Sulphate	$ZnSO_4$, $4Zn(OH)_2$	55
Zinc Oxide[1]	ZnO	50-80
Zinc Carbonate[1]	$ZnCO_3$	50-56
Zinc Chloride	$ZnCl_2$	50
Zinc Nitrate	$Zn(NO_3)_2$, $3H_20$	23
Sulphurous Zinc	ZnS	67
Zinc Frits	Fritted Glass	10-30
Ammoniated Zinc Sulphate Solution	$Zn(NH_3)_4SO_4$	10

[1] *Not water soluble*

Source: Alloway, Brian. "Micronutrients: Think Zinc." New AG International. 2004.

Considerations for fertilizer forms:

- Liquid, solid or granular forms
- Banded or broadcast application
- Foliar or soil application
- Specific crop, soil needs

Competing sources

Current secondary sources of zinc for micronutrient fertilizers:

Material	Annual Generation (tons)	Annual Amount Used in Fertilizer Production (Tons)	Typical RCRA Status	Zinc Content (%)
EAF Dust	925,000	10,000	Hazardous (Pb, Cr, Cd)	15-25
Brass fume dust	32,200	842	Hazardous (Pb, Cd)	40-60
Tire ash	7500	3120	Hazardous (Cd)	27-35
Zinc fumes from galvanizing	Unknown	10836	Non-hazardous	80

Forms typically produced:
Zinc Sulfate, Zinc Oxide, Zinc Oxysulfate, Ammoniated Zinc Sulfate, Zinc Chloride

Source: EPA, The Micronutrient Fertilizer Industry: From By-Product to Beneficial Reuse

Fertilizer Regulations

In general, no regulations on fertilizer from non-hazardous secondary sources

State specific limits:

i.e. Colorado, Texas, Washington

Washington State Standards for Metals in Fertilizers

Constitute	WA Standards (lbs/ac/yr)
Arsenic	0.297
Cadmium	0.079
Cobalt	0.594
Lead	1.981
Mercury	0.019
Molybdenum	0.079
Nickel	0.713
Selenium	0.055
Zinc	**7.329**

Source: Rogowski, Golding, Bowhay and Singleton. Screening Survey for Metals and Dioxins in Fertilizer Products and Soils in Washington State. Olympia, WA : Washington State Department of Ecology, 1999. Ecology Publication No. 99-309

Fertilizer sourcing specifications

Requirements are plant specific and negotiable, but *as a blueprint for sourcing:*

- **Zinc concentration:** at least 30% dry weight
- **Aluminum and iron**: flexible but low, i.e. Fe: <1%, Al: 0.5% or less.
- **Cadmium and lead**: less flexible, i.e. Cd: <2% Pb: <5%
- **Calcium and Magnesium**: less than 2%

Concentrations for EAF dust (hazardous) are a little different:

- Zn 62% as a minimum
- Fe, Pb, K, Cu, Na, Chlorides less than 5%
- Cd, Mn, As less than 0.05%

Argo Tunnel Specifications

Filter Cake Concentrations

Constituent	% dry weight
Zinc	7
Aluminum	2.3
Iron	18
Cadmium	0.019
Lead	0.003
Lime (as $CaCO_3$)	35.4
Total solids	15.1 (of wet weight)

Source: Energy Laboratories, Laboratory Analytical Report for Filter Cake from the Argo Tunnel Water Treatment Facility, 02/02/04

- Not currently viable for micronutrient fertilizer or smelting sourcing.

Economic Costs and Benefits

- Transportation costs
- Capital costs
- O&M costs
- Savings on disposal
    - Volume based
- Earnings
    - Mass based

Conclusions

The Wellington Oro WTP demonstrated viable zinc recovery and recycling

A paradigm shift is needed towards **beneficial recovery** of multiple metals

Recovery strategies must be included during the feasibility analysis phase

Considerations for recovery include:

- What are the potential end uses?
- What forms are technically feasible?
- What is the economically viable?

Thank for your attention

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Resource recovery from MIW is possible!