# Kroll Institute of Extractive Metallurgy
# &
# Value Recovery from Secondary Slag Wastes

**Prepared for the AmCham Organized Trade Mission – October 25, 2023**

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Kroll Institute for Extractive Metallurgy

KIEM Kroll Institute for Extractive Metallurgy

COLORADO SCHOOL OF MINES

Critical Materials Institute
AN ENERGY INNOVATION HUB

CENTER FOR MINING SUSTAINABILITY
COLORADO SCHOOL OF MINES - UNSA AREQUIPA

CR3 Center for Resource Recovery & Recycling


**Dr. Corby G. Anderson, PE**
**KIEM Director**

Mining Engineering Department
Colorado School of Mines


**Recent Research Partners:**
Newmont Mining, Tata Chemicals, Rio Tinto, Freeport McMoran, University of Wyoming, University of Utah, NREL, Ames Lab, Penn State, UNSA, WPI, KU Leuven, ORNL, INL, U of Tokyo, Lundin Mining, Sibanye Stillwater, Electra Battery Metals, and many others !

# KIEM Kroll Institute for Extractive Metallurgy

## Research Center Located in the Department of Mining Engineering

- KIEM was established in 1974 using funds provided by William Kroll who invented processes to produce titanium and zirconium metal from ores.

- Over the years, the Kroll Institute has provided support for a significant number of undergraduate and graduate students who have gone on to make important contributions to the mining, minerals and metals industries.

- The objectives are to provide research expertise, well-trained engineers to industry, and research and educational opportunities to students, in the areas of : minerals processing, extractive metallurgy, recycling, and waste minimization.


The presentation of the first William J. Kroll Zirconium Medal to Admiral H. G. Rickover by Professor A. W. Schlechten, Director of the Kroll Institute for Extractive Metallurgy in 1975.

# KIEM Kroll Institute for Extractive Metallurgy

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Global Director of Business Development & Marketing - NobelClad

JUDITH VIDAL

Group Manager, Building Energy Science - NREL

KIEM Kroll Institute for Extractive Metallurgy

# Recycling Metals Short Course

- 29th Year of success
- Offered again in Summer of 2024

KIEM Kroll Institute for Extractive Metallurgy

# New Directions in Mineral Processing Short Course

- 35 plus years and again in 2024

# Recent/Current Kroll Projects: Resulting in High Impact Professional Papers and Patent Applications

**Recently Completed Examples**

- Sortation of Coarse Trona Ore for the Production of Soda Ash.
- Producing Iron Pellets from Automotive Airborne (overspray) Paint Sludge - patent pending technology.
- Optical Recognition for Copper Removal from Auto Scrap using machine learning (AI)
- Indium extraction and recovery from zinc residue rich in zinc ferrite.
- Novel method of REE bearing bastnaesite leaching – two patent pending technologies.
- Direct Lithium Extraction.
- Recovery of Critical Metals from Slag and modelling of the La Oroya smelting complex.

**Current Examples**

- CORE-CM, Critical Minerals from Coal Penn State, Northern Appalachia Coal Basin.
- CORE-CM, Critical Minerals from Coal Wyoming, Green River and Wind River Coal Basin.
- CORE-CM, Critical Minerals from Coal Utah, Unita Basin.
- Electrochemical Purification of Molten Chloride Salts.
- Flotation of REE bearing Monazite.

# A specific example of Recovery from Waste Slag

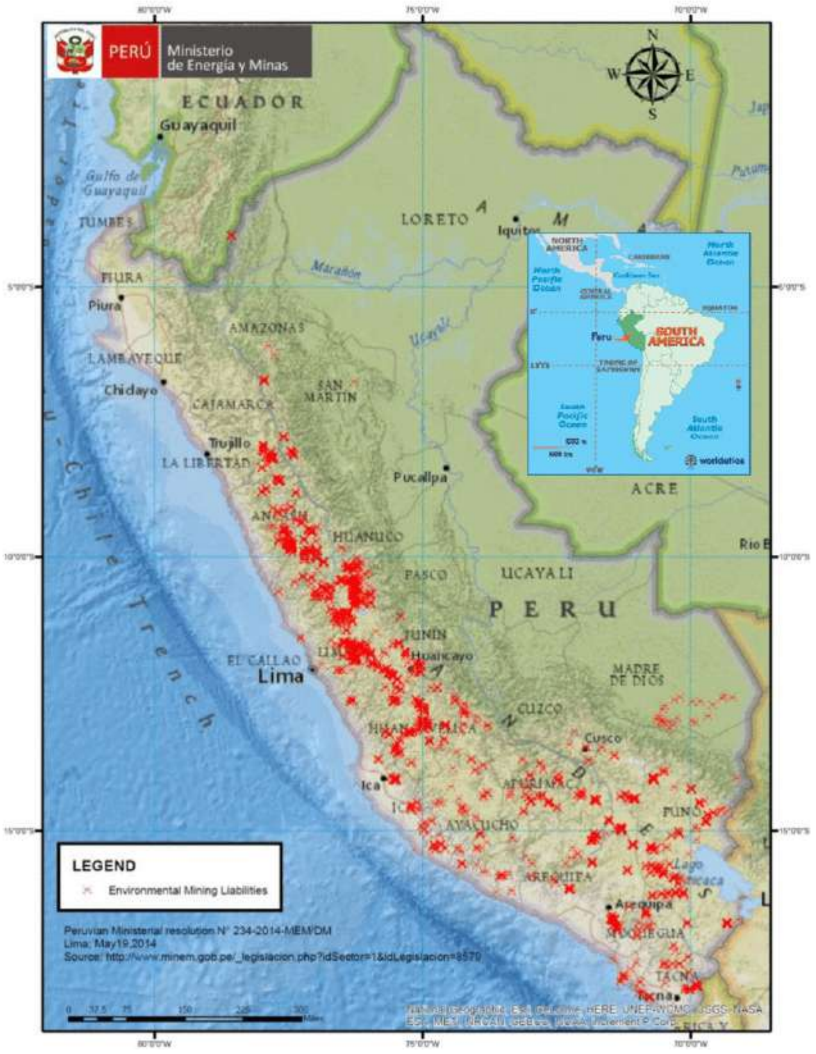
# UNSA Project P2.8
# Hydrometallurgical Reprocessing of Peruvian Pyrometallurgical Slags

Excerpted from Michael Caplan PhD Thesis, Defended April 3rd, 2023

Advisers: Dr. Corby Anderson, Prof. Erik Spiller, Dr. Patrick Taylor & Dr. Paul Santi

# Project Introduction & Motivation

- Peru has history with the mining and refining industries.
- Currently a substantial number of historical stockpiles of wastes.
- Universidad de San Agustin de Arequipa (UNSA) has two goals related to mining and refining in Peru.
  - Improve in-house R&D capabilities.
  - Develop safe methods to utilize existing resources.



# Project Goal:

- Characterize Peruvian smelting and/or refining wastes.
- Identify constituents that are likely to be economically recoverable.
- Develop a process(es) to recover value constituents in the waste material(s)

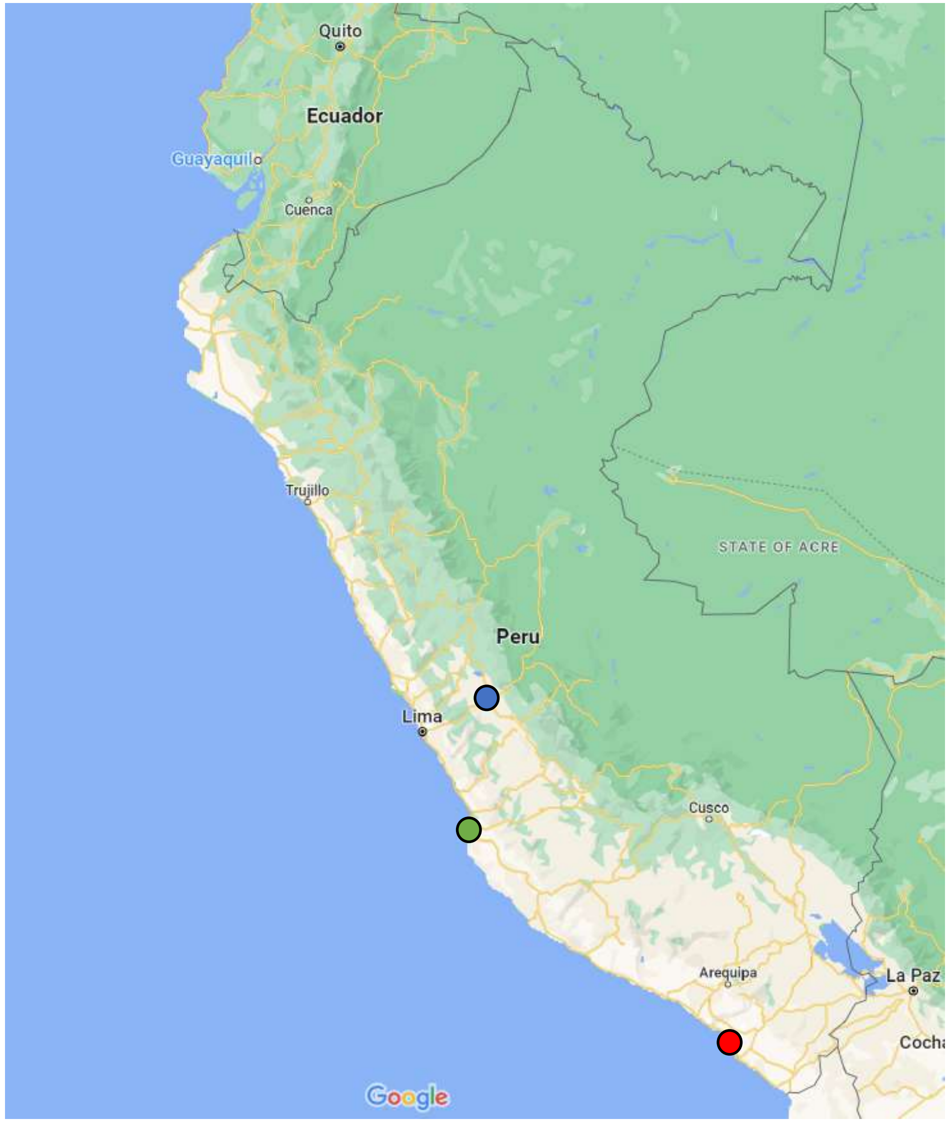
# Characterization – Samples Provided in Cooperation with UNSA Faculty Partners

# Smelting Facilities

**La Oroya** (blue)
- Polymetallic facility previously operated by Doe Run.
  - Primary: Cu, Pb, Zn
  - Secondary: Au, Ag, Bi, In, Se, Te, As, etc.
- Shut down in 2009

**Funsur** (green)
- Tin smelting & refining facility of Minsur mining company.

**Ilo** (red)
- Copper smelting & refining facility owned by Southern Peru Copper Corp (SPCC).
- Processes material primarily from the Cuajone mine.



# Economic Constituents

**La Oroya**

- Potential Targets: Cu, Pb, Zn
    - Cu – 0.5%
    - Pb – 2.4%
    - Zn – 7.2%
    - Trace Au & Ag

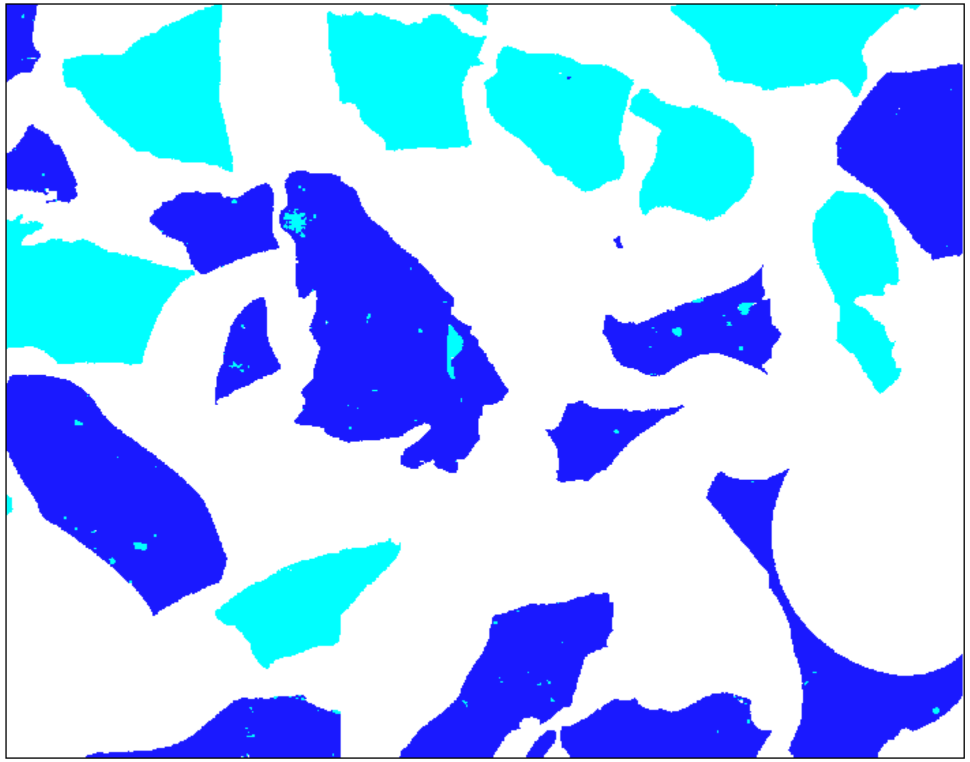
**Funsur**

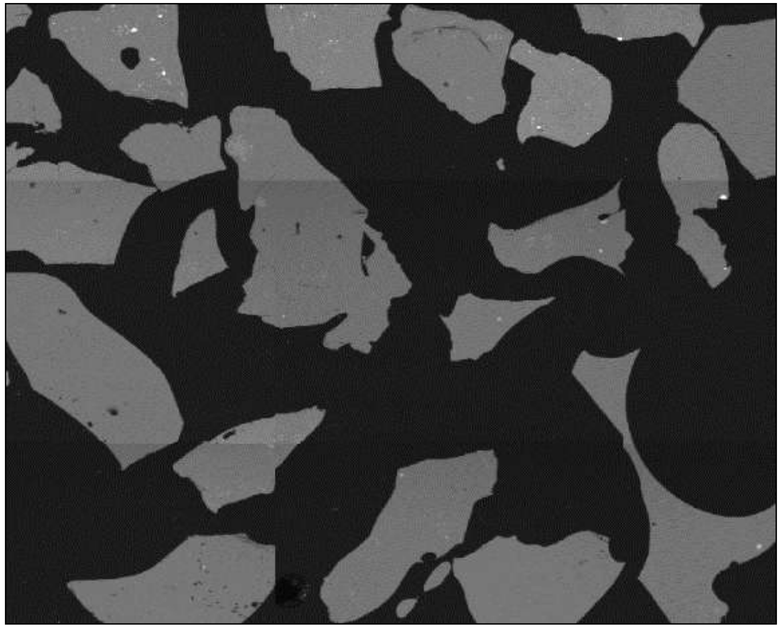
- Potential Targets: Mg & Ti
    - Mg – 1.39%
    - Ti – 1.24%

**Ilo**

- Potential Targets: Cu – 0.84%

# La Oroya - Main





| Element | | |
|---|---|---|
| Lead | 2.30% | 2.60% |
| Iron | 33.00% | 28.00% |
| Zinc | 4.40% | 15.50% |
| Calcium | 4.50% | 14.00% |
| Magnesium | 0.30% | 0.80% |
| Aluminum | 1.20% | 1.30% |
| Silicon | 13.10% | 7.80% |
| Potassium | 0.00% | 0.40% |
| Manganese | 0.00% | 2.90% |
| Titanium | 0.00% | 0.00% |
| Sodium | 0.00% | 0.00% |
| Copper | 0.01% | 0.70% |
| Oxygen | 41.20% | 26.70% |

# Funsur

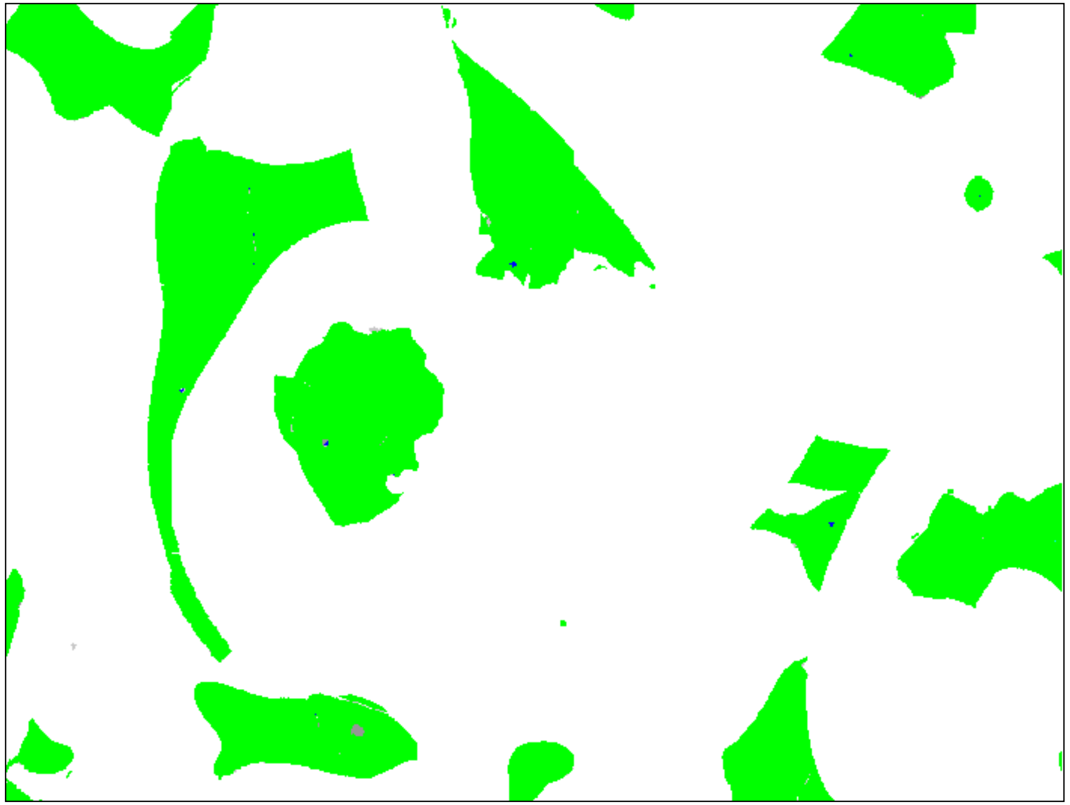
## Automated Mineralogy

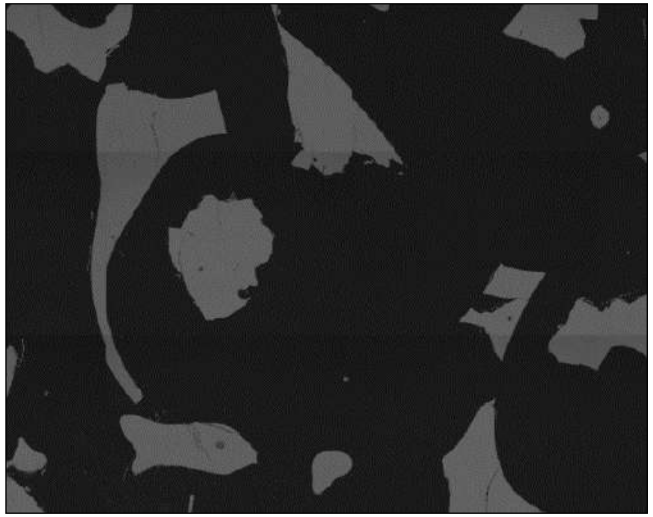
| Element | % Abundance | Element | % Abundance |
|---|---|---|---|
| Lead | 0.2 | Potassium | 0.6 |
| Iron | 10.6 | Manganese | 0 |
| Zinc | 0 | Titanium | 1.3 |
| Calcium | 17.5 | Sodium | 0 |
| Magnesium | 1.6 | Copper | 0 |
| Aluminum | 7.5 | Oxygen | 44.5 |
| Silicon | 15.4 | | |

## ICP-MS

| Element | Al | As | Ba | Be | Bi | Ca | Cd | Ce | Co | Cr | Cu |
|---|---|---|---|---|---|---|---|---|---|---|---|
| % | 7.52 | <0.005 | 0.014 | 0.0010 | <0.005 | 17.0 | <0.005 | 0.0386 | <0.005 | 0.049 | <0.0025 |
| Element | Fe | K | La | Li | Mg | Mn | Mo | Na | Ni | P | Pb |
| % | 9.86 | 0.531 | 0.0184 | 0.015 | 1.39 | 0.136 | <0.001 | 0.758 | 0.061 | 0.406 | <0.005 |
| Element | Re | Sb | Sr | Te | Th | Ti | Tl | V | Y | Zn | Zr |
| % | 0.0008 | <0.005 | 0.021 | <0.005 | 0.0052 | 1.24 | <0.01 | 0.0104 | 0.0084 | 0.05 | 0.0927 |

# Funsur





| Element | |
|---|---|
| Lead | 0.20% |
| Iron | 10.60% |
| Zinc | 0.00% |
| Calcium | 20.10% |
| Magnesium | 1.60% |
| Aluminum | 7.50% |
| Silicon | 15.40% |
| Potassium | 0.60% |
| Manganese | 0.00% |
| Titanium | 1.30% |
| Sodium | 0.80% |
| Copper | 0.00% |
| Oxygen | 41.90% |

# Ilo

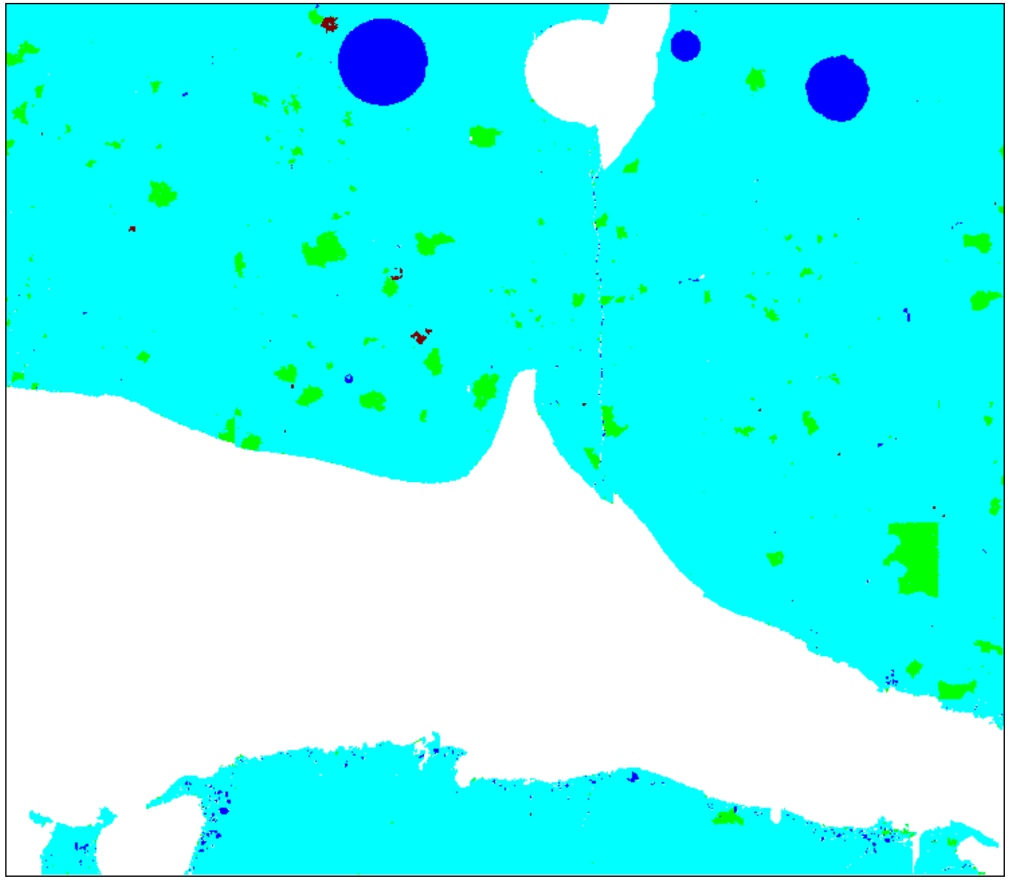
## Automated Mineralogy

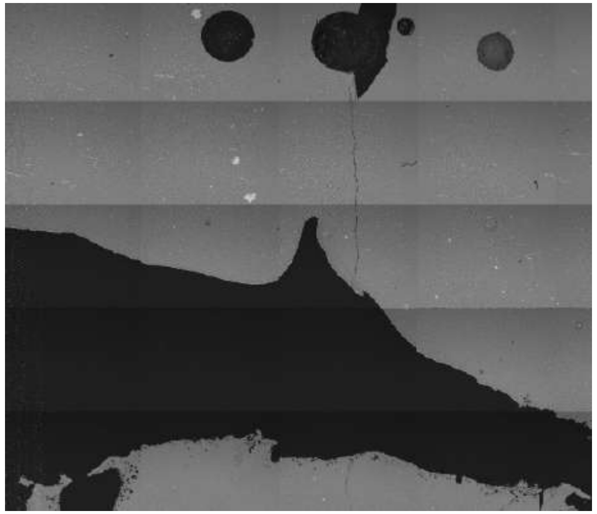
| Element | % Abundance | Element | % Abundance |
|---|---|---|---|
| Aluminum | 3.51 | Calcium | 3.43 |
| Sodium | 0.39 | Copper | 0.78 |
| Sulfur | 1.75 | Potassium | 1.46 |
| Silicon | 11.29 | Manganese | 0.01 |
| Magnesium | 0.36 | Antimony | 0.02 |
| Iron | 36.43 | Arsenic | 0.02 |
| Zinc | 0.66 | Lead | 0 |
| Oxygen | 39.88 | | |

## ICP-MS

| Element | Weight % | Element | Weight % |
|---|---|---|---|
| Al | 3.41 | Mo | 0.060 |
| As | 0.015 | Na | 0.424 |
| Ba | 0.030 | Ni | 0.023 |
| Be | <0.0005 | P | 0.017 |
| Bi | <0.005 | Pb | <0.005 |
| Ca | 3.40 | Re | 0.001 |
| Cd | <0.0005 | Sb | <0.005 |
| Ce | 0.0051 | Sr | 0.024 |
| Co | 0.006 | Te | <0.005 |
| Cr | 0.015 | Th | <0.0005 |
| Cu | 0.841 | Ti | 0.209 |
| Fe | 37.4 | Tl | <0.01 |
| K | 1.35 | V | <0.0005 |
| La | 0.0018 | Y | 0.0011 |
| Mg | 0.352 | Zn | 0.605 |
| Mn | 0.0616 | Zr | 0.0088 |

# Ilo



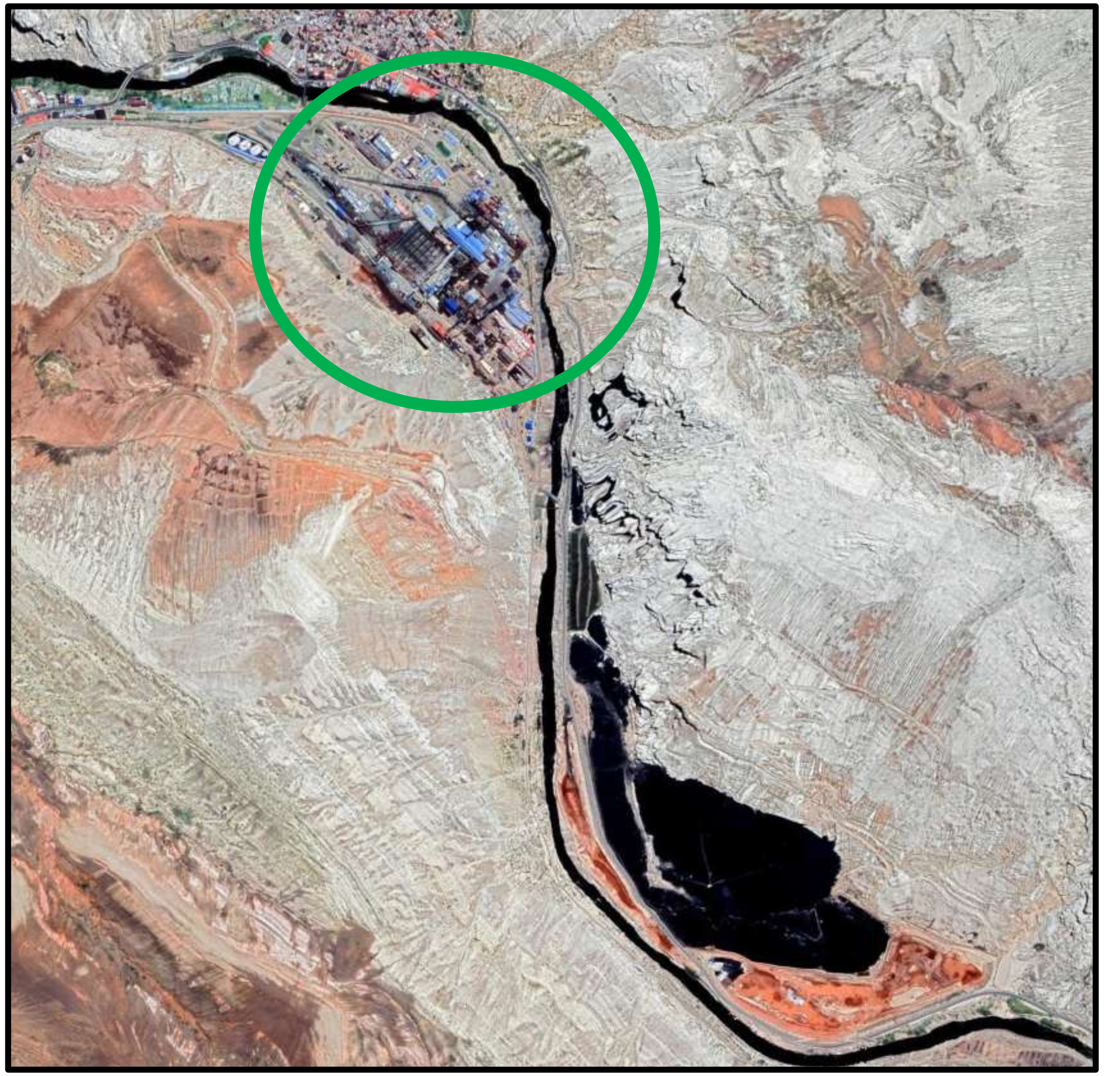


| Element | (teal) | (green) | (cyan) | (dark red) Chalcopyrite |
|---|---|---|---|---|
| Aluminum | 3.50% | 3.50% | 4.00% | |
| Sodium | 0.40% | 0.40% | 0.15% | |
| Sulfur | 1.60% | 1.80% | 0.00% | |
| Silicon | 7.50% | 12.60% | 13.20% | |
| Magnesium | 0.35% | 0.35% | 0.60% | |
| Iron | 40.00% | 35.40% | 32.20% | |
| Zinc | 1.20% | 0.50% | 0.00% | |
| Calcium | 1.00% | 4.00% | 8.70% | $CuFeS_2$ |
| Copper | 0.00% | 1.00% | 0.00% | |
| Potassium | 0.00% | 2.00% | 1.50% | |
| Manganese | 0.00% | 0.00% | 0.30% | |
| Antimony | 0.00% | 0.00% | 0.50% | |
| Arsenic | 0.00% | 0.00% | 0.50% | |
| Lead | 0.00% | 0.00% | 1.10% | |
| Oxygen | 44.45% | 38.45% | 37.25% | |

# La Oroya

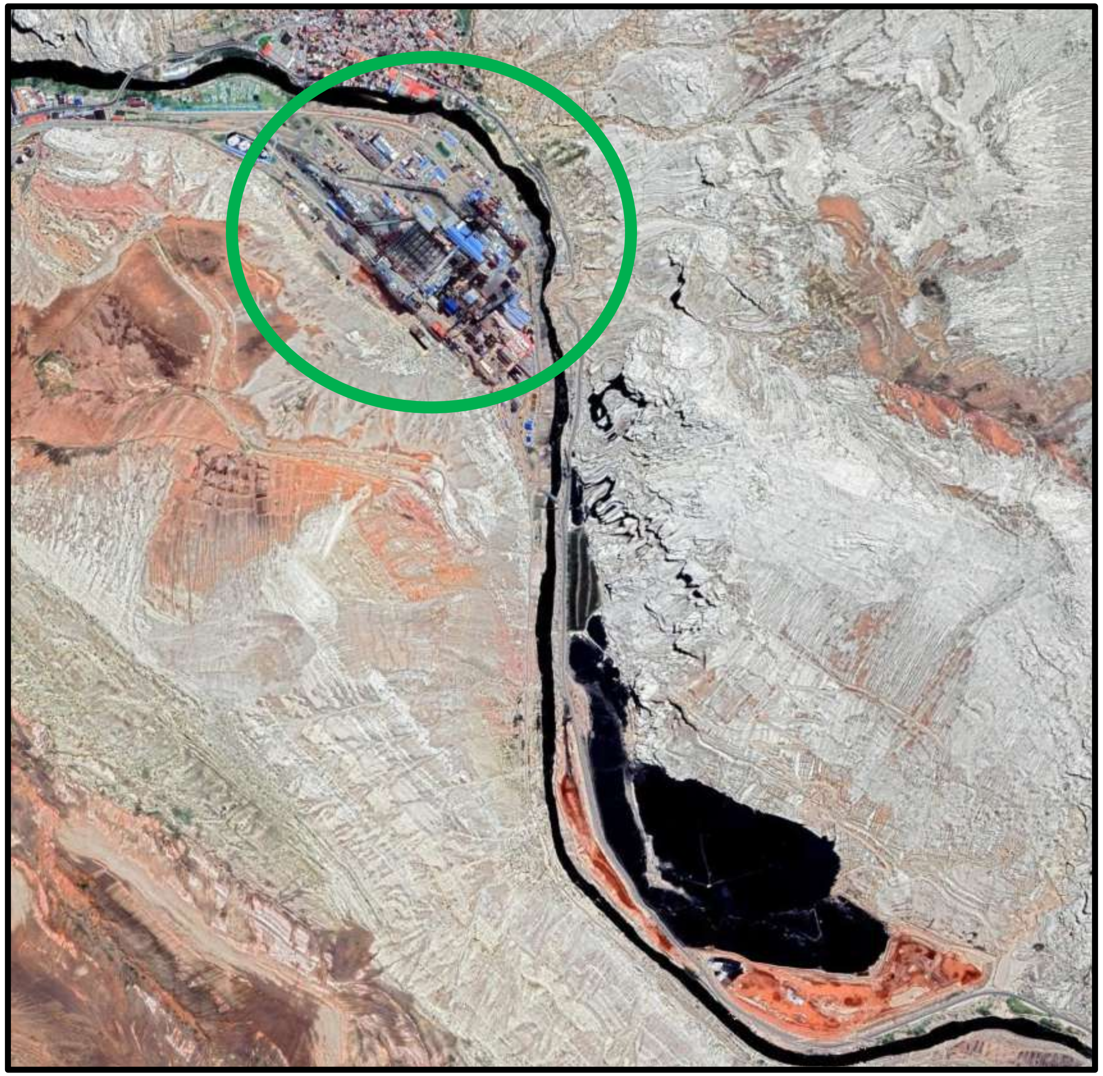
Operation: early 1900’s to 2009

- Cerro De Pasco Corp.
  - Started operation in early 1900’s
    - Full production in 1922.
- Centromin
  - Nationalized by Peruvian government in the mid-70’s.
- Doe Run Peru
  - Purchased La Oroya in 1997.
  - Shut down in 2009.



# La Oroya

- Polymetallic Facility
  - Copper
  - Lead
  - Zinc
  - Byproducts:
    - Gold
    - Silver
    - Indium
    - Cadmium
    - Tellurium
    - Bismuth



# La Oroya Slag

- Environmental problems
  - Release of toxic elements
  - Dust pollution
- 60/40 split of copper and lead slag
- 14 millions tons

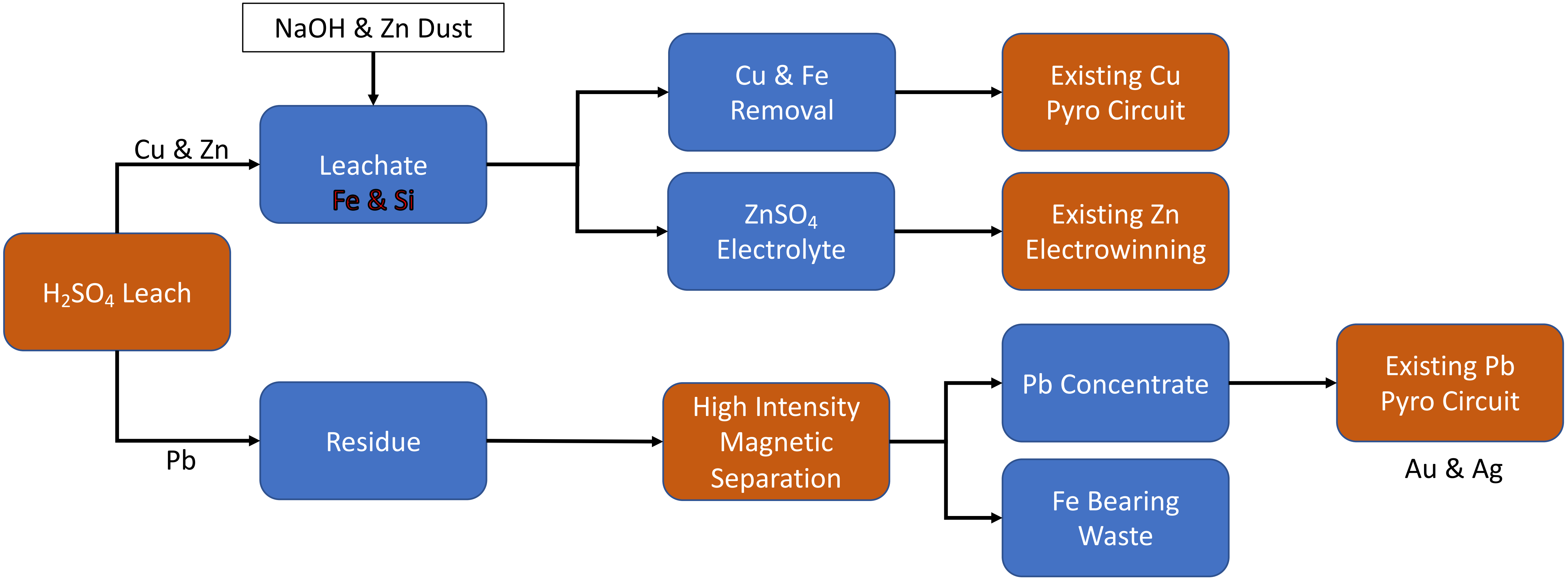
# La Oroya – Slag Value (April 2023)

| Commodity | Price | Amount | Value |
|---|---|---|---|
| Copper | $ 3.40/lb | 67,900 ton | $ 461,720,000 |
| Lead | $ 1,860.10/tonne | 337,400 ton | $ 569,347,000 |
| Zinc | $ 3,010.50/tonne | 1,021,300 ton | $ 2,789,252,000 |
| Gold | $1,656.00/T Oz | 75,541 T Oz | $ 125,097,000 |
| Silver | $ 19.33/T Oz | 19,497,907 T Oz | $ 376,895,000 |

Total Value: US$4.3 Billion

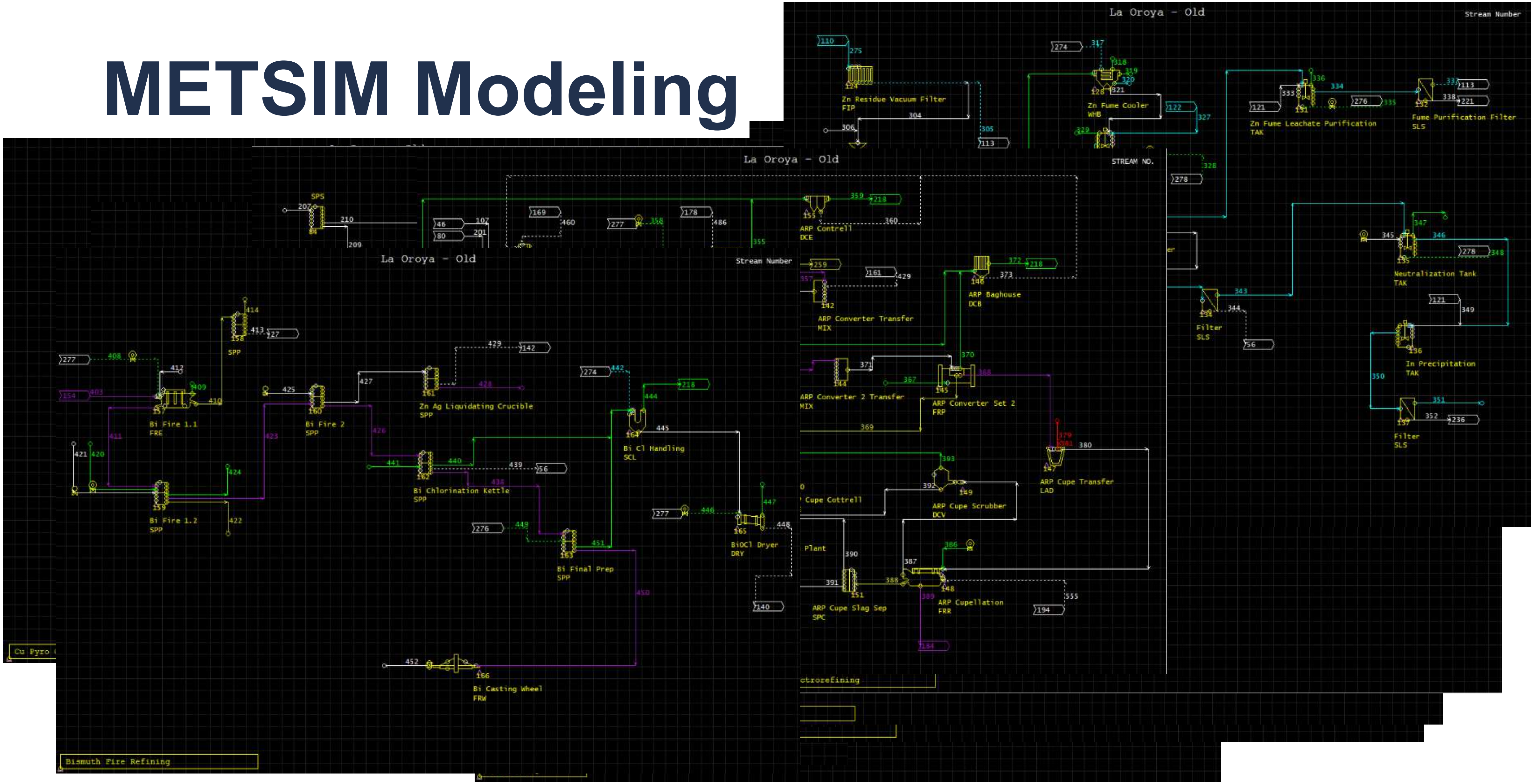
# The Process

# Overall Process



# METSIM Process Modeling

# METSIM Modeling



# Preliminary Techno-Economic Analysis

# NPV & IRR

| Discount Rate, i | NPV Process A | NPV Process B |
|---|---|---|
| **10%** | $131,015,593 | ($161,217,658) |
| **15%** | $80,055,177 | ($106,315,972) |
| ***17%*** | **$68,216,199** | **($93,420,150)** |
| **20%** | $55,025,890 | ($78,932,903) |
| **25%** | $40,329,269 | ($62,554,478) |
| **IRR** | 129% | N/A |

# Conclusions

- 3 Peruvian slags were characterized, La Oroya slag was selected for further work.
- Initial test work indicated full devitrification and beneficiation via flotation not likely to be successful.
- A potential process to recover copper, lead, and zinc was developed.
- METSIM models of the proposed and historical La Oroya processes were developed.
- A preliminary techno-economic assessment was conducted to show the proposed process is viable.

# Acknowledgements

Center for Mining Sustainability

Universidad Nacional de San Agustin de Arequipa

Dr. Corby Anderson

Prof. Erik Spiller

Dr. Patrick Taylor

Dr. Paul Santi

Lennard Harris

Eagle Engineering

# End

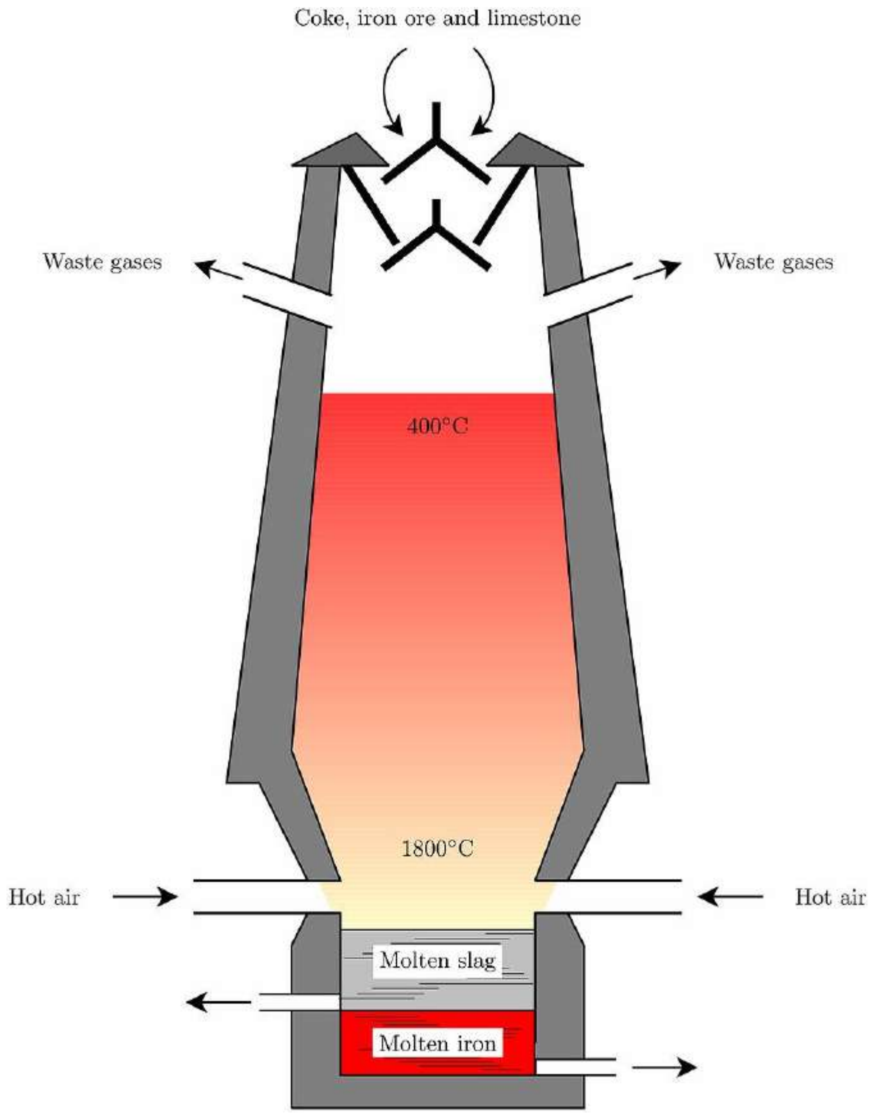
# Outline

- Project Introduction & Motivation
- Sample Characterization
- Scoping Studies & Preliminary Testing
- Developed Process
- METSIM Models
- Preliminary Techno-Economic Analysis
- General Conclusions

# Pyrometallurgical Slag

- What is Slag - During the smelting process, the gauge constituents are turned into a less dense phase and float to the top.

- Entrained matte
- Metal Values
  - Base Metals: Cu, Pb, Zn
  - Precious metals: Au, Ag, PGM's
  - Critical metals: Rare earths, Ga, In, Co



# Smelting Facilities

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- Polymetallic facility previously operated by Doe Run.
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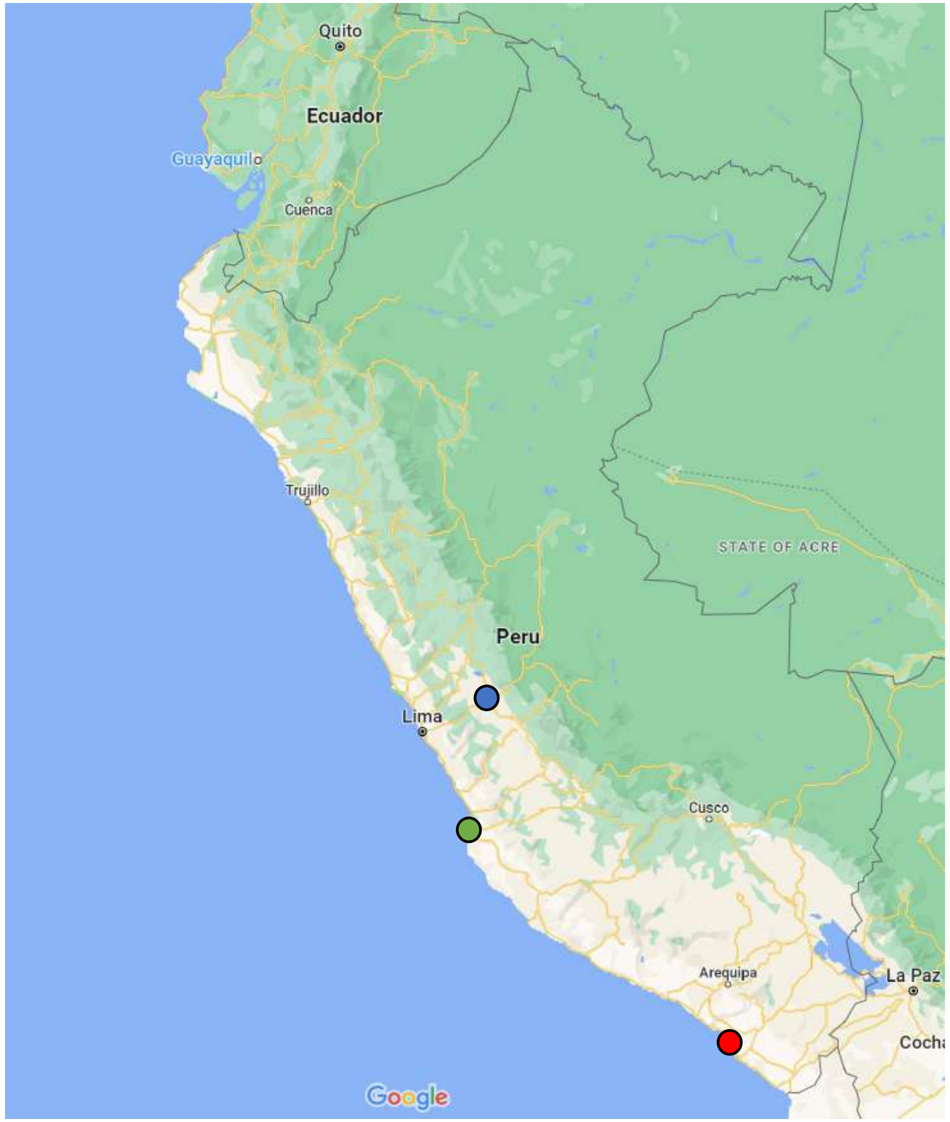
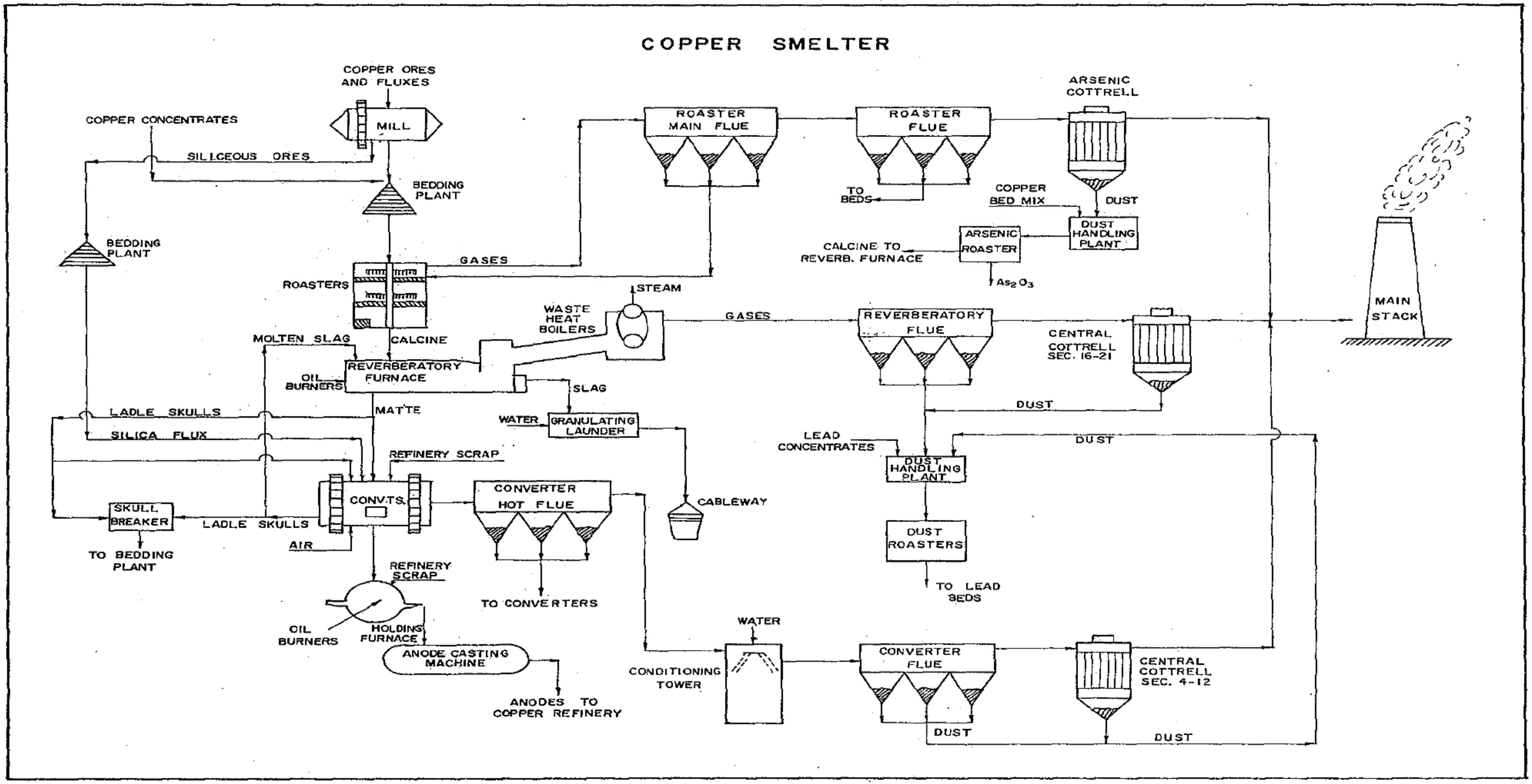
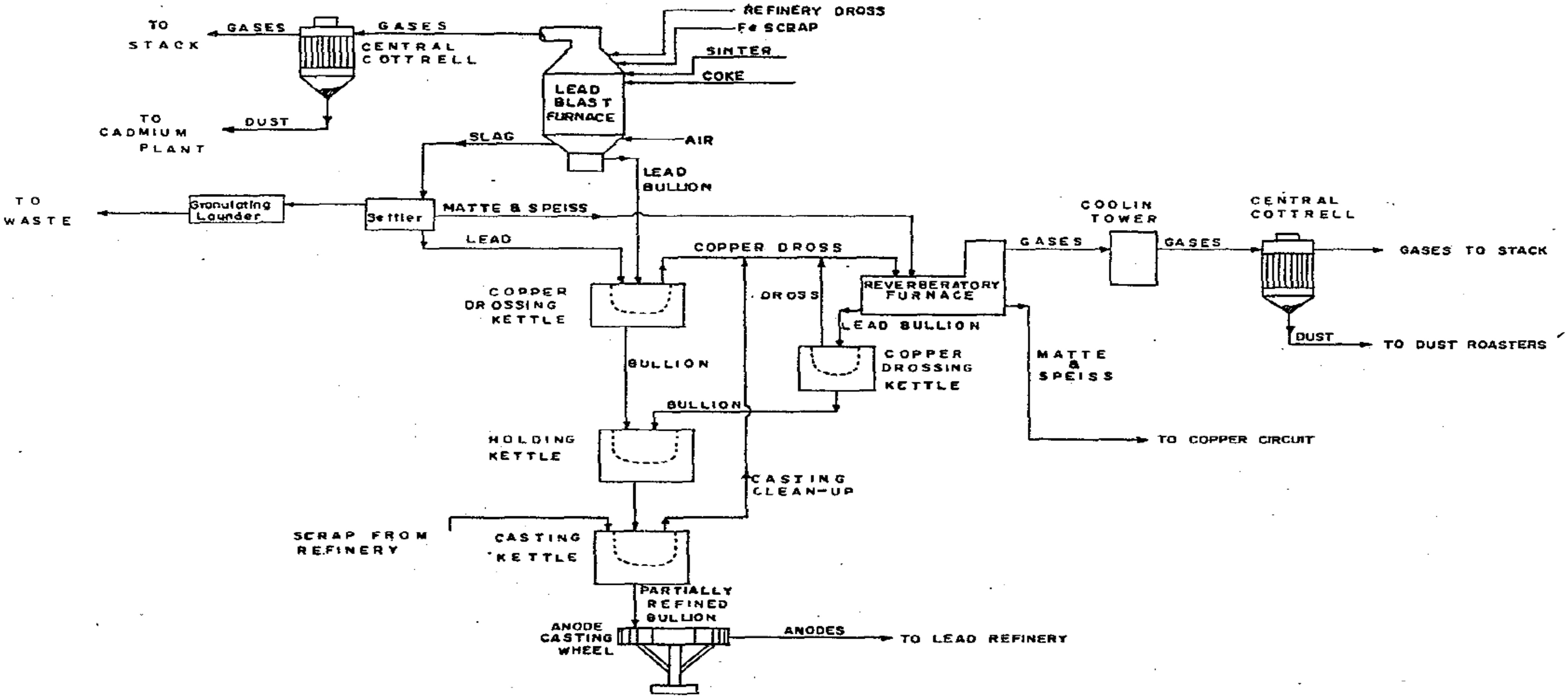



COPPER SMELTER
COPPER ORES AND FLUXES
MILL
COPPER CONCENTRATES
SILICEOUS ORES
BEDDING PLANT
BEDDING PLANT
ROASTERS
GASES
ROASTER MAIN FLUE
ROASTER FLUE
TO BEDS
ARSENIC COTTRELL
COPPER BED MIX
DUST
DUST HANDLING PLANT
ARSENIC ROASTER
CALCINE TO REVERB. FURNACE
$As_2O_3$
STEAM
WASTE HEAT BOILERS
GASES
REVERBERATORY FLUE
CENTRAL COTTRELL SEC. 16-21
MAIN STACK
MOLTEN SLAG
CALCINE
REVERBERATORY FURNACE
OIL BURNERS
SLAG
MATTE
DUST
LADLE SKULLS
SILICA FLUX
WATER
GRANULATING LAUNDER
LEAD CONCENTRATES
DUST
DUST HANDLING PLANT
REFINERY SCRAP
CONVTS.
CONVERTER HOT FLUE
CABLEWAY
SKULL BREAKER
LADLE SKULLS
AIR
TO BEDDING PLANT
DUST ROASTERS
REFINERY SCRAP
TO CONVERTERS
TO LEAD BEDS
OIL BURNERS
HOLDING FURNACE
ANODE CASTING MACHINE
ANODES TO COPPER REFINERY
WATER
CONDITIONING TOWER
CONVERTER FLUE
CENTRAL COTTRELL SEC. 4-12
DUST
DUST

# LEAD SMELTER



# Process Options

| Leachate A (no peroxide) | | | | | |
|---|---|---|---|---|---|
| Element | Cu | Zn | Fe | Si | Pb |
| Recovery | 55% | 92% | 86% | 84% | 0.6% |
| Grade | 0.0012% | 0.34% | 1.20% | 0.49% | 0.0007% |

- Unheated
- 50 g/L
- $P_{80}$: 74 micron
- 3 hours
- 25 °C
- 0.783 M $H_2SO_4$

| Leachate B (peroxide) | | | | | |
|---|---|---|---|---|---|
| Element | Cu | Zn | Fe | Si | Pb |
| Recovery | 88% | 92% | 82% | 82% | 1.0% |
| Grade | 0.018% | 0.30% | 1.00% | 0.42% | 0.0012% |

- Unheated
- 50 g/L
- $P_{80}$: 74 micron
- 3 hours
- 25 °C
- 1.26 M $H_2SO_4$
- 30 mL/L/Hr. 30% $H_2O_2$