



**Use of Alkaline Additives and a Soil Cover for  
Prevention of Acid Mine Drainage from Sulphidic  
Tailings in Lavrion**

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**NATO CCMS Pilot Study  
Prevention and Remediation Issues  
In Selected Industrial Sectors Pilot Study  
Non-Ferrous Mining Sector**

**Baia Mare, Romania**





## Overview

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- **The Lavrion site**
- **Sulphidic tailings**
- **Rehabilitation Approach**
- **Laboratory Experiments**
- **Field Tests**
- **Full Scale Application**
- **Monitoring**
- **Conclusions**

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## The Lavrion History

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- **Lavrion, Greece is an historical mining site**
- **The great era of the Athens city state was based on the exploitation of Lavrion argentiferous ores**
- **Mining started in 7th century BC**
- **Mining during 5th-4th Century BC:**
  - 3,500 t Ag**
  - 1,400,000 t Pb**
- **Modern-era mining: 1865-1980**
  - 860,000 t Pb**

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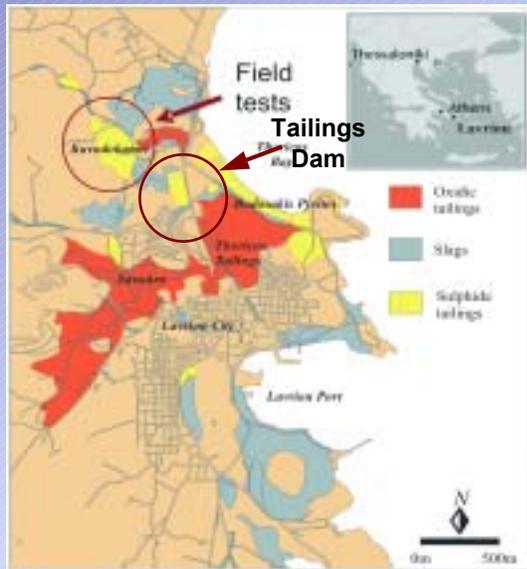
## The Lavrion Site

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- **Generation of hazardous wastes:**
  - ✓ **Mining wastes**
  - ✓ **Beneficiation tailings**
  - ✓ **Metallurgical slags**
  
- **Severe contamination of soils:**
  - ✓ **Pb: 800 - 23,000 mg/kg**  
**(limit 530)**



# The Lavrion Site



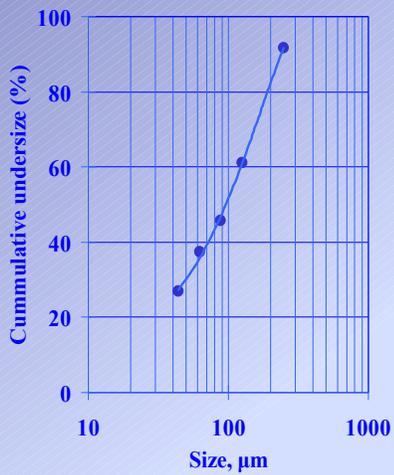
| Physical Properties Tailings Dam |  |
|----------------------------------|--|
| Total quantity                   | 150,000 t                                  |
| Total area                       | 25,000 m <sup>2</sup>                      |
| Average dry bulk density         | 1.26 g.cm <sup>3</sup>                     |
| Specific gravity                 | 2.71 g.cm <sup>3</sup>                     |
| Moisture                         | 8 - 14.3 %                                 |
| Hydraulic Conductivity, k        | 1.44 x 10 <sup>-4</sup> cm.s <sup>-1</sup> |

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## Sulfide tailings dam



### Physical Properties Tailings Dam

|                           |   |
|---------------------------|---|
| $d_{50}$                  | 100 $\mu\text{m}$                           |
| Average wet bulk density  | 1.40 $\text{g.cm}^3$                        |
| Average dry bulk density  | 1.26 $\text{g.cm}^3$                        |
| Specific gravity          | 2.71 $\text{g.cm}^3$                        |
| Moisture                  | 8 - 14.3 %                                  |
| Hydraulic Conductivity, k | $1.44 \times 10^{-4}$<br>$\text{cm.s}^{-1}$ |

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## Material Description

### Chemical Analysis

| Size (mm)    | Weight (%) | As (%) | S (%) | Zn (%) | Pb (%) | Ca (%) | Insol. (%) |
|--------------|------------|--------|-------|--------|--------|--------|------------|
| +0.25        | 8.39       | 0.10   | 0.70  | 0.32   | 0.16   | 17.27  | 36.38      |
| -0.25+0.125  | 30.48      | 0.20   | 2.45  | 0.42   | 0.20   | 15.30  | 33.00      |
| -0.125+0.088 | 15.34      | 0.28   | 5.02  | 0.45   | 0.25   | 13.09  | 31.12      |
| -0.088+0.063 | 8.48       | 0.44   | 6.83  | 0.49   | 0.29   | 12.63  | 29.04      |
| -0.063+0.044 | 10.46      | 0.68   | 7.30  | 0.51   | 0.42   | 12.26  | 26.96      |
| -0.044       | 26.83      | 0.56   | 5.32  | 0.52   | 0.53   | 12.44  | 26.14      |
| Total        | 100.00     | 0.37   | 4.34  | 0.46   | 0.32   | 13.81  | 30.19      |

### Mineralogical phases

calcite, quartz, chlorite, muscovite, epidote, pyrite, gypsum, limonite, chalcopyrite, sphalerite, arsenopyrite, baryte

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## Material Description

### Pore Water Quality

| Element  | Pore water (mg/l) | Greek effluent limits (mg/l) |
|--|-------------------|------------------------------|
| Pb   | 2.5               | 0.1                          |
| Zn   | 1,300             | 2                            |
| Cd (ppm)   | 6                 | 0.02                         |
| As   | 0                 | 0.5                          |
| Ca   | 400               |                              |
| Mg   | 2,200             |                              |
| Fe   | 3,200             |                              |
| SO <sub>4</sub>  | 50,000            | 1000                         |
| pH   | 2.3               | 6-8.5                        |
| Oxidation potential (mV)                                 | 400               |                              |
| Dissolved O <sub>2</sub> (mg/l)                          | 1                 |                              |
| Total Suspended Solids (mg/l)                            | 2,000             | 40                           |
| Conductivity (mS/cm)                                     | 26                |                              |
| <b>NNP (kg CaCO<sub>3</sub>/t): -250 (surface) + 310</b> |                   |                              |

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## Risk Assessment

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- **Performed on the Source – Pathway – Target basis**
- **The main significant pollutant pathways identified for the Lavrion tailings dam were**
  - ✓ **Wind/water erosion**
  - ✓ **Direct contact**
  - ✓ **Seepage**





## Rehabilitation techniques examined

| ARD control techniques                                  | Objective of control  |
|---|---|
| Treatment of sulfidic wastes                            | ⇒ Sulfide removal or isolation                                      |
| Alkaline additives<br>(Carbonates/phosphates/silicates) | ⇒ pH control, Fe <sup>3+</sup> control<br>stabilisation of sulfides |
| Bactericides  | ⇒ Control of bacterial action                                       |
| Water cover   | ⇒ Exclusion of oxygen   |
| Dry covers<br>(soils and/or synthetic membranes)        | ⇒ Exclusion of water and oxygen                                     |

### Parameters considered:

Climatic conditions in Lavrion ⇒ Low precipitation, long dry period

Tailings characteristics ⇒ Heterogeneous and oxidised

**Dry covers the most suitable remediation technique**



## Remediation Alternatives

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### ➤ Conventional covers

A cover incorporating a **low hydraulic conductivity soil layer and/or synthetic liner** would limit the infiltration of rainfall waters and/or oxygen within the tailings mass, thus minimising the contaminants load to the downstream environment and inhibiting further oxidation of sulfides.

### ➤ Geochemical barrier (hardpan)

Artificial formation of a low permeability geochemical barrier at the tailings surface that would act as a water transport and oxygen diffusion barrier.

Based on previous laboratory studies, the addition of limestone to partially oxidised sulfide wastes and subsequent neutralisation of the acidity released would promote the precipitation of secondary oxidation-neutralisation products (gypsum, ferric hydroxides) thus enhancing the formation of a hardpan layer.



## Methodology

Literature Data  
Field Observations



Laboratory  
Tests



Field Tests



Full Scale  
Application

- Hard Pan formation is reported worldwide
- Hard Pan is also reported at the Lavrion Site (Bodossakis Pyrites)



## Laboratory tests

Literature Data  
Field Observations



Laboratory  
Tests



Field Tests



Full Scale  
Application

➤ Lysimeter kinetic tests



➤ Humidity Cells



➤ Column Kinetic tests





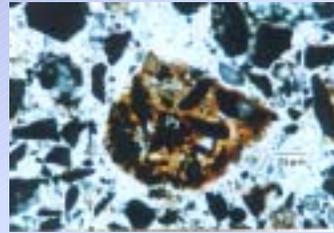
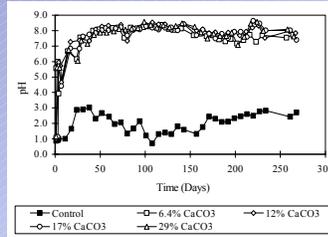
## Laboratory tests

Literature Data  
Field Observations

Laboratory  
Tests

Field Tests

Full Scale  
Application

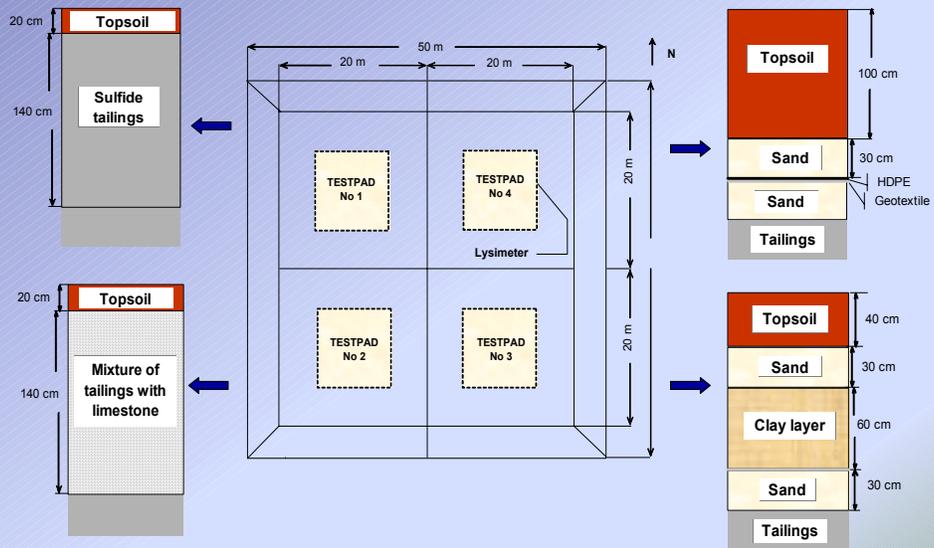


### ➤ Limestone Addition:

- ✓ Neutralization of the acidity
- ✓ Precipitation around the pyrite particles
- ✓ Decrease of the permeability (Hard Pan formation)



# Methodology - Field tests



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## Methodology – Field Tests

Literature Data  
Field Observations



Laboratory  
Tests



Field Tests



Full Scale  
Application

➤ Before  
Construction



➤ After  
Construction

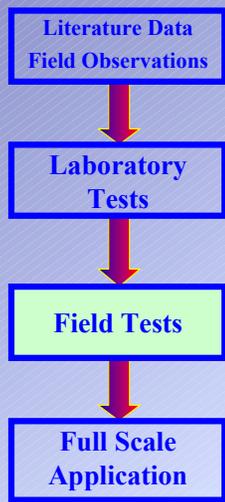


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## Methodology – Field tests



### Formation of a hardpan layer



Soil, 20 cm

Oxidised sulfide tailings, 20 cm

Hardpan layer, 50 cm thick



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## Full scale application

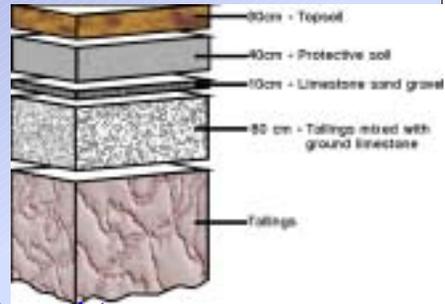
Literature Data  
Field Observations

Laboratory  
Tests

Field Tests

Full Scale  
Application

### Remediation Scheme



### Functions:

- Tailings + Limestone mixture
  - ✓ Provide alkalinity
  - ✓ Decrease water permeability
- Limestone sand gravel – Drainage
- Protective soil – Topsoil
  - ✓ Vegetation
  - ✓ Reduce the risks associated with wind erosion and direct contact



## Full scale remediation of Tailings Dam

Literature Data  
Field Observations

Laboratory  
Tests

Field Tests

Full Scale  
Application

### Before Construction



West



East



- East part was partially empty
- During the winter was full of rain water



## Full scale remediation of Tailings Dam

Literature Data  
Field Observations



Laboratory  
Tests



Field Tests



Full Scale  
Application

- 1<sup>st</sup> step : Initial Leveling (transportation of tailings from the West to the East part – 1% gradient to the East)
- 2<sup>nd</sup> step : Placement of ground limestone



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## Full scale remediation of Tailings Dam

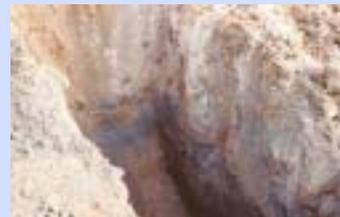
Literature Data  
Field Observations

Laboratory  
Tests

Field Tests

Full Scale  
Application

3<sup>rd</sup> step : Mixing of tailings with limestone  
(Agricultural – mechanical equipment)



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## Full scale remediation of Tailings Dam

Literature Data  
Field Observations

Laboratory  
Tests

Field Tests

Full Scale  
Application

3<sup>rd</sup> step : Mixing of tailings with limestone

### Limestone chemical analysis and physical properties

| Zn (%) | Pb (%) | Cd (ppm) | Fe (%) | Ca (%) | Mg (%) |
|--------|--------|----------|--------|--------|--------|
| 0.01   | 0.02   | 16       | 0.08   | 35     | 2.53   |

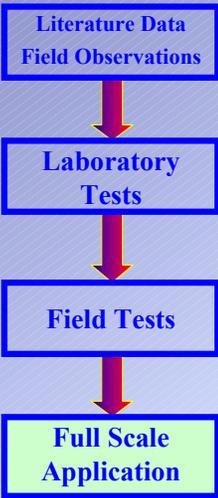
Grain size : -0.8 mm (40% -0.4 mm)

Bulk density : 1.65 t.m<sup>-3</sup>

- Limestone Application rate : 200 kg/t tailings
- Total limestone cost (purchase and transport) : 8.4 USD/m<sup>3</sup>



# Full scale remediation of Tailings Dam



**4<sup>th</sup> step: Placement of limestone sand gravel (drainage layer)**



**5<sup>th</sup> step: Placement of protective soil and topsoil**

**Soil Analyses (mg/kg)**

|                       | Pb  | Zn  | Cd  | As |
|-----------------------|-----|-----|-----|----|
| Topsoil               | 40  | 81  | 3   | 25 |
| Protective soil       | 45  | 7   | 3.8 | 72 |
| topsoil layer limit   | 375 | 600 | 3   | 20 |
| protective soil limit | 500 | 800 | 4   | 25 |





## Full scale remediation of Tailings Dam

Literature Data  
Field Observations



Laboratory  
Tests



Field Tests



Full Scale  
Application

Final View

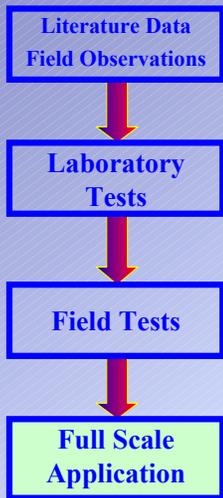


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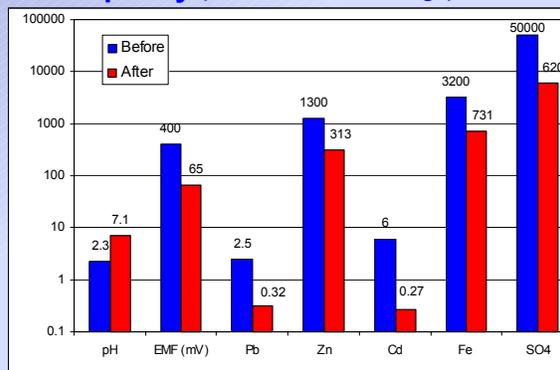
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## Full scale remediation of Tailings Dam - Monitoring



- Drillholes – piezometers were installed for pore water monitoring
- Significant improvement of the pore water quality (elements conc. in mg/l)



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## Full scale remediation of Tailings Dam – Cost data

Literature Data  
Field Observations



Laboratory  
Tests



Field Tests



Full Scale  
Application

### Cost Breakdown

| Cost Categories                 | Quantity (m <sup>3</sup> ) | Cost per Unit (USD/m <sup>3</sup> ) | Total cost (USD)        |
|---------------------------------|----------------------------|-------------------------------------|-------------------------|
| Sand                            | 5000                       | 8.4                                 | 42,000                  |
| Sand gravel                     | 2500                       | 2.5                                 | 6,250                   |
| Protective soil                 | 7500                       | 5.9                                 | 44,250                  |
| Topsoil                         | 10000                      | 7.1                                 | 71,000                  |
| Cost of personnel and machinery |                            |                                     | 171,500                 |
| <b>Total cost</b>               |                            |                                     | <b>335,000</b>          |
| or                              |                            |                                     | 13.4 USD/m <sup>2</sup> |



## Conclusions

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- **A low cost remediation scheme was applied for the Tailings Dam in Lavrion**
- **It involves neutralisation of the upper part of sulphidic tailings with limestone followed by a sequence of layers (drainage, protective soil and topsoil)**
- **The cost of the remediation was 13.4 USD per square meter.**
- **Monitoring results indicated that the applied scheme resulted in significant improvement of pore water quality**