

# TURNING THE “EXTRACTIVE WASTE PROBLEM” INTO A “RESOURCE RECOVERY OPPORTUNITY”

*Teodor VELEA, Vasile PREDICA, Alexandra-Georgiana VATUI, Ioana-Andreea CHIREA, Ionut MACARESCU, Carlos FRIAS GOMEZ, Manuel SEVILLA, Mika PAAJANEN, Lieven MACHIELS*

# ABSTRACT

- The mining of non-ferrous metals, such as Cu, Pb, Zn, Au, Ag, produces a large volume of metals and enormous volumes of waste.
- A particular problem is generated by the sulphidic waste-like pyrites.
- This paper presents the results of experiments for advanced removal of sulphur, in order to obtain near-zero waste and valuable products and by-products.
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# INTRODUCTION

- a) The mining of non-ferrous metals, such as Cu, Pb, Zn, Ni, Co, and precious metals (Au, Ag, and Pt) produces the largest volume of extractive waste in Europe: about 29% of all the waste is produced in the EU-28. Consequently, enormous volumes of this material, known as “tailings”, can cause environmental problems (particularly sulphidic tailings which may cause acid mine drainage).
- b) In its 2016 “Raw Materials Scoreboard” report, the European Innovation Partnership (EIP) on Raw Materials launched a “call to arms” to transform the “extractive waste problems” into a “resource recovery opportunity”.
- c) In response to this call an interdisciplinary consortium from the ‘Near-zero-waste recycling of low-grade sulphidic mining waste for critical-metal, mineral and construction raw-material production in a circular economy — NEMO’ project developed new technologies and new techniques for processing sulphidic tailings arising from the production of Cu, Zn, Pb etc. in some important mines in Spain and Finland.

# MAIN OBJECTIVE

- Pressure alkaline leaching process was investigated to achieve a viable alternative to roasting-smelting sulphidic waste, with the associated environmental and socio-economic benefits:
  - ❖ reducing to zero SO<sub>2</sub> emissions,
  - ❖ eliminating problems with H<sub>2</sub>SO<sub>4</sub> market saturation,
  - ❖ decreasing high capital cost and energy consumption.



**ZERO**   
EMISSION

# EXPERIMENTAL WORK

The specific objectives of the research work were:

- To define and characterize sulphidic mining waste.
- To demonstrate how alkaline oxidation of sulphidic mining waste leads to advanced removal / recovery of sulphur in order to obtain near-zero waste and valuable products and by-products,
- To evaluate the Cu, Zn, As oxidation rate using autoclave alkaline oxidation,
- To validate the parameters of the alkaline leaching process aiming at the recovery of the valuable components from sulphidic mining waste.



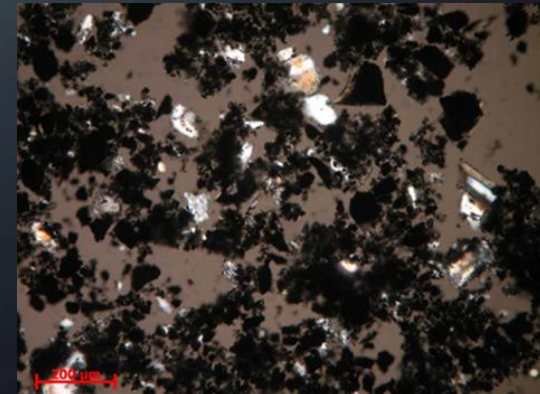
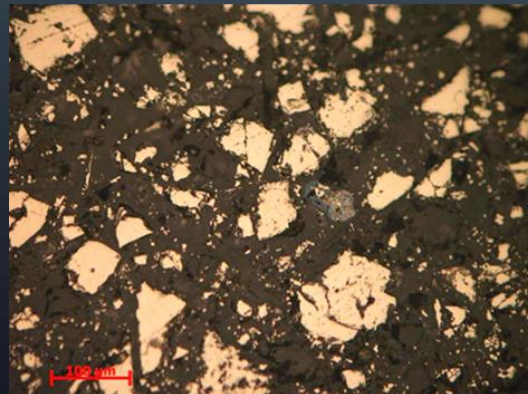
# RAW MATERIAL CHARACTERISATION

Raw materials are tailings from CLC - Copper Mine, Spain.

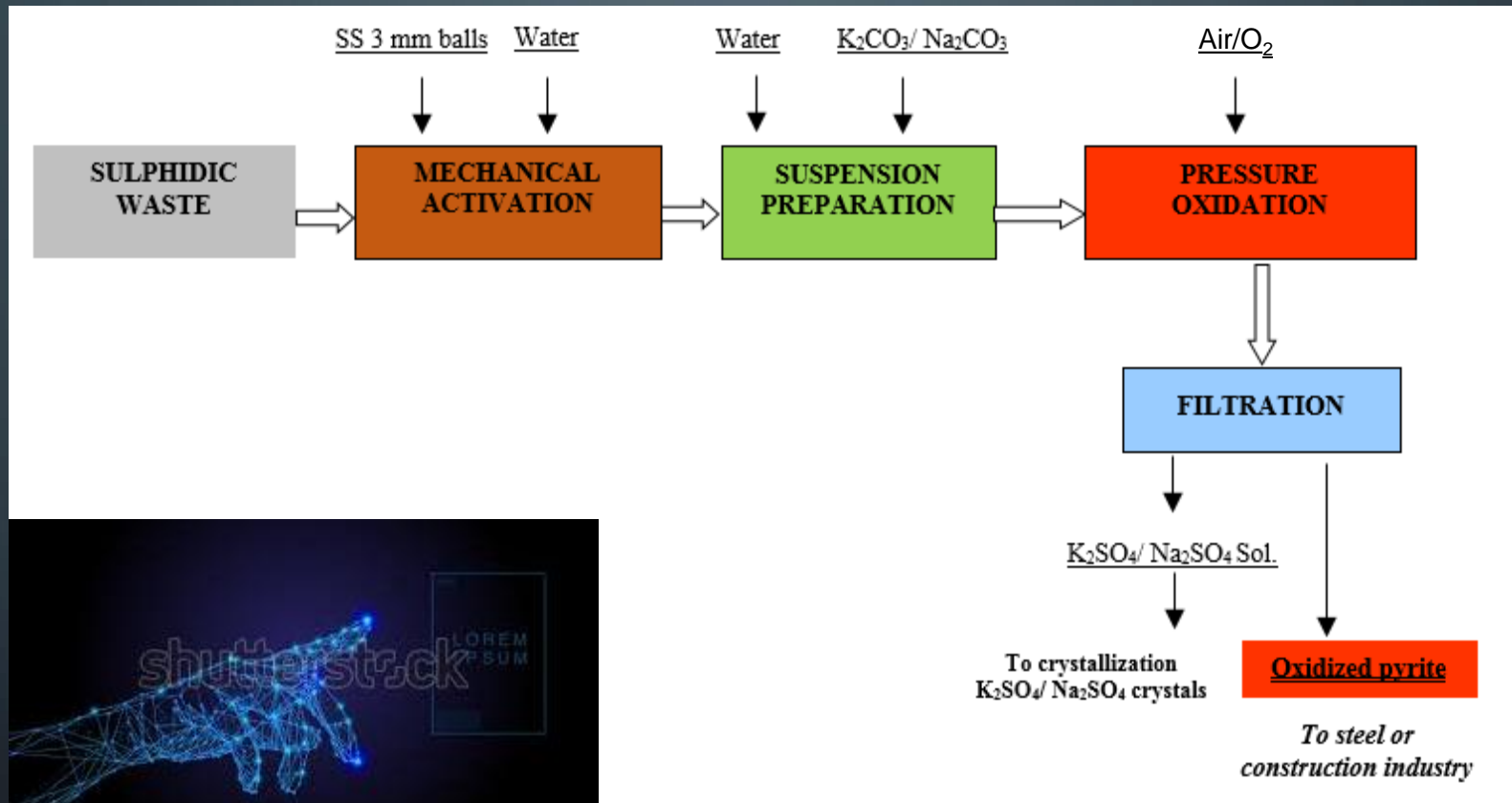
Chemical characterization of CLC sample

Method		ME-ICP81x							
	Analyse	Cu	Fe	Ca	As	Pb	Zn	Mn	S
		%	%	%	%	%	%	%	%
Sample	N11O-001	0.53	29.4	0.13	0.26	0.66	0.13	0.02	35.2
	Analyse	SiO <sub>2</sub>	Al	Co	Ni	Mg	K	Ag	Al
		%	%	%	%	%	%	ppm	%
Sample	N11O-001	33.7	0.52	0.042	<0.005	0.04	0.11	27.8	0.04

Pyrite (FeS<sub>2</sub>) is the predominant mineral in the sample and appears to be associated with: ZnS blend, covellite CuS, galena PbS, bornite Cu<sub>5</sub>FeS<sub>4</sub>, quartz SiO<sub>2</sub>, feldspar plagioclase Ca(Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>).



# TECHNOLOGICAL CONCEPT



# THE MAIN EQUIPMENT

Alkaline oxidation of sulphidic mining waste in 20 litre autoclave with continuous feed





Bench scale experiments used a continuous-feed 20 litre autoclave, made of SS316, with the following facilities.

- Electric heating with constant temperature control and maintenance;
- Cooling system for exothermic processes;
- Continuous gas supply (air, oxygen, etc.) in the liquid mass and continuous gas discharge with constant pressure maintenance;
- Continuous suspension feeding with metering pump (diaphragm pump);
- Continuous drainage of autoclave suspension;
- Sampling during operation.



# CRYSTALLIZATION EQUIPMENT – SPRAY DRYER



Potassium/sodium sulphate

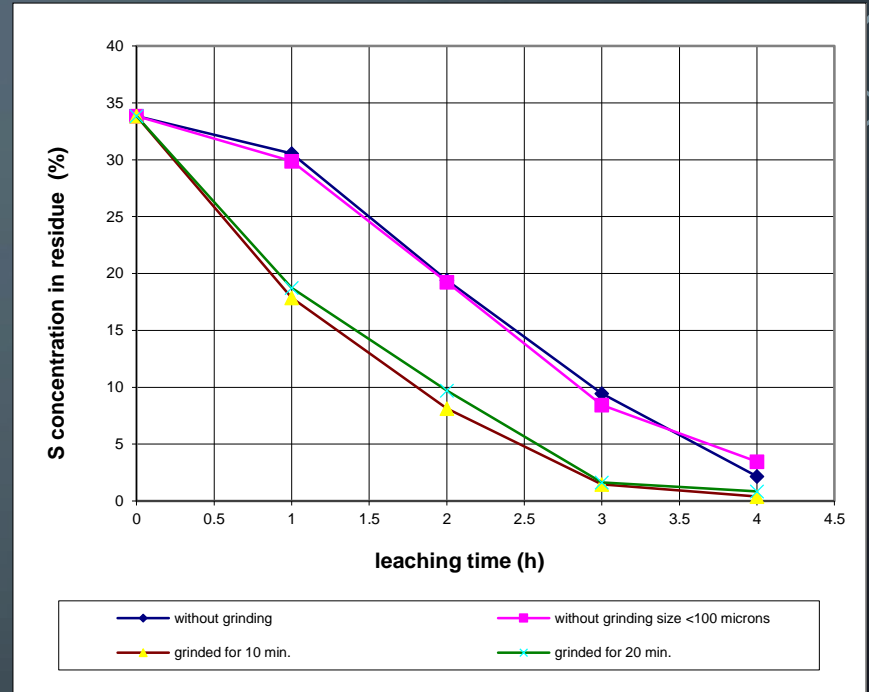
# RESULTS

## 1. Attrition

To demonstrate the effect of mechanical activation on the process of alkaline oxidation of mining waste, alkaline leaching experiments were carried out under constant conditions:

- Temperature 135 °C;
- Total pressure 8 atm.;
- Oxidation time 4 h;
- Oxidizing agent air;
- Reaction media: alkaline  $K_2CO_3$ - oxidized waste, with and without grinding

Thus, the sulphur oxidation efficiency for untreated waste was 92%, for waste milled for 10 minutes it was 94%, and in case of grinding for 20 minutes the sulphur oxidation efficiency was 98%.

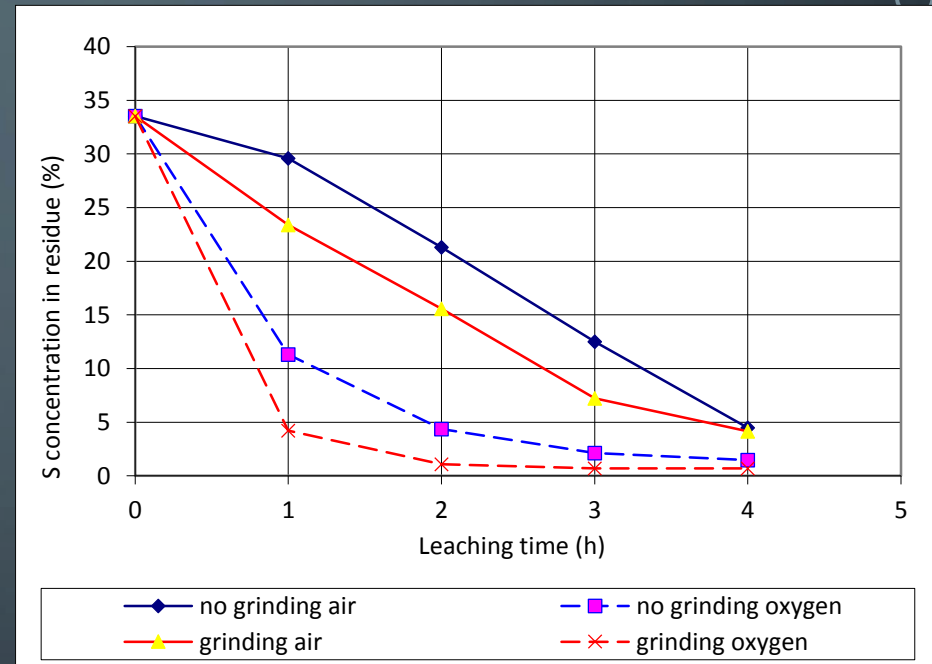


Percentage of S content in residual oxidized waste, with and without grinding

## 2. AUTOCLAVE ALKALINE OXIDATION

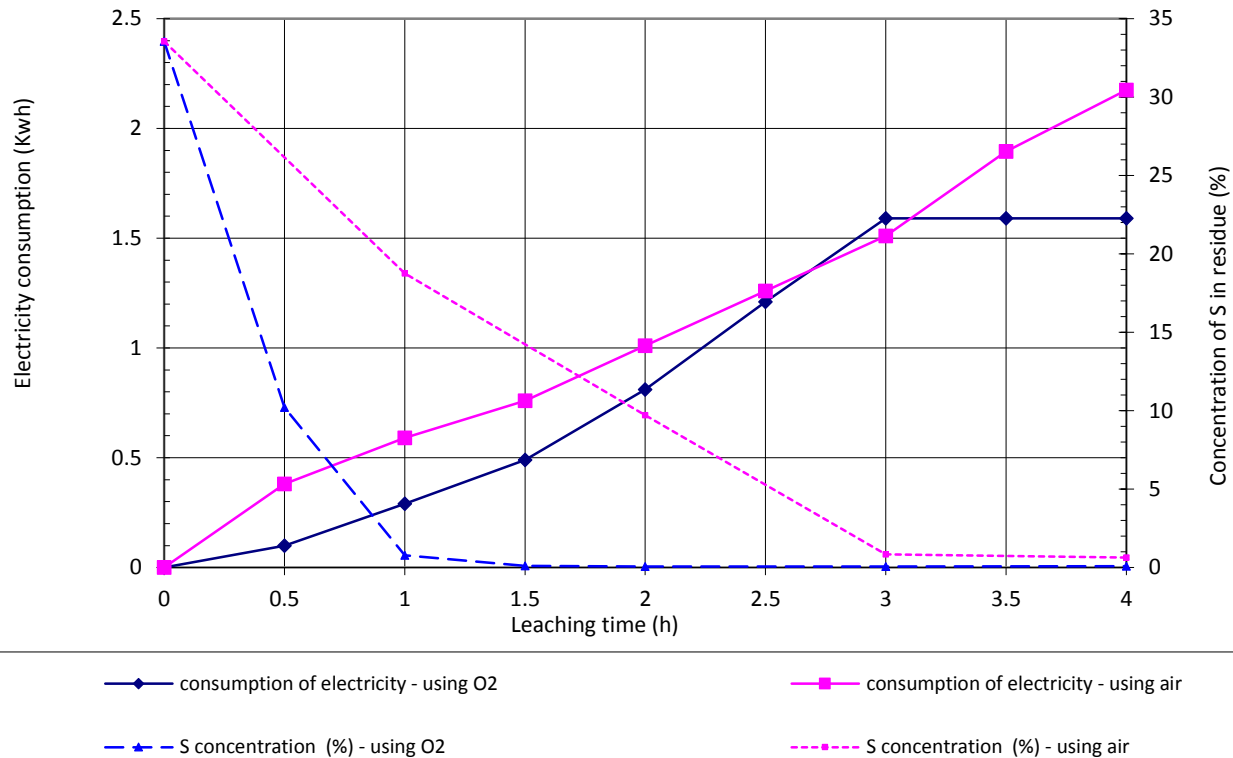
1. Oxidation agent: air / oxygen; alkaline medium  $K_2CO_3$   
In the autoclave leaching experiments, air and oxygen were used.

- Temperature 135 °C;
- Total pressure 8 atm.;
- Grinding time 0-10 min.;
- L/S ratio 15/1-17/1.



Using air as oxidant agent, it was necessary 4 hours to obtain 96-98% sulphur oxidation efficiency and 2 hours when it was used oxygen as oxidant.

S content over time during pressure leaching in potassium carbonate media, as a function of leaching time; air or oxygen as oxidant



## S content over leaching time in potassium carbonate media; electricity consumption as a function of leaching time

Thus, by using air for oxidation reaction after one hour the sulphur content of the oxidized waste drops from 33.54% to 18.75%, with an electrical consumption of 0.6 Kwh.

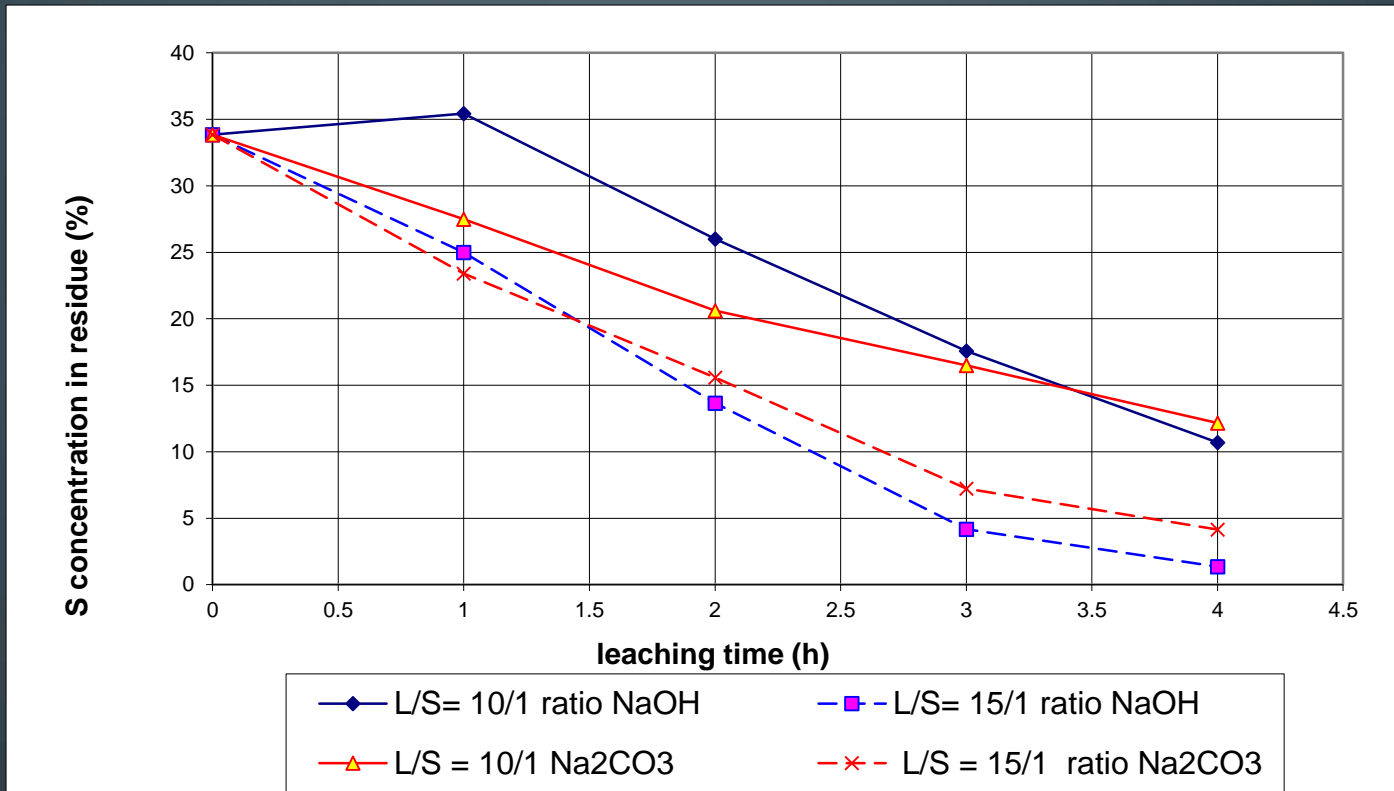
By using oxygen for the oxidation process after one hour the content of sulphur from the oxidized waste drops from 33.54% to 0.78%, with an energy consumption of 0.20 kWh.

**b. Oxidation agent: air / oxygen; alkaline medium  $\text{Na}_2\text{CO}_3$**

**Working parameters:**

- **Temperature**      **135 °C;**
- **Total pressure**   **8 atm.;**
- **Grinding time**      **0-10 min.;**
- **L/S ratio**          **15/1-17/1,**
- **Reaction time**      **1-4 h.**

**The results demonstrated the dependence of the oxidation degree of sulphur using  $\text{Na}_2\text{CO}_3$  / NaOH as oxidants function of the liquid/ solid ratio.**



S content in residue over time during pressure leaching in NaOH/Na<sub>2</sub>CO<sub>3</sub> media, as a function of the L/S ratio

c. Oxidizing agent: air; alkaline medium NaOH

Compared to solubilisation in alkaline Na<sub>2</sub>CO<sub>3</sub>, solubilisation in NaOH medium leads to higher sulphur oxidation rates during the first 2 to 4 hours of reaction.

# •Alkaline sulphate solutions processing (resulted from oxidation under pressure)

- ✓ After alkaline oxidation, sulphur from sulphidic waste passes in the solution as  $\text{SO}_4^{2-}$ , with 96-99% efficiency.
- ✓ The non-ferrous metals from tailings are oxidized and transferred into solution with a very low efficiency if the alkaline medium consists of  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ . When it was used NaOH as oxidant agent, the arsenic is transferred into solution with 50-70% efficiency.
- ✓ The distribution of main metals between solution and waste, after oxidation process (in presence of air) and  $\text{K}_2\text{CO}_3$  (1),  $\text{Na}_2\text{CO}_3$ (2), NaOH (3) as oxidant agents.

%, g/l	Fe	Cu	Pb	Zn	As
<b>Mining waste</b>	29.06	0.47	0.69	0.128	0.236
<b>1. residue</b>	30.3	0.45	0.65	0.12	0.23
<b>1. solution</b>	0.001	0.001	0.0004	0.001	0.001
<b>2. residue</b>	29.9	0.44	0.63	0.11	0.23
<b>2. solution</b>	0.001	0.001	0.0003	0.001	0.001
<b>3.residue</b>	30.22	0.36	0.62	0.12	0.037
<b>3.solution</b>	0.001	0.1	0.0005	0.001	0.145



## $K_2SO_4$ Crystals



Alkali sulphates were crystallized from potassium sulphate solutions, having the following chemical composition.

Sample code	Chemical composition (g/L; %)							
	K	SO <sub>4</sub> <sup>2-</sup>	Fe	Cu	Pb	Zn	As	Sb
<b>K<sub>2</sub>SO<sub>4</sub> crystals</b>	43.8	55.74	0.0010	<0.0005	<0.0002	<0.0005	<0.0002	<b>&lt;0.0002</b>
Sample code	Chemical composition (%) continued							
	Cd	Co	Al	Ca	Mg	Na	Cl <sup>-</sup>	
<b>K<sub>2</sub>SO<sub>4</sub> crystals</b>	<b>&lt;0.0002</b>	<b>&lt;0.0002</b>	<b>&lt;0.0005</b>	<b>0.008</b>	<b>&lt;0.0005</b>	<b>0.058</b>	<b>0.008</b>	

# CONCLUSIONS

- 1) Autoclave alkaline oxidation of tailings leads to a selective and advanced removal of sulphur and its recovery as sodium / potassium sulphate like pure crystals.
- 2) We believe that this concept of sulphidic tailings processing could replace the pyrometallurgical processing methods that are generally based on waste roasting.
- 3) Fortunately, all the results and data can be successfully used as a replication in others cases, to process other types of sulphidic waste, low-grade sulphidic non-ferrous metal concentrates, etc, with realistic changes to solve with high efficiency problems and to ensure environmental protection, with minimal risks.



**THANK YOU  
FOR YOUR  
ATTENTION**

