ZINCEX™ TECHNOLOGY: RECENT INDUSTRIAL OPERATIONS

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ABSTRACT

The Modified ZINCEX™ Process (MZP), developed by Técnicas Reunidas, is an industrially proven flexible process. It can handle a wide range of primary and secondary raw materials, producing SHG zinc. The core of the Modified ZINCEX™ Process is the zinc solvent extraction unit. This unit is an effective barrier for any leachable impurities present in the raw material. As a result of this an ultra-pure zinc solution is always obtained. The high versatility of the process makes the application of the technology in different scenarios possible. MZP can be effectively applied when developing a whole new plant (Skorpion) or adapting its scheme to an existing refinery (Akita), in both cases giving the same results. Flexibility in terms of capacity of the plant is a great advantage of the MZP, there is the possibility to adapt the global process to a wide range of production capacities. Zinc production capacities of over 150 000 t/a may be achieved with a single solvent extraction plant train. The robustness of the Modified ZINCEX™ Process has been recently proven on two new plants currently in operation: Portovesme (Italy) and Horsehead (USA) after start up during 2013. The status of both plants is described in this paper.

KEYWORDS

Modified ZINCEX Process, Zinc, Solvent Extraction, New Plant Operation, Waelz Oxide, Electrolysis

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Zincex™ Technology:

RECENT INDUSTRIAL OPERATIONS

GLENCORE INTERNATIONAL AG

Portovesme s.r.l.

HORSEHEAD

TECNICAS REUNIDAS

MZP – INT

METALQUÍMICA DEL NERVIÓN

- ZINCEX™
- 8,000 tpa SHG ZINC
- secondary zinc materials
- Bilbao (Spain)
- In operation 1976-1992

FIRST WORLD REFERENCE IN SHG ZINC

WITH SOLVENT EXTRACTION TECHNOLOGY

QUIMIGAL

- ZINCEX™
- 11,000 tpa SHG Zinc
- high chloride leach liquors
- Lisbon (Portugal)
- In operation 1980-1995

MZP – INTRODUCTION

TECNICAS REUNIDAS

ZINCEX™ Technology

Modified ZINCEX™ Process (MZP)

MZP is a simplification and optimization of the ZINCEX™ process specifically adapted to treat solid materials or impure sulphate solutions

MZP – INTRODUCTION

TECNICAS REUNIDAS

PILAGEST

- Modified ZINCEX Process
- 2,800 tpa of spent domestic batteries
- Containing mercury and high levels of manganese as main impurities
- In operation from 1997 to 2010
- Barcelona (Spain)

MZP – INTRODUCTION

TECNICAS REUNIDAS

SKORPION ZINC REFINERY

- Modified ZINCEX™ Process
- 150,000 tpa SHG Zinc
- Namibia
- In Operation 2003-Actually
- Operating cost US$ 334/tn Zn
- Overalll Zinc recovery > 92%

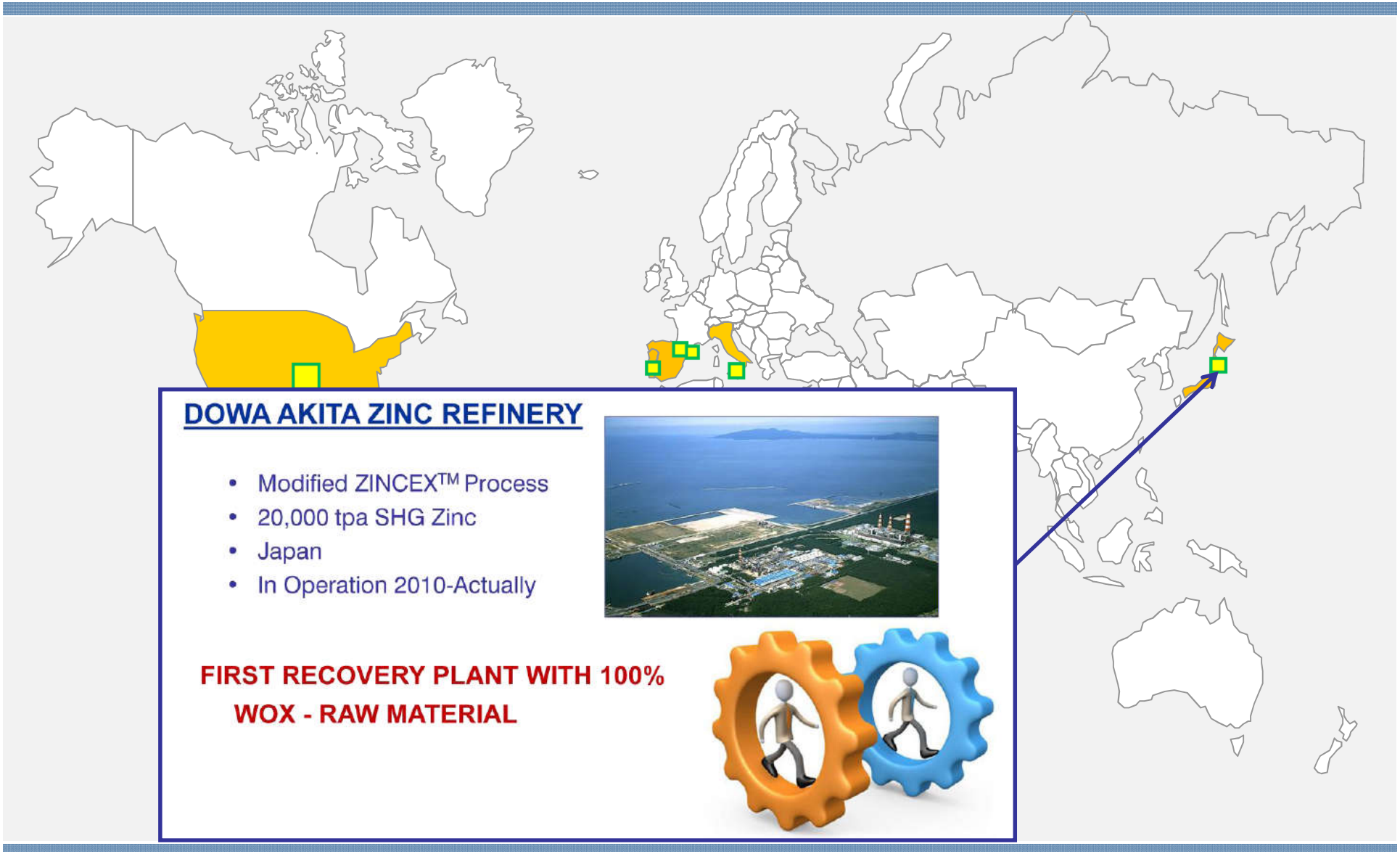
RAW MATERIAL: OXIDISED ORE 10,5%

PROJECT VIABILITY AVAILABLE ONLY

MODIFIED ZINCEX™ PROCESS

MZP – INTRODUCTION

TECNICAS REUNIDAS



DOWA AKITA ZINC REFINERY

- Modified ZINCEX™ Process
- 20,000 tpa SHG Zinc
- Japan
- In Operation 2010-Actually

FIRST RECOVERY PLANT WITH 100%
WOX - RAW MATERIAL

MZP – INTRODUCTION

TECNICAS REUNIDAS

The Industrial plants demonstrate:

- Ability of the Modified ZINCEX® process (MZP) to recover zinc from zinc solutions.
- MZP achieve SHG zinc working with a wide range of raw materials
  - ✓ Solid or liquid.
    - Solids: Primary ores or Secondary raw material
      From 7% of zinc to 60% of zinc
    - Liquid: Sulphate or Chloride media
      From 5 g/l to 160 g/l of zinc
  - ✓ Containing high presence of impurities, including chlorides and fluorides.
- Solvent extraction (SX) is the key step used in MZP to purify the zinc solutions,
  - ✓ Is a very effective barrier for the impurities
  - ✓ And act as buffer for changes in the composition of the Pregnant Liquor Solution (PLS)
  - ✓ The final purified solution produced after SX are available for conventional electrowinning (EW)

WAELZ OXIDES PROCESSING THROUGH ZINCEX™ TECHNOLOGY

TECNICAS REUNIDAS

The use of secondary zinc materials has the following **benefits**:

- Lower raw material costs → recycled zinc is generally more economical than primary zinc concentrates
- Reduced iron removal costs → iron within secondary zinc material is normally low, more easily controlled and managed than that from primary zinc concentrates
- Increased feed diversity → fluctuations in the primary zinc concentrate market have less impact
- Environmental advantages → reuse of materials

WAELZ OXIDES PROCESSING THROUGH ZINCEX™ TECHNOLOGY

TECNICAS REUNIDAS

The use of secondary zinc materials has the following **disadvantages**:

- Presence of relatively high levels of metallic and halide impurities → unsuitable for direct electrolytic processing

  - ✓ EW is extremely sensitive to the presence of traces Metallic impurities → Removed by cementation with Zinc Dust → This unit increases the OPEX

  - ✓ The presence of high levels of Chlorides in EW (<100 mg/l) → corrosion of lead-silver anodes and health hazard for plant workers due to chlorine gas production during the electrowinning

  - ✓ Fluorides cause dissolution of the protective Al_2O_3 layer on the cathode surface → operational problems and shorter cathode life is expected

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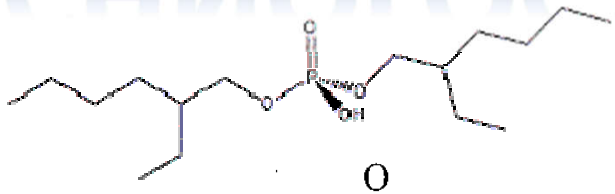
Limitation in the recycling raw material rate

WAELZ OXIDES PROCESSING THROUGH ZINCEX™ TECHNOLOGY

TECNICAS REUNIDAS

ZINCEX™ TECHNOLOGY



MZP Solvent Extraction extractant:

$(C_8H_{17}O)_2POH$

Di-2-ethylhexylphosphoric acid (D2EHPA)

- Selective for zinc over most of the deleterious species to EW (Cu, Cd, Co, Ni and the halides)

- Readily stripped using acid concentrations typical of the spent electrolyte (~180 g/l H_2SO_4)

WAELZ OXIDES PROCESSING THROUGH ZINCEX™ TECHNOLOGY

TECNICAS REUNIDAS

ZINCEX™ TECHNOLOGY

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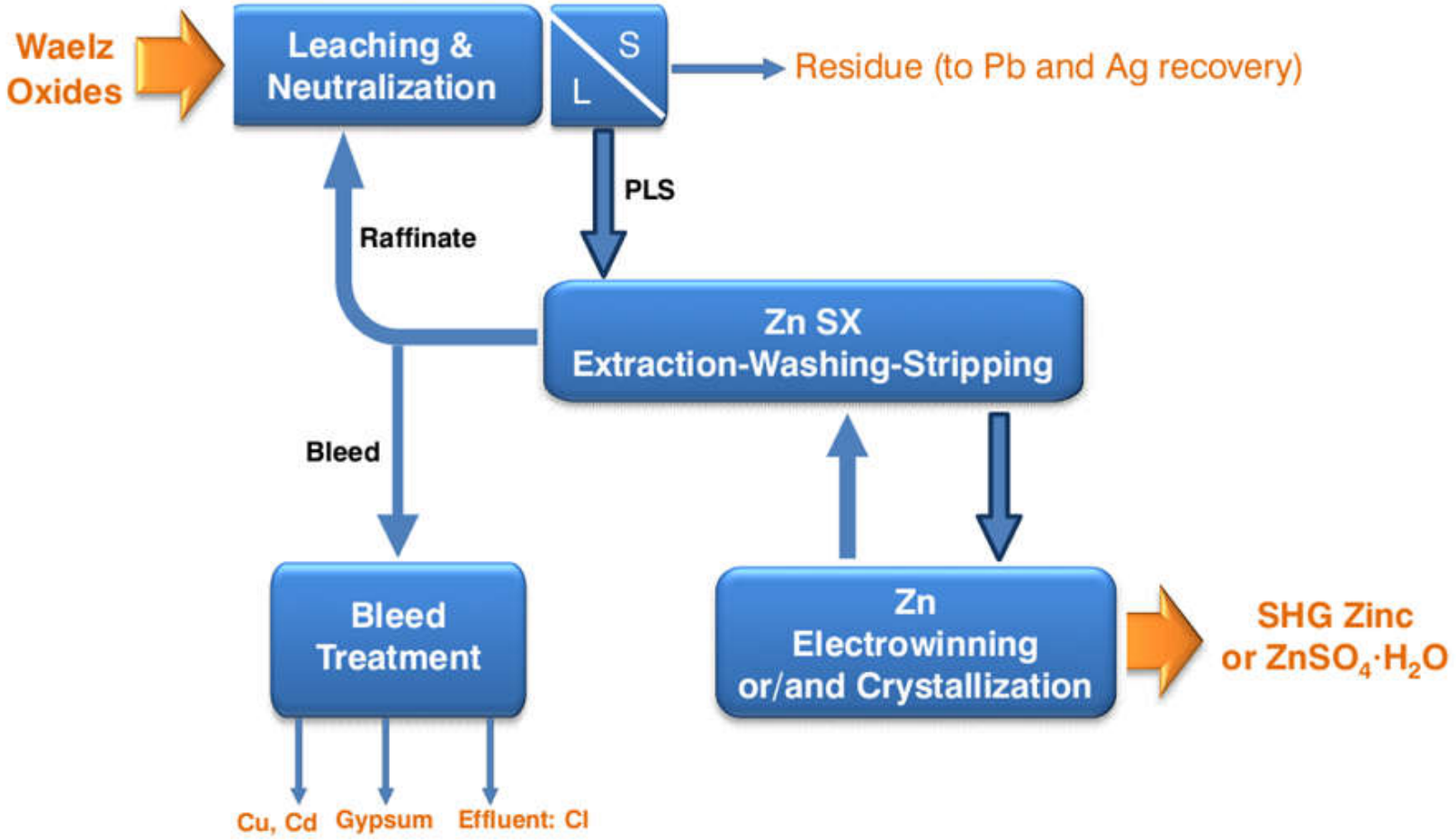
WAELZ OXIDES PROCESSING THROUGH ZINCEX™ TECHNOLOGY

TECNICAS REUNIDAS

Typical Block Diagram for Waelz Oxides Processing through MZP



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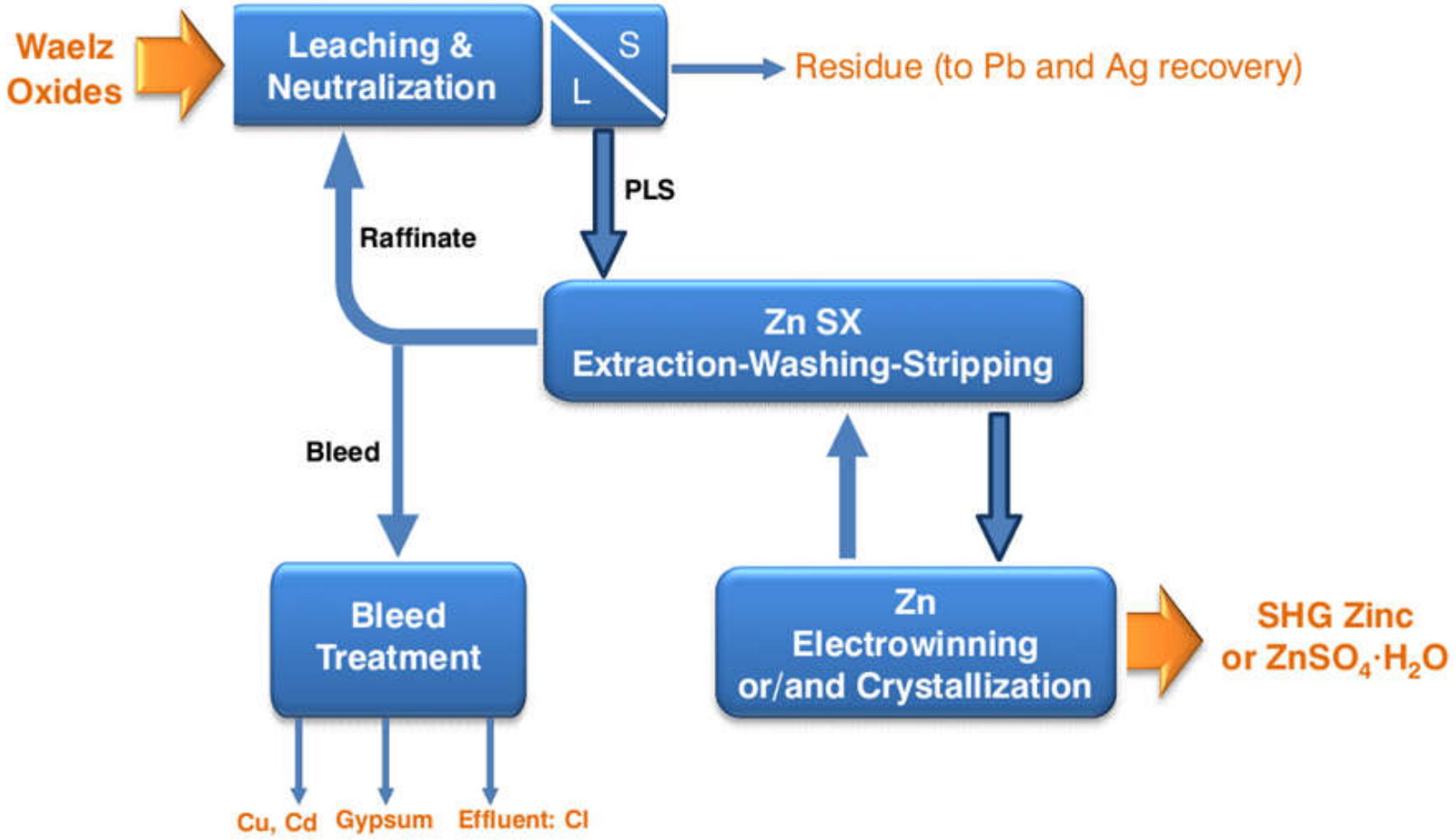

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TECNICAS REUNIDAS

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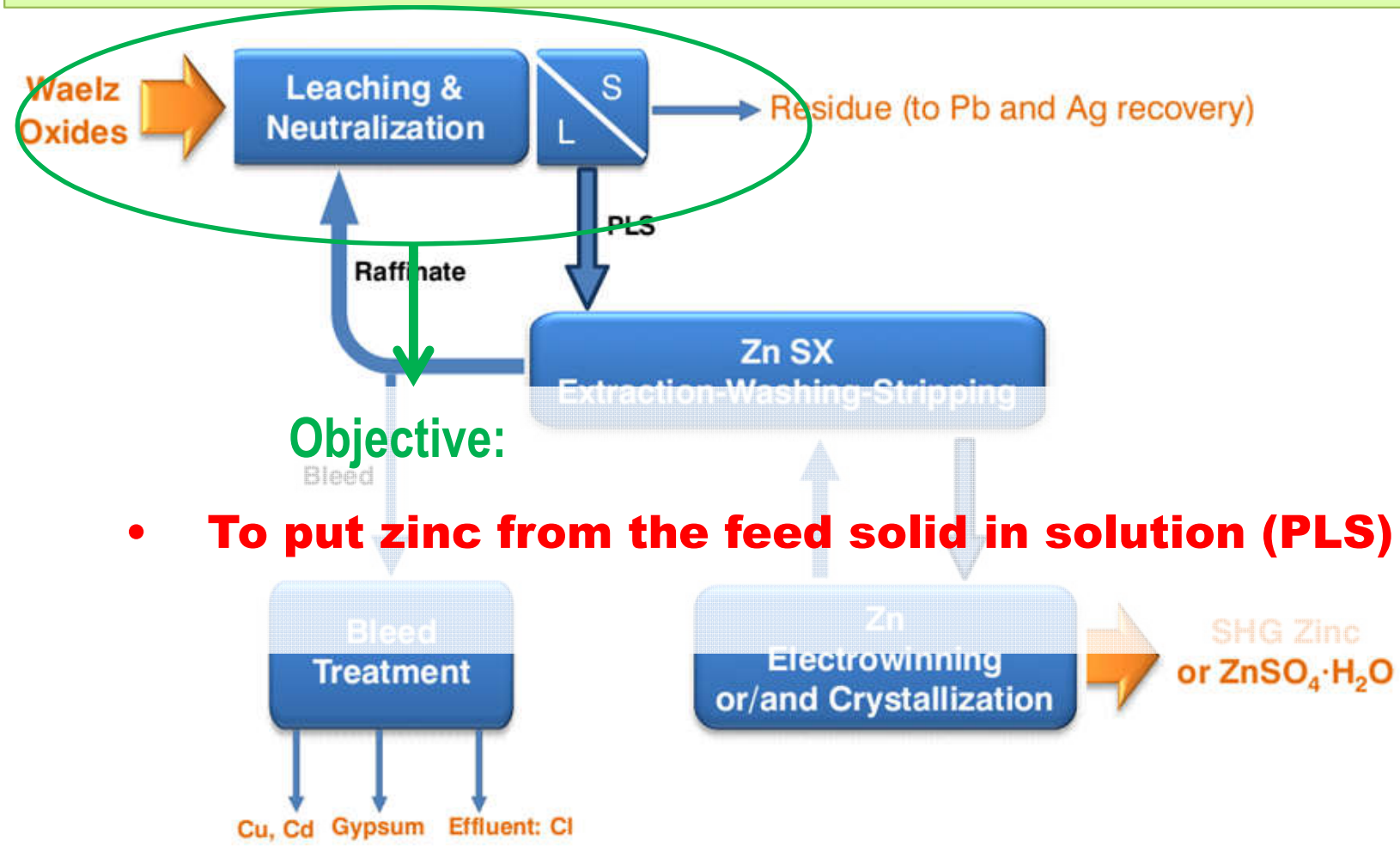


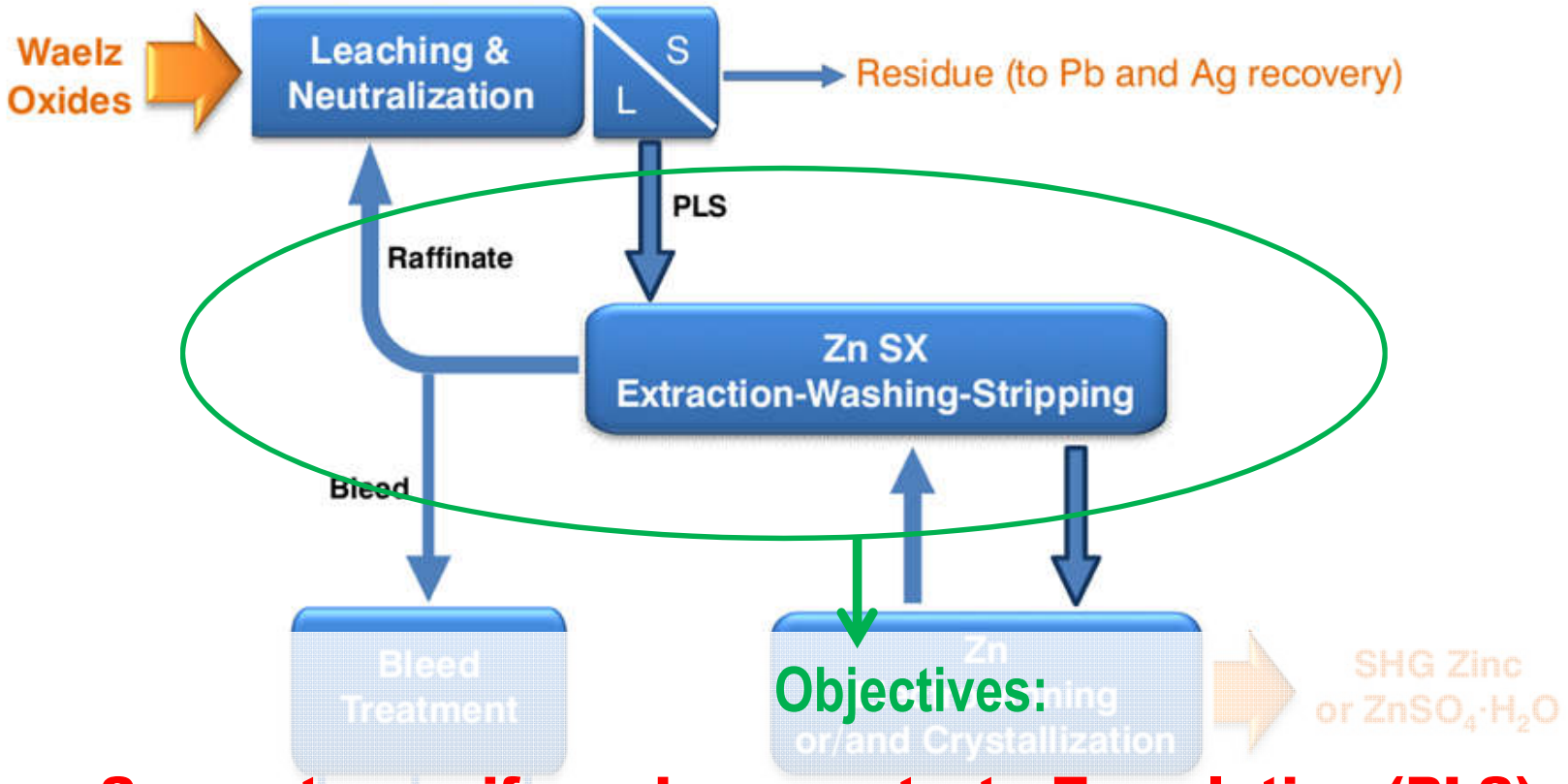
Objective:

- **To put zinc from the feed solid in solution (PLS)**

WAELZ OXIDES PROCESSING THROUGH ZINCEX™ TECHNOLOGY

TECNICAS REUNIDAS

Typical Block Diagram for Waelz Oxides Processing through MZP



Objectives:

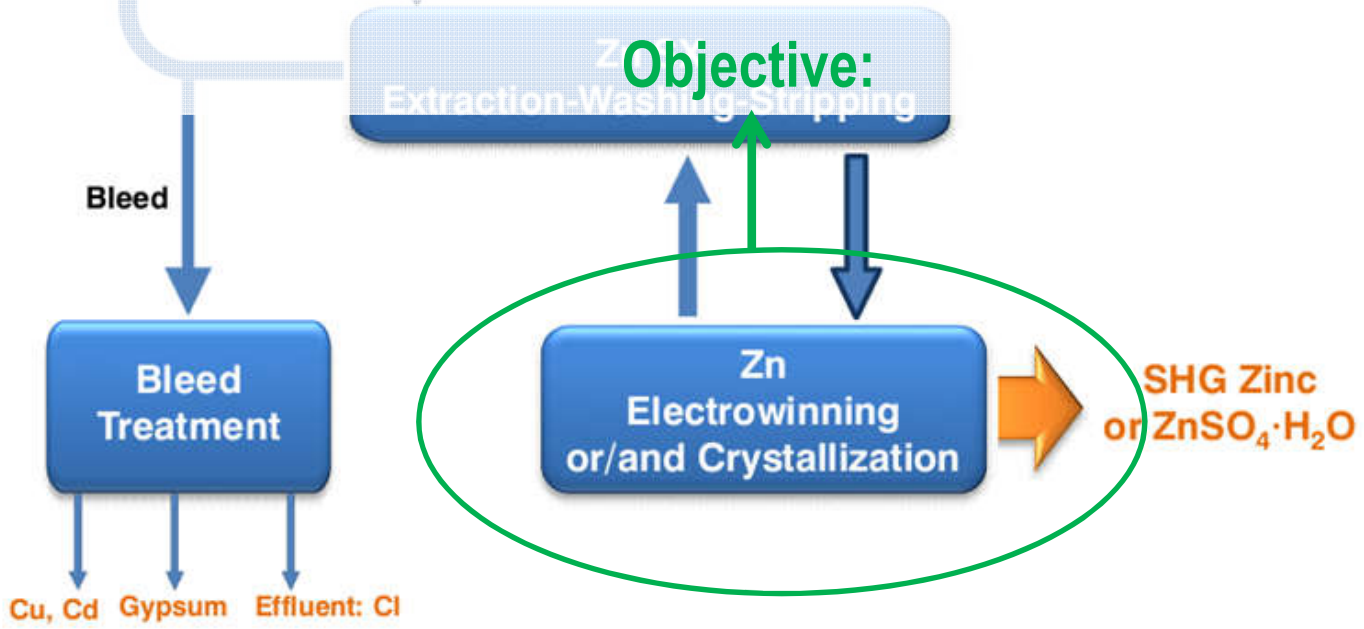
- **Separate, purify and concentrate Zn solution (PLS), rendering an ultra-pure electrolyte for EW (loaded electrolyte)**

WAELZ OXIDES PROCESSING THROUGH ZINCEX™ TECHNOLOGY

TECNICAS REUNIDAS

Typical Block Diagram for Waelz Oxides Processing through MZP

- **Zinc is electrowon onto the cathode sheets**
- **Zinc spent electrolyte produced is fed to SX**
- **Crystallization is an optional operation that can substitute or complement the zinc electrolysis**

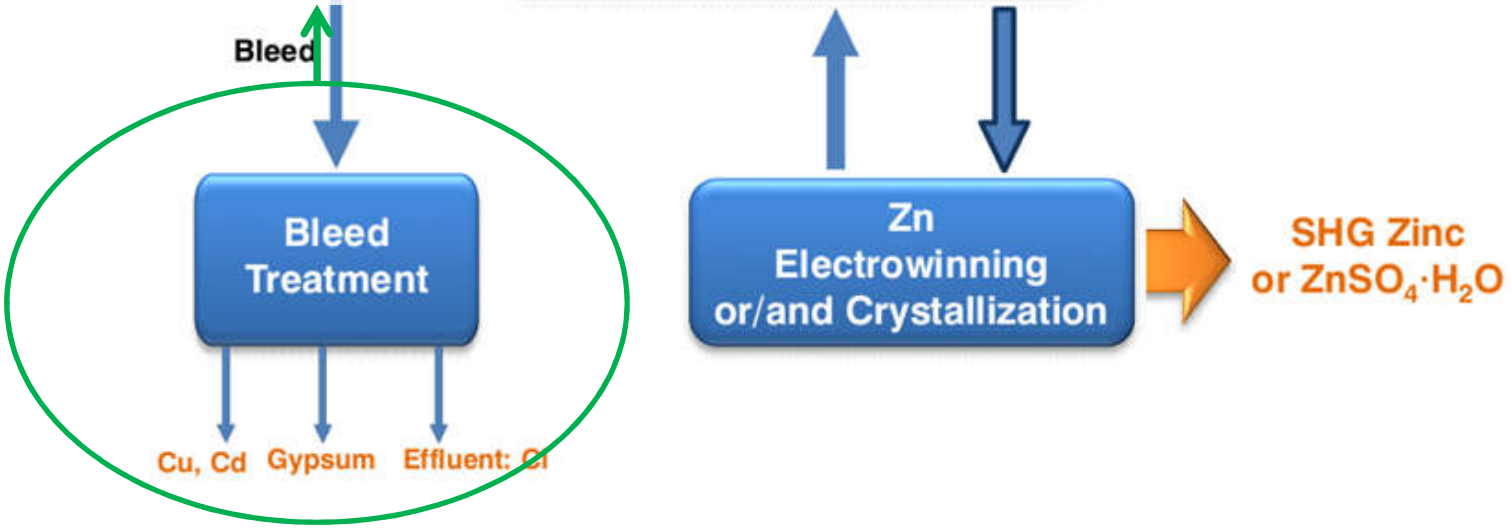


WAELZ OXIDES PROCESSING THROUGH ZINCEX™ TECHNOLOGY

TECNICAS REUNIDAS

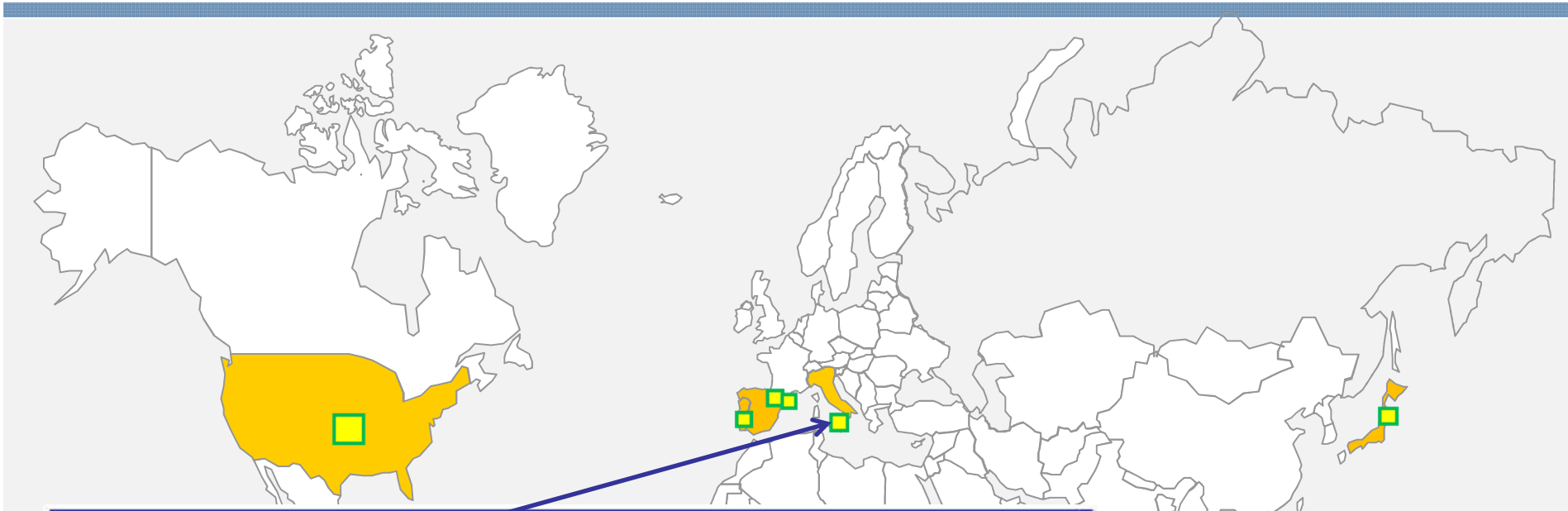
- **Remove impurities from PLS circuit, to prevent build-up**
- **Keep water balance in the plant**
- **Maximize Zn recovery**
- **Minimize residue production, turning some impurities into by-products**

Objectives:



IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS



PORTOVESME ZINC REFINERY

- Portovesme S.r.l facility located in Sardinia (Italy)
- Objetive: increase the existing refinery capacity producing additional SHG zinc and recovering a lead concentrate to be treated in the Kivcet plant
- 52,500 tpa SHG Zinc

RAW MATERIAL: WOX

IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS

Raw Material:

The raw material feed to the MZP plant will be:

- Unwashed Waelz Oxides: approximately 85,000 tpa (dry basis)
- Kivcet oxides: approximately 5,500 tpa (dry basis)

Table 1 - Average composition of the raw materials

COMPONENT	UNWASHED WAELZ OXIDES	KIVCET OXIDES
Zn %	61-64	32.6
Pb %	5-7	43.7
Fe %	0.8-1.5	0.65
Cd %	0.2-0.5	1.14
Cu %	0.05-0.1	0.43
Cl %	5-7	0.31
F g/t	900-1,500	Not av.

IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS

Process Description

High quality zinc sulphate solution

+

Traditional RLE purified solution

sent to → EW section →

SHG Ingots

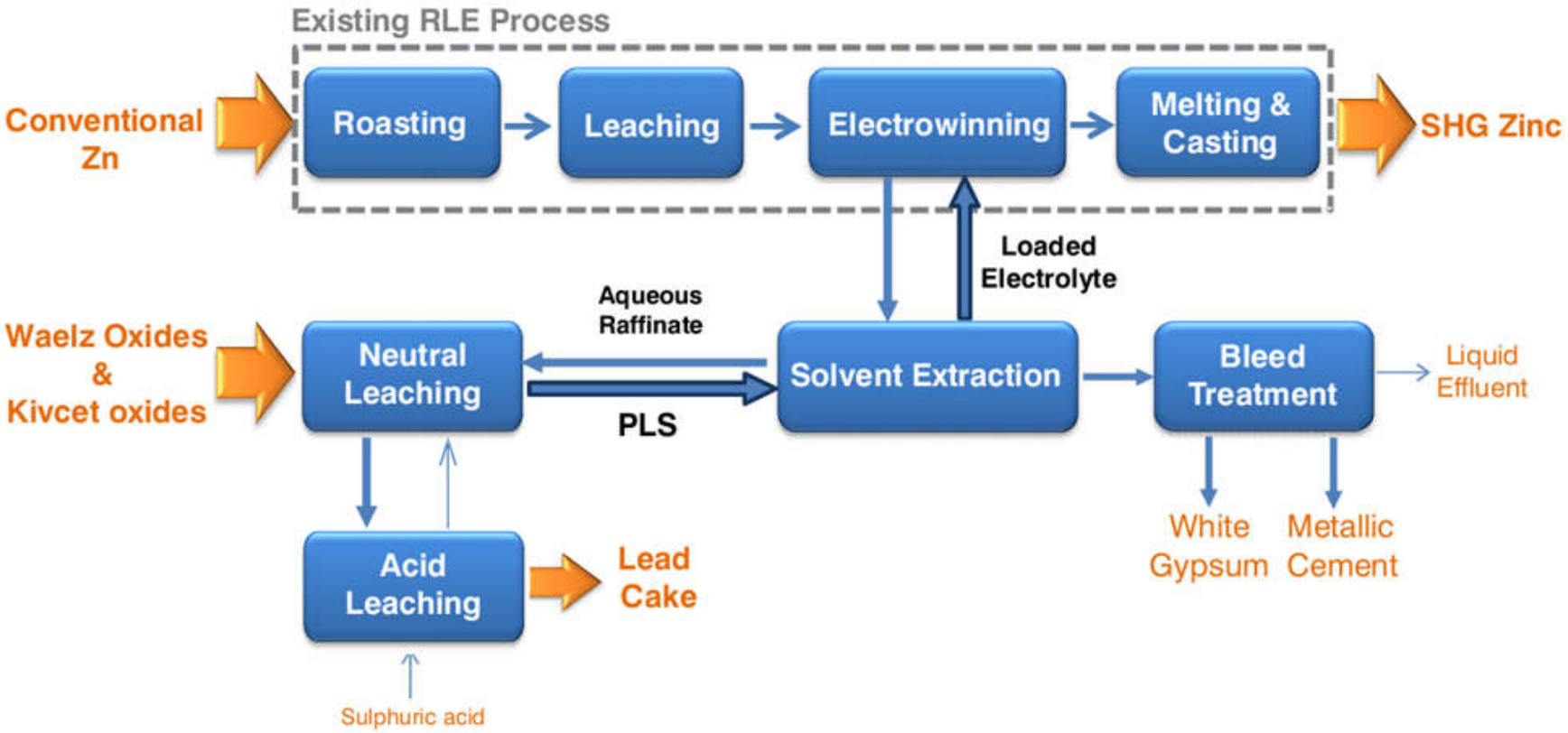
The new processing facilities incorporate the following major areas:

- Leaching
- Solvent Extraction
- Bleed Treatment

IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS

Process Description



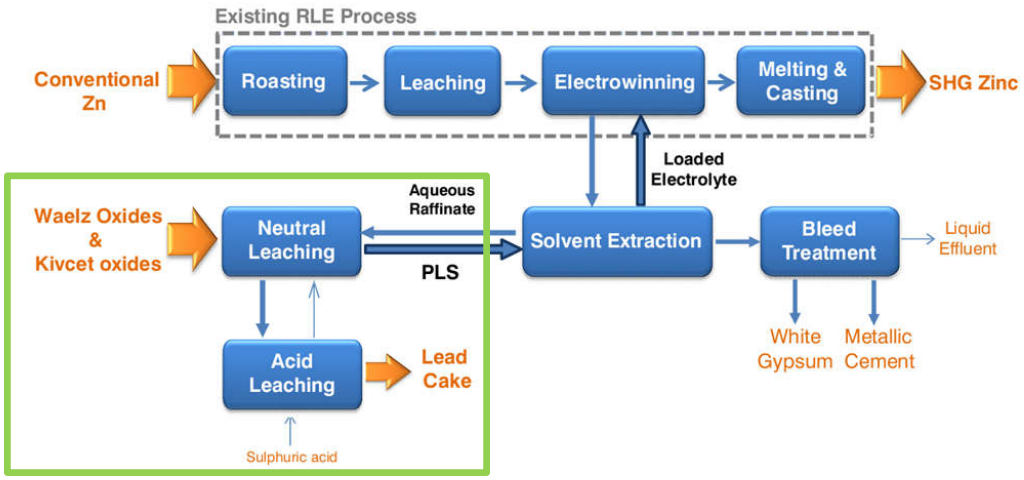
IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS

Process Description

Leaching Unit:

- **Two-stage counter current leaching process**
- **Option selected in order to produce a relatively clean, solid residue with a high lead content, which could be treated in the Kivcet Plant for metal recovery**



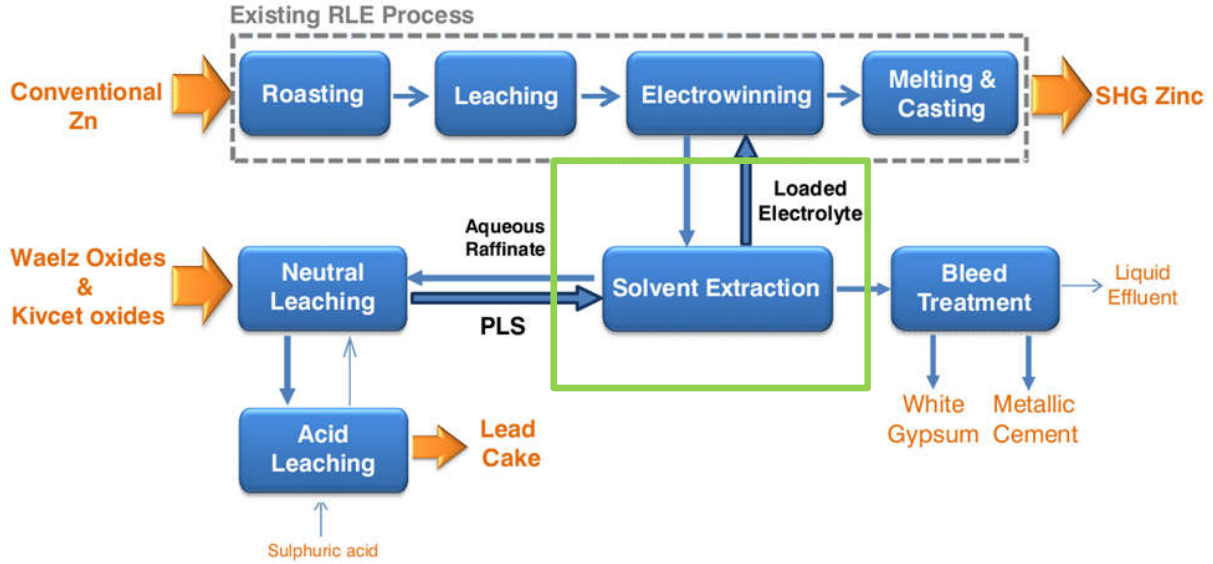
IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS

Process Description

Solvent Extraction area:

- **Connection stage between traditional plant and MZP plant**
- **Produce an ultra-pure rich solution (loaded electrolyte) suitable to be mixed with the typical RLE electrolyte and produce SHG zinc by EW**

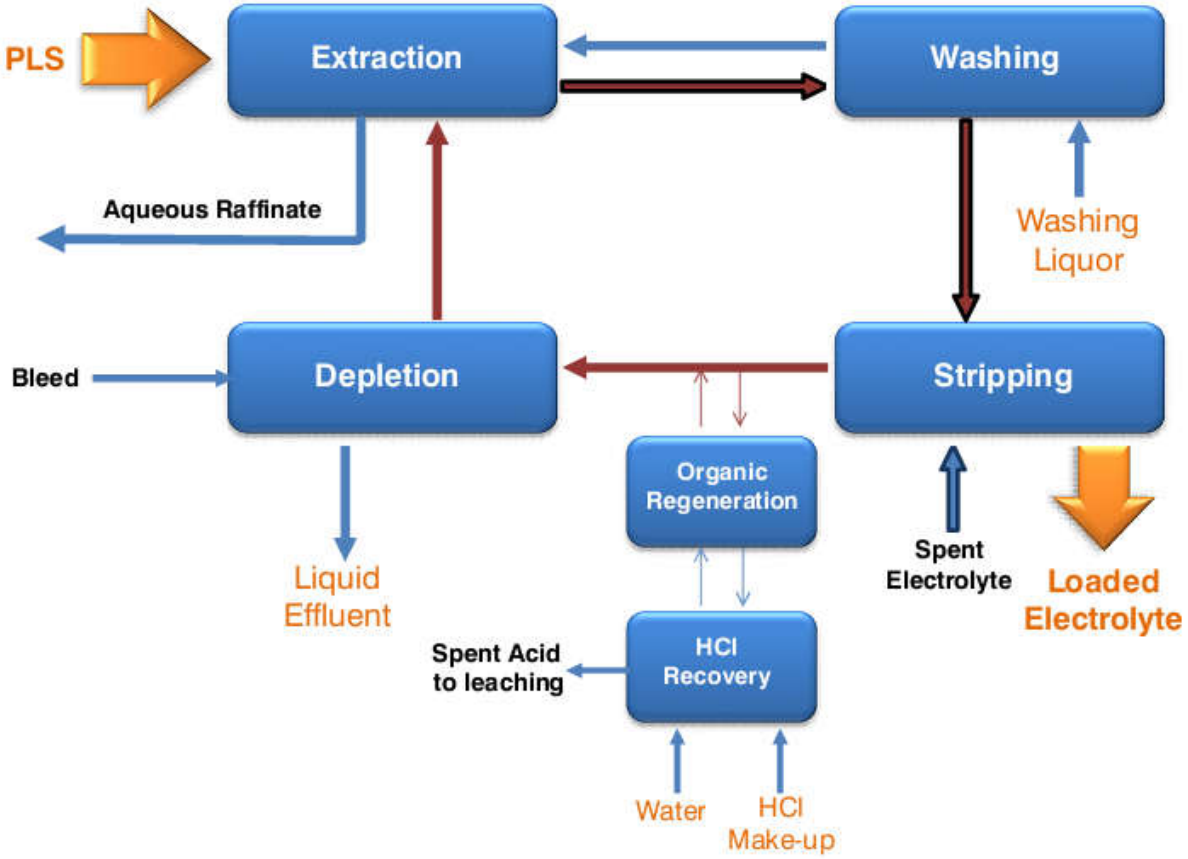


IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS

Process Description

Solvent Extraction area:



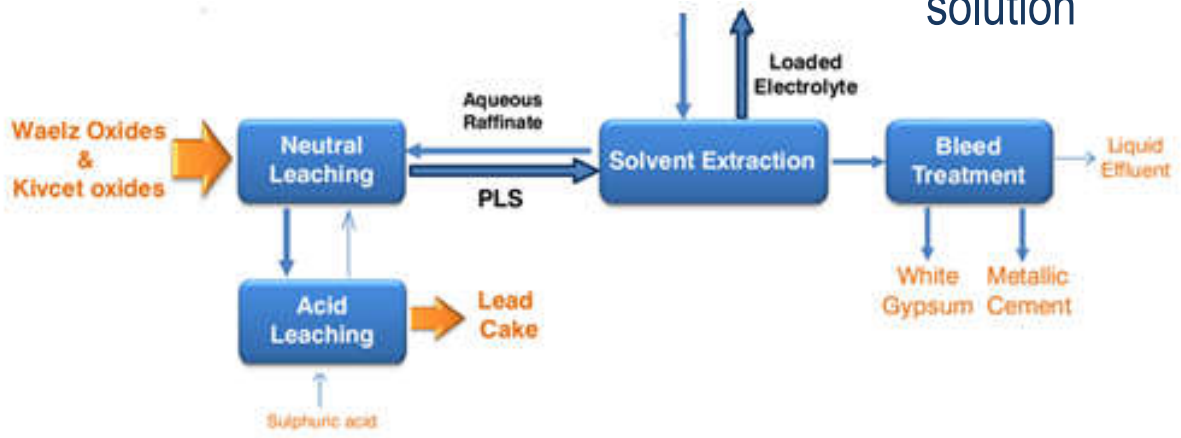
IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS

Process Description

Bleed Treatment:

- **Units:**
  - **Gypsum Precipitation + Depletion** → recovery of Zn from raffinate
  - **Metal Cementation** → deals with Cu and Cd present in the solution

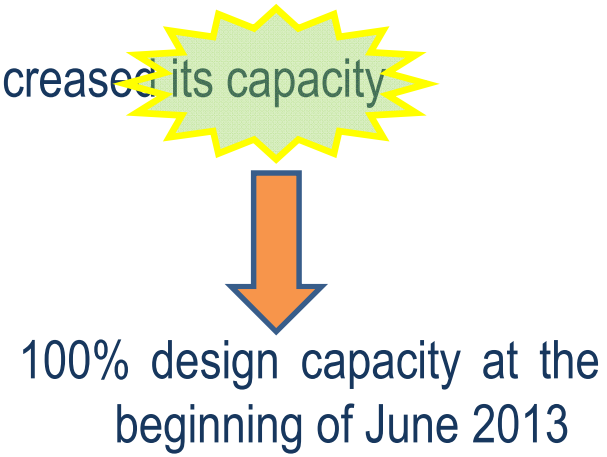


IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS

Plant Status:

- Portovesme MZP plant started production on the 25th of February 2013
- During March, April and May 2013, plant increased its capacity



- To date, plant has been producing SHG Zinc

IMPLEMENTATION OF MODIFIED ZINCEX™ AT PORTOVESME ZINC REFINERY

TECNICAS REUNIDAS

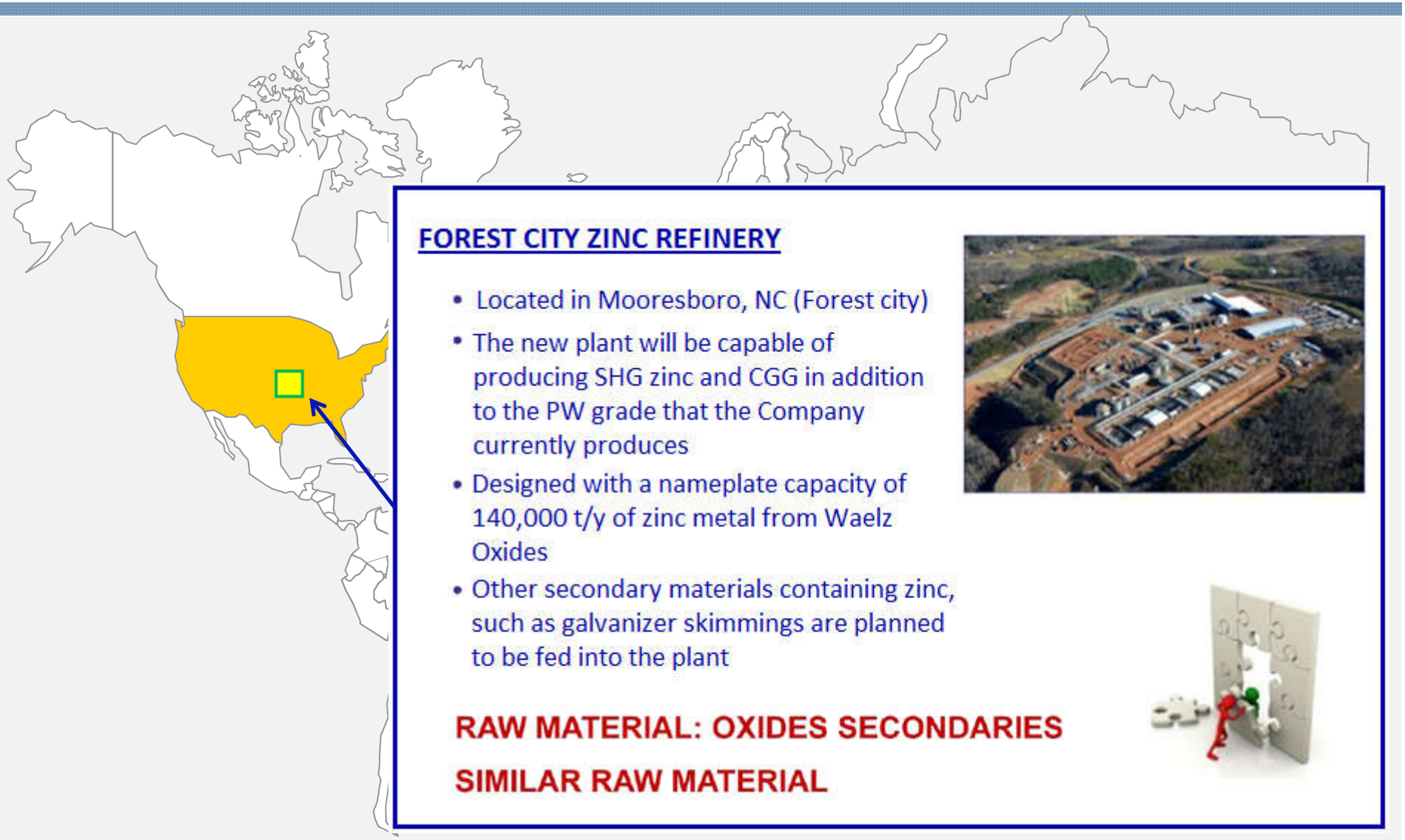
Plant Status:

- The main problem find during de start up is the low quality of the spent electrolyte produced in the main RLE plant, contains a lot of Solid in Suspension (Gypsum, Silica, etc) and High temperature ⇨ during the start-up of the MZP plant significant amount of this solids was detected in stripping stages
- TR and Portovesme were working to minimize the impact in plant operation

The quality of the loaded electrolyte produced through the MZP has been demonstrated during this period, improving substantially the quality of the electrolyte that is fed to the EW unit

IMPLEMENTATION OF MODIFIED ZINCEX™ AT HORSEHEAD ZINC REFINERY

TECNICAS REUNIDAS



FOREST CITY ZINC REFINERY

- Located in Mooresboro, NC (Forest city)
- The new plant will be capable of producing SHG zinc and CGG in addition to the PW grade that the Company currently produces
- Designed with a nameplate capacity of 140,000 t/y of zinc metal from Waelz Oxides
- Other secondary materials containing zinc, such as galvanizer skimmings are planned to be fed into the plant

RAW MATERIAL: OXIDES SECONDARIES

SIMILAR RAW MATERIAL

IMPLEMENTATION OF MODIFIED ZINCEX™ AT HORSEHEAD ZINC REFINERY

TECNICAS REUNIDAS

Raw Material:

The raw material feed to the MZP plant will be:

- Waelz Oxides: approximately 241,000 tpa (dry basis)
- Zinc Skimmings

Table 2 - Average composition of the raw materials

COMPONENT	WAELZ OXIDES	SKIMMINGS
Zn %	61.2	70
Pb %	2.97	0.6
Fe %	4.23	3.1
Cd %	0.18	N/A
Cu %	0.05	0.21
Cl %	4.56	N/A
F %	0.29	N/A

IMPLEMENTATION OF MODIFIED ZINCEX™ AT HORSEHEAD ZINC REFINERY

TECNICAS REUNIDAS

Process Description

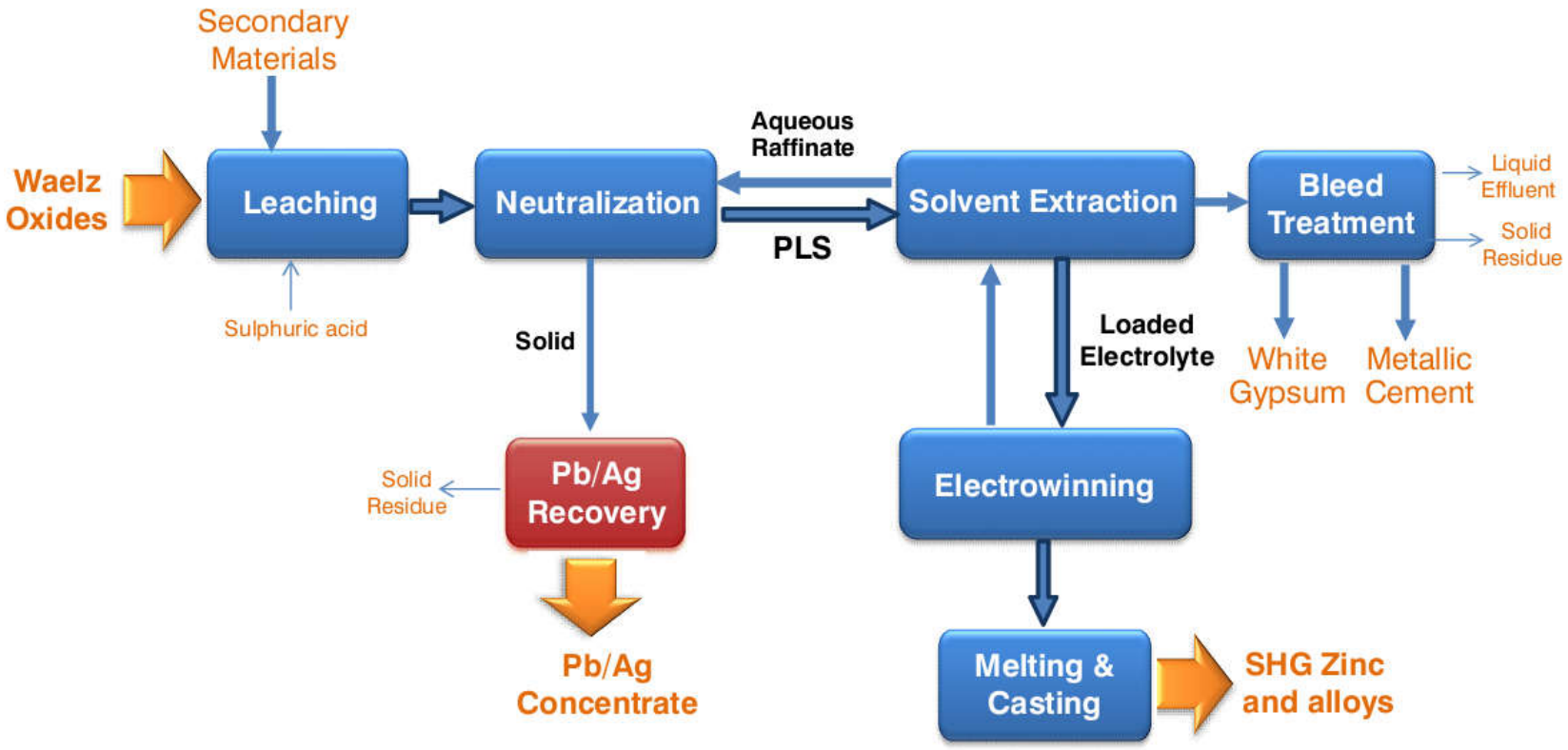
- Is a New Factory
- Able to produce SHG Zinc and different alloys (CGG and/or PW) using MZP technology
- Annexed to the MZP plant a process plant to recover the lead and silver present in the leaching residue will also be implemented. The final product of that plant will be a Pb/Ag concentrate

IMPLEMENTATION OF MODIFIED ZINCEX™ AT HORSEHEAD ZINC REFINERY

TECNICAS REUNIDAS

Process Description

The new processing facilities incorporate the following major areas:



IMPLEMENTATION OF MODIFIED ZINCEX™ AT HORSEHEAD ZINC REFINERY

TECNICAS REUNIDAS

Plant Status:

- Horsehead MZP plant started production on the 28th of May 2014
- Now they are involve in the ramp up of the plant
- To date, plant has been producing SHG Zinc

CONCLUSIONS

TECNICAS REUNIDAS

The Modified ZINCEX™ Process represents the optimum solution to deal with WOX:

- Successfully demonstrated with the start-up of two new plants:
  - Portovesme
  - Horsehead
- Since 2010, Akita plant is also working with this type of raw material producing SGH zinc
- The integration of the traditional RLE plant and the Modified ZINCEX™ process has also been well established at industrial scale with the start-up of the Portovesme plant

Thank you very much!

QUESTIONS WELCOME!

GLENCORE INTERNATIONAL AG

Portovesme s.r.l.

HORSEHEAD

TECNICAS REUNIDAS