



# Highly Efficient and Low Cost Zinc Electrolyte Purification Using ZINCEX™ Solvent Extraction

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**Keywords:** zinc, zinc electrolyte purification, Zincex, zinc solvent extraction

## Abstract

In hydrometallurgical zinc production, the purity of loaded electrolyte is critical in order to assure electrolytic SHG zinc quality and at the same time yielding high current efficiency. Metallic impurities adversely affect the zinc electrodeposition process and exert a negative influence on the purity and the morphology of the zinc cathodes. Besides, some impurities decrease the current efficiency due to hydrogen evolution and, as a consequence, the unit energy consumption (kWh/kg Zn) is increased.

In the conventional Roasting, Leaching and Electrowinning (RLE) zinc production process, purification of the solution is achieved by adding zinc dust. Zinc displaces elements below it in the electrochemical series and removes the impurities that have a negative effect on the electrowinning process. Conventional purification techniques using zinc dust are complex and labour intensive, usually requiring large additions of dust (frequently ranging from 5 to 15 kg of zinc dust per cubic metre of solution) and other specific reagents in several unit operations. Careful and extensive analytical control is also compulsory. In spite of the above, there are many harmful impurities such as Mg, Ca, Halogens, Na, K, etc. that cannot be removed at all by conventional purification processes and can significantly impair electrowinning performance.

The ZINCEX™ technology owned by Tecnicas Reunidas represents a simple, highly efficient, and low cost purification process which removes impurities from zinc electrolytes. This commercially available solvent extraction system is a perfect barrier to all metallic impurities, and in addition, Mg, Ca, Halogens, Na, K, etc, are also rejected. As the ZINCEX™ solvent extraction process does not consume zinc dust, the electrolytic zinc production and the income of the zinc refinery is 5-10% higher in comparison to the RLE technology; as a result, this innovative technology presents around 15% lower operating cost and similar capital cost compared with the conventional purification process.



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This paper was published in the Proceedings of EMC 2011, which can be acquired in the following link:

<http://emc.gdmb.de/previous-proceedings/proceedings-of-emc-2001/>

The following presentation for commercial use describes the content of this paper.

# **Highly Efficient and Low Cost Zinc Electrolyte Purification Using ZINCEX™ Solvent Extraction**

**Proprietary Technology Development Division**

**TECNICAS REUNIDAS, S.A., Spain**



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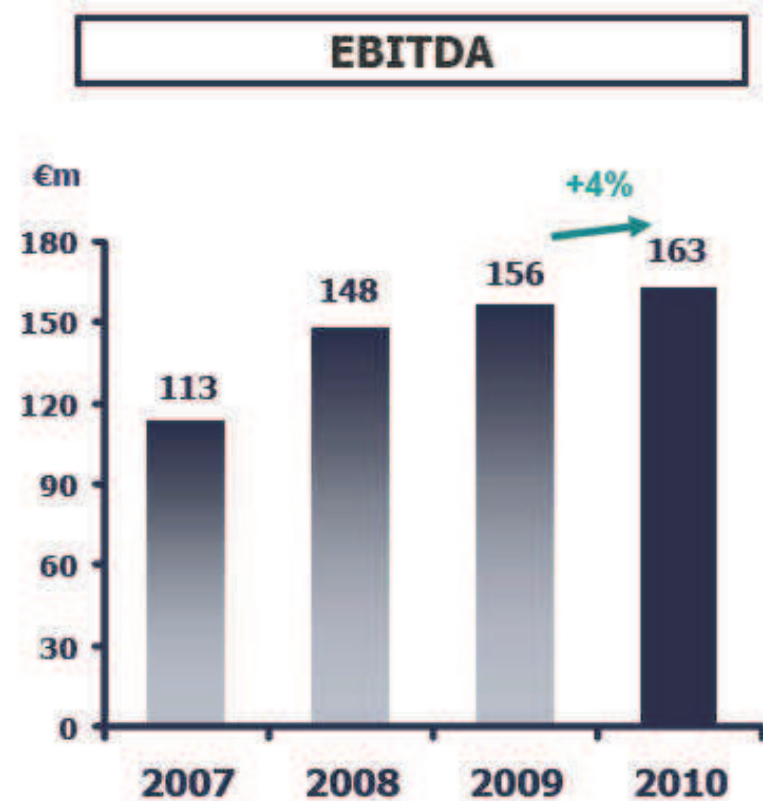
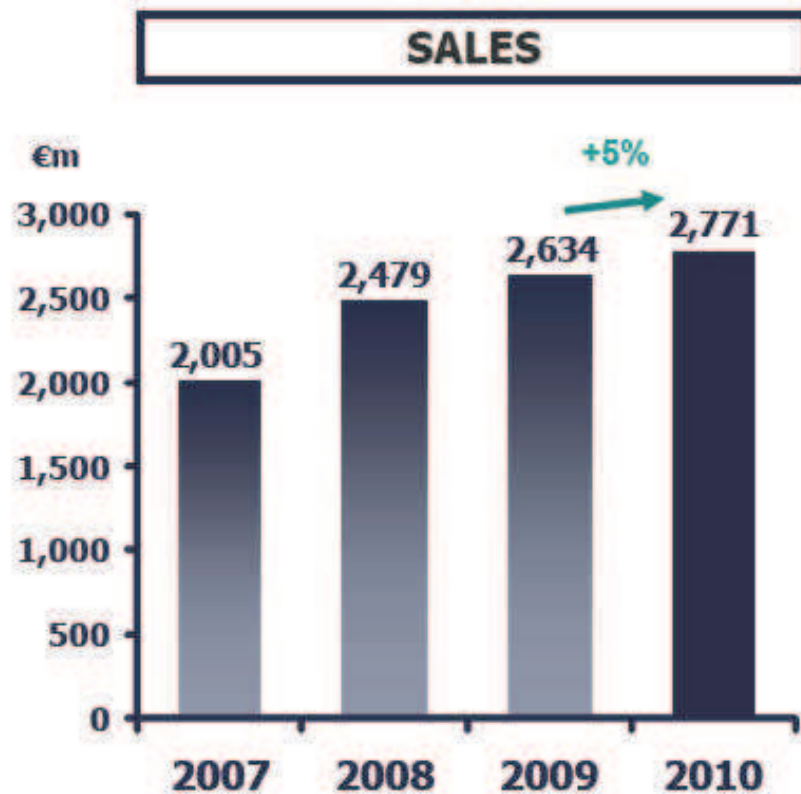
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## COMPANY BACKGROUND

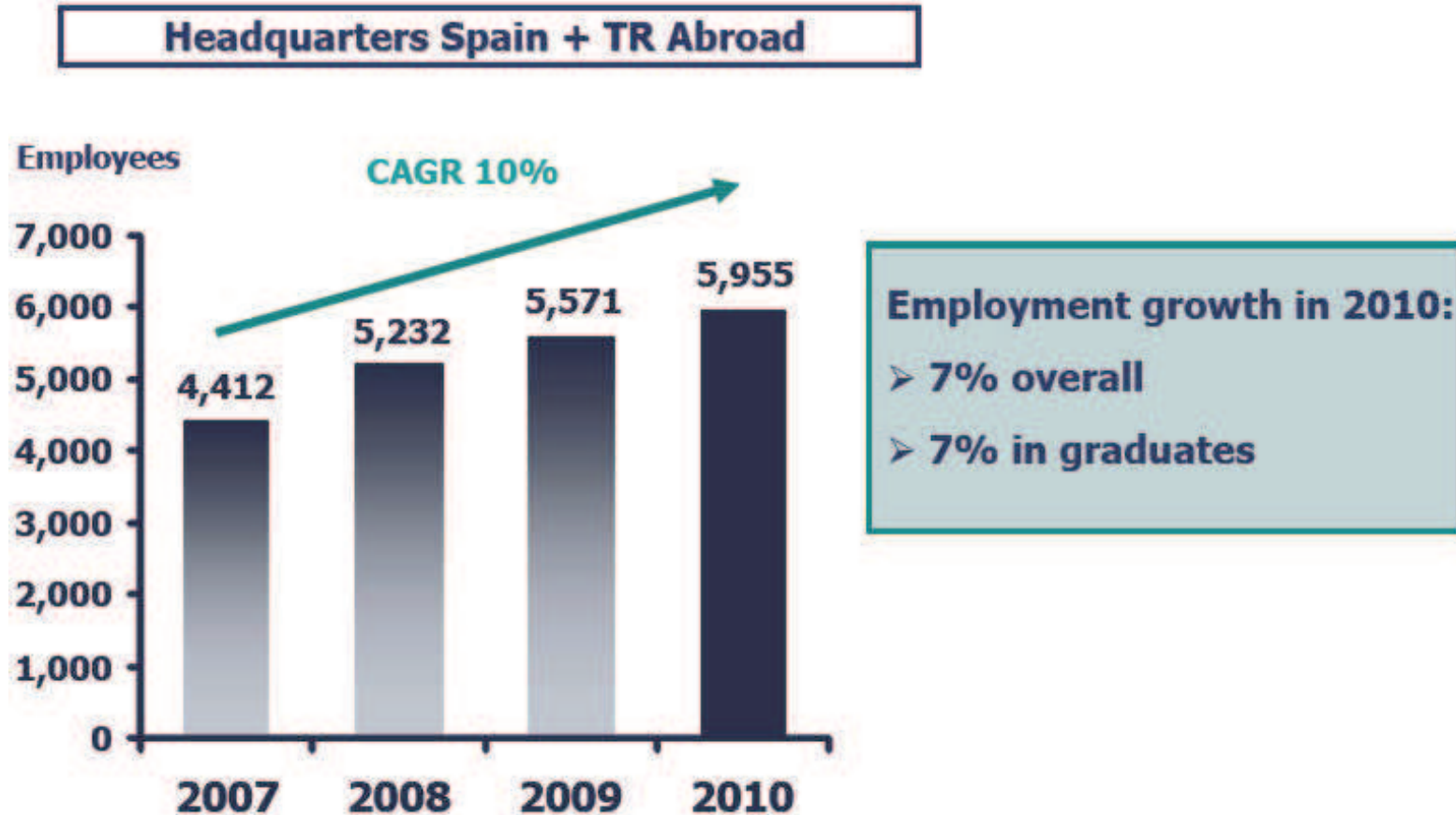
⇒ **Leader & Largest EPC Contractor in Spain and second in Europe**



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## COMPANY BACKGROUND

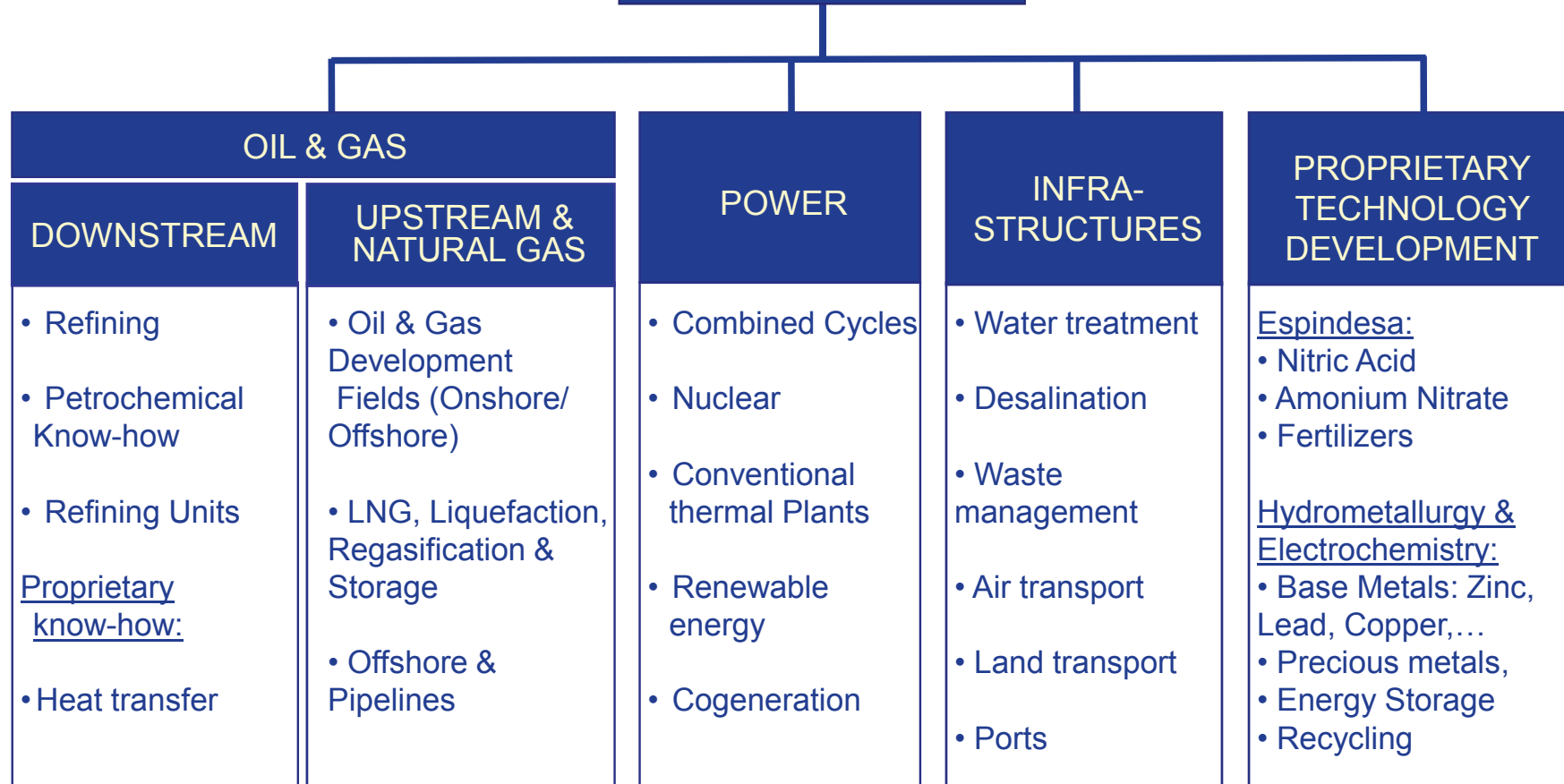
⇒ 50 Years Experience; More than 1000 Projects worldwide



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# BUSINESS AREAS

## TR Group



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# **OVERVIEW:**

- **INTRODUCTION**
- **CONVENTIONAL ZINC DUST PURIFICATION**
- **ZINCEX™ SOLVENT EXTRACTION PURIFICATION**
- **COMPARISON OF THE PURIFICATION TECHNOLOGIES**
- **INDUSTRIAL CASE STUDY**
- **CONCLUSIONS**



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## INTRODUCTION

- ☺ In hydrometallurgical zinc production, the purity of loaded electrolyte is critical in order to assure:
  - Electrolytic SHG zinc quality
  - Yielding high current efficiency
- ☺ Impurities adversely affect the zinc electrodeposition:
  - Negative influence on cathode purity
  - Bad deposit morphology: dendrites, sticky, etc
  - Current efficiency decreasing: H<sub>2</sub> evolving
- ☺ In consequence:

**Loaded electrolyte purification is likely the most important and critical unit process in any zinc refinery**



## INTRODUCTION

- ☺ In the conventional Roasting, Leaching and Electrowinning (RLE) zinc production process, purification of the pregnant solution is achieved by adding zinc dust:
  - Complex and labour intensive operation where careful and detailed analytical control is compulsory
  - Large addition of dust: 5-15 kg Zn dust/m<sup>3</sup> solution
- ☺ In spite of the above, there are many harmful impurities that are not removed at all by zinc dust purification:
  - Mg, Ca, Halogens, Na, K, etc

**Such impurities can impair electrowinning performance**



## INTRODUCTION

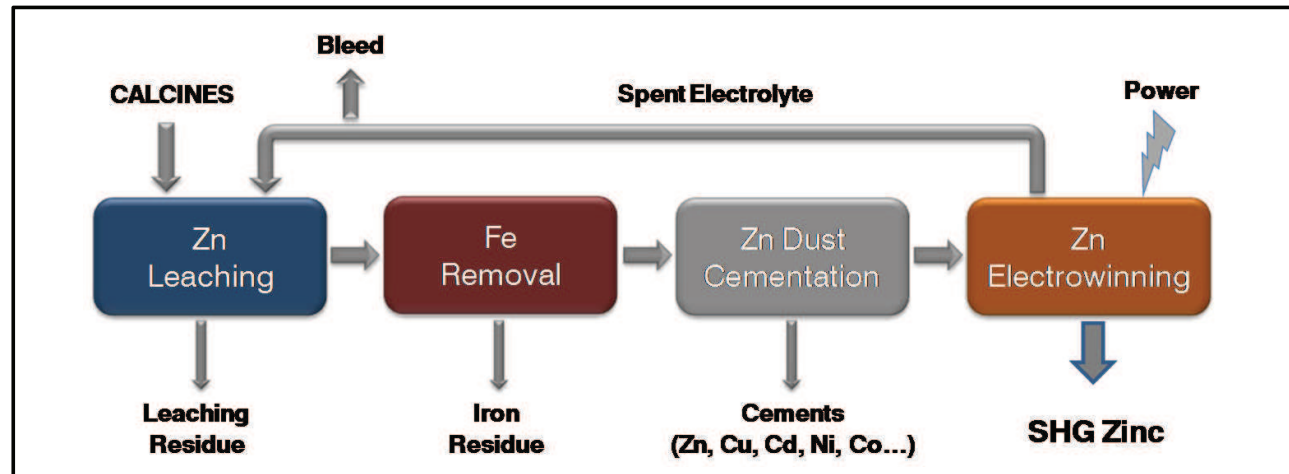
- ☺ **The ZINCEX™ solvent extraction technology owned by Tecnicas Reunidas is a highly efficient and low cost purification process for zinc electrolytes and represents an ideal solution versus conventional purification:**
  - **Given that zinc dust is not required, the income of the zinc refinery increases by 5-10% because all zinc plates is sold, none is recycled as zinc powder**
  - **Solvent extraction is totally automatic, requiring low labour and maintenance: low-cost process**
  - **Solvent extraction system is a perfect barrier to all metallic impurities, and in addition, Mg, Ca, Halogens, Na, K, etc, are fully rejected**

**This presentation compares the conventional purification versus the new ZINCEX™ solvent extraction purification from technical and economic viewpoints**

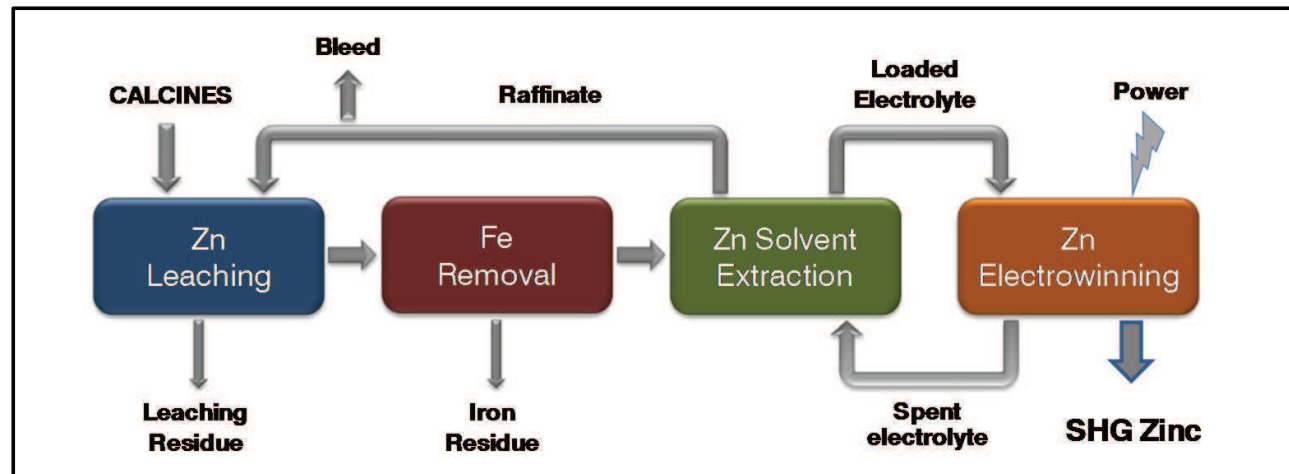


# CONCEPTUAL BLOCK DIAGRAMS

R.L.E.  
Process



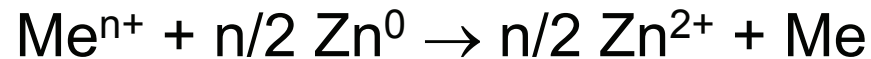
ZINCEX™  
Process



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## CONVENTIONAL ZINC DUST PURIFICATION

- ☺ **Electrolyte purification is achieved by means of zinc dust cementation:**

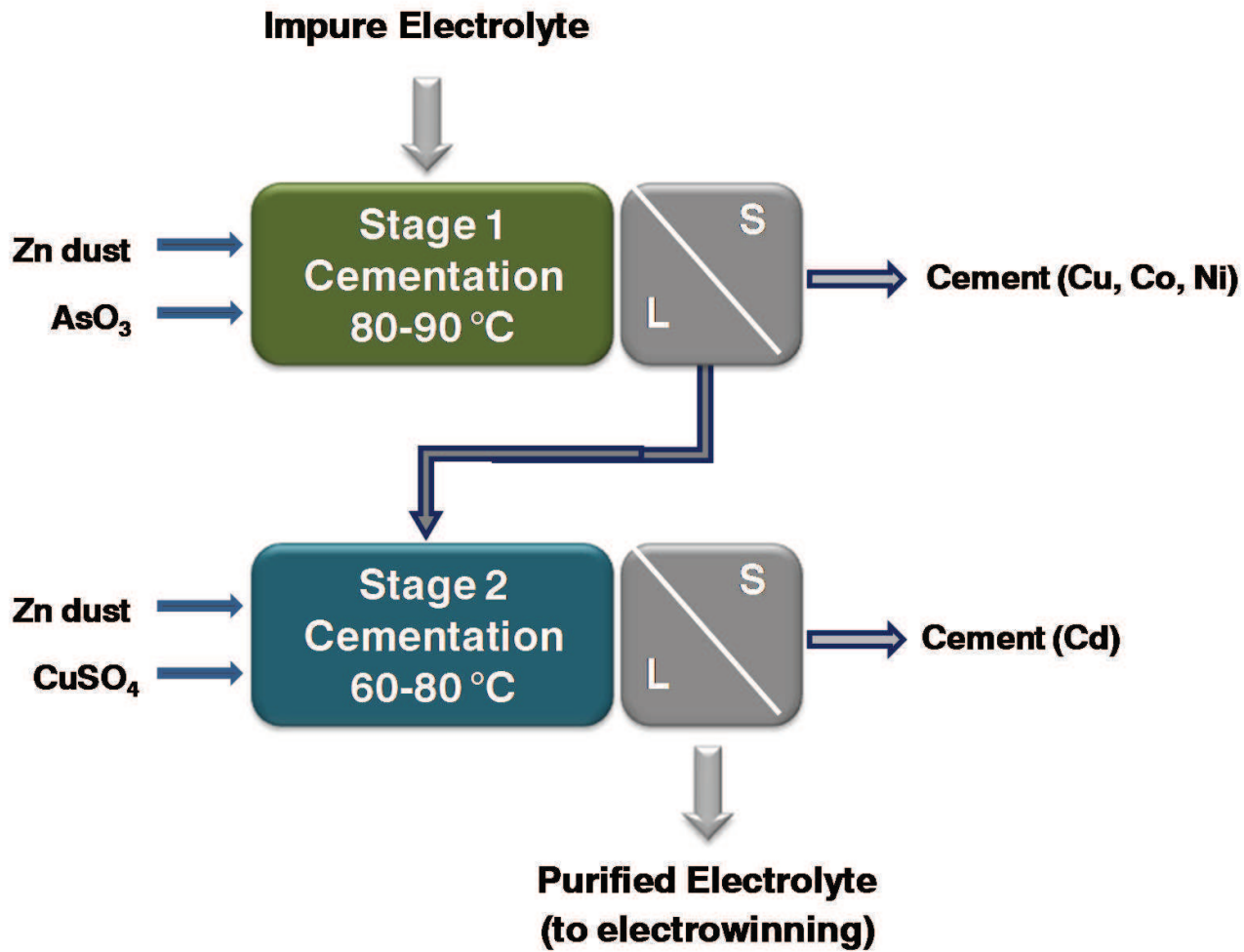


(“Me”= Cu, Cd, Ni, Co, Ge, etc)

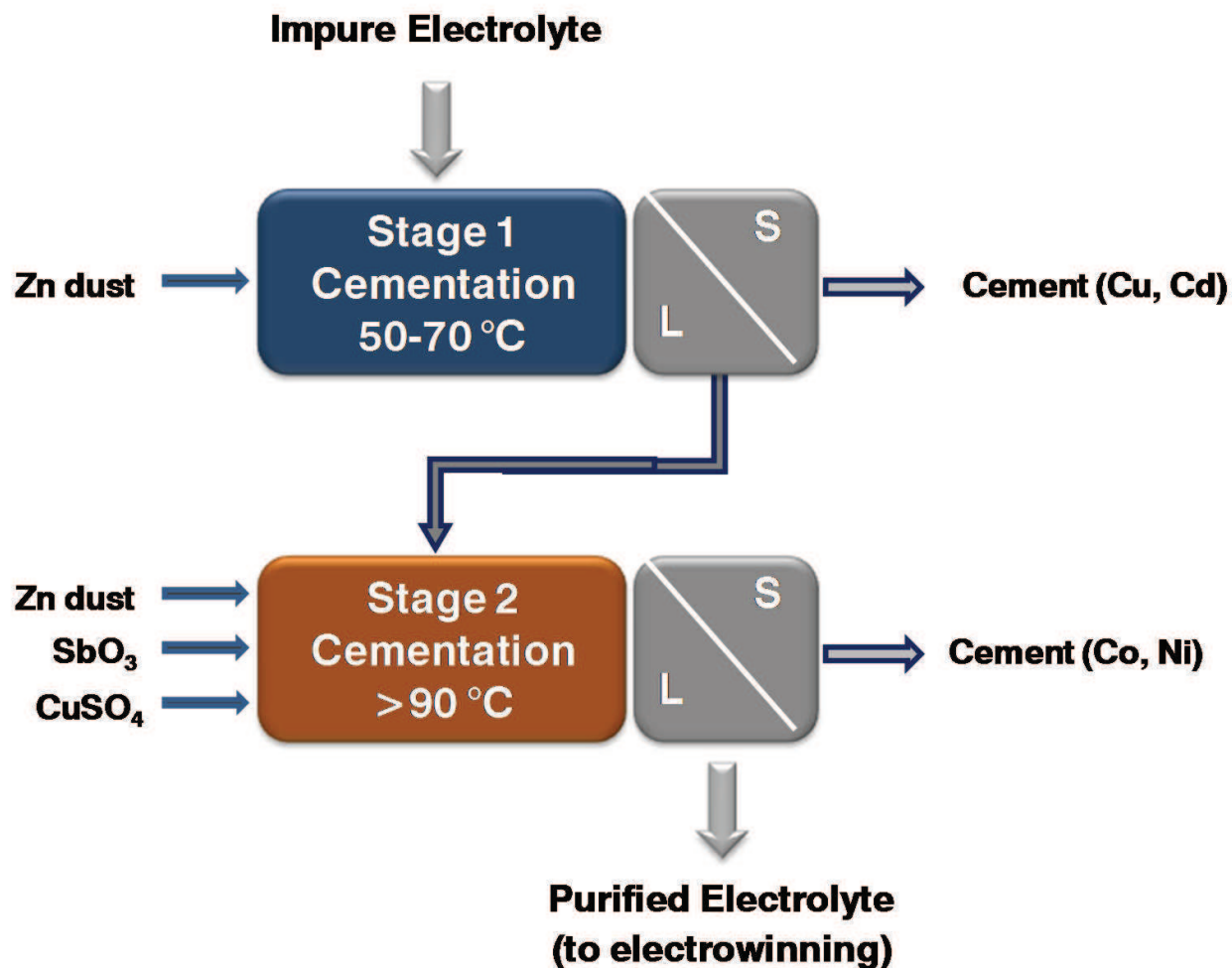
- **Achieving an extremely low level of impurities is a complex process that requires high excess of zinc dust and also specific additives to catalyse the reactions**
- **Several mechanisms are proposed, e.g. formation of inter-metallic compounds that promotes impurities deposition**
- **The cementation procedures are tailored and adapted to every zinc refinery depending on the composition and characteristics of the impure solution, the capacity, batch or continuous process, etc**
- **Most applied methods are summarised as follows:**



**-Two-stage “hot-cold” arsenic trioxide process-**

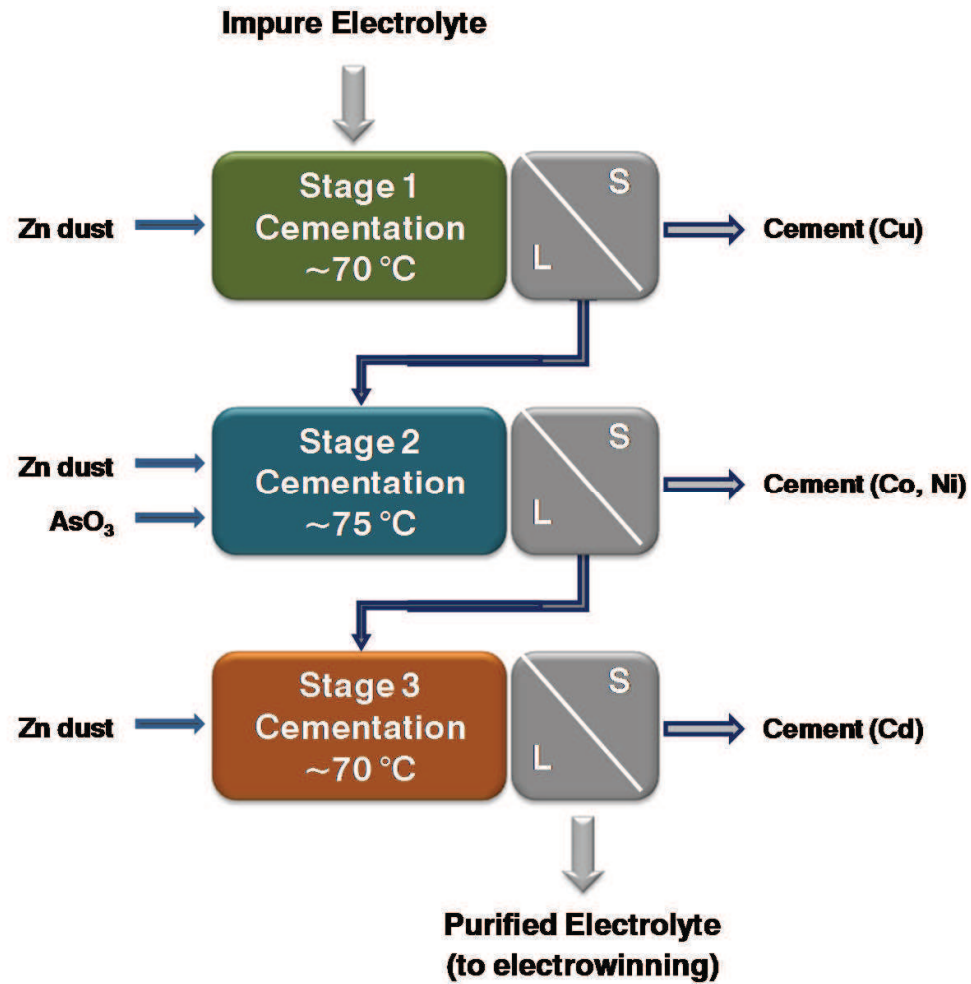


## -Two-stage “cold-hot” antimony trioxide process-



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## -Three stage process-

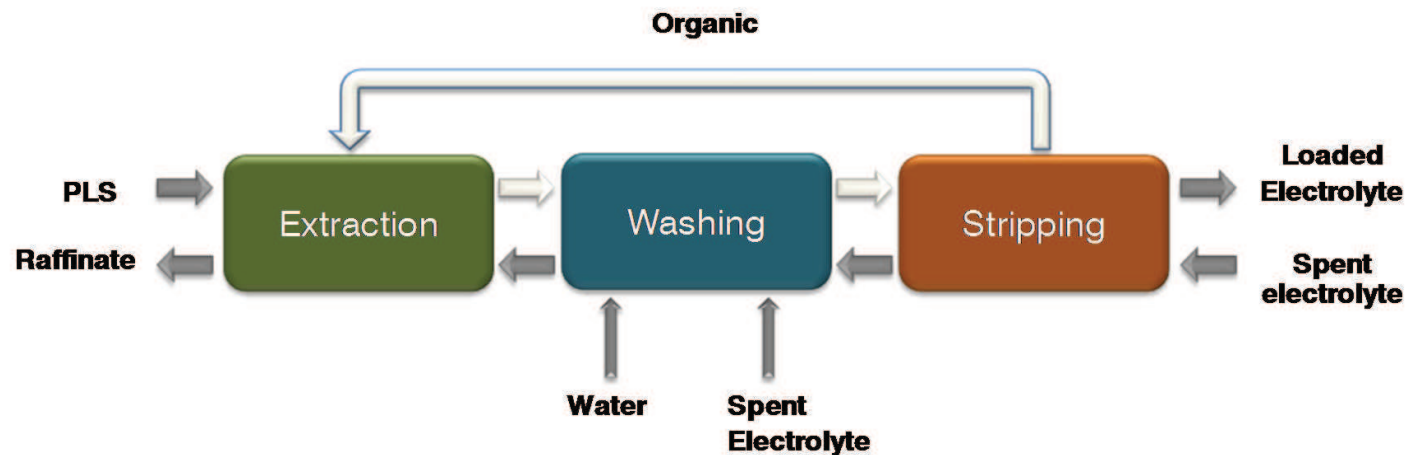


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## ZINCEX™ SOLVENT EXTRACTION PURIFICATION

- ☺ The solvent extraction process consists of three main stages: Extraction, Washing, and Stripping running in counter-current, which enables production of an ultrapure loaded electrolyte that guarantees SHG zinc quality production:

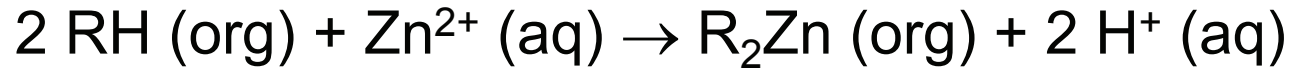


- The organic phase contains di-2-ethyl-hexil phosphoric acid (D2EHPA) diluted in kerosene, and the operating conditions are adapted to achieve a perfect separation of the zinc metal from the remaining impurities



# ZINCEX™ SOLVENT EXTRACTION

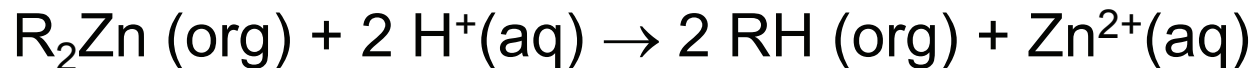
## ☺ Extraction stage:



## ☺ Washing stage:

The organic phase is contacted with water and (acidic) spent electrolyte in order to remove the entrained or co-extracted impurities

## ☺ Stripping stage:



- **This zinc solvent extraction system operates automatically and on a continuous basis: low labour and low energy; it is a simple and cost-efficient process**



## PROCESSES COMPARISON: Reagents

Zinc Dust Cementation	ZINCEX™ Solvent Extraction
5-10% of zinc production is converted to zinc dust	Zinc dust is not required
Yearly income is 5-10% reduced due to zinc dust production	Yearly income increased by 5-10% because zinc dust is not required and all produced electrolytic Zn is sold
5-10% overdesign of the tankhouse due to zinc dust production	Capex of the tankhouse is 5-10% lower as zinc dust is not required
Reagents include zinc dust, arsenic or antimony trioxide, copper sulphate, etc	The only reagent required is the organic make up
Formation of H <sub>2</sub> gas due to reaction of zinc dust and acid, and possible formation of AsH <sub>3</sub>	No formation of H <sub>2</sub> or AsH <sub>3</sub> gas
Organic compounds are not used	Risk of fire due to organic compounds. A safe design is required to avoid any trouble
Organic compounds are not used	Risk of traces of organic material passing to the tankhouse. This is avoided through proper design and operation of active carbon columns



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## PROCESSES COMPARISON: Labour & Control

Zinc Dust Cementation	ZINCEX™ Solvent Extraction
Labour is required for: strict analytical control, filtration and handling of cements, preparation and dosing of additives, sometimes batch purification operations, etc	Automatic and continuous process with minimum analytical control; as a consequence, little labour is required
The process sometimes fails to meet the target level of impurities in the electrolyte	The solvent extraction process is based on equilibrium, therefore impurity levels in the electrolyte are always kept constant
Re-dissolution of impurities from zinc cements when the retention time is long	No risk of re-dissolution of impurities because zinc cements are not produced



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## PROCESSES COMPARISON: Temperature

### Zinc Dust Cementation

Electrolyte is heated to 90-95 °C in order to achieve efficient purification

High solubility of gypsum due to high temperature, creating scaling and crystallisation problems in the cellhouse

### ZINCEX™ Solvent Extraction

Electrolyte temperature is kept constant at 40-45 °C

The loaded electrolyte is gypsum free because this solvent extraction system runs as a barrier to calcium



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## PROCESSES COMPARISON: Purification Effic.

Zinc Dust Cementation	ZINCEX™ Solvent Extraction
Purification is carried out on the main process stream, so any problems in the purification process may affect tankhouse operation	Purification is carried out on the effluent bleed, so any operating problems will never affect the tankhouse performance
Single circuit, thus any perturbation of the purification stage may lead to Fe, Ni, As, etc, being fed to the tankhouse with very detrimental consequences	Independent solvent extraction and electrowining circuits, thus surges of Fe, Ni, As, etc, are buffered by the organic phase, and in consequence, the loaded electrolyte quality remains unchanged
Efficient process for removal of metallic impurities, but unable to reject other ions such as Mg, Ca, Cl, F, Mn, Na, K, etc	This solvent extraction system is a perfect barrier for metallic impurities and other elements such as Mg, Ca, Mn, Na, K, Cl, F, etc, which are fully rejected



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## PROCESSES COMPARISON: Zinc Losses

Zinc Dust Cementation	ZINCEX™ Solvent Extraction
The copper cements is contaminated with As or Sb arising from purification additives	Cements are not produced
The complex composition of the cements makes processing them difficult	Cements are not produced
Losses of zinc content in zinc cements	Cements are not produced, losses of zinc are therefore minimal



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## PROCESSES COMPARISON: Effect on EW

### Zinc Dust Cementation

Ultrapure electrolyte production is not possible because some elements such as Mg, Ca, Mn, Na, K, Cl, F, etc, are not rejected

Loaded electrolyte produced is saturated with gypsum

### ZINCEX™ Solvent Extraction

Produces ultrapure loaded electrolyte presents the following advantages: (i) Lower cell voltage and power consumption (alkalines), (ii) Longer electrode life (Cl, F), (iii) Minimisation of cell sludge (Ca, Mn), (iv) Highest zinc quality, (v) Lower anode cleaning frequency (Ca, Mn)

Produces ultrapure loaded electrolyte, free of gypsum, presents the following advantages: (i) No gypsum scaling problems, (ii) Simpler and lower cost cooling system, (iii) Minimises maintenance requirements in the cooling towers



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## PROCESSES COMPARISON: Process Stages

Zinc Dust Cementation	ZINCEX™ Solvent Extraction
Cu, Cd Removal	<p>Solvent Extraction (This single process stage is equivalent to 8 process stages required in a conventional zinc refinery)</p>
Cl, F Removal	
Ni, Co Removal	
Gypsum Removal	
Magnesium Removal	
Manganese Removal	
Zinc Dust Production Unit	
Heating and Cooling Electrolyte System	



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## INDUSTRIAL CASE STUDY

- ☺ A comparative techno-economic study has been undertaken for a zinc refinery having a capacity of 100,000 t/a SHG zinc:

**OPEX** (reagents and consumables, manpower, maintenance and 10% contingency)

Operating Cost	Zinc Dust Cementation	ZINCEX™ Solvent Extraction
TOTAL, USD/t SHG Zn=	105	58

### **CAPEX**

Investment Cost (license excluded)	Zinc Dust Cementation (including gypsum removal)	ZINCEX™ Solvent Extraction
TOTAL, Million USD=	50	52



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## CONCLUSIONS (1)

- Zinc electrolyte purification using ZINCEX™ solvent extraction technology presents many advantages in comparison with conventional zinc dust purification process, such as:
  - Better overall process performance
  - Enhanced electrowinning
  - Lower operating cost (approximately 40% saving per ton of Zn)
  - Yearly income increased by 5-10% because zinc dust addition is not required, and therefore, all produced electrolytic zinc is sold
  - Ability to treat difficult materials, e.g. containing high Mn, Cl, F, Mg, etc



## CONCLUSIONS (2)

- 😊 The positive economic results obtained in this preliminary study confirm that ZINCEX™ solvent extraction is a reliable and cost-efficient alternative able to substitute the conventional zinc dust purification in RLE zinc refineries



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**THANK YOU FOR YOUR ATTENTION!!!**