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IMPROVING ZINC SMELTER PROFITABILITY. IS SECONDARY ZINC THE SOLUTION? USE ZINCEX^{TM} SOLVENT EXTRACTION

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ABSTRACT

Secondary zinc oxides are a growing zinc resource mainly due to the continuous increase in galvanised scrap recycling. Feeding secondary zinc to primary refineries represents an advantageous alternative to conventional concentrates; however, there are process limitations due to some detrimental impurities in the cell-house. These limitations are fully overcome when purification by solvent extraction ZINCEX^{TM} technology is used. Treating up to 100% secondary zinc in existing zinc refineries is a profitable investment. This paper describes the implementation of a ZINCEX^{TM} plant annexed to the largest zinc refinery in Japan aiming to produce 20000 t/y SHG Zn from secondary zinc.

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FOLLOWING THE PAPER IS A PRESENTATION FOR COMMERCIAL USE WHICH DESCRIBES ITS CONTENT.

INTRODUCTION

In recent years there has been a marked increase in zinc consumption triggered by increased demand from developed countries as well as emerging economies such as China. This, coupled with market shortage of zinc sulphide concentrate, is forcing zinc refineries to consider supplementing primary zinc feedstocks with secondary zinc oxide materials in order to remain competitive.

A large proportion of secondary zinc oxide material is generated in electric arc furnaces (EAF) or basic oxygen furnaces used to recycle galvanised steel scrap. In 2007, it was reported that above 90% of the EAF dusts produced in Europe (EU27) by the steel industry are recycled to recover zinc. This corresponds to an annual production of 1.2 million tpa of EAF dust. Around 80% of the recycled EAF dusts are treated using the Waelz Process, whilst the remaining 20% is processed by other means such as the rotary hearth furnace or multiple hearth furnace (Primus Process) [1].

Other sources of secondary zinc material include wastes from the smelting and metal refining industries such as: skimmings from pyrometallurgical processes, spent furnace linings, abatement system wastes (flue gas dust, sludge, etc.) waste water treatment sludge containing metal hydroxides and sulphides, sludge originating from leaching, purification and electrolytic processes.

This paper covers the advantages of utilizing secondary zinc oxides, their drawbacks and how these drawbacks may be overcome using Zincex^{TM} Technology. It also includes a brief over-view of the implementation of the Zincex^{TM} Solvent Extraction Plant in Japan which has been designed to recover 20,000 tpy SHG zinc from secondary zinc oxides.

BENEFITS OF PROCESSING SECONDARY ZINC MATERIALS

In recent years more and more zinc refineries are supplementing their primary zinc feed-stocks with secondary zinc oxides. The use of secondary zinc materials in this manner poses a number of benefits, which include [2]:

- Lower raw material costs - recycled zinc is generally more economical than primary zinc concentrates.
- Reduced iron removal costs - the iron content of secondary zinc material is generally lower than that of primary zinc concentrates.
- Lower energy costs – less energy is required to process secondary zinc material.
- Increased feed diversity – fluctuations in the primary zinc concentrate market have less impact.

Although use of secondary zinc materials has many economic and environmental advantages, the presence of relatively high levels of metallic and halide impurities in these materials renders them unsuitable for direct electrolytic processing. For zinc electrowinning, the levels of chlorides and fluorides are critical, recommended concentrations in zinc electrolytes are as follows: Chloride <100 mg/l and Fluoride <10 mg/l.

Exceeding the recommended chloride levels mainly accelerates corrosion of lead-silver anodes and other equipment within the zinc plant, which leads to higher lead levels in electrowon zinc plates and shorter anode life. Furthermore, chlorine gas evolved during the electrolytic process also presents a health hazard for plant workers.

Apart from corroding plant equipment, fluorides cause dissolution of the protective Al_2O_3 layer on the cathode surface causing the zinc deposits to adhere to the cathode surface. This creates operational problems as the zinc plates stick to the cathodes and furthermore shorten cathode life.

Prior to feeding secondary zinc oxide materials such as Waelz oxides to primary zinc refineries, the oxides are first washed to reduce the chloride and fluoride content to approximately 0.2%. The most commonly used method of introducing the washed oxides to the zinc refining process is by blending it with the zinc sulphide concentrate fed to the roaster. Halides present in the washed oxides are partially vaporized and eliminated in gas phase. In order to maintain the energy balance and to control impurity levels in the zinc electrolyte produced, usually the plant can treat a maximum of 15% washed oxides in the total feed.

Plants using the goethite process or pyrometallurgical treatment of leaching residues may also utilise washed zinc oxides as a raw material source. In this case, part of the fluorides dissolved in the leaching stage is removed in the iron precipitation stage. As in the previous case, the portion of washed zinc oxides fed to the refining process is limited. Approximately 5-7% of the zinc input into the plant can be in the form of washed zinc oxides.

The limitations posed by the presence of halides and other impurities ceases to exist when Zincex™ technology is used to process secondary zinc. This technology is highly versatile and is capable of treating washed and unwashed Waelz oxides as well as other zinc secondary materials. Zinc feed-stocks containing up to 100% zinc secondaries may also be processed using Zincex™ technology, ensuring the production of SHG Zn quality.

OVERVIEW OF THE ZINCEX™ TECHNOLOGY

Zincex™ is an industrial benchmark in zinc hydrometallurgical processing [4, 7, 8, 9]. This process has been designed and developed by Técnicas Reunidas over a number of years and implemented on four industrial plants, the most well known is the Skorpion Zinc plant in Namibia (owned by Anglo American Company) which has a nominal capacity of 150,000 tpy SHG Zn [5].

The Zincex™ technology is highly versatile and has been industrially proven to provide a feasible, efficient and profitable means of processing zinc raw materials of varying composition to produce SHG zinc over throughout the life of the refinery. A Zincex™ plant to produce SHG Zinc is comprised of the following unit operations: Leaching, Solvent Extraction and Electro-winning. Auxiliary facilities such as a Melting and Casting unit would complete the whole facility. These unit operations can be tailor made and adapted for each specific application of the Zincex™ technology, enabling the process to be operated as a stand-alone process or integrated into an existing zinc refinery. A brief description of these unit operations is provided in the following paragraphs:

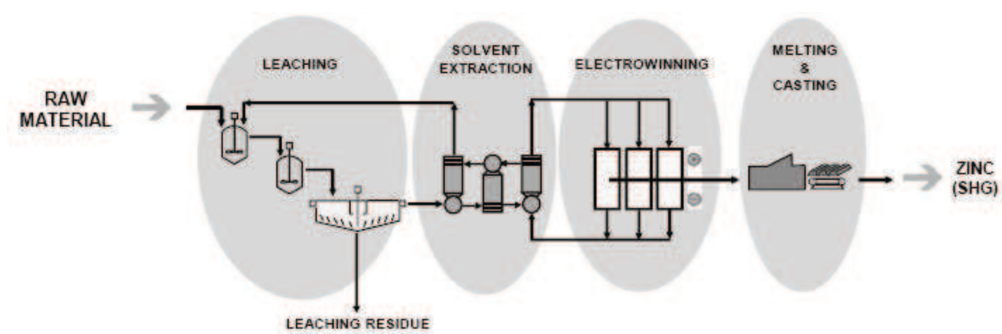

Figure 1 - Simplified flow diagram of the Zincex™ Process

Leaching

Zinc oxides, sulphuric acid and acid raffinate produced in the solvent extraction section of the process are fed to leaching reactors where the pH is carefully controlled to ensure soft leaching conditions.

In most of the secondary zinc oxides tested, the zinc recovery efficiency is close to 99%. The leached zinc goes into solution along with minor quantities of other impurities such as silica, iron, aluminium, cadmium, copper, etc. Some of these impurities are precipitated out of solution in a posterior neutralisation stage where they are removed along with the refractory part of the feed material giving rise to a leaching residue. The pregnant liquor solution produced (PLS) is fed to the zinc solvent extraction unit.

Solvent Extraction

Zinc is selectively extracted from the PLS by solvent extraction, yielding an ultra pure zinc sulphate electrolyte solution from which SHG zinc can be produced. Zincex™ solvent extraction is comprised of 4 stages: extraction, washing, stripping and organic regeneration.

Extraction

During the extraction stage zinc is selectively transferred from the aqueous PLS phase to an organic phase containing the extractant di-2-ethylhexyl phosphoric acid. The hydrogen ions released from the organic extractant are transferred to the aqueous phase producing an acidic aqueous raffinate which is returned to the leaching stage.

The selective extraction of zinc is represented by equation 1 below:

$$2\ RH\ (org) + Zn^{2+}\ (aq) \rightarrow R_2Zn\ (org) + 2\ H^+\ (aq) \qquad (1)$$

Washing

The organic phase loaded with extracted zinc is properly washed with a suitable aqueous solution in order to remove impurities arising from co-extraction and aqueous phase entrainment.

Stripping

In this stage, the zinc contained in the organic phase is once again transferred to the aqueous phase. This is carried out by contacting the washed organic phase with spent electrolyte from the electrowinning cell-house.

The stripping reaction is represented by equation 2 below:

$$R_2Zn\ (org) + 2\ H^+\ (aq) \rightarrow 2\ RH\ (org) + Zn^{2+}\ (aq) \qquad (2)$$

The stripping stage produces an ultra pure zinc electrolyte which is fed to the electro-winning cell-house. The stripped organic phase is recycled to the extraction stage, closing the loop in the solvent extraction system circuit.

Regeneration

In the extraction phase of the process, a small quantity of iron is co-extracted with zinc into the organic phase. In order to prevent this iron building up within the solvent extraction circuit, a small portion of the organic phase is regenerated using a hydrochloric acid solution.

Electro-Winning and Melting & Casting

Ultra pure zinc electrolyte from the solvent extraction stage is fed to the electro-winning cells to produce SHG zinc plates. Spent electrolyte leaving the electro-winning cells is returned to the solvent extraction circuit where it is used in the washing and stripping steps.

The zinc plates produced in the electro-winning process are then melted and casted by conventional units to produce SHG Zn ingots.

BENEFITS OF ZINCEX™ SOLVENT EXTRACTION

The use of Zincex™ solvent extraction provides the following benefits:

- Zinc plants with the capability of treating a 100% zinc oxide secondary feed-stock without experiencing the operational problems caused by impurities previously described.
- Lower operating costs than conventional zinc purification methods because use of zinc powder is not required.
- Consistently high quality electrolyte even when fluctuations in impurity levels and process flow-rates are experienced.
- Lower cell voltage and power consumption due to decreased impurity levels in the zinc electrolyte.
- Reduced corrosion of cell electrodes as chloride and fluoride levels in the zinc electrolyte will be lower than those achieved by other purification methods.
- Electro-winning free from scaling by gypsum and other insoluble compounds such as manganese dioxide.

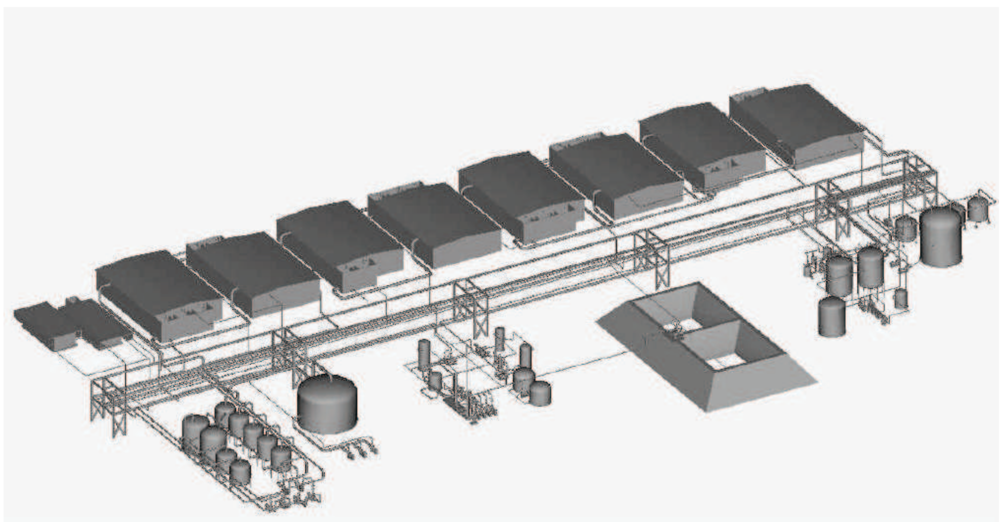

Figure 2 - Three-Dimensional model of the Zincex™ Solvent Extraction unit

IMPLEMENTATION OF ZINCEX™ TECHNOLOGY AT AKITA ZINC REFINERY

A new Zincex™ plant designed to produce 20,000 tpa SHG Zinc from secondary zinc oxides is to be implemented in Japan. This facility belongs to the Akita Zinc Recycling Co, established in March 2008 by DOWA Metals and Mining Co. Ltd and forms part of the environmental initiative to recycle zinc from dusts obtained from Japan´s Iron and Steel Industry. The new plant will be annexed to the existing zinc refinery owned by Akita Zinc Co. in Iijima, Akita.

In August 2008, Técnicas Reunidas was contracted by Dowa Metals and Mining under a Know-How Licence and Supply Agreement to provide the following services for the Akita Zinc Recycling Project:

- Licence of Use and Commercial Exploitation of the Zincex™ Solvent Extraction Technology.
- Basic Engineering Design of the zinc solvent extraction process.
- Detailed design of Special Proprietary Equipment for the solvent extraction process.

- Supply of Proprietary Equipment for the solvent extraction process.
- Technical Assistance during detailed engineering design, procurement, construction, commissioning and plant start-up.

Basic Engineering Design

During the Basic Engineering Design, Técnicas Reunidas utilised engineering tools such as the METSIM® Metallurgical process simulation program. Once the basic engineering design work for the Zincex™ solvent extraction plant was completed, the required information to proceed with the detailed engineering design was provided to DOWA Metals and Mining Co.

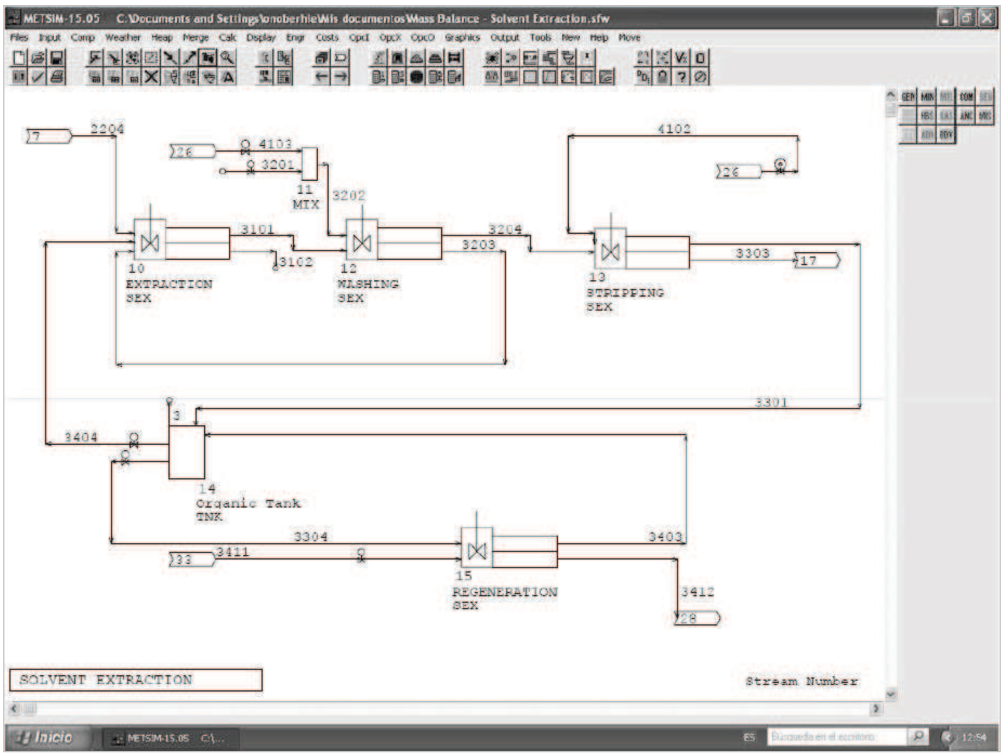

Figure 3 - METSIM® process simulation output

Special Proprietary Equipment

Técnicas Reunidas was responsible for the detailed design of Special Proprietary Equipment required for the solvent extraction process, which includes the mixer-settler vessels and systems for removal of entrained organic phase. Detailed design of these items of equipment was completed according to the project schedule.

Proprietary equipment

The detailed design of Proprietary Equipment required for the Zincex™ Solvent Extraction Process was also carried out by Técnicas Reunidas. Proprietary Equipment includes the pump mixers, agitators, internal parts for the mixer-settler vessels and interface control valves, which are based on Técnicas Reunidas' in depth experience in design and supply. This equipment improves and optimizes key conditions in order to maximise process performance. Selectivity is carefully controlled so as to minimize the transfer of impurities.

In addition to Técnicas Reunidas' zinc solvent extraction technology design database, computational fluid dynamics and 3-D modelling techniques were also used to optimise and perfect the detailed design of proprietary equipment [6]. Detailed design of proprietary equipment was completed as scheduled.

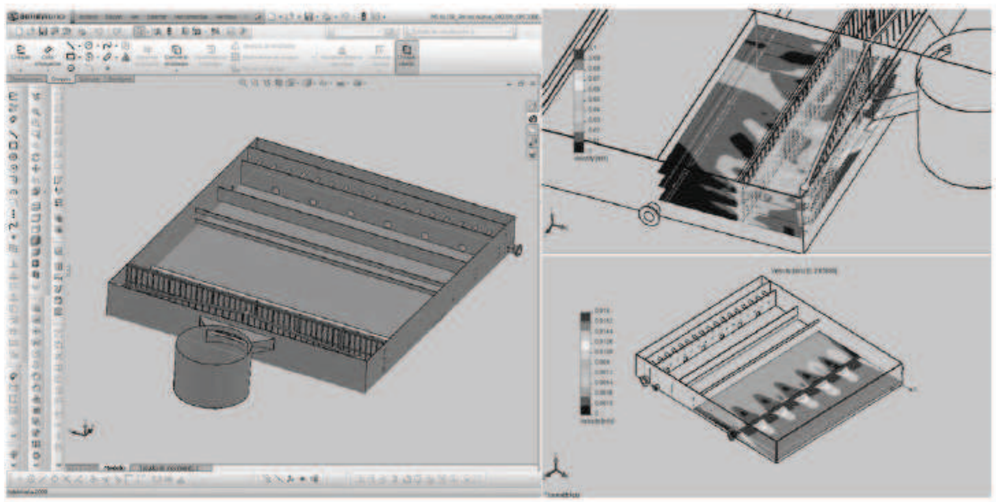

Figure 4 - Three-Dimensional & computational fluid dynamic modelling of mixer-settler vessels and internal parts

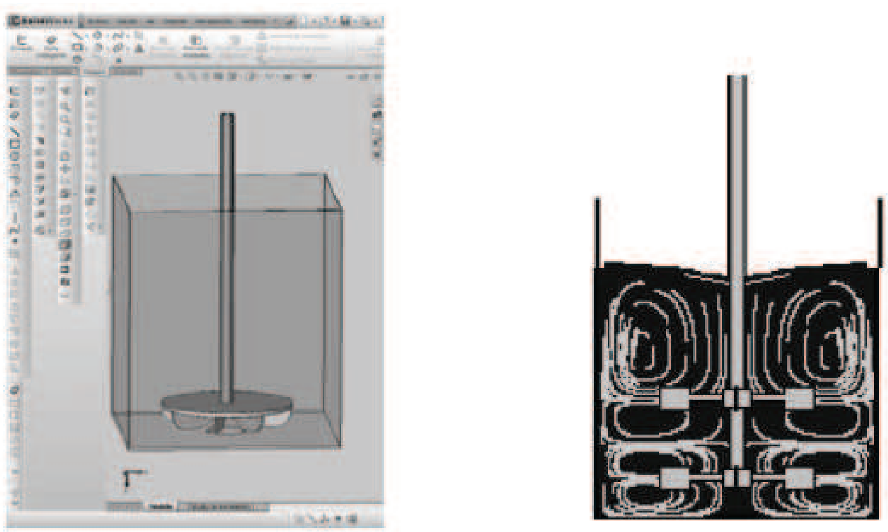

Figure 5 - Three-Dimensional & computational fluid dynamic modelling of solvent extraction agitators

To date, the majority of the engineering work has already been completed and construction work is currently underway. Thus, this new Zincex^{TM} plant is scheduled for start-up at the end of 2010.

CONCLUSIONS

Use of secondary zinc materials to complement zinc concentrate feed-stocks provides a viable means of improving the profitability of primary zinc refineries. The limitations posed by the presence of impurities in these secondary materials are now a thing of the past. Zincex™ Solvent Extraction provides a feasible and profitable solution, enabling zinc refineries to utilize feedstocks containing up to 100% secondary zinc oxides.

Zincex™ technology, designed and developed by Técnicas Reunidas, has been industrially proven on four industrial plants (Metalquímica del Nervión, Quimigal, Pilagest, and Skorpion Zinc), all of which have consistently produced high quality zinc product. A new plant designed to produce 20,000 tpa of SHG Zinc from secondary zinc oxides is currently under construction in Japan.

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PROPRIETARY TECHNOLOGY DIVISION

IMPROVING ZINC SMELTER PROFITABILITY,

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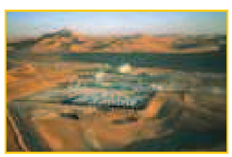
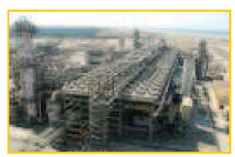


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  - Services provided
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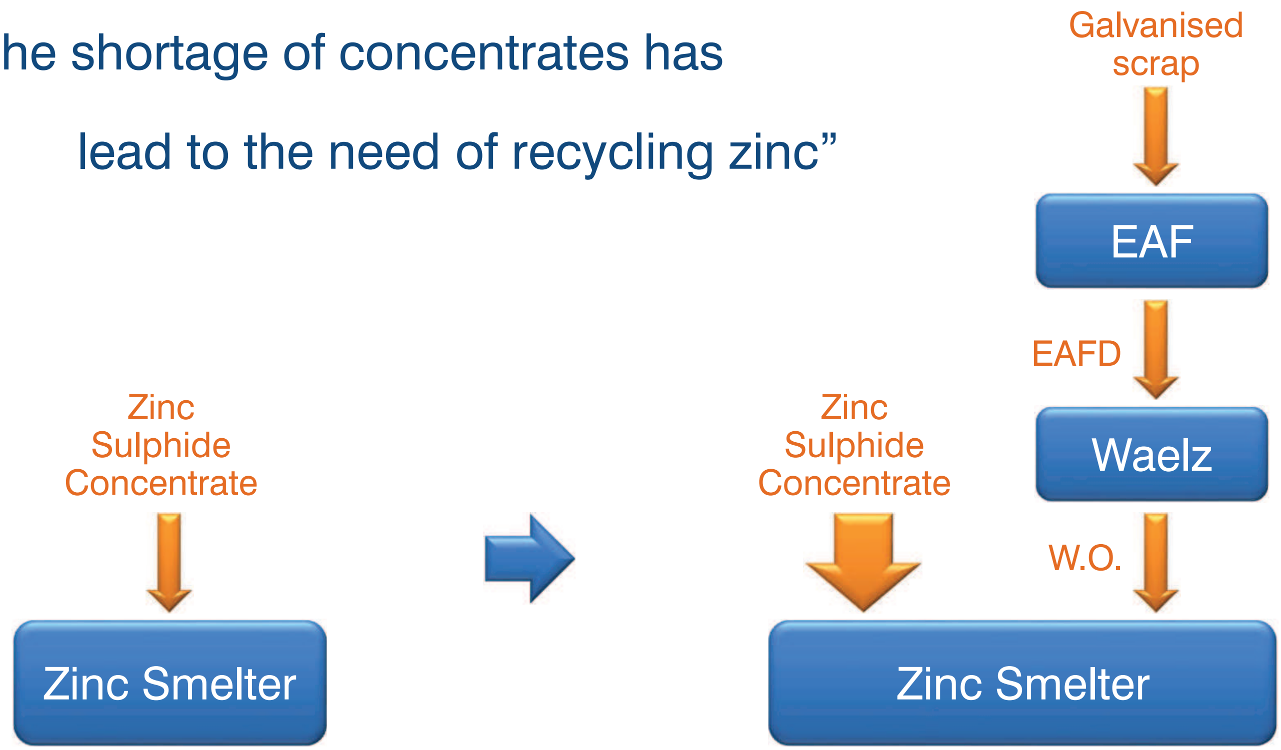
Demand of secondary Zinc & Zinc recycling

"The increase of zinc demand and
the shortage of concentrates has
lead to the need of recycling zinc"



Pros & Cons of smelting secondary Zinc

Smelting secondary zinc has advantages and disadvantages…

PROS	CONS
Lower raw material costs	Metallic and Halide impurities
Reduced iron removal costs	• Electrode Corrosion
Lower energy costs	• Chlorine gas in Tankhouse
Increased feed diversity	• Sticky zinc plates
• Less dependency on market	Limited ratio of oxide feedstock
	Feeding through the roaster
	Washing required but inefficient

With Zincex™ we can get advantage of the Pros and solve the Cons:

- Halides and impurities are removed
- Smelting secondary materials 100% is now possible

Zincex^{TM} a new solution or a complement for Zinc smelters

Overview of the Zincex^{TM} Process

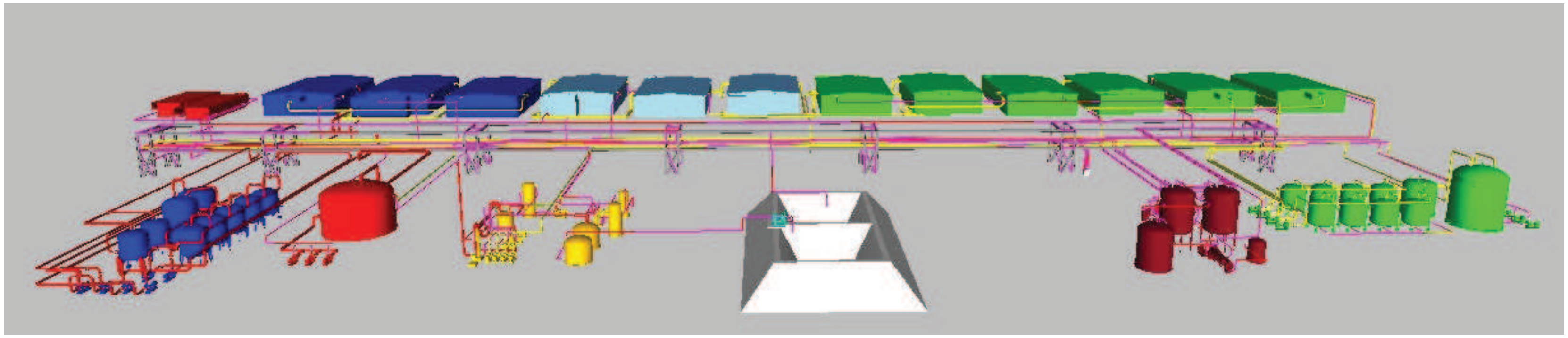
- Industrial Benchmark in Zn hydrometallurgical processing.
- Industrially proven in four plants.
- Process zinc materials of varying composition.
- SHG Zinc life-time guaranteed.
- Highly Versatile, Robust and Reliable.
- Possible up-to 100% from Zn oxide Secondaries.
- **Stand-Alone or Integrated in existing refinery.**
- High recoveries of zinc (> 98%).
- Three more projects in the pipeline.

SHG zinc Ingots

Zincex™ a new solution or a complement for Zinc smelters

Overview of the Zincex™ Process

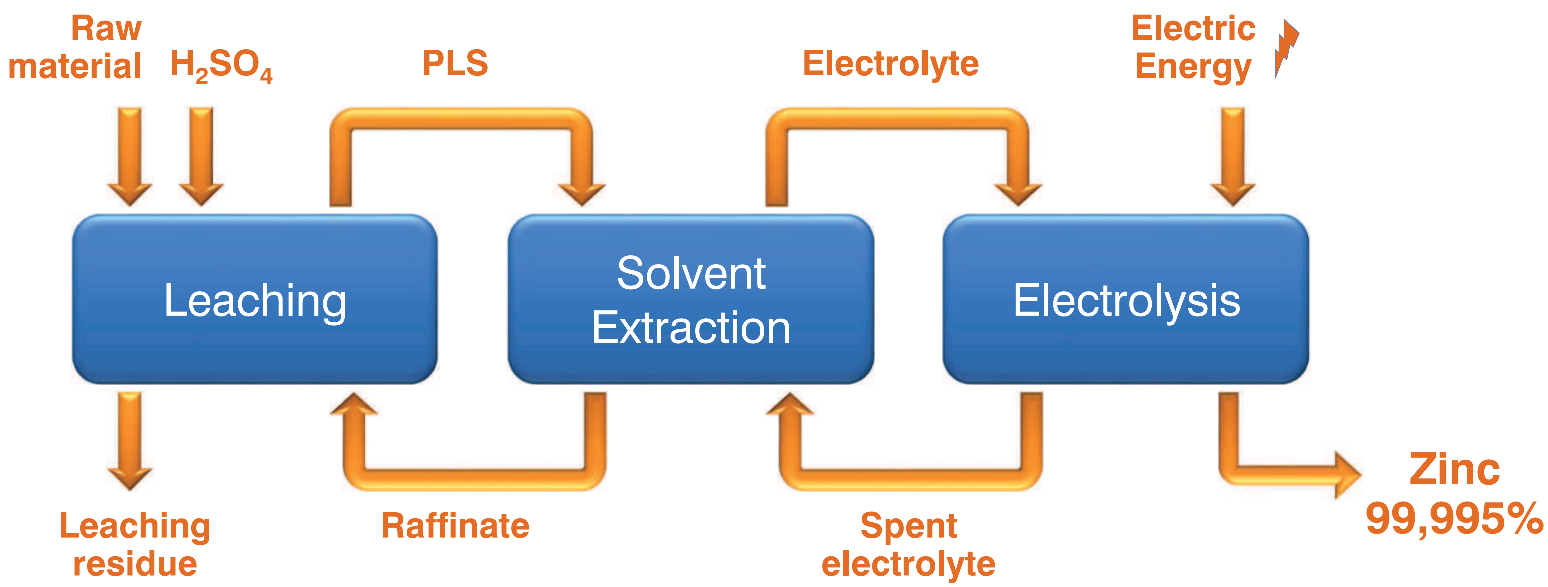
- **Lower operating costs** (-15% of Conventional RLE Technology)
  - No need of zinc dust cementation. (+5% capacity)
  - No Magnesium in the electrolyte.
  - Lower cell voltage (-7%)
  - No gypsum scaling in tank-house
  - Reduced electrode corrosion



3D Model of a complete Zincex™ Plant

Zincex™ a new solution or a complement for Zinc smelters

Stages



Leaching in H_2SO_4 and Neutralisation
(Fe, Si, Al… removal)

Extraction, Washing and Stripping

High purity electrolyte
=
↑↑↑ efficiency

Zincex^{TM} a new solution or a complement for Zinc smelters

Stages

Leaching

- Zinc oxides + H_2SO_4 + acid raffinate from SX feed the leaching reactors
- Zinc recovery efficiency often ≈99%
- Precipitation of some impurities in the neutralization stage
- Obtained pregnant liquor solution (PLS) feeds solvent extraction (SX) unit.

Pilot plant I at the TR technology centre. Pilot facilities for Leaching, Solvent extraction and Electrowinning

Zincex™ a new solution or a complement for Zinc smelters

Stages

Solvent Extraction I. Extraction

- The aqueous PLS is put in contact with an organic phase that has a strong and selective avidity for Zn^{++} cations.
- The PLS is now converted to Acid Raffinate after taking the released H^+ exchanged by Zn^{++}.
- Acid Raffinate is fed back to Leaching stage for using H^+ again

Solvent Extraction facilities at Skorpion Zinc Refinery

Zincex^{TM} a new solution or a complement for Zinc smelters

Stages

Solvent Extraction II. Washing

- The zinc loaded organic phase is washed with an aqueous solution to remove impurities and aqueous phase entrainment.


Solvent Extraction Demonstration plant and Pilot plant I at the TR technology centre.

Zincex^{TM} a new solution or a complement for Zinc smelters

Stages

Solvent Extraction III. Stripping

- The organic phase is put in contact with spent electrolyte.
- Zinc is transferred to the electrolyte obtaining ultra pure zinc loaded electrolyte.
- The stripped organic phase is fed back to Extraction.

Demonstration Solvent Extraction facilities at the TR Technology centre

Zincex™ a new solution or a complement for Zinc smelters

Stages

Solvent Extraction IV. Regeneration

- In the extraction phase, a small quantity of iron is co-extracted into the organic phase. To prevent iron building up, a small portion of the organic phase is regenerated using a hydrochloric acid solution.
- Crud, if any, produced in some settlers is removed, filtered and washed ready for disposal or feeding back to Waelz kiln.

Solvent Extraction Pilot plant II at the TR technology centre.

Zincex^{TM} a new solution or a complement for Zinc smelters

Stages

Electro-Winning and Melting & Casting

- Ultra pure zinc electrolyte is fed to the electro-winning cells to produce SHG Zn plates.
- The zinc plates are melted and casted by conventional units to produce SHG Zn ingots.

Electrowinning Pilot plant I and electrowon zinc plates at the TR technology centre.

Zincex^{TM} a new solution or a complement for Zinc smelters

References

- Skorpion Zinc Refinery (Namibia)
  150,000 tpa SHG Zinc
  In Operation since May 2003

- Pilagest (Spain)
  2,000 tpa domestic batteries (400 tpa SHG Zn)
  In Operation since 1998

- Quimigal (Portugal)
  11,500 tpa SHG Zinc
  In Operation 1980-1995

- Metalquimica d.N. (Spain)
  8,500 tpa SHG Zinc
  In Operation 1976-1992

From top to bottom: Industrial plants of Skorpion zinc refinery, Pilagest, Quimica de Portugal, Metalquimica del Nervion.

The case of Akita refinery (Japan)

Project Overview

- A new Zincex^{TM} plant to produce 20,000 tpa SHG Zinc
- Recycle zinc solid wastes from Japanese Industry
- Construction underway at Akita (Japan) by DOWA Metal and Mining Co.

- Technology Packaged supplied:
  - Licence of Use of Zincex^{TM}
  - Basic Engineering Design
  - Detailed design and/or supply of Proprietary Equipment for SX
  - Technical Assistance

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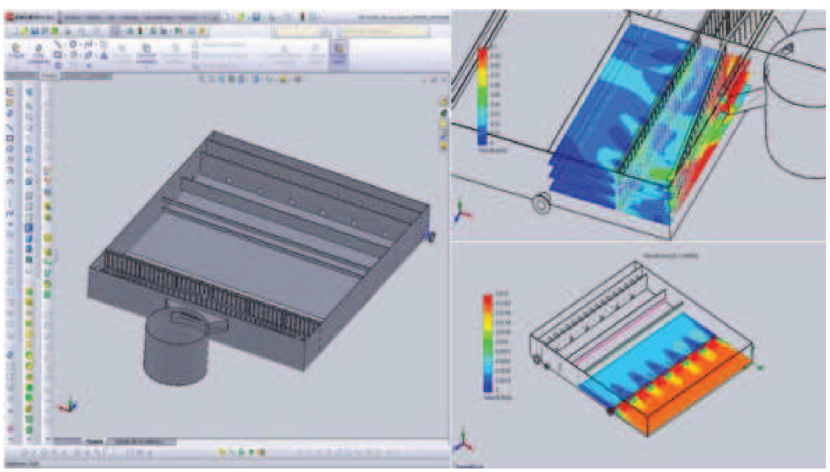
Aerial view of the Akita plant in Japan

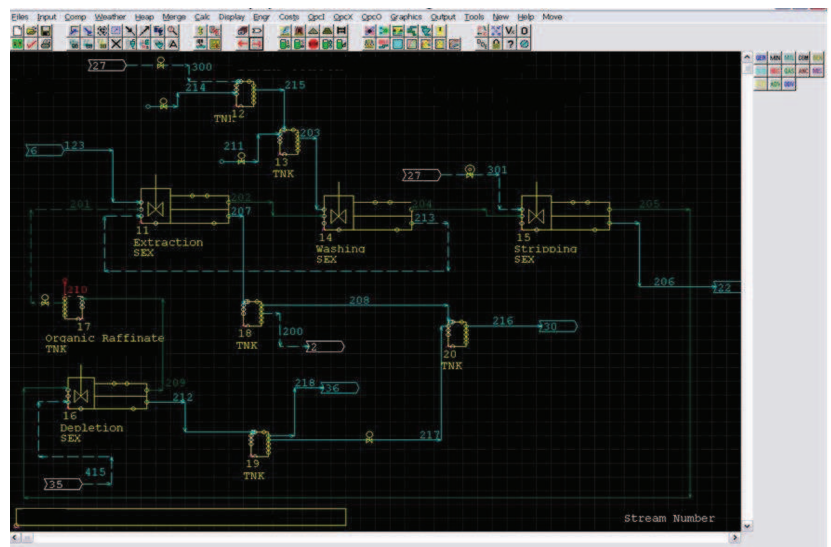
The case of Akita refinery (Japan)

Basic Engineering Design

- BED package accomplishment for a Zincex^{TM} solvent extraction plant.
- Provide the required information for procurement and detailed engineering design.
- Use of Engineering tools and Metallurgical process simulation programs (Flow-Works, METSIM, etc.).



Modeling and scale-up capacities at the TR Technology Centre.



Process Simulation Tools (METSIM)

The case of Akita refinery (Japan)

Other Supplies

Proprietary Equipment Supply

- Pump mixers, agitators, internal parts for the mixer-settler and interface control valves.
- This equipment improves and optimizes process performance and minimizes the transfer of impurities.

Detailed Design of Special Proprietary Equipment

- Mixer-settler vessels and systems for removal of entrained organic phase.

Prototypes and proprietary equipment manufacturing capacities at the TR Technology Centre.

The case of Akita refinery (Japan)

Project Current Status

- Construction underway, but almost completed.
- Mechanical completion date arriving.
- Commissioning date next November.
- Start-up date next December.
- Ramp up and steady nominal production early 2011.

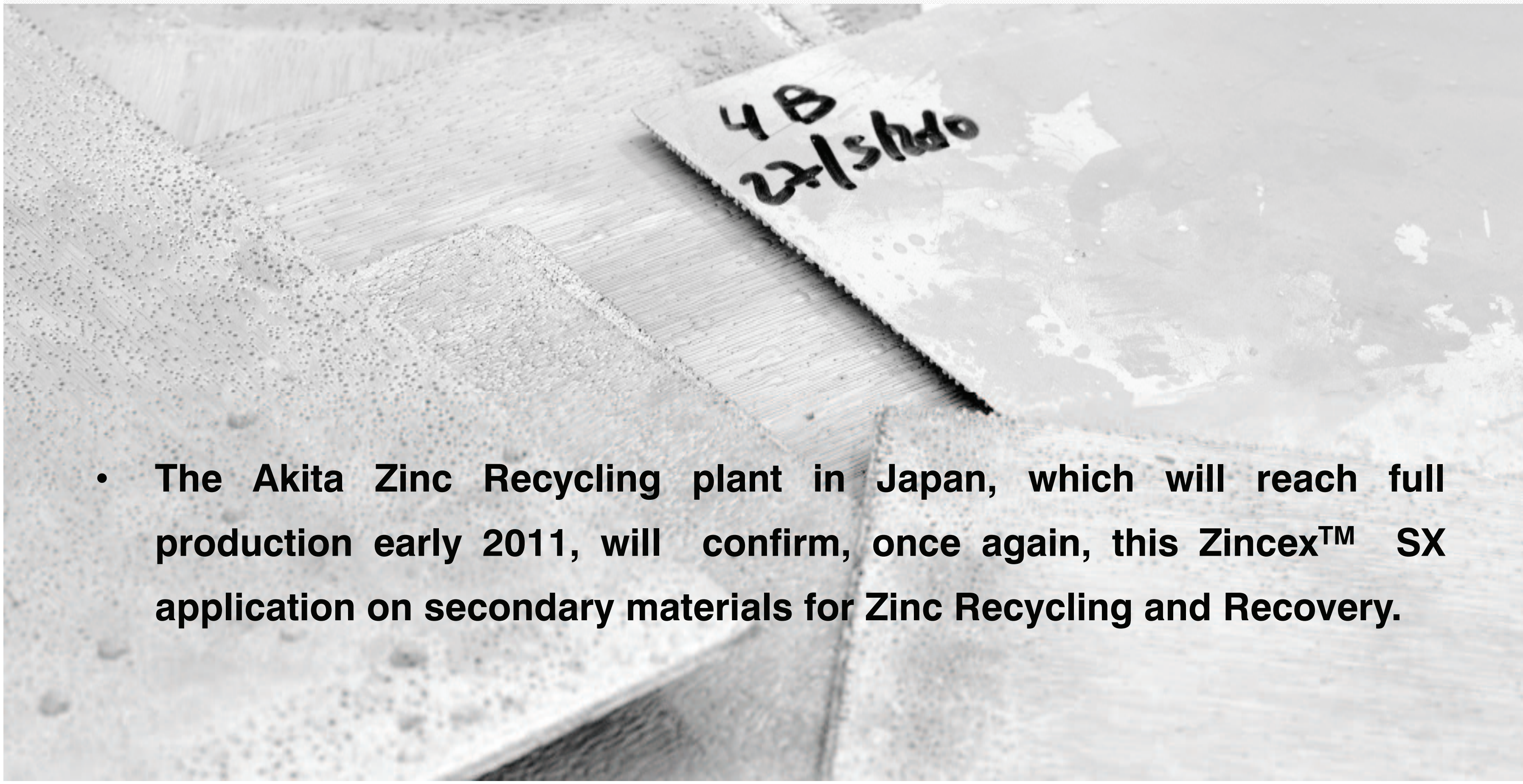
Picture Dowa courtesy at September 2010

Conclusions

- Use of secondary materials can improve the profitability of primary zinc refineries based on lower OPEX and more income.
- The limitations posed by impurities can be overcome and are actually overcome by using Zincex^{TM} SX process.
- Zincex^{TM} SX process permits refinery feed-stocks from 0% to 100% zinc oxides.
- Zincex^{TM} SX technology has been industrially proven on four industrial plants.
- Three more projects in the pipeline, two of them applied on unwashed Waelz Oxide and one on Lead-Zinc Concentrate. (50 to 150 kt Zn/y)

Electrowon zinc plates at the TR Technology Centre.

Conclusions



- The Akita Zinc Recycling plant in Japan, which will reach full production early 2011, will confirm, once again, this Zincex^{TM} SX application on secondary materials for Zinc Recycling and Recovery.

Electrowon zinc plates at the TR Technology Centre.

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Thank you very much for your attention.

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End of Presentation