The Modified ZINCEX™ Process is an advantageous smelting hydrometallurgical process licensed by Técnicas Reunidas to produce ultra-pure Zinc cathodes and enable the recovery of other valuable metals.

The main advantages provided by this process when compared to the conventional route are: Lower OPEX at similar CAPEX, Flexibility regarding raw material composition and Added value through saleable by-products and environmental efficiency.

![Figure 1: Advantages of the Modified ZINCEX™ Process.](image)

The reduction of Operation Costs is achieved mainly in two fronts: First in purification stage, where no zinc dust is required, because purification is made by solvent extraction (this also implies investment reduction in EW cell house); and Second in electrowinning, where the purity of the electrolyte permits achieving lower cell voltage --what leads to lower power consumption--, a gypsum free electrolyte and longer electrode life cycle.

The feed material flexibility is achieved through a leaching approach that permits processing a wide range of Raw Materials. The Modified ZINCEX™ Process can treat most types of Zinc raw materials, not being limited to conventional zinc concentrates: primaries like sulfides, oxides, carbonates and silicates with no limitation in Zinc content or impurities content (Zn-Pb concentrates, High Mn or As concentrates, in some cases run-off-mine, etc...) and secondary materials (unwashed and washed WOX, CZO, etc.) This can also provide an advantage to miners unable to achieve a commercial grade of concentrates. Regarding impurities, there are also much fewer restrictions.

The Modified ZINCEX™ Process ensures the production of SHG Zinc along the whole plant life at proper plant operation. Also other valuable metals like Pb, Ag, Cu, Cd, Rare Earths, In, Ge and other high value metals can be recovered if they are present in economical quantities. This provides a significant improvement of plant feasibility. Finally, the environmental impact is also reduced: less energy consumption, no air pollution (as there is no roaster) and manageable wastes and effluents, including much less if any jarosite or goethite production.
The history of Modified ZINCEX™ Process starts in the early 70’s with the development of the (former) Zincex™ process. This process was aimed to recover Zinc from Zinc complex solutions or solids with high presence of impurities hardly separable by conventional routes. The first industrial implementation of the (former) ZINCEX™ process took place in 1976. After two successful industrial implementations a further development of the technology resulted in the current “Modified ZINCEX™ Process”.

Nowadays, the Modified ZINCEX™ Process is in commercial use for processing oxidic zinc ore at Skorpion in Namibia (150,000 MTPY SHG Zinc) and for secondary materials at Akita in Japan (25,000 MTPY SHG Zinc), at Portovesme in Italy (52,500 MTPY SHG zinc from WOX) and at Horsehead in the USA (135,000 MTPY SHG zinc from WOX).

Figure 2: History of the Modified ZINCEX™ Process.

1.- Process Description

The Modified ZINCEX™ Process is a technology for zinc refining (the word “refining” is used rather than “smelting” as no roaster or furnace are used) based on three main stages: (Direct) Leaching, Solvent Extraction and Electrowinning.
Leaching is carried out at proper conditions to produce a Pregnant Liquor Solution (PLS) of very low zinc concentration. This has the following advantages: high recoveries of zinc (as high as in hot acid leaching) while iron and other impurities remain mostly intact in the leaching residue - therefore very low jarosite or goethite formation. The concentration of zinc in the PLS may be as low as 20gpl, although 30-50gpl is standard. This can be done because Solvent Extraction stage, besides being a complete purification unit, concentrates the liquor solution to achieve suitable concentrations for EW. This leaching approach is applied for both sulfidic and oxidic raw materials.

The leaching residue can be used as raw material for Lead, Silver and other valuable metals recovery. Tecnicas Reunidas has industrial proprietary processes that can be applied for this aim. This new stage can improve significantly the feasibility of a project when Lead, Silver and other valuable metals are present in the raw material.

Solvent Extraction is the core of the technology. It works as a perfect barrier for impurities and as a transfer vehicle for zinc to EW and acid to Leaching. There are three units in this stage: Extraction, Washing and Stripping.

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**Figure 3: Main process stages of the Modified ZINCEX™ Process**

**Figure 4: The three Aqueous/Organic/Aqueous circuits and zinc-acid countercurrent transfer**
**Modified Zincex Process by Técnicas Reunidas**

Zinc Extraction from the PLS is performed using D_{2}EHPA (di-2-ethyl hexyl phosphoric acid) as the organic extractant in a kerosene type diluent. In the proper design and operating conditions, D_{2}EHPA can ensure very high and selective affinity for zinc. The exhausted acid raffinate is recycled to leaching stage.

A small bleed stream may be taken in order to control circulating impurity levels. Other valuable metallic elements, like Copper and Cadmium, which have been concentrated in this bleed, may be recovered if they are present in economic quantities. MZP also enables in this stage the recovery of high value metals such as Rare Earths, Indium, Germanium, etc.

The Washing unit performs a physical and chemical wash of the loaded organic to remove entrained and co-extracted impurities.

Finally in the Stripping unit, the loaded and washed organic passes to the stripping unit where it is put in contact with spent electrolyte. Zinc is thus stripped into the electrolyte producing an ultra pure Loaded Electrolyte ready for zinc Electrowinning. After zinc stripping, a small bleed of stripped organic is regenerated, thus preparing the whole organic phase to restart the cycle in the Extraction stage.

The Loaded Electrolyte produced in the Solvent Extraction stage is extremely pure, free of impurities and gypsum that would affect the zinc electrowinning plant and increase maintenance expenses. The highest performance of the tankhouse can be achieved by this process, provided that proper maintenance and housekeeping policies are applied by operators. Another benefit is the longer life of the electrodes. Tecnicas Reunidas ensures the suitability of the electrolyte for any commercial Electrowinning process.

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**Figure 5: Schematic of the Skorpion Zinc SX flowsheet. Source Skorpion Zinc and TR; ISEC 2011.**

2.- Advantages of the Modified Zincex Process

The main advantages provided by this process when compared to the conventional route are: Lower OPEX at similar CAPEX, Flexibility regarding raw material composition and Added value through saleable by-products and environmental efficiency.
Technical Advantages

The main differential advantage of MZP over RLE comes from the existence of two independent circuits that lead to safer and more robust operation; one circuit for leaching and another for electrowinning. These circuits are separated by the organic cycle of SX, which behaves as a physical and chemical barrier.

This makes the process very flexible to deal with unexpected amounts of impurities coming into the system or in general with operational disturbances. This in addition improves the performance of the electrowinning unit due to the extreme purity of the electrolyte produced by SX system.

In the leaching stage the zinc concentration in the PLS can be reduced because MZP Solvent extraction not only purifies zinc-rich solutions but also increases their concentration. This leads to the following advantages:

- Leaching can be achieved in softer conditions without any loss in zinc total recovery.
- A lower amount of iron is leached. Therefore jarosite/goethite production is significantly reduced, if any at all.
- Direct leaching of various types of zinc raw materials is technically and economically feasible. This includes primaries without limitation of impurities or lead content, grade, nature (oxidic or sulfidic) and secondaries.
- The contained lead and silver can be recovered through other Tecnicas Reunidas technologies.
- Lower concentrations of zinc in the leaching stage imply in practice less zinc losses.
Modified Zincex Process by Técnicas Reunidas

The SX unit yields an extremely pure electrolyte free of impurities like Co, Ni, Cu, Cd, Mn, Fe, Mg, Ca, Na, K, Cl, F, etc. This permits the recovery of zinc from secondaries (high Cl and F) or high-Mn concentrates without limitation. In addition Minor metals such as Cadmium, Copper, Silver, Gallium, Indium, Nickel, Rare Earths, etc, can be recovered as by-products enhancing plant feasibility.

![Diagram of Modified ZINCEX™ Process]

Figure 7: Modified ZINCEX™ Process as a perfect barrier for impurities

In the electrowinning stage several advantages are found like:

- The high quality of the electrolyte leads to a lower cell voltage, which results in lower power consumption.
- The cellhouse is free of gypsum. This makes tankhouse maintenance less intensive and cooling equipments smaller and cheaper. Heat exchanger works perfectly with no gypsum scaling at all.
- The level of chlorides and fluorides is much lower. EW atmosphere is chlorine gas free. Cathode corrosion is negligible and zinc crystallography is better. This improves stripping. Electrodes wear and tear is reduced.
- No chlorides and gypsum leads to improvement in the morphology of the activation layer of the anodes and this to a lower requirement of anode cleaning and flattening. Therefore, anode life is extended.
- The level of magnesium and other alkaline cations is at ppm level, which decreases cell voltage.
Modified Zincex Process by Técnicas Reunidas

- The conventional RLE purification system consumes zinc powder, and therefore, the zinc tankhouse is >5% overdesigned. No zinc powder is needed in MZP plants for purification purposes.

The environmental advantages are: less energy demand, much less iron leaching, higher recovery of other valuable metals and no roasting. All these factors enhance the environmental sustainability of MZP Plants.

This process can provide a benefit to miners that have big losses of zinc in their flotation stage. As lower quality concentrates can also be treated.

Economical Advantages

All above technological advantages produce the following economical advantages:

OPEX: On average savings of 15% of total operation costs are achieved operating a Modified ZINCEX™ Process Plant instead of a conventional smelter.

CAPEX: On average savings between 1% to 10% of total investment costs are achieved in the construction of a Modified ZINCEX™ Process Plant instead of a conventional smelter.

In addition plant feasibility is significantly enhanced with the recovery of other valuable metals like Pb, Ag, Cu, Cd, Rare Earths, In, Ge and other high value metals.

<table>
<thead>
<tr>
<th>PROCESS STAGES</th>
<th>MZP CHEAPER?</th>
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<td>Crushing and Milling</td>
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Modified Zinex Process by Técnicas Reunidas

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*Table 1: Economical advantages of Modified ZINEX™ Process*