A Brief Summary of Zinc Oxide Processing Methods Available for the Bongará Deposit

Introduction

Bongará oxide deposit is a typical calamine type deposit containing several zinc minerals: smithsonite, hydrozincite and hemimorphite. A large number of similar deposits were exploited from the beginning of the 19th century. The majority of these deposits are today exhausted. They have been progressively replaced by sulfide deposits located more deeply in the ground.

The composition of Bongará oxide deposit is quite similar to Electric Arc Furnace Dust (EAFD), a residue from the steel industry. The quantity of EAFD processed around the world today is 3,400,000 tpy.

The process applied by the previous Bongará mine owner, the Waelz kiln, can be applied to process the Bongará oxide deposit but other more recent processes (thermic or non-thermic processes) that are proven technologies can also be applied.

The specific location and associated constraints of the Bongará deposit (zinc ore cut-off grade, local communities impact, water availability, power,) will have a determinant influence on the process selection.

This report covers various proven technologies that could potentially be applied to the Bongará oxide deposit.

Thermic processes (zinc fumed at high temperatures)

- Waelz Kiln
- Rotary Hearth Furnace
- Scanarc
- Flame Reactor

Non-thermic processes

- Floatation
- Direct H_2SO_4 Acid Leaching
- Direct Basic Leaching

All these technologies are industrially well-known, with various worldwide equipment Suppliers.

Table 1 summarizes some of the industrial references where thermic processing technology is used to extract zinc from oxides.

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Engineering assistance (BFS – Bankable Feasibility Study)

Waelz Technology

Developed by German firms at the beginning of 20^{th} century, with the first operating plant in 1925.

The material containing zinc (oxide, silicate, carbonate, zinc ferrite) must be pelletized with a carbon reductant. The carbon reductant must be a coal with low volatiles content, only the carbon units which are not volatilized are useful for the zinc fuming reaction:

$$ZnO_{(ore)} + C_{(coal)} \rightarrow Zn_{(gas)} + CO_{(gas)}$$

The volatile part of the coal is liberated at the very beginning of the kiln, with little part of this thermal energy being valorized inside the kiln.

Pellets preparation reduces dust formations, they are fed into a rotary kiln where temperature is progressively increased up to 1100-1400 °C.

Pellets and combustion gases flow counter-currently in the kiln rotating at low speed (0.4-0.7 rpm). Solids residence time is about 3-10 hours depending on the feed material.

The gases at the outlet of the kiln are mixed with air to re-oxidize the zinc vapor into solid zinc oxide while CO is converted to CO_2. Gases are cooled by adding water and zinc oxide produced is collected in bag houses. This zinc oxide can be used as feed for zinc smelters.

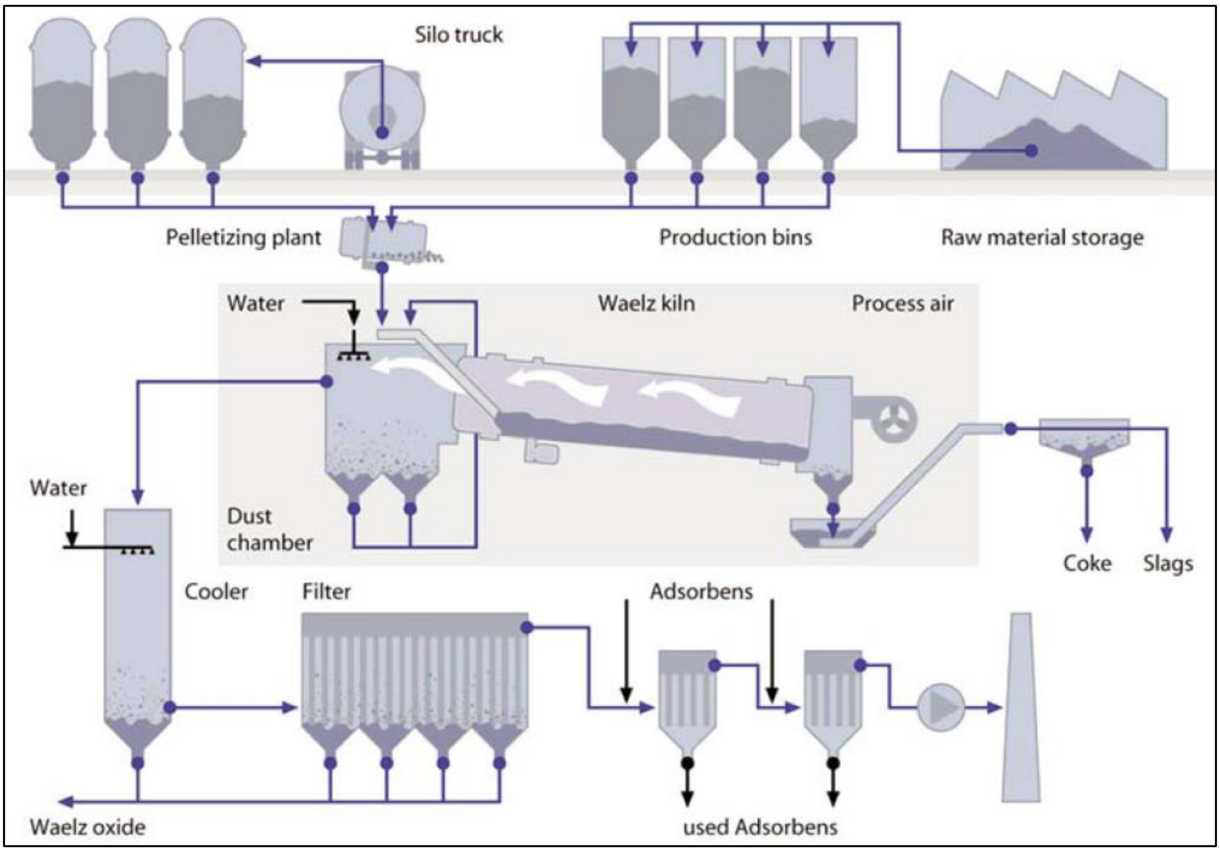
The zinc oxide product quality range could be 70-85% ZnO, it depends on zinc material feed as other elements and compounds are volatilized with zinc: e.g. lead, cadmium, chlorine, fluorine, sodium and potassium. If needed, a further calcination of the zinc oxide produced can occur in a secondary rotary kiln at 1000°C to separate the zinc oxide from other elements increasing the product quality to above 90% ZnO, depending on the lead content.

Gases leaving the bag filters are treated to meet environmental regulation standards in terms of dioxins.

The un-fumed material (slag) leaves kiln at 1050-1150°C and is quenched in water before disposal. Depending on their chemical composition and stability, the slag could be re-used as aggregate or be utilized for other purposes.

Stable and homogeneous pellet feed, as well as stable suction conditions of the gases treatment, is critical for kiln performance efficiencies. Instability will cause an imbalance of chemical reactions resulting in poor zinc recovery and accretions in the kiln as solids (which are in continuous contact with the kiln wall refractory) may stick on walls and block the flows.

A dust settling chamber is installed on the gas outlet to reduce the carry-over of pellet fines in the zinc oxide dust in order to minimize the contamination in the final zinc product. The remaining CO is changed to CO_2 in this chamber.



The Waelz kiln technology is a well-known, understood and proven technology developed from the beginning of the 20th century.

This technology can process various materials containing oxidized zinc: e.g. zinc oxide ore, EAFD dusts and smelter residues.

Waelz technology is recognized to efficiently process electric arc furnace dust EAFD.

Zinc material feed to Waelz kilns can be:

- Oxidized zinc ore
- EAFD electric arc furnace dust
- Zinc ferrite residue from zinc smelter
- Pure zinc oxide production

Oxidized zinc ore

The Waelz process has been was initially developed to process zinc oxidized ore containing between 15 and 30% zinc.

The PBSIM & BFS team was directly involved (process tests and development, engineering concept) with the Shairmerden zinc oxide ore deposit located in Kazakhstan where 200,000 tpy of ore is processed by the Kazzinc Ridder plant utilizing 2 existing rotary Waelz kilns.

Zinc recovery from the Waelz kiln was 95% and the zinc oxide produced was directly leached in the zinc smelter which produced zinc metal. The processing of stockpiled Shairmerden zinc oxide ore continues at the smelter although the mine is now closed due to accelerated mining and ore body depletion.

The analysis of the Shairmerden deposit is very similar to the analysis of Bongará deposit. The gangue composition can be adjusted with addition of fluxes.

Bongará deposit: Zn: 23.76%, Pb: 1.24%, Fe: 15.16%, Mn: 0.52%, SiO_2: 10.27%, Al_2O_3:4.30%, CaO: 3.54%, MgO: 1.57%, Cl: 0.41%, F: <0.1%, S: 0.06%

Shairmerden deposit: Zn: 21.05%, Pb: 1.1%, Fe: 6.42%, Mn: .0,73%, SiO_2: 24.73%, Al_2O_3: 8.91%, CaO: 6.19%, MgO: 0.5%, Cl: 0.29%, F: 0.29%, S: 0.46%

Electric Arc Furnace Dust

Worldwide approximately 6,750,000 tpy of EAFD are produced annually. These dusts contain 1.600.000 tpy of zinc.

About 35 Waelz kilns with an average capacity of 75,000tpy are installed worldwide (see partial list below). They process every year 3.400.000 tons of EAFD.

Table 1

Company	Year built	Capacity (tpy EAFD)
Horsehead – Palmerton, USA	1981	245,000 (3 kilns)
Horsehead – Calumet, USA	1988	72,000
Horsehead – Rockwood, USA	1990	200,000 (3 kilns)
Horsehead – Nucor, USA	2010	180,000 (2 kilns)
Steel Dust Recycling – Millport, USA	2008	120,000 (2 kilns ?)
Zinc Nacional – Monterey, Mexico	1982	150,000 (2 kilns ?)
Befesa Recytech – Noyelles-sous-Lenz, France	1993	83,000
Befesa – Freiburg, Germany	1991	100,000
Befesa – Duisburg, Germany	1992	105,000
Nuova Samia – Ponte Nossa, Italy		87,000
Ponte Vesme – Sardinia, Italy	1991	180,000 (2 kilns)
Aser – Bilbao, Spain	1987	100,000
Befesa – Metoks, Turkey	2008	60,000
Cinkur, Turkey	1980 (zinc ore)	200,000 (2 kilns)
Befesa – Chungbuk, South Korea	2012	100,000
Himeji – Himeji, Japan	1975	35,000
Sotetsu Metal – Alzu, Japan	1974	60,000
Sumitomo – Shisaka, Japan	1987	120,000 (2 kilns)
Taiwan Steel Union, Taiwan	1996	180,000 (2 kilns)

A typical analysis of EAFD (average of 15 EAFD worldwide)

Zn: 28.24%, Pb: 1.27%, Fe: 28.24%, Mn: 2.71%,SiO_2: 2.14%, Al_2O_3: 1.23%,
CaO: 6.17%, MgO: 2.95%, Cl: 3.80%, F: 0.13%; S: 0.56%.

The difference with the Bongará oxide deposit is the higher iron, chlorine and fluorine content.

The higher content of iron will require more of the reducing agent and the higher chlorine and fluorine content will require an elimination stage of these elements prior to shipping to the zinc smelter.

The recovery yield is also around 95%.

Zinc ferrite residue from zinc smelter

The countries from East Block (ex USSR plus the satellites countries) have applied the Waelz kiln technology to process zinc containing residues from hydro metallurgical smelters.

These residues are similar to EAFD except chlorine and fluorine are much lower.

Rotary hearth furnace technology

Developed by Japanese firms at the end of the 20th century, with a first operating plant in 1965 on iron product.

Rotary hearth furnace is a rotating torus ring hearth to which a uniformly layer of pellets has been spread on the floor of the hearth. The hearth is moved on rail cars while the refractory wall structure is fixed.

The zinc feed material is pelletized (or briquetted) with a carbon reductant.

The carbon reductant can be a coal with low or high volatiles content, only the carbon units which are not volatilized are useful for the zinc fuming reaction:

$$ZnO_{(ore)} + C_{(coal)} \rightarrow Zn_{(gas)} + CO_{(gas)}$$

As per the Waelz Kiln the volatile part of the coal is liberated at the very beginning of the furnace, the associated thermal energy being valorized inside the furnace.

Pellets (briquettes) are dried before feeding the furnace where the temperature is progressively increased up to 1200-1300 °C. The temperature is adjusted by fuel burners and air injectors installed all around the torus ring.

Pellets and combustion gases are flowing cross-currently in the furnace rotating at very low speed (0.03-0.05 rpm). Solids residence time is about 15-30 minutes depending on the feed material.

The gases inside the furnace are continuously mixed with air (from forced air injectors installed all around the furnace) ensuring the re-oxidization of zinc vapor into solid zinc and the burning of CO in CO_2 inside the furnace.

Energy from gases leaving furnace at approximately 1200-1300°C is partially recovered in dedicated heat exchangers to produce hot air (300-500°C) which feeds the furnace via forced air injectors.

Gases at 850-950°C are then cooled down rapidly by the addition of water and the resultant zinc oxide is then collected in bag filters. This zinc oxide can be used as feed for zinc smelters. The fast cooling down ensures that no dioxin & furans are generated. Further energy recovery apparatus (heat exchangers) are installed after the bag filter which produces hot air around 130-140°C suitable for the pellets (briquettes) drying stage.

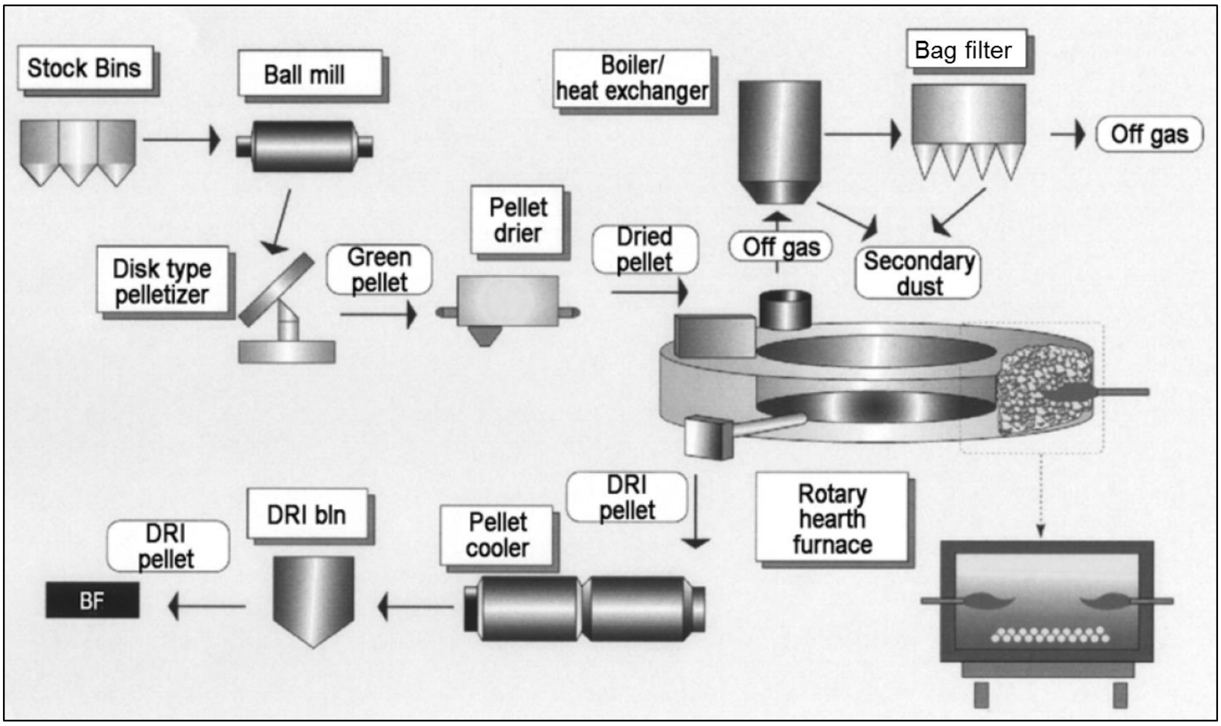
The zinc oxide product quality range could be 70-90% ZnO, it depends on zinc material feed as other elements and compounds are volatilized with zinc: e.g. lead, cadmium, chlorine, fluorine, sodium and potassium.
A simple water washing (with minor addition of Na_2CO_3) of the zinc oxide produced can separate the zinc and lead oxide from those other elements, reaching a more valuable product for zinc smelter (>98% ZnO+PbO).

The un-fumed material (iron mainly metalized) leaves the furnace at 1000-1050°C, it is extracted through a water-cooled screw and then recycled as iron-units to steel industry; or quenched in water before disposal.

For Bongará ore, the iron grade will be too low for iron-units valorization in the steel industry but there is a possibility it may be of use in the cement industry as iron and combustible input (carbon excess and metallic iron). Disposal conditions will have to be defined through inertness testing of the pellets (briquettes) leaving the furnace.

Due to the residence time for the pellets (briquettes) and to the fact that zinc and coal are perfectly mixed in the adequate ratio inside the pellets, the rotary hearth furnace has high flexibility in feed flow and feed homogeneity.

Excluding the pellet feeding distribution system and the un-fumed material extraction screw, the pellets are fully static (only the hearth is moving). This means solids are never in contact with refractory reducing accretions thereby increasing the refractory life.



The Rotary hearth furnace technology is a proven technology developed from the end of the 20th century.

They have mainly been installed on steel mills that generate various kinds of dust during the steel making process. Among these, iron dust containing large quantities of zinc cannot be directly recycled. Use of rotary hearth furnace allows for removing zinc from that iron dust; zinc is volatilized and collected in the gases as zinc oxide while iron containing mainly metallic iron (usually called DRI – direct reduced iron) is leaving the furnace as pellets/briquettes suitable for recycling into the steel making process.

Typical analysis of steel dust: Zn: 7.39%, Pb: 0.07%, Fe: 57.51%, Mn: 0.91%, SiO_2: 6.10%, Al_2O_3: 0.13%, CaO: 8.07%, MgO: 1.57%

To our knowledge, 10 Rotary hearth furnaces with a capacity of 200,000 tpy of iron waste are operating worldwide. They produce zinc oxide for zinc smelters and DRI (Direct Reduced Iron) which is recycled in blast furnaces. Four Rotary hearth furnaces, each with throughput of 500,000 tpy of iron ore, are operating worldwide producing DRI.

Based on this technology, ZincOx built a Rotary hearth furnace in South Korea for the treatment of 200,000 tpy of EAFD. This furnace is operated today by Korea Zinc and has a zinc recovery above 95%. The same technology is under development for a plant in Vietnam.

Location	Company	Supplier	Status	Feed type	Feed tpa	Product(s)
South Korea, Chungbuk	ZincOx - Korea Zinc	"ZincOx"	Q2 2012	EAFD	200,000	DRI, *HZO*
South Korea, Pohang	Posco	Nippon Steel Eng.	Q3 2009	Iron Waste	180,000	DRI, *HZO*
South Korea, Gwangyang	Posco	Nippon Steel Eng.	Q3 2009	Iron Waste	180,000	DRI, *HZO*
Japan, Hirohata	Nippon Steel	Midrex/Kobelco	Q3 2009	Iron Waste	190,000	DRI, *HZO*
Thailand	Nakorn Thai Group	Inmetco	Q1 2009	Iron ore fines	500,000	DRI
Italy, Piombino	Lucchini Steel	Inmetco/Demag	Q1 2009	Iron Waste	60,000	DRI, *HZO*
USA, Minesota	Erie Nugget	Midrex/Kobelco	Q4 2008	Iron ore fines	500,000	PI
Taiwan	China Steel Corp.	Nippon Steel Eng.	Q4 2007	Iron Waste	180,000	DRI, *HZO*
Japan, Hirohata	Nippon Steel	Midrex/Kobelco	Q1 2005	Iron Waste	190,000	DRI, *HZO*
Italy, Piombino	Lucchini Steel	Inmetco/Demag	Q3 2003	Iron Waste	60,000	DRI, *HZO*
Japan, Kimitsu	Nippon Steel	Nippon Steel Eng.	Q4 2002	Iron Waste	180,000	DRI, *HZO*
USA, MI, Senatobia	Hartford Steel	Hartford Steel Technologies	Q1 2002	EAFD	80,000	DRI, *HZO*
Japan, Hirohata	Nippon Steel	Midrex/Kobelco	Q2 2000	Iron Waste	190,000	DRI, *HZO*
USA, Indiana	Iron Dynamics	IDI	Q3 2000	Iron ore fines	500,000	DRI
Japan, Kimitsu	Nippon Steel	Nippon Steel Eng.	Q2 2000	Iron Waste	120,000	DRI, *HZO*
USA, Michigan	Rouge Steel	Maumee	Q2 1999	Iron Waste	300,000	DRI, *HZO*
Thailand	Nakorn Thai Group	Inmetco	Q4 1997	Iron ore fines	500,000	DRI
USA, Arkansas	Nucor Yamato	Allmet	Q4 1997	EAFD	100,000	DRI, *HZO*

Rotary Hearth Furnace Technology Offers Several Advantages:

- If EAFD are treated metallic iron (DRI) is produced that can be recycled instead of disposed as slag, (it will not be the case for Bongará zinc deposit).
- Higher value of the zinc oxide produced due to lower contamination by feed dust carry-over, lower carbon, and no organics material (highly harmful for zinc smelter). This feed allows for a simpler process for the treatment of zinc oxide which is required before feeding a zinc smelter.
- No dioxin production in the gas, meaning simplified gas treatment.
- No requirement of fluxes. In Waelz kilns the addition of fluxes may be necessary to prevent the accretion of slag rings on the refractory walls.
- The size of Waelz kiln is limited at 100,000 tpy of feed and RHF goes from 100,000 tpy to 500,000 tpy.
- Every kind of reductant can be used, from coal with high volatiles to coke.
- High flexibility in feed flow and feed homogeneity.
- Easy adjustment of the temperature profile all along the furnace.

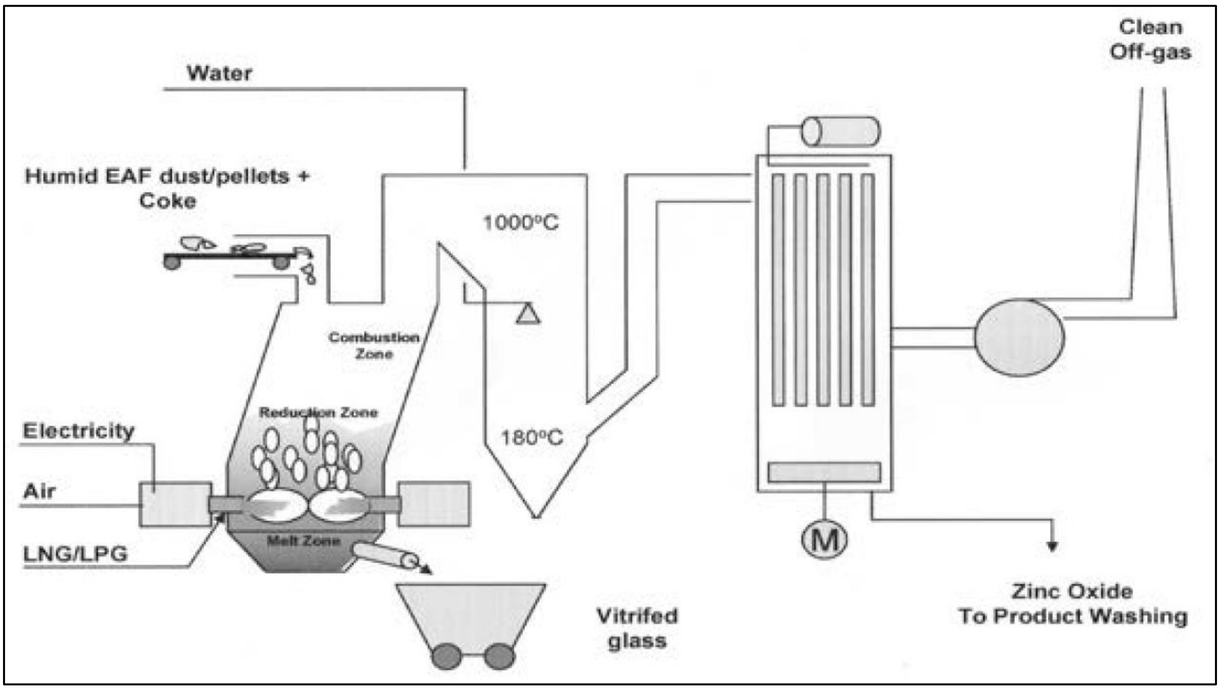
Other Thermic Processes

A lot of other thermic technologies have been developed to process zinc ores or residues but only two have been in real operation: the Scanarc and the Flame reactor technologies.

Scanarc technology

Technology developed by Scan arc and applied by Nyrstar at Hoyanger in Norway, 40,000 tpy EAFD plant capacity with a zinc recovery of about 94%.

Partly the required energy is brought in the system by electricity that produces a plasma of the gas (O2) injected in the furnace. This technology can only be economic in regions where the electricity is very cheap.



Flame reactor technology

Developed by Horsehead (USA) capacity of the plant: 30,000tpy of EAFD. Horsehead has never developed more this technology and now applies only the Waelz kiln technology to process +/- 1,000,000tpy of EAFD.

Non-Thermic Processes

The thermic technologies previously described are definitively suitable to efficiently recover the zinc from an oxidized zinc ore (above 95%), producing a dry disposable residue, but they require a large quantity of thermal energy (coal, fuel, natural gas) and electricity. Their capital cost and operating cost is also important.
Non-thermic processes such as floatation or leaching (in acidic or basic media), depending on the ore quality can be an alternative to thermic processes. Their zinc recovery from oxidized ore can also reach suitable levels. But a drawback could be the wet residue disposal, although this can be solved by specific stabilization technologies transforming those into dry disposal residue.

Some of those non-thermic processes may also not be suitable to specific areas where water availability is an issue, nevertheless, there are technologies to minimize water consumption by increasing the water recycling's (e.g. slurry filters with low moisture in residue, crystallizers, or reverse osmosis to concentrate salts).

Floatation

Floatation of zinc oxidized ore was developed after the Second World War. Before that, it was the recognized technology applied to concentrate sulfide ore.

This technology is more adapted to process complex ores of sulfide and oxide containing several elements.

Different concentrates like a zinc concentrate on one side and a lead/silver concentrate on the other side can be produced.

The recovery yield and the purity of the zinc concentrate produced are lower than the yield and the purity of the zinc oxide obtained with a thermic process. The floatation recovery yield is of the order of 85% compared with 95% for a thermic process.

Floatation can process zinc grades around 5% zinc whereas a thermic process is limited to values well above 10%.

Direct H_2SO_4 Acid Leaching

In the 80's, an innovative technology was developed by Vieille Montagne (Belgium) to process oxidized zinc ore.

The zinc oxide concentration stages, through either thermic process or floatation, are not required anymore with this innovative technology. The low-grade zinc ore is fed directly to a zinc smelter where zinc is leached in H_2SO_4 and finally recovered as zinc metal. This process generates a good zinc recovery (>95%) and has the benefits of having the capital and operating cost lower than the conventional method utilizing a concentration stage before the zinc smelter.

Two plants processing zinc oxide ore had been in operation but are now close due to mine exhaust. Padeang (Thailand) with 70,000 tpy zinc metal and Skorpion (Namibia) with 150,000 tpy zinc metal.

Padeang ore was similar to the Bongará oxide deposit (calamine: 23% zinc) whereas the Skorpion ore is a clay containing 10% zinc.

Both plants are based on H_2SO_4 acid leaching with the H_2SO_4 being recycled during the zinc electrowinning stage minimizing the fresh acid input.

Direct basic leaching

Ammoniac direct leaching is a proven technology in other non-ferrous metals such as copper, nickel, cobalt.

Ammonia leaching has been studied by ZincOx on the Jabali ore (Yemen). Jabali is an oxidized zinc ore containing 10% zinc as smithsonite and hemimorphite. The high purity zinc oxide produced (70,000 tpy) can be used as technical oxide in the rubber and the ceramic industry.

Jabali mine is open and the metallurgical plant is in construction, but the project stopped due to the political situation in Yemen.