

Top submerged lance direct zinc smelting

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ABSTRACT

A long history of zinc processing starting with pilot plant studies in the 1980s has progressed to the treatment of close to 800,000 tonnes a year of zinc bearing feeds in Top Submerged Lance (TSL) furnaces in the form of residues and slags. Whereas these Ausmelt TSL applications are end-of-pipe applications treating residues from classical Roast-Leach-Electrowinning (RLE) process routes, this paper discusses Direct Zinc Smelting (DZS) Process. In Stage 1 of this novel two stage TSL application the sulphide sulphur from the zinc concentrate is the energy carrier used to smelt the concentrate and fume 60–65% of the zinc content. Subsequently in Stage 2 zinc is fumed from the already molten Stage 1 slag to create a final discard slag with a total zinc recovery of 99%. The use of sulphide sulphur as fuel to smelt has economic advantage over the present end-of-pipe TSL applications, that require two steps (for smelting and sulphur removal) and then fuming using primary fuels. The slag product of the DZS process overcomes inherent environmental liability and ever increasing economic burden associated with the traditional RLE processes by eliminating the creation of large volumes of iron bearing residues (mainly jarosite and goethite) while complementing high recoveries of Zn with those of the valuable elements e.g. Cu, Ag, Au, Pb, Ge, and In. High levels of Fe, Mn, SiO₂, and MgO in some concentrates render them unsuitable for processing in RLE, however are elegantly directed by DZS to the benign slag. This paper will discuss Ausmelt's applications in zinc processing with a focus on DZS to show how this process can extend the life of present RLE sites.

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1. Introduction

With growing pressure on the margins for the processing of zinc feeds as a result of increasing costs of energy and labour, the ever increasing drive for sustainable use of zinc resources, interest in the economical processing of secondary feed material sources has surged. In addition the drivers for environmental conformity and stricter health regulations in an increasingly educated and environmentally aware and active society will affect the future of metal production. Intensifying the processes in metallurgy by maximizing mass and energy transfer in state-of-the-art furnace technology will be a key. Since its invention, Top Submerged Lancing (TSL) Technology has gained widespread commercial acceptance in non-ferrous metal production by doing exactly this.

The processing of among others copper, lead, tin, and zinc bearing primary, secondary (residue) or recycled materials in TSL is commercial reality. Close to 40% of Sn will be produced through TSL furnaces in the next years, while an ever increasing amount of copper is produced in TSLs while e-waste processes, lead battery recycling and copper recycling are already commercial reality (Matuszewicz and Reuter, 2008). Producing these various metals

in close to 50 commercial Ausmelt TSL furnaces is testimony to this technology's flexibility to economically process both primary and/or secondary feeds, while using varying fuels, oxygen and good process control to produce high metal recoveries.

Being environmentally compliant in regions for example such as Europe, Japan, and South Korea evidences TSL's excellent environmental performance by operating within all norms for offgas emissions and other environmental legislation.

This paper describes the technical and commercial aspects of Ausmelt's progress in the field of zinc processing. The discussion briefly provides an overview of Korea Zinc's commercial applications for the treatment of zinc leaching residues (and other materials) and subsequently focussing on the developments of Direct Zinc Smelting (DZS). The DZS process has the potential to make an important contribution to treating lower grade unclean concentrates in an innovative combination of the pyrometallurgical recovery of zinc as a ZnO fume and subsequent processing it in a simplified leach and electrowinning circuit while harnessing the sulphide sulphur as a fuel. This complements the success TSL already has in the processing of iron containing residues from the classical Roast-Leach-Electrowinning (RLE) primary zinc industry, fuming zinc from slags and treating secondary materials such as Electric Arc Furnace (EAF) dusts to recover both the iron and zinc units.

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1.1. Zinc processing – current commercial solutions

Traditional RLE processes are complex flow sheets that incorporate a number of fundamentally simple steps to produce zinc sulphate liquor that undergoes electrolysis to produce the final zinc metal product. The complexity in the flowsheet comes from the need to purify the leach liquor to remove the iron, copper, cobalt, nickel, and other elements such as arsenic and bismuth to prevent them affecting the final product or reducing the efficiency of the electrowinning processes. The leach residue (usually jarosite or goethite) is already a cost driver in terms of disposal and increasing dumping costs, as well as negative publicity around them is continuing to be a major concern as stricter environmental standards are enforced preventing the creation of ponds and other storage mechanisms for economically viable disposal. In addition, the RLE process is less efficient in the recovery of valuable minor elements such as Indium (In) or Germanium (Ge), which are commonly found with zinc ores.

TSL zinc processing technology has been implemented in various commercial applications for the efficient recovery of zinc from these intermediate industrial products (residues, slags) in South Korea, Japan, and Australia (Hughes et al., 2008). Therefore, retrofitted to existing zinc smelting installations, the TSL furnace can treat primary leach residues to recover the zinc units and minor valuable elements such as In and Ge to produce a discard saleable slag low in zinc (<2%) enabling maximum zinc recovery from a concentrate source. The zinc is returned in the form of zinc oxide fume can easily be treated in simplified existing zinc RLE works for which only a neutral leach step is required (see Fig. 1).

The Korea Zinc facility in Onsan (South Korea) is the most comprehensive evidence to date as to the success of TSL technology (Lee and Park, 2003; Kim and Lee, 2000; Lee et al., 2006). It comprises an integrated flow sheet of seven interdependent projects utilising twelve TSL furnaces (10 for the specific recovery of zinc) that allows Korea Zinc to maximize the recovery of values from these intermediate industrial residue products (e.g. goethite, QSL slag, old residue ponds, indium, and germanium, etc.). This demonstrates the flexibility of the TSL furnace and zinc technology in particular as depicted by Fig. 2. According to Korea Zinc’s 2008 annual report the Korea Zinc Group (Korea Zinc, its wholly owned subsidiary Sun Metals Corporation, and its sister company Young Poong) ranks second in the global zinc market and has refined zinc smelt-

ing capacity of 925 kt/a. It is notable that this processing recovers through its TSL technology (Fig. 2) 63.5 kt/a Zn, 39.0 kt/a Pb, 267 t/a Ag, 600 t/a Cd, and 75 t/a In (substantial amount on a global basis), adding considerably to the profit margin (Korea Zinc, 2008 Annual Report). These fuming activities make Korea Zinc the only zinc smelter free from environmental pollution issues. While fuming recovers all the valuable metals from waste it also turns the leftovers into environmentally stable slag to be used as construction materials.

These fully commercialized TSL applications are complemented by TSL flowsheets to process EAF dusts (Hughes et al., 2007; Lee et al., 2006) as well as direct processing of zinc concentrates, which is the topic of this paper.

1.2. Direct zinc processing – future solutions

Over the past 25 years, fundamental investigations have been conducted into the direct smelting of zinc sulphide concentrates with the objective of producing crude zinc metal directly by condensation of the zinc metal vapour from the SO₂ bearing gas stream or technologically best as oxidized ZnO fume.

Thermodynamic calculations by Yazawa (1979) on the volatilization of zinc as metal vapour from pure ZnS material during oxidation of sulphide showed that 99% of the Zn as sulphide is converted to zinc metal vapour. However, this tends to convert to ZnO and ZnS during cooling, because of the presence of SO₂ and CO₂, i.e. the pO₂ is high enough for this to occur. These experiments were extended to industrial concentrates by Davey and Turnbull (1980), producing similar results, claiming as well that the process is thermally autogenous. However, it has proven challenging and elusive to produce metal zinc by condensation from zinc vapour/gas mixtures other than for the Imperial Smelting Furnace. Test work has been conducted by Minproc (Foo et al., 1992) for producing ZnO from Bolivian sulphide ores in a submerged combustion smelting process with zinc recoveries exceeding 92%.

In the late 1990s Ausmelt carried out extensive R&D resulting in a two stage ZnS concentrate smelting–fuming process being proposed and developed in conjunction with BUKA Minerals Ltd., Australia. In this process finely grained Zn–Pb bulk concentrate from their existing operations were treated. The Buka Zinc Process (BZP) was based on a two stage smelting process in the TSL furnace

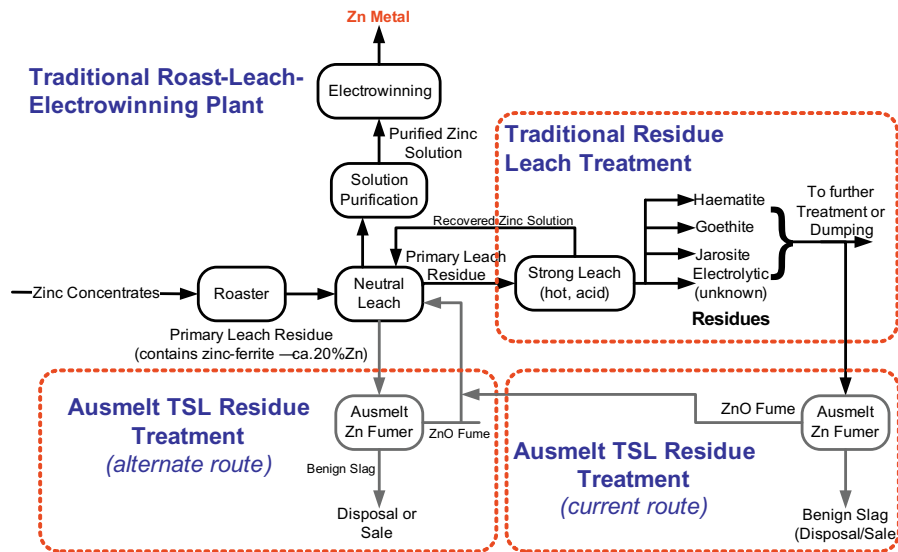


Fig. 1. Commercialized TSL zinc technology solutions for processing zinc residues.

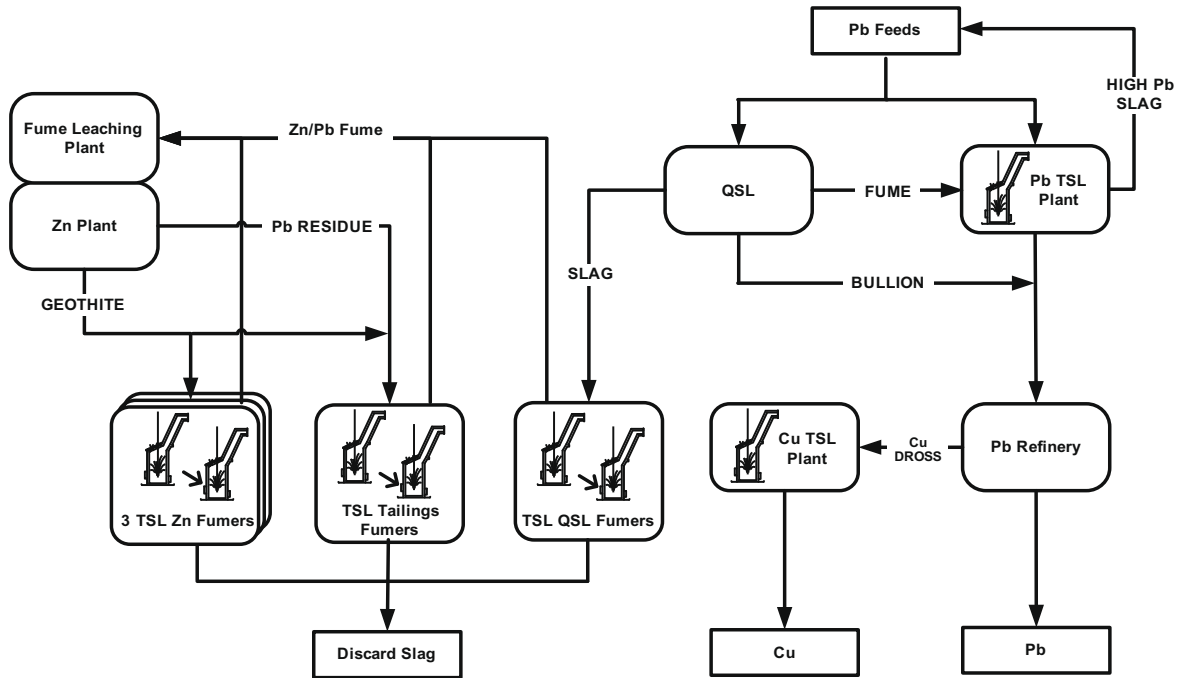


Fig. 2. Korea Zinc's integrated flowsheet using TSL Technology to recover zinc and lead from various slags and residues created during primary zinc and lead concentrate processing producing benign discard slags while complying with all South Korean environmental legislation.

(Buckett and Sinclair, 1998). It was shown that high levels of zinc (>50%), lead (>90%) and silver (>90%) are recovered as fume in the 1st Stage smelting process, with the majority of the balance of the zinc (>40%), lead (<5%) and silver (<10%) recovered in the 2nd Stage reduction/fuming step. It was observed that in excess of 5% of the sulphur input reported as sulphate to the Stage 1 fume, principally due to sulphatisation of the lead present in the Stage 1 fume in the gas handling system.

In the BZP process the treatment of the lead-rich ZnO fumes was conducted via a hydrometallurgical ammoniacal leaching process (ammonia-ammonium carbonate (AAC)-leach solution). The advantage of this process is its good separation of the lead from the zinc, as lead largely remains un-dissolved in the residue as lead

carbonate, whereas zinc dissolves as a zinc-amine complex. After solution purification (by cementation using Zn-dust), the zinc is recovered from solution by steam distillation of the ammonia and precipitation of zinc in the form of a basic zinc carbonate. The distilled ammonia is absorbed and re-circulated.

In order not to contaminate the closed ammonia solution circuit with sulphate, the ZnO fume is pre-leached in an alkaline Na₂CO₃-solution in order to remove sulphate in the form of Na₂SO₄. While the selected treatment of the fume by the above method was ideal due to its small scale (i.e. pilot plant scale), it is disadvantageous when used in large scale due to its economics and intermediate residue streams etc. Due to renewed market interest coupled with the expected growth in the supply of concentrates that cannot be

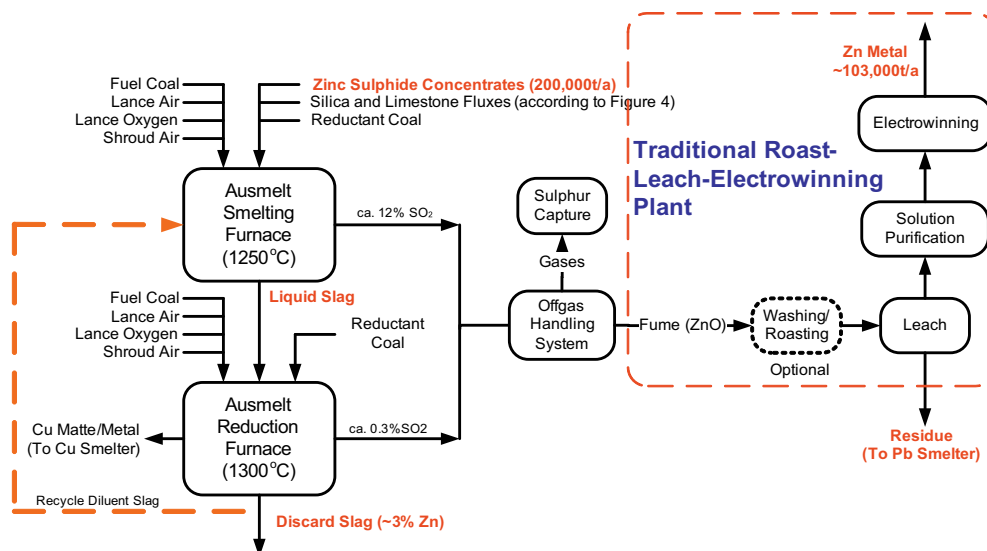


Fig. 3. Conceptual flowsheet for zinc sulphide processing (the block on the right is the front end of a traditional zinc hydrometallurgical plant – hence the DZS process can run parallel to a RLE route extending an old processing plant's life with dumping issues).

readily processed in the traditional RLE process, a process was developed in which zinc is recovered from ZnS concentrate by the direct ZnS concentrate smelting/volatilization in a Top Submerged Lance (TSL) furnace process. The recovered zinc in the form of a crude zinc oxide product is suitable to be treated by the conventional zinc RLE process. This will be discussed in more detail in the next section.

2. Features of the Direct Zinc Smelting (DZS) Process

In this section the various main operating steps of the DZS process are presented and discussed in some detail based on a 200,000 t/a feed rate of concentrate. The main steps of the DZS process are depicted by Fig. 3 noting that the furnace details are depicted in Fig. 4:

- During Stage 1 the zinc concentrate is smelted and zinc fumed directly as zinc metal. The basic reaction is: $ZnS + O_2(g) = Zn(g) + SO_2(g)$ ($\Delta G^\circ_{1250^\circ C} = -168.1$ kJ/mol). Oxygen and air pass through the TSL lance, while the concentrate and fluxes are fed through the roof of the furnace. Conditions are controlled

according to Fig. 5 e.g. by slag recycle or zinc residues and oxygen partial pressure.

- During the reductive Stage 2 the slag, which contains around 25% zinc, is fumed to produce ca. 3% zinc in slag producing zinc vapour. 40% of Stage 2 slag is recycled back to Stage 1 to dilute the zinc content in the smelting Stage 1 to 25%. The basic equation is: $ZnO + C = Zn(g) + CO(g)$ ($\Delta G^\circ_{1300^\circ C} = -101.7$ kJ/mol) controlled by the slag chemistry of Fig. 6.
- The zinc vapour is reoxidized according to $Zn(g) + 0.5O_2(g) = ZnO$ ($\Delta H^\circ_{1750^\circ C} = -455.5$ kJ/mol), which is highly exothermic. The dust is collected in a Bag-house or electrostatic precipitator (ESP) optionally washed to remove halides/sulphate/lead and subsequently leached in a neutral leach leaching circuit (which could be an available RLE circuit).
- The created SO_2 is converted to sulphuric acid, while all other particulates are collected to environmentally acceptable levels.

To remove lead, halides and sulphur from the fume it can be co-treated in the roaster of a RLE if this is operating parallel to the DZS process, otherwise a leaching step could be used to remove halides, sulphates, etc., which would however make Na_2SO_4 recovery (or

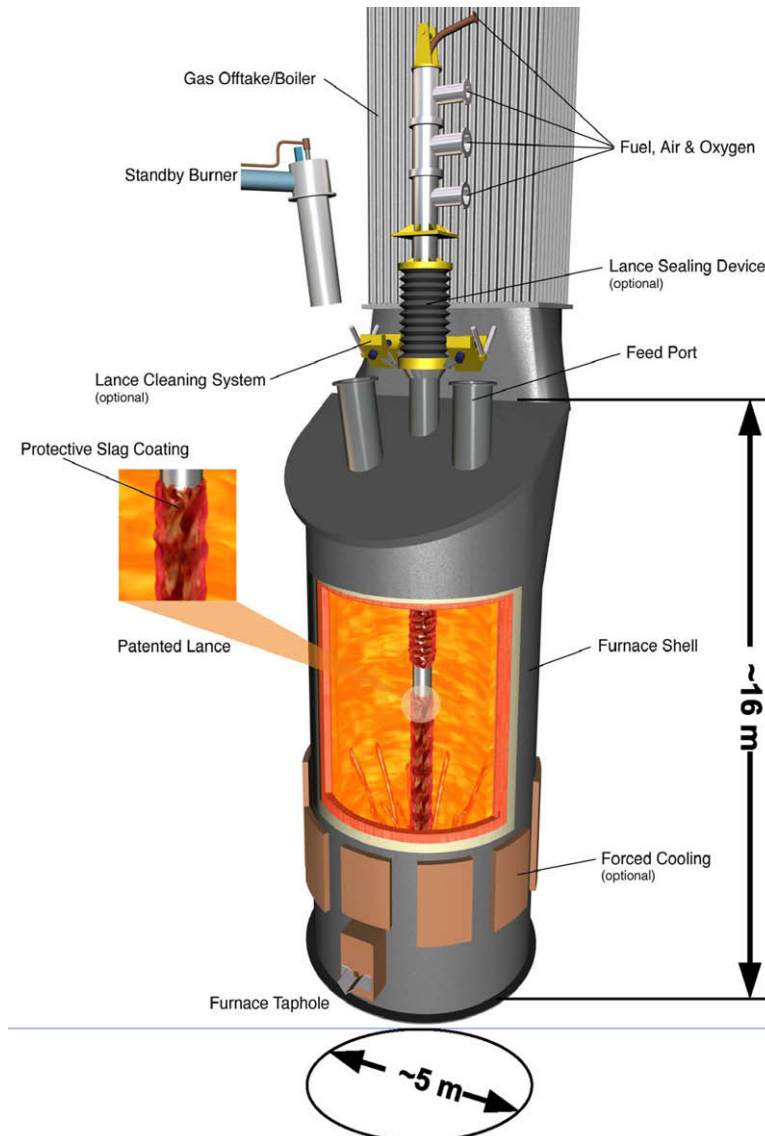


Fig. 4. A typical TSL furnace showing among others dimensions, architecture, lance structure, refractories, cooling panels, taphole, boiler system, and the basics of the lance operation.

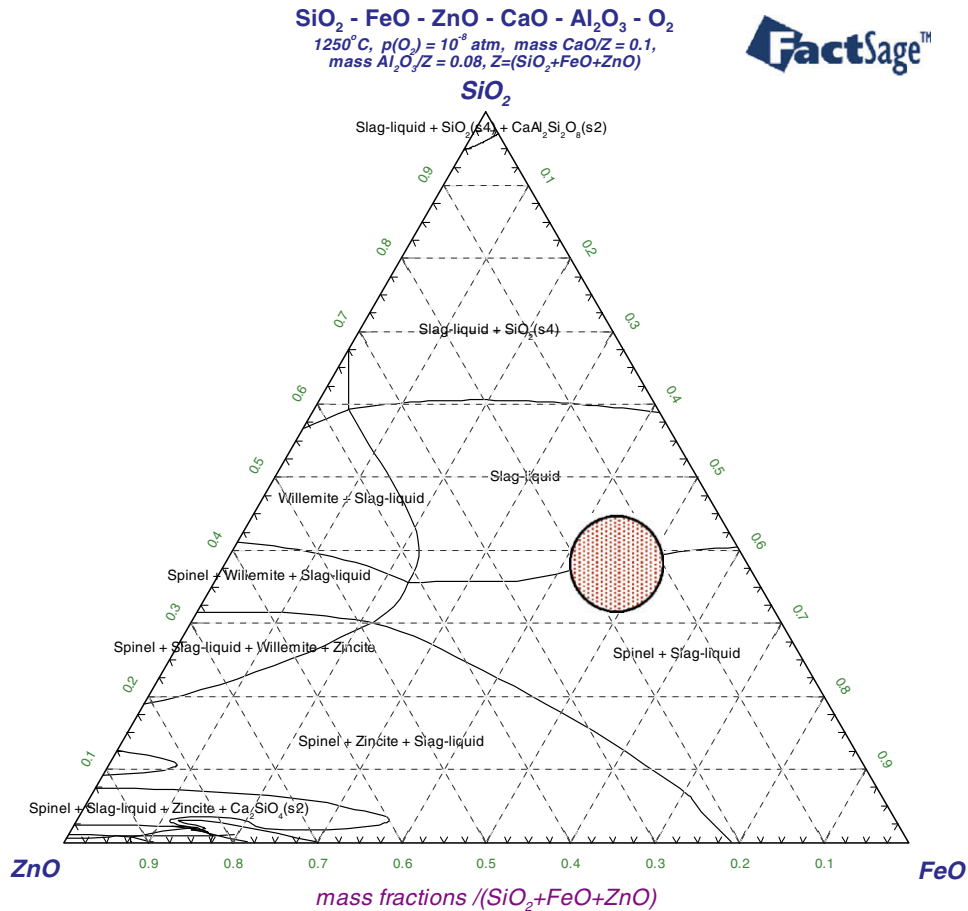


Fig. 5. Simplified slag phase relationships for zinc direct smelting (Stage 1 at 1250 °C) in a TSL furnace showing the Slag-liquid area and typical operating point for smelting conditions. Note that only a few major components were selected, i.e. FeO_x, CaO, ZnO, Al₂O₃, and SiO₂ (FeO must be read FeO_x).

other means) from the leach solution necessary to control the sulphur balance of the leaching circuit.

2.1. Stage 1: smelting at 1250 °C

In the first stage, the concentrate is introduced to a starter slag bath, whereby the smelting of ZnS concentrate under controlled partial oxygen pressure conditions begins according to the theoretical considerations elaborated on by Yazawa (1979). A substantial part of the zinc is eliminated by volatilization as metal vapour, which is subsequently post-combusted to zinc oxide fume. From our industrial experience the zinc content in the slag should in practice not exceed 25% to ensure that the liquidus temperature is sufficiently low. Fig. 5 reflects (noting that the diagram simplifies the industrial situation due to only considering the given slag components) that at the smelting conditions a maximum theoretical limit is around 37% as limited by the phase fields around the molten slag phase field at 1250 °C and $pO_2 = 10^{-8}$ atm (FactSage™, 1976–2007). However, this scenario can change sharply if much higher Zn contents in the slag are achieved i.e. the operating point moves into the adjacent fields that contain among others precipitated phases. The pO_2 , which can be controlled well in a TSL furnace, must also ensure that the magnetite levels are controlled well as shown in the phase field around FeO_x (bottom right) to ensure that the slag remains liquid. The Zn-content of the slag is also controlled by the pO_2 as well by the well-controlled internal recirculation of slag from Stage 2 containing only ca. 3% Zn. This dilutes the Zn content of the Stage 1 smelting slag. Note that about 60–65% of the zinc input is eliminated during Stage 1.

The reduction of the zinc level in Stage 1 slag is vital, since a high ZnO content increases the slag melting point and decreases the fluidity. It has been demonstrated that by maintaining the sufficiently low partial pressure of O₂ during Smelting Stage 1 up to 25% Zn in slag can be tolerated with ease as shown by the large liquidus area in Fig. 5 for the given concentrations of lime and alumina in the slag. Furthermore, a low partial O₂ pressure prevents the oxidation of ferrous oxide in the slag to ferric oxide the latter combining with ZnO to form high melting zinc ferrite (bottom right corner in Fig. 5). In addition lime is added to the slag in order to increase the activity coefficient of zinc.

The process gas of Stage 1 Smelting is rich in SO₂ (~12 vol.%). After heat recovery in a Waste Heat Boiler (WHB) and separation of the fume by Bag-house or ESP, the process gas is wet-gas-cleaned, further treated if required, and then processed in an acid plant to produce sulphuric acid.

2.2. Stage 2: reduction at 1300 °C

The Zn content of the Stage 1 slag is reduced from 25% to ca. 3% by volatilization reduction/fuming. The volatilized zinc is post-combusted and collected from the fume as ZnO dust. The bulk of the remaining zinc is eliminated via the slag in Stage 2. This slag has a final zinc content of between 1% and 3% Zn, which represents 1% of the original feed as the total zinc recovery is 99%.

Fig. 6 gives only a thermodynamic indication of the reduction step as it must be noted that fuming in a TSL furnace is also kinetically driven due to the large volume of gas flowing through the slag. This figure does show a large molten phase field in which zinc

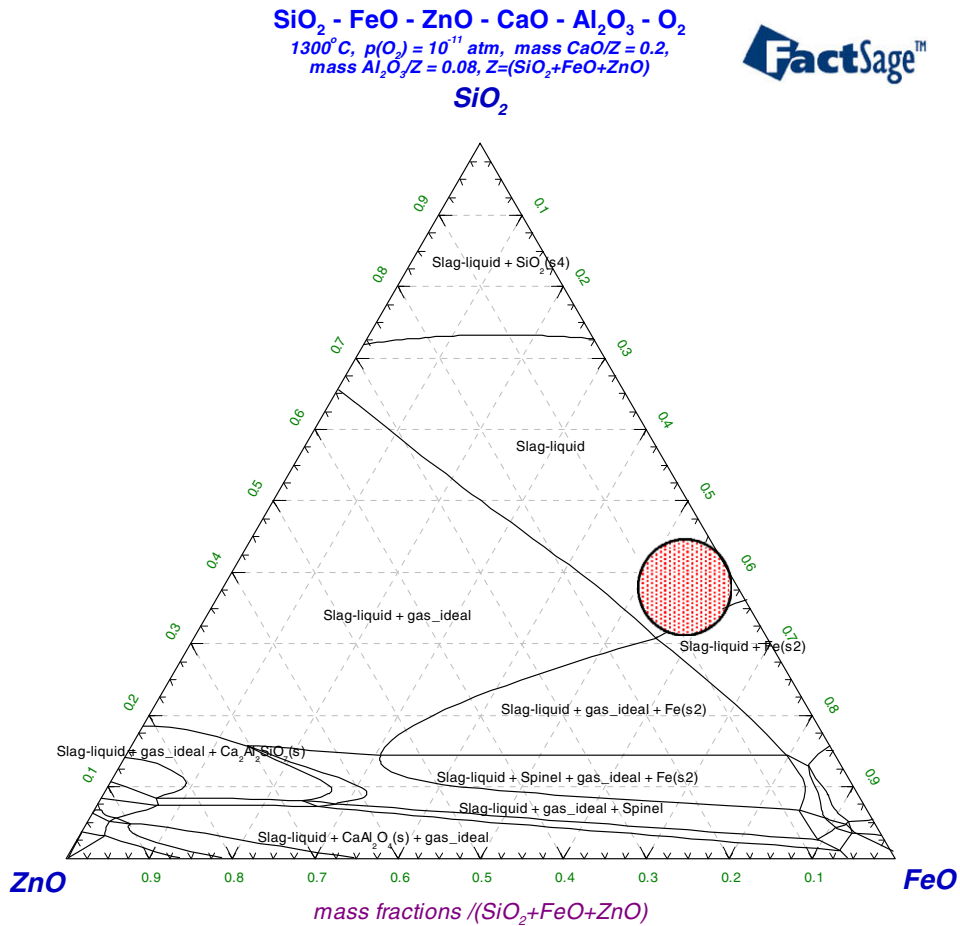


Fig. 6. Simplified phase relationships for the reduction Stage 2 at 1300 °C in a TSL furnace for the components FeO_x, CaO, ZnO, Al₂O₃, and SiO₂ (FeO must be read FeO_x) and the typical operating point.

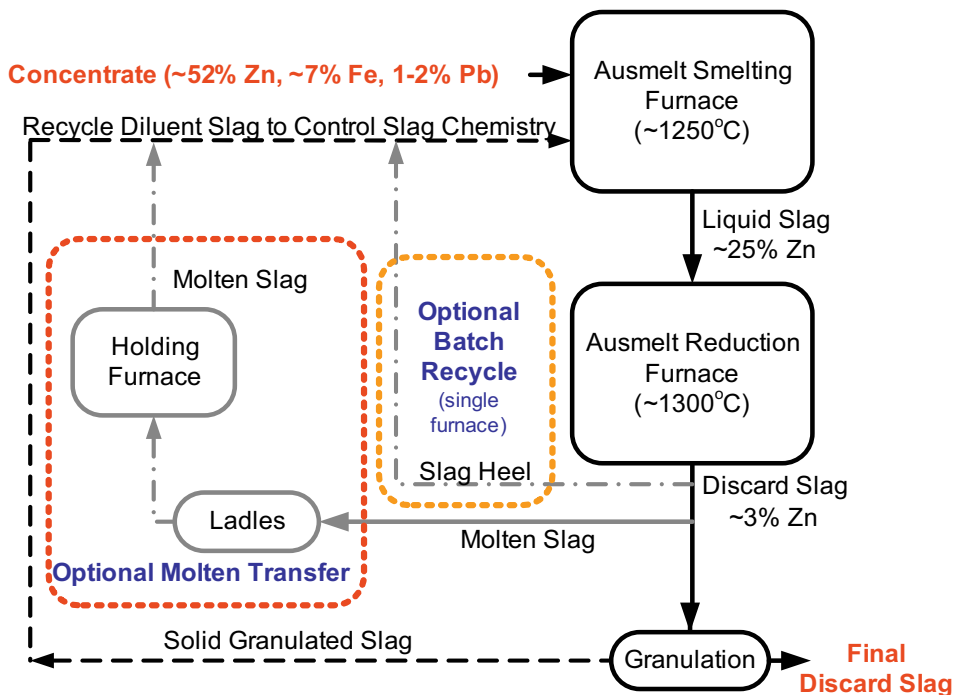


Fig. 7. Optional transfer methods for diluting the Zn in slag. (Slag recycle can be replaced by the use of zinc containing residues to control the slag chemistry.)

partially also exists as metal vapour at the simulated conditions at 1300 °C and $p_{O_2} = 10^{-11}$ atm (FactSage™, 1976–2007).

2.2.1. Stage 2: slag recirculation

A proportion of the total slag that is generated is re-circulated to Stage 1 smelting in order to dilute the Stage 1 slag to achieve the required zinc levels in the slag as dictated by the slag chemistry depicted by Fig. 5. The simplest way to perform the recirculation is, obviously, to granulate the second Stage 2 slag and to re-circulate the required quantity to Stage 1 smelting. In order to ensure sufficient Stage 1 slag dilution, the quantity of slag to be re-circulated can be high, i.e. about 40% of the concentrate feed based on a 52% zinc containing concentrate of ZnS.

Obviously the granulated re-circulated slag needs to be re-melted consuming energy in the form of coal. An alternative would be not to granulate the Stage 2 slag but to re-circulate it in the liquid state to the Stage 1 Smelting, of which there are two options available, either by ladle transfer or by batch operation keeping the molten slag bath as a starter heel for the next cycle (see Fig. 7).

The benefits of using molten slag recycle (ca. 80,000 t/a) may present some engineering issues that need to be addressed and weighed against the extra costs of solid slag recycle. Fig. 8 shows the energy balance in a system with cold slag recycle and Table 1 shows the changes when changing to molten slag recycle to help gauge the relative cost benefits of liquid slag recycle. It can be seen that as the coal fuel contribution to the energy balance is only minor (4%) as compared to the contribution from the concentrates, and the enthalpy of reaction, there is only a marginal (~10%) gain in fuel and energy costs from using molten transfer as opposed to solid slag transfer. This is however reflected in a 10% decrease in the heat available for recovery in the offgas. Molten transfer may only be of use where energy costs are extremely high, or the sulphur content of the concentrates (the main source of energy) is lower than usual.

Note as well that zinc containing residues such as jarosite (ca. 3% Zn), goethite (ca. 6% Zn), neutral leach residue (ca. 20% Zn), Electric Arc Furnace dust (>25% Zn) can be used to control the slag chemistry, as these also contain Fe. This has the advantage that residue ponds can be processed recovering e.g. In but also contained zinc and freeing up land. This would make slag recycling unnecessary.

Although molten slag transfer has its merits, it does detract from TSL's commercially proven environmental track-record due to it being a closed system, as zinc and other metals could fume from open ladles. Therefore, due to environmental reasons, granulated slag transfer would be recommended.

If DZS were operating parallel to an existing RLE plant, the iron containing residues that are created (jarosite, goethite, neutral

Table 1

Changes in consumptions using molten slag recycle instead of solid for 200,000 t/a feed and 40% slag recycle.

Consumptions	% Change
Lump coal	-9.16
Fuel coal	-19.38
Lance air	10.57
Lance oxygen	-11.59
Shroud air	-6.93

leach residue) could be used as diluents for the Stage 1 slag, hence making slag recycling unnecessary. Their high iron content would be favourable the slag metallurgy of TSL. This would be the most attractive solution as it does process the old residue material with the advantage that it alleviates capacity issues as well is unlocks the metal value in it e.g. indium that left RLE route through this.

2.2.2. Metal phase generation during Stage 2

Under the reducing conditions of Stage 2 as well as in the absence of sulphur a metallic phase will be formed collecting the non-volatile reducible elements such as copper and (residual) silver. In addition, gold, if present, would also be recovered to a large extent in the metal phase as will (residual) arsenic.

The entrainment of non-volatile inert solids with the process gas during the direct Smelting of ZnS concentrates amounts to about 1.6% of the non-volatile fraction of the total input, distributed equally (50%) between Stages 1 and 2. As a consequence the dilution of the ZnO fumes by inert material will be quite low. The fume is expected to contain 1–2% inert material (Fe_2O_3 , SiO_2 , Al_2O_3 , MgO, etc.).

2.3. Element distribution

The distribution of various elements is summarized by Table 2, which provides an overview of the degree of volatilization of important elements in the feed. A more detailed discussion follows below as well as a general flow sheet for the leaching is depicted by Fig. 9. Various of these elements are recovered as sulphides under sulphide smelting conditions (e.g. $AgS(g)$, $SbS(g)$, $InS(g)$, etc.) or under reducing conditions fumed off as metals that re-oxidize and report to the zinc fume as oxides (HSC, 1974–2007), while copper will report to a metal phase during reduction.

2.3.1. Non-volatile accompanying elements/compounds

Non-volatile accompanying elements or substances are:

- Fe, Cu, Ni, Co, Au, Mn, Cr, and
- SiO_2 , Al_2O_3 , CaO, MgO, and TiO_2 .

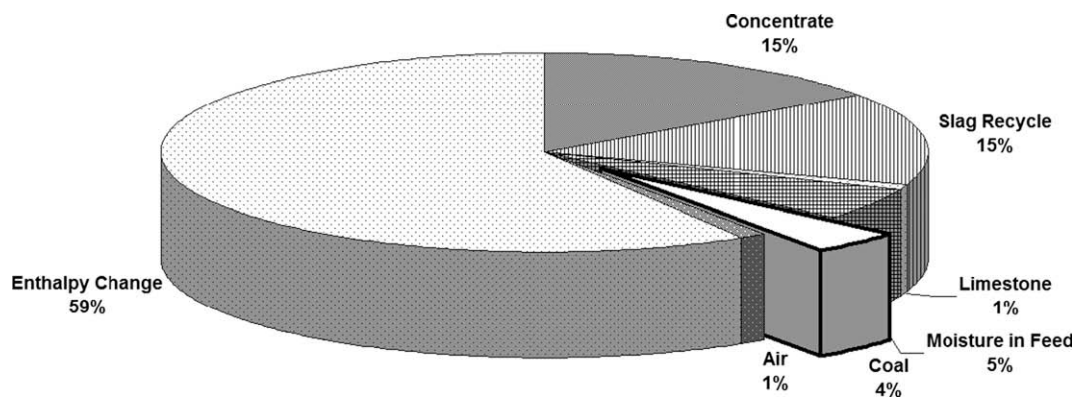


Fig. 8. Indicative energy balance in the smelting furnace based on 200,000 t/a concentrate feed (52% Zn) in Figs. 3 and 7 and ca. 40% cold slag recycle as depicted by Fig. 7.

Table 2
Approximate behaviour of elements during direct smelting of ZnS concentrates.

% of input with conc.	Zn	Pb	Ag	Cd	As	Sb	Cl	In	Ge	Hg	S
Stage 1	62	93	87	68	72	24	~100	63	59	~100	7
Stage 2	37	6	12	27	17	62	0	31	35	0	0
Total volatilized	99	99	99	95	90	86	~100	94	94	~100	100
Reporting to Zn fume	99	99	99	95	90	86	100	94	94	0	7
Reporting to metal/speiss	0	0	0	0	6	5?	0	3	3	0	0
Reporting to discard slag	1	1	1	5	4	9	0	3	3	0	0

These elements will report either to the slag or to the metal alloy phase (Cu, Au). This means that their presence in the ZnS concentrate, even at more elevated concentrations, will not significantly affect the Zn-winning process. Of the valuable elements only Cu and Au will be recovered, while Ni and Co are expected to be lost with the slag as will be manganese and chromium. The fact that especially Fe and Mn (and some of the gangue oxides) are recovered to a benign slag makes this an extremely interesting process route as these are problematic during RLE.

2.3.2. Volatile accompanying elements

Volatile accompanying elements are:

- Zn, Pb, Ag, Cd, As, Sb, In, Ge, Tl, Se, (Te) and probably Sn, and
- Cl, F, Na, K, and Hg.

With the exception of Hg, all of these elements will report to the ZnO fume in a more concentrated form. The degree of collection to the fume might vary due to the difference in volatility as a function of whether the dry gas cleaning is performed at a higher temperature ESP or at lower temperature in a bag-filter. This has an impact particularly on Cl and F, as well as possibly also Se.

All of these elements will dissolve up to their solubility level during the sulphuric acid ZnO fume leaching process (Fig. 9), which is low for Pb, Ag, Sb, and Sn, which will therefore mainly report to the Pb/Ag residue. The other elements are removed from the leach circuit by means of:

- Selective precipitation from the (weak acid) leach solution in the case of As, In, Ge and residual dissolved Sn,
- Cementation during the neutral leach solution purification: Cd, traces of As, Sb, Se and Tl, and

- Bleed of solution: Cl, Na, and K (the latter two only present at low concentration in ZnS concentrate).

It must be noted that some sulphate is created in the zinc fume e.g. insoluble lead sulphate but also soluble sulphates that do affect the sulphur balance in the leaching circuit, which will therefore have to be bled from the system as gypsum. This does have a negative economic impact.

2.4. Leach liquor purity affecting current efficiency

The most critical issue for the ZnO fume leach process is the ability to produce a purified solution at acceptable costs in order to be able to achieve high current efficiencies during zinc electro-winning. The concentrations of very critical impurities such as Co, Ni, In, Ge, As, Sb, and Tl must be sufficiently low in order to be able to purify the neutral leach solution to the very low concentrations required for electrowinning, all obviously at a reasonable or acceptable cost.

2.5. Special considerations with regard to lead and tin

Since there is a high lead recovery in this process, high lead containing ZnS concentrates could create a zinc fume with high sulphated lead content (or rather partially sulphated lead) as well as PbO. This would create a PbSO₄ product that would need further processing as suitable separation of sulphur and lead may not have been achieved. This would necessitate additional processing steps which could be readily undertaken in a conventional TSL lead smelter thereby realising the lead and silver credits.

Tin is rarely present in ZnS concentrate. However, since tin can be volatilized as SnS(g) (as in the tin fuming process) or as SnO(g)

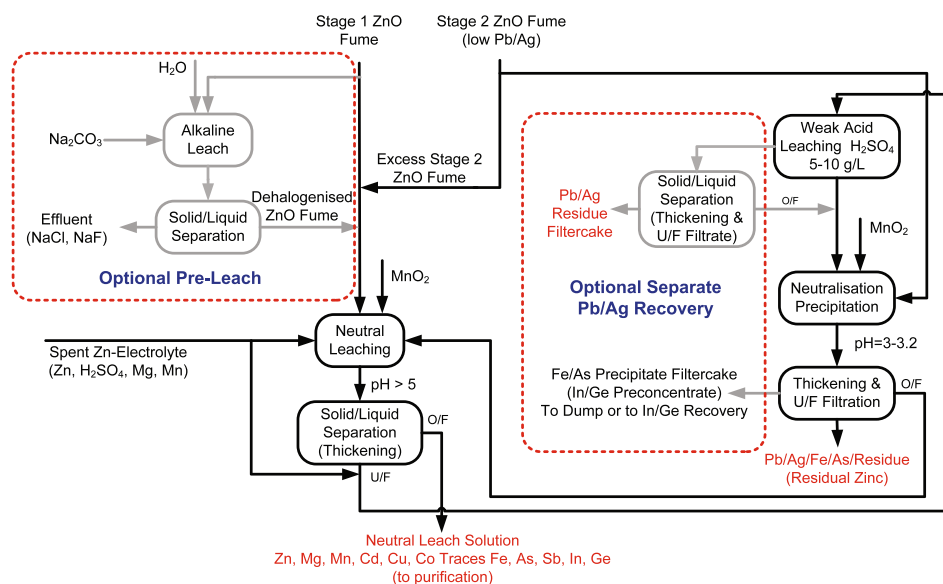


Fig. 9. Flowsheet for the sulphuric acid leaching of the ZnO fume from the DZS process with an optional dehalogenation leaching step shown.

(as in the converting process for black copper in the secondary copper smelting process) it may be assumed that tin will report to a large extent to the ZnO fume. During the sulphuric acid leaching of the fume tin will dissolve in the leach solution up to its solubility level. The removal of dissolved tin from sulphate leach liquors is believed not to be without any problems. Since generally tin is not present in ZnS concentrate information on the purification of neutral leach solution with regard to tin is extremely scarce. A dedicated process for tin removal may be required, particularly with regard to the difficulty of separation of the hydrolyzed gelatinous tin precipitate. As a similar condition would apply in the case of the RLE process, it is not expected that the DZS process would present a particular disadvantage as compared to the RLE process with respect to tin behaviour.

2.6. Economic and environmental advantages

The cost of residue deposition has often been an argument in favour of the implementation of processes which do not generate residues but valuable products. For example metallurgical slags could be used as building materials or can safely be deposited as they pass elution criteria in a much reduced volume than precipitates from hydrometallurgical processing. However, the cost of deposition of a wet solid residue (e.g. gypsum sludge, jarosite, etc.) in 2008 for Europe is assumed not to exceed €20/t of dry material.¹ If the residue is stabilized with cement at an addition of about 15% by weight of dry residue, and the stabilized residue is stacked on a tailor-made pad area, the deposition costs are expected to be slightly higher but not to exceed €25/t of dry material.² It may, therefore, be concluded presently that the cheapest way of disposal of wet solid residues is by ponding, or in a stabilized form.

However, the real issue with regard to the deposition of residues is not the cost of deposition itself, but the possibility of deposition, i.e. this is affected by public opinion, public awareness and ever increasing education concerning issues around environment, scarcity of land and past failures due to improper handling or solid waste mismanagement, just to name but a few issues. These issues have led the authorities to introduce legislative barriers, which are a deterrent to the implementation of new residue ponding facilities and extending new licenses (e.g. Belgium) or prohibiting them in total (e.g. The Netherlands). The introduction and application of eco-taxation for residue deposition is an example of a deterrent. It is expected that, in future, new operations generating wet solid residues will not be granted permission to be erected in areas of dense population, or suitable for agricultural and other industrial applications. These issues will all increase these deposition costs and hence the industry does need to act now. Due to dynamic change in zinc prices and changing treatment charges it is refrained from providing an exact analysis, but DZS does become attractive at relatively low dumping costs.

3. Conclusion

Since the early 1980s Ausmelt has been developing novel processes to recover zinc from both primary concentrates and secondary/recycle/residue resources. The success at Korea Zinc and the innovation of Ausmelt is a clear example as to the technological advantages that can be gained by using TSL technology in the pro-

cessing of residues originating/slugs from primary hydrometallurgical and pyrometallurgical processing of zinc and lead concentrates.

The DZS process as proposed and discussed has the potential to provide excellent metallurgical performance that recovers 99% of the Zn to a high grade ZnO fume, which is better than any other known metallurgical process. The major economic benefits are the use of sulphide sulphur (instead of fossil fuel) as the energy carrier and the ability to fume the zinc from the Stage 1 slag, without the need to remelt the slag. In addition, the DZS process enables the high recovery of Pb, Ag, Au, In, Ge, and Cu, which only could be recovered up to a level of 50–70% by the conventional RLE process (including residue treatment). In excess of 99% of Pb and Ag input will report to the fume, with Ge and In ranging from 90% to 95%. This is superior to any other known process, including the Waelz kiln process. It is subsequently relatively easy to recover these values from the fume, provided their concentrations are sufficiently high, ensuring that revenues exceed the cost of their extraction from the fume. The elements As and Sb will also concentrate into the fume. These two elements can be eliminated either with the Pb–Ag residue (when leaching the fume) or be separated as a separate residue depending on whether or not the recovery of In/Ge is economically warranted. About 93% of the sulphur input will be recovered as sulphuric acid, which is similar to the recovery of sulphur in the conventional RLE process.

The DZS process provides distinct metallurgical and economic advantages with reference to the RLE process for the processing of ZnS concentrates that have higher concentrations of non-volatile elements/compounds than the usual level encountered in ZnS concentrates which are used in the RLE process. These refer in particular to Fe, Mn, SiO₂, MgO but also to Ni, and Co, which in the DZS process report to a benign slag, making this extremely interesting for processing of high manganese and iron containing zinc ores.

Increasing dumping costs, the lack of dumping space and the non-issue of dumping permits in certain parts of the world are likely scenarios that will and does already confront the zinc industry in an ever increasing environmentally conscious playing field. This provides an interesting inclusion within the basis for comparison between the economics of the DZS vis-à-vis the RLE process, especially also if the positive aspect of harnessing the sulphur as energy carrier is considered in the analysis.

In summary, the DZS process is a (virtually) residue-free process that can be tailored to the needs of the zinc smelting industry, running possibly also parallel to classical RLE routes to clean up residue ponds and extend the life of well established RLE site. The slag, which is generated as an environmentally friendly benign slag, can be valorised to meet increasing strict environmental control for the disposal of metallurgical intermediate residues.

Potentially running RLE and DZS in parallel does increase the flexibility of a present facility to process a wide variety of feeds including residues and hence does lengthen the present life of well established RLE sites by decreasing their reliance on jarosite/goethite ponds. In addition, a wealth of metals present in the residues such as indium will be recovered.

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¹ An example out of practice to corroborate these values is the investment cost for a new deposition facility for jarosite, stabilized with cement according to the "Jarofix Process". The investment is quoted to be USD 15 Million for a period of 15 years, corresponding to USD 1 Million/a for a quantity of dry residue of 170 kta. The specific capital costs would, therefore, amount to about €5/t, reaching €20/t if operating cost of about €12–15/t (for cement, etc.) are added.

² As above.

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