

# EVALUATION OF PROCESSING OPTIONS FOR THE TREATMENT OF ZINC SULPHIDE CONCENTRATES AT SKORPION ZINC

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## ABSTRACT

Skorpion Zinc, an integrated zinc mine and refinery located in the South of Namibia, has a production capacity of 150 000 t/a of special high grade (SHG) zinc. The Skorpion zinc oxide resource will be depleted by 2017. Extensive exploration drilling for additional zinc oxides was conducted without success. With the abundant availability of zinc sulphide concentrates regionally (Black Mountain and Gamsberg in the Northern Cape or Rosh Pinah Zinc and new deposits in the Rosh Pinah region) the life of the operation can be extended by processing of zinc sulphide concentrates.

Leach kinetics of zinc sulphides are substantially slower than oxides, preventing the processing of zinc sulphides in the existing process under current conditions, and Skorpion Zinc faces the challenge to identify a suitable zinc sulphide treatment process that can be integrated with the existing plant. Various zinc sulphide processing options were identified through an extensive literature search and non-viable options were eliminated. Mass and energy balances were established for potential options and an economic evaluation (including capital and operating cost estimation) was conducted to identify a suitable process.

It is concluded that ferric leaching of sphalerite in a sulphate medium under atmospheric or pressure leach conditions are suitable processes for Skorpion Zinc. These processes present advantages over all other options when elemental sulphur is preferred as the final department for sulphide sulphur. Both these processes can be integrated into the existing refinery and will be able to process concentrates with a wide composition range.

## INTRODUCTION

Skorpion Zinc, an integrated zinc mine and refinery, located near Rosh Pinah in southern Namibia, produced its first metal in May 2003. The refinery has a production capacity of 150 000 t/a of special high grade (SHG) zinc (> 99.995 % Zn). The ore body, a substantial oxide resource averaging 10.9 % Zn, was discovered in 1976. The main minerals are sauconite (a zinc-bearing clay mineral), smithsonite (zinc carbonate), and hemimorphite (zinc silicate). The elevated silica levels and the presence of halides and challenges to upgrade the zinc ore resulted in a delay in developing a processing route that includes direct leaching of the ore, purification with via a solvent extraction process and conventional electrowinning to produce the final zinc product on site.

The Skorpion zinc oxide resource will be depleted by 2017. Extensive exploration drilling for additional zinc oxides was conducted without success. With the abundant availability of zinc sulphide concentrates regionally, from Black Mountain and Gamsberg in the Northern Cape or Rosh Pinah Zinc and new deposits in the Rosh Pinah region, consideration is given to convert the Skorpion Zinc refinery to process zinc sulphides. Concentrates can also be imported via Luderitz harbor, approximately 400 km from Skorpion Zinc. Leaching kinetics of zinc sulphides are significantly slower than those of oxides, preventing the processing of zinc sulphides in the existing process.

For sulphide ores, a concentrate containing zinc sulphide as sphalerite or marmatite is usually produced. The standard process for zinc sulphide concentrate treatment is the Roast-Leach-Electrowinning (RLE) process. This process is highly efficient in converting the zinc to special high grade zinc metal by roasting to zinc oxide, acid leaching and purification and electrolysis to zinc metal. The economics of this process are favorable when a market for sulphuric acid exists.

There is a whole host of alternative hydrometallurgical processes for zinc. Sphalerite and marmatite are highly leachable in a variety of solutions including sulphuric and chloride media. As is often the case in hydrometallurgy, the sulphate route for zinc recovery has received the most commercial application with the Dynatec Zinc pressure Leach, the Outotec (previously Outokumpu) atmospheric leach and the Union Minière atmospheric leach installed at a number of sites. These processes essentially avoid the roasting step of the RLE by directly dissolving zinc from the sulphide mineral followed by purification and electrolysis. These three processes have all been used to add incrementally to zinc production by being installed alongside existing RLE plants. The Dynatec pressure leach and the atmospheric leach processes have been installed in few instances as “stand alone” facilities (Filippou, 2004).

The challenge for Skorpion Zinc is to identify a suitable zinc sulphide treatment process to be integrated with the existing plant. The selection of a process option will have to consider the cost of implementation, i.e. the time and capital required to convert the existing refinery to process zinc sulphides, including the impact on production output. Consideration has to be given also to various feed sources available, ensuring Skorpion Zinc remains a low cost zinc producer in a volatile market and economic climate. Important considerations for a suitable process for Skorpion Zinc are:

- A process with more favorable economics will be preferred. This implies low operating and capital cost with high zinc recovery.

- Low technical risk. A process that is commercially proven will be preferred against other options to reduce the risk of achieving design production and operating cost.
- Schedule of implementation. The oxide resource will be depleted by 2017 and the new process must deliver the first zinc in 2017. Any process delivering zinc after this date will be discarded.
- Skorpion Zinc is located remotely and cannot competitively deliver sulphuric acid to market. A process that produces sulphuric acid will be considered as undesirable.
- A low impact on safety and health of employees and low environmental impact will be preferred.
- Skorpion Zinc is committed to a low carbon footprint and to reduce the use of natural resources. Processes with low energy and water consumption will be preferred.

This paper will present the process followed to identify a suitable zinc concentrate processing route for Skorpion Zinc. The initial screening and evaluation on potential processes will be discussed with the objective to eliminate unfavorable processes. The remaining process options will be further developed in order to establish technical integration with the existing refinery and to establish the capital and operating costs of each selected option. A suitable process will then be identified.

### **SCREENING OF OPTIONS**

Figure 1 presents an overview of possible zinc concentrate processing routes compiled through a literature study. The pyrometallurgical processes involve the fuming of zinc, condensation as zinc oxide that is further processed by an electrolytic process (dissolution, solution purification and electrowinning) (Sannikov, 1998; Bartlett, 1985; Hughes et al, 2008; Buckett et al, 1998). In the Roast Leach Electrowinning (RLE) process, zinc sulphide is oxidized to form a zinc oxide that is also processed by an electrolytic process (Filippou, 2004; Huggare et al, 1973; Svens et al, 2003). The pyrometallurgical and RLE processes produce SO<sub>2</sub> gas as byproduct which is converted to sulphuric acid. Other processes involve the direct leaching and processing of zinc sulphides and can be further divided into atmospheric, pressure or percolation leach options. From all the processes, the Roast Leach Electrowinning (RLE) has been applied more widely and is the most popular process option in the 21<sup>st</sup> century (Figure 2). Several of the other processes have been established commercially and many hydrometallurgical routes proposed (but not developed commercially) to process more complex sulphides that could not be economically processed through the RLE or pyrometallurgical processes (Filippou, 2004). These processes will also be considered and evaluated.

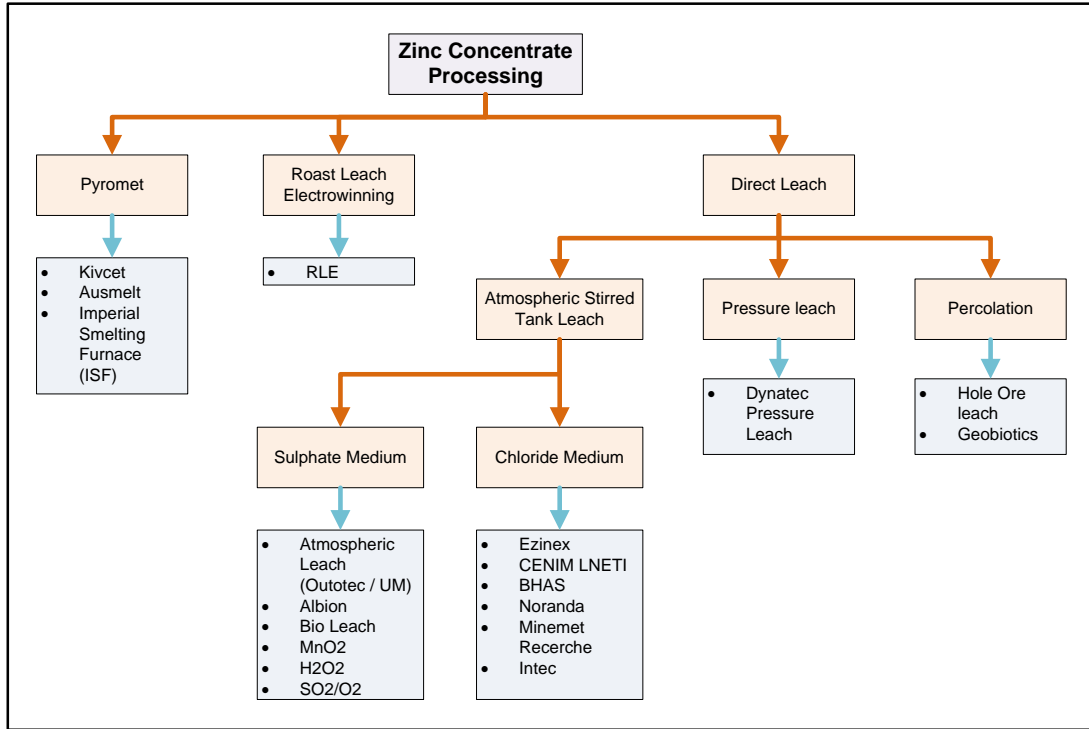


Figure 1: Overview of zinc sulphide concentrate process options

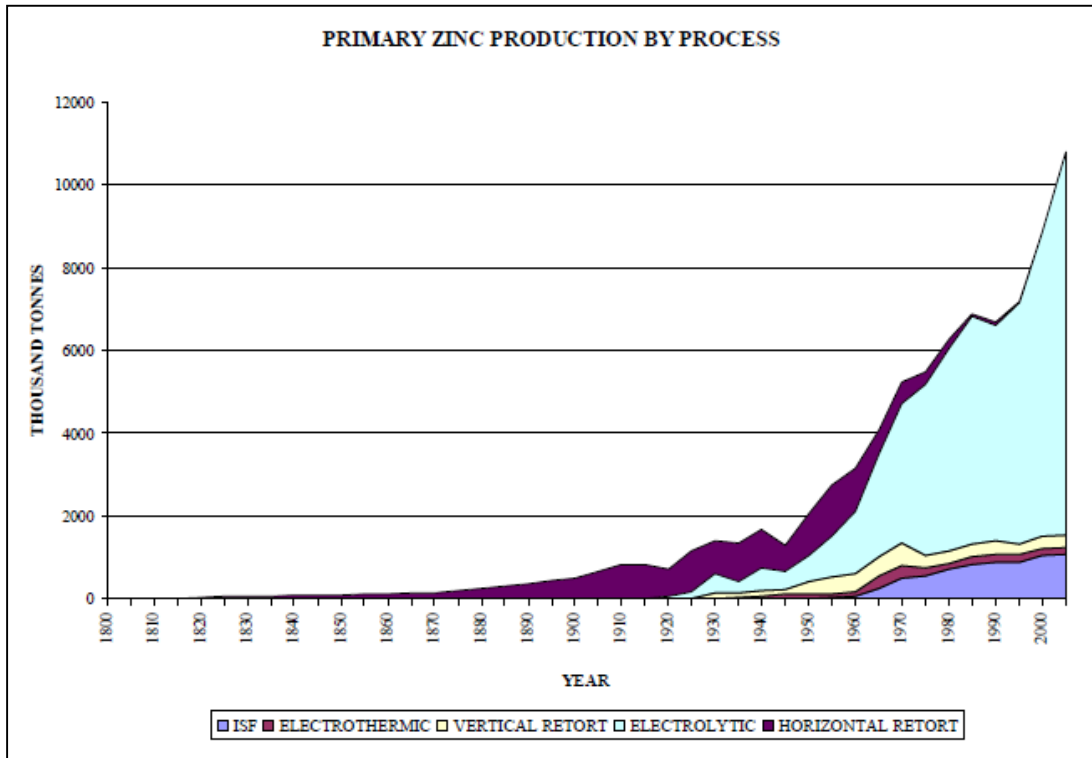


Figure 2: Primary zinc production by process (Brook Hunt, 2004)

**Pyrometallurgical** and the **RLE** processes produce sulphuric acid as byproduct. This acid is sold to a downstream user / local market for sulphuric acid. If no offset exists, it may result in stopping zinc production due to full sulphuric acid stock tanks or it will have to be neutralized and disposed of at high cost. Sulphuric acid is produced as a by-product in many refineries and a sensitive balance in the sulphuric acid market exists. The demand is also highly integrated with the world sulphur market. Sulphur is produced as a by-product in the oil refining industry at an oversupply and the long term forecasts is that an oversupply in the sulphuric acid and sulphur market will remain ([www.crugroup.com](http://www.crugroup.com)). Large consumers for sulphuric acid are typically the phosphate industry and other hydrometallurgical processes. Within South Africa there is a good balance between sulphuric acid supply and demand. The Uranium industry located near Swakopmund in Namibia is a net consumer for sulphuric acid. Skorpion zinc is very remotely located in the south of Namibia and will not be able to deliver sulphuric acid competitively to any of the two markets due to high transport costs. A pyrometallurgical or the RLE process at Skorpion will therefore increase the business risk. Having your primary business linked to another market, especially a by-product market, will be a disadvantage. The pyrometallurgical and RLE processes will therefore be discarded as options Skorpion Zinc.

There are two options to consider when the **percolation leach** process is considered. The first is the 'Geocoat' process from Geobiotics where the zinc sulphide concentrate is coated on an inert substrate before stacked and leached ([www.geobiotics.com](http://www.geobiotics.com)). The leaching process takes place in a sulphate medium at low pH. Zinc sulphide is leached by ferric as oxidant. The ferric is regenerated by oxygen and bacteria. Although it has not been commercialised to process zinc concentrates, it was applied at Agnes (South Africa) to leach refractory gold concentrates. This mine is no longer operational. Some other projects are also under evaluation but not implemented yet. Harvey et al (2002) reported 95% recovery from concentrates on laboratory scale. This recovery is expected to reduce on commercial scale due to the inherent challenges of solution distribution and percolation in heaps. It will be hard for this option, processing high grade concentrates, to compete with alternative options with high recovery and slightly higher capital investment. This option is discarded based on the limited commercial implementation and the long time associated with heap leach piloting and demonstration test work.

The second heap bioleach option (Teck Cominco's HydroZinc process) is to process the mined ore directly (Lizama et al, 2003; Hunter et al, 2004). This option therefore, cannot be compared directly to the other options discussed in this chapter as it does not process a concentrate. This option is therefore compared to the crushing, milling, flotation and leaching capital and operating costs. This process can only be considered as an option for Skorpion Zinc if a complete new mine is to be developed, where capital investment for a milling and concentrator plant can be offset with the capital cost of setting up a heap leach operation and where the mine is located close to Skorpion. At present, potential feed sources are not close to Skorpion Zinc and trucking of a low grade whole ore will not be viable due to the high transportation cost and therefore this option is eliminated.

The Dynatec **pressure leach** process involves the ferric leach of zinc sulphide at 150°C in a sulphate medium. Ferric is regenerated by pure oxygen injected into the autoclave. It is a mature technology with successful implementation at various sites in the gold, platinum and base metals industries. The Dynatec (previously Sherrit Gordon) pressure leach was first applied to treat zinc sulphide concentrates

commercially in 1981 in the Cominco Zinc plant at Trail, British Columbia. The zinc pressure leaching plant included a single autoclave designed to treat 188 t/d of zinc concentrates (Ashman et al, 1990). It was an add-on to the existing RLE plant to expand capacity. Following Cominco, the pressure leach has been added to existing RLE plants to expand capacity at Kidd Creek (now Falconbridge) and a third plant at Ruhr Zink in 1991 (Buban et al, 2000). The first two-stage pressure leach for zinc sulphide concentrates was commissioned during 1993 as a replacement for the RLE process at Hudson Bay Mining and Smelting Co., Ltd. (Barth et al, 1998). The two-stage pressure leach (stand-alone) option will be applicable to Skorpion. The two stage process has significantly less free acid in the PLS solution compared to the single stage process, which developed as an add-on to an existing process flow sheet where the residual sulphuric acid is consumed.

One of the primary advantages of this process is that sulphur reports to elemental sulphur which can be recovered or discarded with the residue. This is a critical consideration for Skorpion as discussed earlier. This process further has high zinc recovery with lower capital investment compared to the RLE process and has more flexibility to treat concentrates containing iron, silica and lead. It can tolerate a higher amount of pyrite and hence could positively impact zinc recovery at the concentrators. Silicates are essentially inert to the zinc pressure leach process and concentrates with high silica content are readily treated (unlike the RLE process).

The downside of this process is a higher energy cost (compared to the RLE process) as the energy released by converting elemental sulphur to sulphuric acid is not harvested. It further requires pure oxygen for the process at high cost. Although proven technology, operating at high pressure increases safety risks and requires a higher level of attention during operation and maintenance. No fatal flaws associated with this process option have been identified so far. Further development is required to establish the economics of this process.

The **atmospheric leach** processes can broadly be divided into two categories based on the leaching medium - chloride or sulphate. The leaching mechanisms in these media include acid leaching, alkaline leaching and oxidative leaching. Various **atmospheric leach processes in chloride media** have been developed including: CENIM-LNETI (Figueiredo, 1993, 1995), EZINEX (Olper, 1998), INTEC ([www.intec.com.au](http://www.intec.com.au)), BHAS (Ricketts et al, 1989), Noranda (Allen et al, 2001), Minemet Recherche (Demarthe et al, 1978). The challenge to process complex sulphide ores economically and the need to achieve a residue-free process have driven the development of the various chloride based processes. The Noranda process could not deliver a high quality zinc product and recovery is low and therefore never developed past the laboratory scale. Though the inventors claim reduced operating and capital cost for the INTEC process with environmental benefits, it has not been developed beyond a locked-cycle batch processing pilot plant. The same applies for the CENIM-LNETI, EZINEX, BHAS and Minemet Recherche processes. Material of construction is also costly in a chloride leach environment in at elevated temperature (50-100°C) and is a disadvantage compared to sulphate medium processes. The chloride media processes might have some advantages when complex sulphides have to be processed to maximize recovery of all valuable elements. Due to the time required to develop these processes to commercial scale and the fact that Skorpion Zinc will process a typical zinc concentrate none of these processes will be further considered.

To simplify the discussion of **atmospheric leach** of zinc sulphide **in sulphate media**, three categories will be considered. First the development of atmospheric leach process with oxygen injection (Outotec, Union Minière and Albion), second, the bioleach process and thirdly all other processes developed to laboratory stage.

Outotec (previously Outokumpu) and Union Minière independently developed an **atmospheric leach** process, initially as add-on process to existing RLE operations (Filippou, 2004; Van Put et al, 1999; Fugleberg, 1998). This process involves the ferric leach of zinc sulphide just below 100°C. Ferric is regenerated by pure oxygen injected into the reactors. The key to success of the atmospheric leach processes is the special designed reactors to enhance the oxygen dispersion in the slurry. The technology can be considered mature with low technical risk for implementation. This process has a high recovery with the primary advantage of producing elemental sulphur and not sulphuric acid. It has the perceived advantage over the pressure leach to have lower capital and maintenance cost due to operation at atmospheric pressures. This process also requires oxygen supply and has a net energy requirement, similar to the pressure leach process. As it operates below the melting point of sulphur, it has the advantage over pressure leach by not requiring a surfactant (such as Lignosulphonate or Quebracho). There are no fatal flaws associated with the atmospheric leach process and the economics compared to other potential options for this process will have to be evaluated further.

The **Albion** process depends on a fine grind to achieve fast reaction kinetics to achieve reasonable economics (Hourn et al, 1996, 1999). Although this process has not been proven commercially on refractory minerals or zinc concentrates, aspects of the Albion process are being applied in industry. Fine milling technology is being applied successfully in the minerals processing industry and atmospheric leach processes for zinc sulphides have been proven to be successful. The first commercial scale project (Certej project in Romania to process a gold refractory ore – [www.albionprocess.com](http://www.albionprocess.com)) was due for commissioning towards the end 2011. Sphalerite is a sulphide mineral that leaches relatively easily compared to other sulphide minerals, which enables it to be leached under atmospheric conditions, as proven by Outotec and Union Minière. Test work has also proven that kinetics are enhanced by a finer particle size distribution. The solution chemistry is very similar to the pressure and atmospheric leach processes. The decisive question to be answered is whether the additional capital and operating costs for fine grinding can be offset by the reduced capital cost and operating costs of atmospheric leach by speeding up kinetics. There is no fundamental flaw but also no clear advantage to this process. Further development is required to establish true capital and operating costs more accurately.

Although the stirred tank **bioleach** process has not been commercialised in zinc processing, it is commercially applied in the gold industry and can therefore not merely be rejected (Filippou, 2004; Steemson et al, 1994; Nilsson, 1996; Sandstrom et al, 1997a,b). The role of the bacteria in the leaching process is to oxidise the ferrous to ferric for the leaching of sphalerite. Oxygen is provided by sparging air through the slurry, eliminating the need for expensive pure oxygen supply. Sulphur oxidising bacteria, also present, oxidise the product sulphur layer formed on the sphalerite surfaces. The downside of the bioleach process is the long residence time required. The sphalerite dissolution is surface reaction rate controlled (Harvey et al, 1993; Souza et al, 2007) and the kinetics is strongly driven by reaction temperatures. This explains the long residence times required for bio-leach (typically at

temperatures of 45-65°C compared to the atmospheric leach process at temperatures of 95-100°C. It further explains the reduction in residence time required when extreme thermophilic organisms are used allowing to operate at temperatures of 65°C compared to the MIM Bioleach process that operates at ~45°C with moderate thermophilic bacteria. In the order of 3-5 days of residence time is required to leach a zinc concentrate with a particle size distribution of 90% passing 45micron. At 15% solids concentration and the long residence time of the bioleach process, the reactor volume for the sphalerite leach would substantially higher than the atmospheric leach. Work by Sandstrom et al (1997a) indicated that residence time can be shortened by fine grinding (90% passing 20µm). This compares to a feed size distribution of the Albion process, but still with a much longer residence time due to the low leach temperatures. Due to the relatively low slurry densities, typical solution inventories in the bioleach process are substantially larger than in other processes, necessitating larger vessels for all downstream equipment. Xstrata (Hourn et al, 2005) conducted an economic trade-off study for a refractory gold ore where the Albion, Pressure Leach and Bacterial oxidation options were compared. This indicated that the bacterial oxidation process had the highest capital and operating cost.

Pyrite, the most noble sulphide mineral in the electrochemical series, also starts to oxidise under the conditions of the bioleach. All pyrrhotite is dissolved and some pyrite, resulting in the total iron dissolution between 30 and 90%, depending on the mineralogy, temperature, redox potential and leach conditions. At 65°C and redox potentials necessary to achieve high sphalerite dissolution, between 60 and 90% iron is dissolved, depending on the residence time (Sandstrom, 1997a). This is significantly higher than the atmospheric, pressure and Albion leach processes, putting it in a less advantaged position compared to the other processes, as a higher amount of iron has to be removed from solution (most likely as a jarosite due to the high iron content and relatively lower acidic conditions – jarosite is the least preferred iron residue).

This process has a further disadvantage compared to the pressure, atmospheric and Albion processes due to the oxidation of sulphur to sulphate. The additional sulphate is removed from solution by jarosite formation and excess sulphates have to be precipitated.

Zinc tenor from the bio-leach process (~30g/l) is not suitable for direct electrowinning which require zinc tenors in solution around 150-160g/l. A solvent extraction step is therefore required to upgrade the solution to become suitable for electrowinning. Although no capital cost will be required if this process is chosen for Skorpion Zinc, as a SX plant is already installed, it has higher sulphuric acid and neutralisation costs compared to conventional purification processes and hence is at a disadvantage compared to the pressure and atmospheric leach processes.

As this process presents some clear disadvantages relative to the pressure, atmospheric and Albion leach processes, it will not be considered further as an option for Skorpion Zinc. It has a potential application in the gold industry where the objective is to dissolve the pyrite and other sulphide gangue to liberate gold.

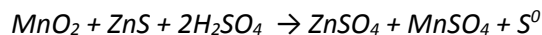
The processes discussed in the previous paragraphs, involves the leaching of sphalerite under oxidising conditions in an acidic ferric solution. **Other oxidative leach processes in sulphate media** have also been tested at laboratory scale:



- Mixture of SO<sub>2</sub> and O<sub>2</sub>
- Pyrolusite (MnO<sub>2</sub>)
- Hydrogen peroxide

Adams et al (1981) describe the leaching of metal sulphide concentrates at atmospheric pressure using SO<sub>2</sub>/O<sub>2</sub> mixtures. Their laboratory testwork indicates that SO<sub>2</sub>/O<sub>2</sub> mixtures of appropriate composition rapidly leach a variety of zinc concentrates at atmospheric pressure in aqueous solution containing sulphuric acid and ferrous iron. Their work indicates that oxygen to sulphur dioxide ratio of 1:1.5 is required for the reaction to occur. The oxygen consumption will therefore be fairly high if the gas is not recycled. This process has not been commercialised with the main challenge of the scale-up of this process due to the large airflow volumes required.

Filippou et al (2004) cited work by many others regarding the use of manganese dioxide as an oxidant for zinc sulphide. MnO<sub>2</sub> is a very effective oxidant at low pH and can directly leach zinc from zinc sulphides as follow:



However, electrowinning of zinc from solutions containing high levels of Mn is virtually impossible. A method to separate the Mn from the zinc rich solution needs to be found for this process to be successful.

The leaching of sphalerite concentrate by means of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an oxidant in sulphuric acid solutions was examined by Pecina et al (2008) and Aydogan (2006). Hydrogen peroxide is a strong oxidizer which forms water during the oxidation of sulphides. An increase in sulphuric acid and hydrogen peroxide concentration, temperature and decreasing particle size increased the leaching rate. Test work indicated a recovery of between 60% and 80%. With this low recovery and high cost of hydrogen peroxide it is unlikely that this process will be economical.

None of these processes (SO<sub>2</sub>/O<sub>2</sub>, MnO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>) have been developed commercially and will not be further considered due to the time it would take to develop these processes and the associated technical risks risk.

To summarise, the favored processes for Skorpion Zinc are the ones not producing sulphuric acid as by-product and which have been developed to commercial scale. The pyrometallurgical process and electrolytic (RLE) processes have been eliminated as they produce sulphuric acid as by-product. Hydrometallurgical processes in chloride media and processes involving oxidants other than ferric in a sulphide media have been discarded based on lack of development past laboratory scale. Bioleach processes have been rejected due to dilute sulphuric acid produced and the need for a subsequent solvent extraction process to upgrade the zinc tenor, suitable for electrowinning. Hydrometallurgical processes that involve ferric leaching in sulphate media (**pressure leach, atmospheric leach and the Albion process**) are favored and will be considered for further economic evaluation.

## DETAILED ANALYS OF FAVOURABLE OPTIONS

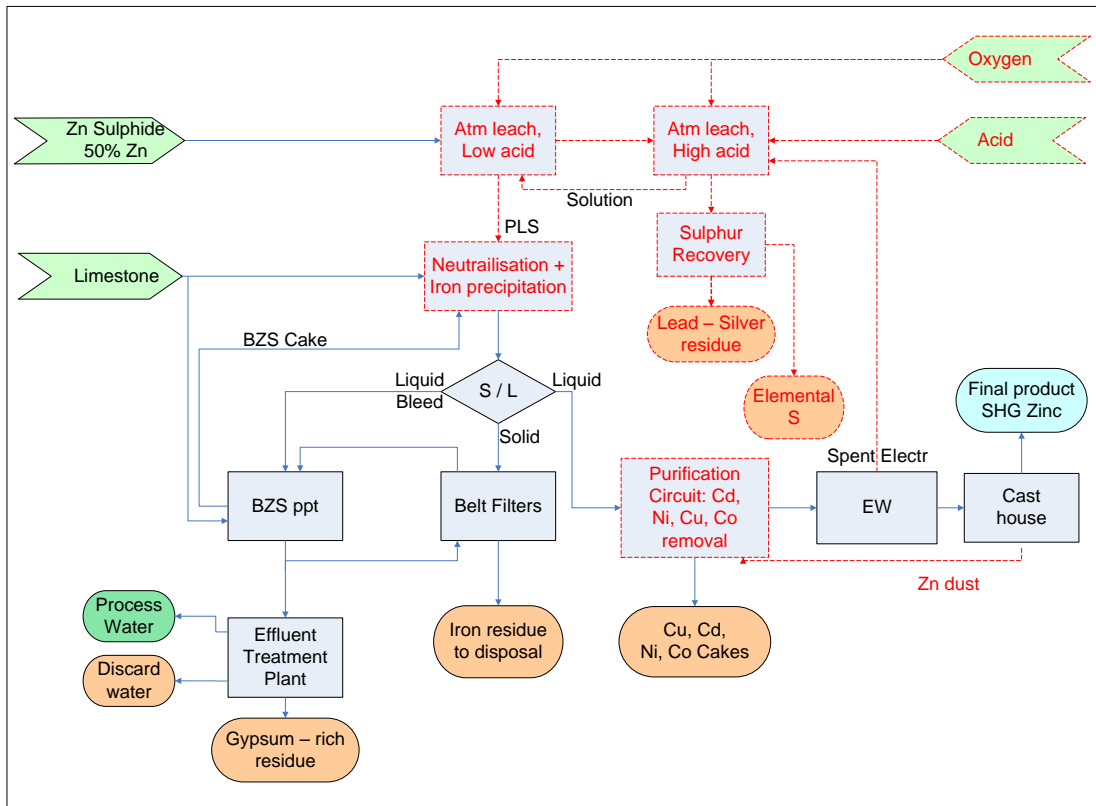
The selected process options will be further developed in order to establish technical integration with the existing refinery and to conduct an economic assessment. For the economical assessment a capital and operating cost estimate was established. A flow sheet and mass & energy balance for each process was developed and capital costs were estimated by establishment of mechanical equipment costs by HATCH Africa, using their database of recent completed projects (post 2001). Total capital cost was then estimated from mechanical cost by factoring of other costs (electrical, civil, instrumentation, project management, etc). Accuracy of the capital cost estimate is  $\pm 30\%$ . Operating costs were established by factoring maintenance cost, compiling organizational structure with personnel requirement and costing of reagents by actual reagent prices at Skorpion Zinc and volumes from the mass & energy balance.

Although the commercial pressure and atmospheric acid leach processes do not require a solvent extraction stage to upgrade the zinc, there could be a potential benefit from the solvent extraction plant as it provides an additional buffer to impurities for the zinc electrowinning stage. As a solvent extraction circuit is installed as part of the oxide process, no additional capital would be required. The impact of incorporating the SX with the proposed processes was evaluated by incorporating it as part of the pressure leach process for comparison. The pressure leach can be substituted with any of the atmospheric leach or Albion processes.

The flowsheet developed for each option will first be presented in this section followed by a discussion on the economics of the various processes.

### Atmospheric Leach

The process flow of the atmospheric leach is presented in Figure 3. Zinc sulphide concentrate is fed to a two-stage counter current atmospheric leach circuit at a rate of 34t/h. The two-stage process will be applied in order to reduce the residual free acid concentration in the PLS (reducing neutralisation cost). PLS solution from the Low Acid Leach (LAL) contains  $\sim 10\text{g/l}$  free acid and total soluble iron of  $\sim 8\text{g/l}$  by careful control of acid and oxygen addition. Solids from the first stage are transferred to the High Acid Leach (HAL) stage where it is subjected to a high concentration sulphuric acid leach for another 15hrs close to  $100^\circ\text{C}$ . Reaction enthalpy is sufficient to maintain temperature without any external heating required (Lahtinen et al, 2005). Solution from the HAL contains 13-14g/l Fe,  $\sim 48\text{g/l}$   $\text{H}_2\text{SO}_4$ ,  $\sim 134\text{g/l}$  zinc. Solids concentration is around 9% in both leach stages and oxygen is sparged into the leach trains to oxidise ferrous to ferric. The solids from the HAL contain elemental sulphur, some unreacted sulphides (pyrite and chalcopyrite) and insoluble sulphates (lead sulphate). A total residence time of 30 hrs has been used for this process (even though 24 hrs are recommended by Lahtinen, 2005). This is to ensure high zinc recovery of 98% is achieved at a concentrate feed particle size distribution of 90% passing 45 micron.



**Figure 3: Atmospheric Leach of zinc concentrates (dashed lines indicate new process units)**

The HAL solution is thickened and can be further processed to recover the elemental sulphur through a flotation and melting process. The PLS solution, with zinc tenors suitable for electrowinning (156g/l) is sent to sequential purification steps. Iron is firstly removed in an iron precipitation process. Any type of iron removal (jarosite, goethite or hematite) can be applied (Haakana et al, 2008). It is assumed for this study that a goethite removal step will be used due to the availability of Basic Zinc Sulphate (BZS) from the BZS process and limestone as neutralisation reagents. Limestone is present in the oxide resource and can be mined locally and milled to 90% passing 45  $\mu\text{m}$ . Iron will be precipitated at a pH between 3 and 4, with oxygen sparging to oxidise the ferrous to ferric. This process typically takes place at 60-90°C. The iron content in solution is reduced to 6-10 mg/l, suitable for electrowinning. Solid precipitated iron residue is filtered and washed with a zinc free solution, provided by the BZS plant.

Solution from the iron removal process is further purified by a cold and hot conventional zinc cementation process to remove Cu, Cd, Ni, Co and rare earths before processed in the zinc electrowinning plant, where zinc is plated.

New equipment that has been costed is represented by the dotted (red) lines in Figure 3. As specially designed reactors are required for the concentrate atmospheric leach process, the existing agitated leach tanks cannot be utilised and will be replaced. An oxygen plant will be constructed to supply oxygen for the atmospheric leach and iron precipitation processes.

The sulphuric acid consumption will be 4.6 t/h, about 10% of the design capacity of the existing sulphur burning acid plant, well below its turn-down capacity. This study assumes the buy in of sulphuric acid

and a trade-off study to construct a low capacity acid plant is recommended for a later stage. Offloading and storage facilities do exist at Skorpion.

Iron removal, especially the goethite removal described in literature, is typically conducted at temperatures between 60°C and 95°C. This is primarily done in order to achieve high reaction rates and reduces equipment sizing. In most of the processes the feed solution is already at high temperatures (from the leach processes) and no additional heating is required. In the proposed atmospheric leach circuit the LAL solution feeding the precipitation circuit will be around 70-78°C. The existing neutralisation equipment is designed for a temperature up to 55°C and therefore not suitable for the proposed neutralisation process. The reaction kinetics of the goethite iron removal process at 55°C need to be understood better to assess if the existing equipment could provide sufficient residence time for this process at lower temperatures, before a final conclusion on existing equipment can be made. The second challenge will be the high cost (capital and operating) required for cooling the solution down to 55°C to use the existing equipment and then heating it back up to 85°C for the following hot zinc cementation circuit. For the purpose of this study it was therefore assumed that the existing equipment will not be used, and the cost of a new iron removal circuit will be included.

The mass balance indicates that the flow rate of iron free PLS to the purification circuit is 177 m<sup>3</sup>/h, with a copper tenor of 0.9 g/L. The existing copper cementation circuit is designed for a flow rate of ~350 m<sup>3</sup>/h and solution tenor of 0.88 g/L. This indicates that the existing copper removal circuit is sufficient. However, the existing hot purification circuit (for Ni and Co removal) is sized for 70 m<sup>3</sup>/h and will have to be upgraded to process the targeted 177 m<sup>3</sup>/h.

The iron residue to be disposed of is estimated to be 22 dry tonnes per hour with significantly lower filtration fluxes than the current residue. The existing residue filtration is modular and able to process 195 t/h material. The existing system will be able to process the projected iron residue. The BZS circuit will provide wash solution for the iron residue as well as the lead-silver residue. The projected required feed rate to the BZS circuit is around 61 m<sup>3</sup>/h, which is within the turn-down ratio of the BZS plant. No capital is therefore required for modification of the BZS circuit.

Iron and the lead-silver residue may contain heavy metals that could be mobilised during high rainfall years. For the purpose of this study it has been assumed that all residue will be disposed on lined facilities. The selection of the goethite process above the jarosite will require a smaller footprint and reduce disposal capital requirements.

### **Dynatec Pressure Leach**

The Dynatec pressure leach (150°C) process flowsheet (Figure 4) is very similar to the atmospheric leach process flow. The leach process will also be conducted in a two-stage counter-current flow to achieve a lower final acid concentration of 8g/L and 2g/L dissolved iron. Zinc tenor in the LAL discharge slurry is 160g/l, sufficient for electrowinning without upgrading. The HAL solution contains 30g/L acid and 15g/L dissolved iron (Barth et al, 1998). The process chemistry of pressure leach and atmospheric leach is very similar, with the main difference in reaction kinetics and stability regions of jarosites. At elevated temperatures, the reaction kinetics are significantly faster (Harvey et al, 1993; Butinelli et al, 1992). At 150°C an overall residence time of around 2 hours (~ 1hr per stage) is sufficient to achieve 98%

dissolution of zinc sulphides. The downside is that special equipment (autoclave) is required to operate at elevated temperatures to keep water in the liquid state. This equipment requires high capital and skills for maintenance. The other downside of high pressure leaching is scaling that takes place in the autoclaves, resulting in bi-annual shut-downs to clean the autoclaves. To achieve high availabilities, typically a third standby autoclave is constructed and piped in to be used either as LAL or HAL stage. This further increases capital cost. The advantage though is a smaller footprint and associated civil and structural costs. Heat required for the pressure leach process and iron removal step is supplied by the exothermic reactions. Sulphur is also in the molten state, requiring the use of surfactants to prevent the coating of unreacted zinc sulphides.

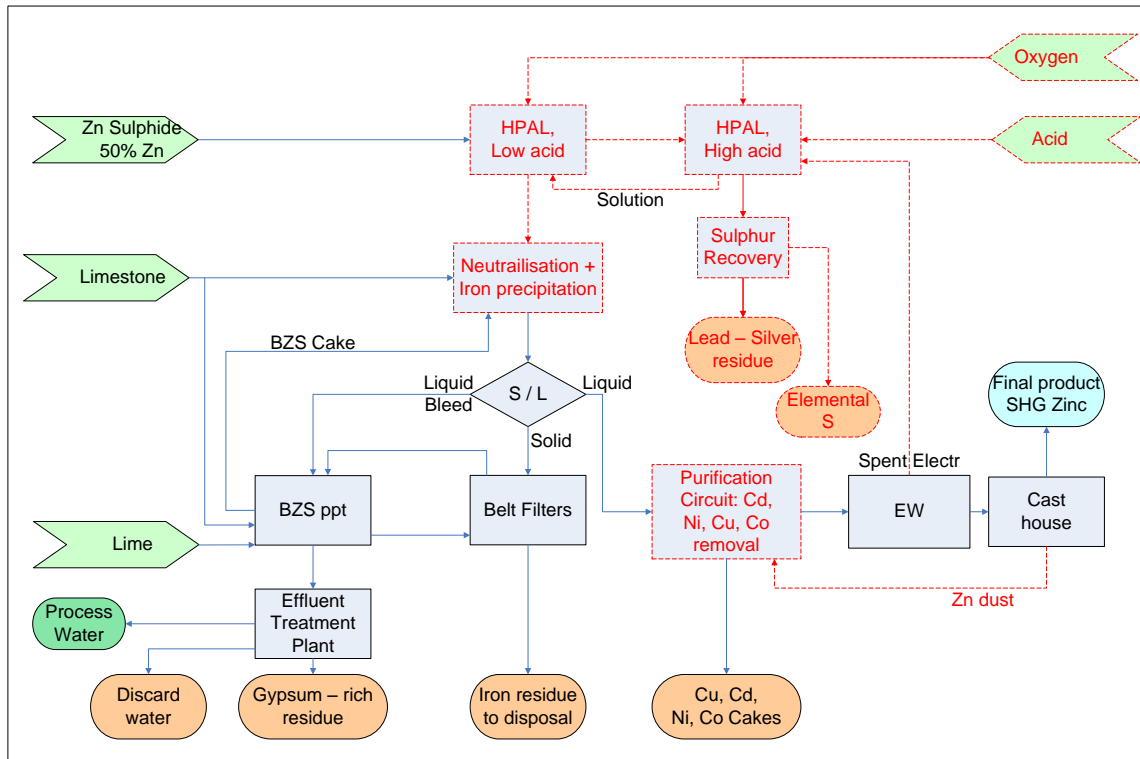


Figure 4: Pressure leach of zinc concentrates (dashed lines indicate new process units)

### Pressure Leach combined with SX

The leach section of this process is the same pressure leach as described earlier, with the difference that spent electrolyte is not returned to the autoclave, but rather the raffinate from the extraction circuit. PLS from the leach section will go through an iron removal step and residue through a wash step before disposed on a lined tailings facility.

As in the Skorpion Oxide process, Cu, Cd, Ni, Co will build up in the leach circuit and a removal step needs to be introduced. This can be achieved by either via a bleed circuit or by processing the total PLS stream, depending on the allowable copper tenor in PLS. When a certain threshold copper tenor in PLS is reached, there is some carry-over to electrolyte via entrainment. For this study, it was assumed that the threshold copper concentration is 0.9 g/L and therefore the full PLS stream will have to be processed through the impurity removal process.

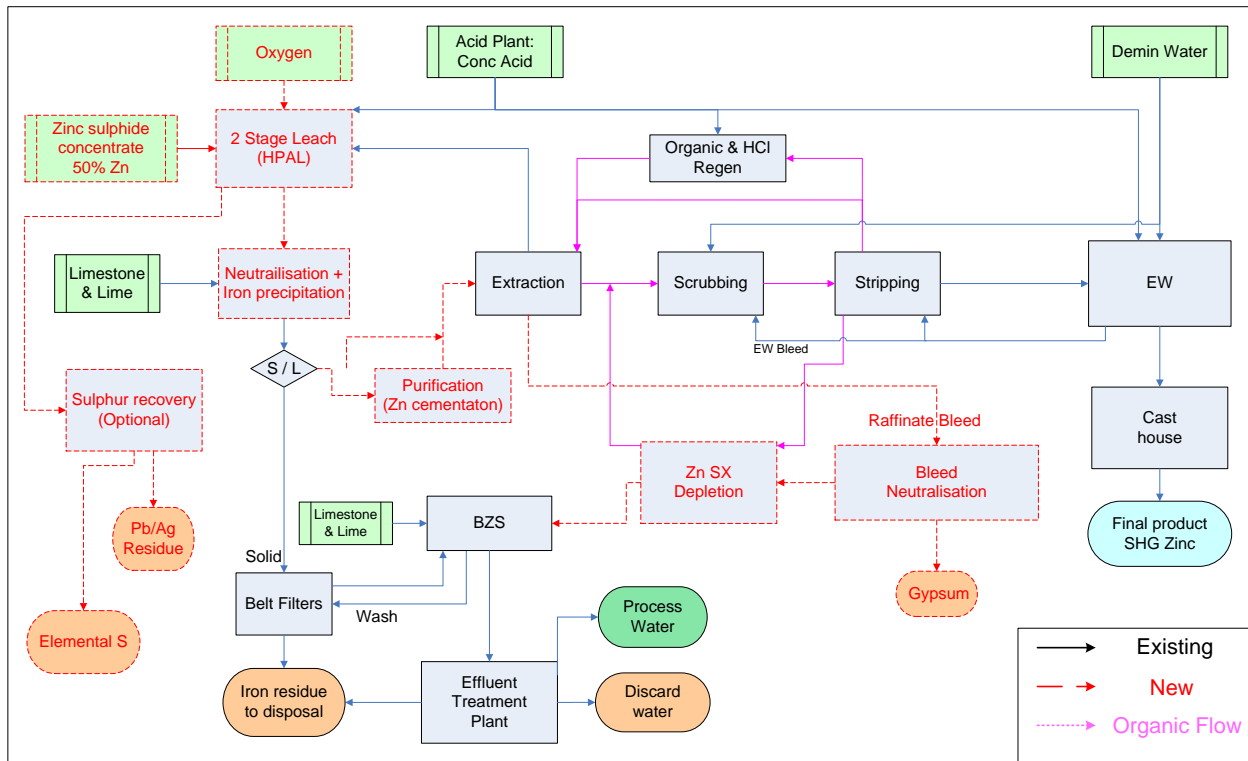


Figure 5: Pressure Leach with SX (dashed lines indicate new process units)

Zinc rich solution (145 g/L Zn) from the iron removal/purification circuit is extracted in the solvent extraction, leaving a raffinate with zinc tenor of ~55.4g/L. The expected percentage extraction is scaled up linearly from the current operating circuit. Isotherms for extraction at elevated temperatures and PLS zinc tenors will have to be developed if a more accurate estimate is required. For the purpose of this study the linear scale-up would be sufficient. Zinc is stripped from the loaded electrolyte and recovered in a conventional zinc electroplating process. Electrolyte has to be bled from the electrowinning process to prevent a build-up of impurities in the closed circuit electrolyte solution. Lost electrolyte is replaced with demineralised water and chemically pure sulphuric acid.

Excess water and sulphuric acid present in the circuit, mainly from the electrolyte bleed, scrubbing stages and acid requirement for the organic regeneration, necessitate a liquid bleed from the process. This is done by scavenging zinc from a raffinate bleed stream in a zinc depletion SX step and a final polishing step in the BZS circuit. From here the solution is bled from the circuit. Excess sulphuric acid is removed by a neutralisation step in front of the zinc SX depletion step. Acid consumption could potentially be reduced by 50% by using alternative technologies (such as resin or evaporative regeneration) to regenerate the hydrochloric acid used to remove iron from the stripped organic. The acid requirement to replace bled electrolyte will remain.

Acid consumption of this circuit at 8 t/h is roughly 18% of the design of the existing acid plant. This is significantly below the turn-down ratio of 30-40%. Significant modifications to the acid plant will have to be done in order to produce sulphuric acid at the required rate. It has been assumed for this study that the acid will be bought in.

The only benefit from this circuit is to provide an additional buffer for impurities, allowing production of producing SHG zinc in a more consistent manner. However, this will add much more complexity to the design and operation of the plant. The high sulphuric acid consumption and associated neutralisation and tailings disposal costs make this option very unattractive.

### Albion Leach

The process flow of the Albion process is presented in Figure 6. It is very similar to the atmospheric leach process with the difference of a milling step before the leach. Received concentrates (90% passing 45µm) is milled to ~90% passing 20 µm. The objective is to improve kinetics and reduce residence time in the leaching process, hence reducing capital required. Leach reactors will also require less power input compared to the Outotec reactors, as a more conventional stirred tank reactor with lower power input can be used. Oxygen is sparged into the tanks using a supersonic oxygen injection lance in combination with hydrofoil impellers to achieve the required mass transfer and leaching rate.

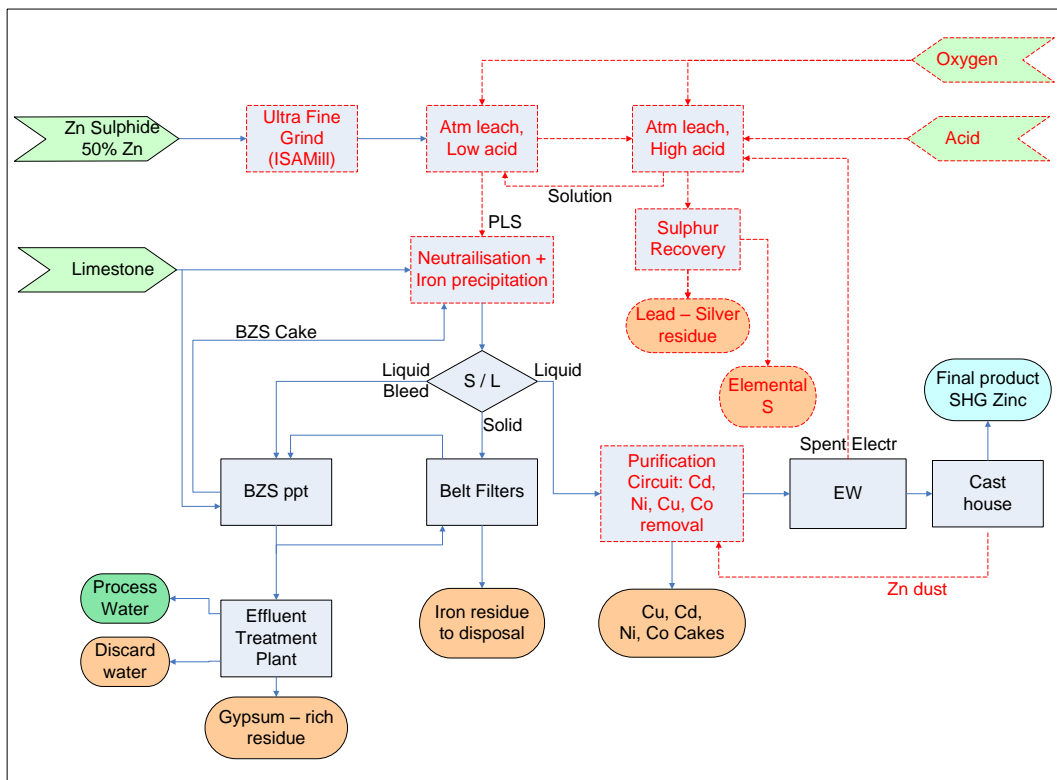


Figure 6: Albion process flow

The leaching process for the Albion process is very similar to the atmospheric leach process and the same reactions and rates have been assumed for the Albion process. The only difference is the required residence time that is reduced to 24hrs to achieve the same reaction extent.

When considering the fit with existing infrastructure and equipment, the same arguments as for the atmospheric leach prevail for the Albion leach. The existing oxide ore ball mill is not suitable for the ultra-fine grinding and will have to be replaced with the ISAMill technology provided by Xstrata Technology.

## Operating Cost

The reagent consumptions of the various options are presented in Table 1 below.

		Atmospheric L	Pressure L	Pres L & SX	Albion
Reagents	Units	Flow	Flow	Flow	Flow
Sulphuric Acid	t/hr	4.6	2.1	12.7	4.6
Limestone	t/hr	12.5	6.4	30.9	12.5
Hydrated lime (CaOH <sub>2</sub> )	t/hr	0.6	0.5	0.5	0.6
Oxygen	t/hr	7.6	7.6	7.6	7.6
Organic diluent	m <sup>3</sup> /a	-	-	1,593	-
Extractant	m <sup>3</sup> /a	-	-	103	-
Zn Dust	t/hr	-	-	-	-
Flocculant (total)	kg/hr	15.4	14.5	22.1	15.4
Lignosulphonate	kg/hr	-	79.5	80.7	-
Flotation Reagents	kg/hr	0.5	0.5	0.5	0.5
Water	m <sup>3</sup> /h	73.7	26.3	26.3	73.7
Demineralised Water	m <sup>3</sup> /h	-	-	107.6	-
Steam	t/hr	9.8	7.1	9.9	9.8
Grinding media	kg/t	-	-	-	0.5

**Table 1: Reagent consumption**

Sulphuric acid consumption for the atmospheric leach is twice the consumption of the pressure leach. This is a direct result of the leach conditions selected for the two processes – specifically the outlet acid, ferrous and ferric concentrations. Reaction extent for both processes was the same with the exception of jarosite that was allowed to form in the pressure leach process, also impacting on the acid consumption. Jarosite precipitation liberates acid and reduces the overall acid consumption. The process effluent tenors for sulphuric acid, ferric and ferrous chosen were sourced from literature. Extensive research and development were conducted and published on the pressure leach process since it was introduced in the 1980s. The atmospheric leach process was only commercially introduced in the late 1990s with comparatively less research and actual data published. Lathtinen et al (2005) report that the conditions in the atmospheric leach can be manipulated to achieve a wide range of acid tenors and redox potentials in the atmospheric leach process. This can very well be achieved by variation of the oxygen injection and slurry density in the leach. However, for the purpose of this study, parameter selection was based on published data. The mass and energy balance indicate that reagent consumption is very sensitive to the actual leaching kinetics and conditions and the form of iron precipitation.

The acid consumption for the pressure leach with SX is six times the acid consumption for the pressure leach alone, a major disadvantage of this process option. This is primarily a result of the water requirement of the washing stages of SX and the electrolyte bleed which consumes acid. Demineralised water is used to top up the water losses in the SX and EW circuits - further increasing the cost of this option.

The limestone requirement for the pressure leach with the solvent extraction results from the high acid consumption, as the refinery bleed stream (to balance Mg tenors and total solution) has a higher acid tenor, which has to be neutralised. Likewise, the higher limestone requirement for the atmospheric leach compared to the pressure leach is due to higher sulphuric acid tenor in the solution to the neutralisation section.



Oxygen consumption for all the options in the mass balance was assumed to be the same. The number reported in Table 1 is based on stoichiometric requirement. In reality, the oxygen conversion efficiency will differ between the atmospheric and pressure leach. Although Lathinen et al (2005) mentioned that oxygen consumption in the pressure leach is higher than in the atmospheric leach, it is expected that the oxygen will have lower efficiency due to the ambient operating pressure and the higher volumes of the atmospheric reactors. It has been assumed that the oxygen conversion rate for the atmospheric leach will be 87% of the conversion rate in the pressure leach reactors. This has been accounted for in the numbers presented in Table 2.

Although it is reported in literature that both the atmospheric and pressure leach processes operate autothermally due to the heat released by the exothermic reactions, there is a steam requirement in the sulphur melting process, the hot purification circuit and to pre-heat solutions to the leach sections. The pressure leach with SX has an additional heat requirement due to the cooling of PLS before the SX circuit that result in a heating requirement of the raffinate before it is fed back to the pressure leach circuit.

The calculated operating costs for each option are presented in Table 2. Again, it is expressed as a percentage of the total cost of the atmospheric leach. Around 55% of the cost is locked in fixed costs which include maintenance, labour, management, administration and support services. These were based on actual operating costs at Skorpion Zinc.

For the Albion process, the grinding cost includes energy consumption (assuming 25kWh/t energy requirement), grinding media cost and maintenance cost. Maintenance cost includes wear items like the shell, disks and other wear items.

Zinc dust consumption is indicated as zero. Zinc dust will be produced internally and circulated back to the purification circuit, with no requirement to buy in zinc dust.

<i>Cost as % of Atm leach operating cost</i>	<b>Atmospheric L</b>	<b>Pressure L</b>	<b>Pres L &amp; SX</b>	<b>Albion</b>
<b>Sulphuric Acid</b>	10.0	4.6	27.7	10.0
<b>Limestone</b>	4.7	2.4	11.6	4.7
<b>Hydrated lime (CaOH<sub>2</sub>)</b>	0.7	0.6	0.6	0.7
<b>Oxygen</b>	2.8	2.4	2.4	2.8
<b>SX reagents</b>	-	-	1.7	-
<b>Zn Dust</b>	-	-	-	-
<b>Water</b>	0.6	0.2	0.2	0.6
<b>Demineralised Water</b>	-	-	1.1	-
<b>Steam</b>	1.4	1.0	1.5	1.4
<b>Electricity</b>	18.8	18.8	18.8	18.8
<b>Reagents other</b>	0.4	0.7	0.9	0.4
<b>Consumables (Anodes &amp; Cathodes)</b>	4.3	4.3	4.3	4.3
<b>Labour variance</b>	-	-	0.6	0.3
<b>Maintenance cost</b>	9.0	9.9	12.9	9.0
<b>Fine Grind variance</b>	-	-	-	1.2
<b>Fixed Cost Incl Labour, admin, overheads</b>	47.2	47.2	47.2	47.2
<b>Total</b>	<b>100.0</b>	<b>92.2</b>	<b>131.7</b>	<b>101.5</b>

**Table 2: Operating cost comparison**

The major contributors to the variable cost are electricity, sulphuric acid, limestone and consumables (anodes and cathodes). The reagent cost estimate is based on consumption rates presented and recent quotations from suppliers.

The pressure leach has the lowest operating cost, roughly 8% below that of atmospheric leach. This is primarily driven by the assumptions made for the leaching conditions and iron precipitation. Maintenance cost is expected to be lower for the atmospheric leach equipment as specialised components and brick lining are not required for the atmospheric reactors. This is reflected in the factored maintenance cost estimate (2% of capital cost).

### **Capital Cost**

The atmospheric leach capital cost estimate includes 12 reactors (7 for LAL and 5 for HAL), each with 5m diameter and 25m high to achieve the 30hrs residence time. The atmospheric leach tanks are equipped with 90kW and 75kW motors for the LAL and HAL respectively. Some uncertainty exists on the mechanical costs for the atmospheric leach reactors. The reactors of Outotec and Union Minière are both specialised and proprietary equipment and actual costs not available in the open domain. Costs were estimated based on the reactor dimensions and assumption on the material of construction. It is known that the agitators require a high power input and the above power requirements were assumed. One spare reactor was included for each of the HAL and LAL stages.

For the capital cost estimate of the pressure leach circuits (with and without SX), three carbon steel brick lined autoclaves were included - two operational and a third one as standby. The standby autoclave can be tied into the circuit into the place of any one of the HAL or LAL autoclaves. The standby autoclave is to ensure a plant availability of 98% is achieved despite the maintenance stops required for brick lining and de-scaling. The size required to achieve a retention time of 60 min per autoclave is estimated at 4.5m diameter and 22.5 m long, 4 compartments with 5 agitators (45kW each).

Capital cost for the Albion process included an ISAmill for the fine grind duty and atmospheric leach tanks. The M3000 model ISAmill with 1.1 MW drive was selected for this process. It was sized based on a conservative power consumption estimate of 35kWh/t to grind from  $P_{90}$  of 45 $\mu$ m to 20  $\mu$ m. A percentage runtime of 85% was assumed and considered conservative. The capital estimate for the Albion atmospheric leach circuit was based on a total of 11 reactors (including 2 stand-by) and power duty of 72kW and 60kW drives for the LAL and HAL respectively. A conventional reactor with length to diameter ratio of 1:1 was assumed for the costing.

The zinc concentrate handling, iron removal, hot and cold purification circuits were all assumed to have the same duty for all the options. Table 3 presents the duty of all various unit operations for the capital cost estimates.

<i>Design Duty: unit processes</i>		<b>Atm Leach</b>	<b>Press Leach</b>	<b>Press. L &amp; SX</b>	<b>Albion</b>
Leach	dry t/h concentrates	34	34	34	34
Sulphur Recovery	t/h solids	16	16	16	16
Purification	m <sup>3</sup> /h solution	177	177	195	177
Bleed neutralisation	m <sup>3</sup> /h solution	-	-	23	-
Fe removal	m <sup>3</sup> /h slurry	145	145	165	145
SX	t/h Zn	-	-	17	-

**Table 3: Design duty for unit processes**

Capital is expressed as a percentage of the total cost of the atmospheric leach for discussion purposes and presented in Table 4. The total capital cost for the pressure leach is around 22% more expensive than the atmospheric leach. This is a result of the higher capital cost of the autoclaves and auxiliary equipment compared to the atmospheric leach reactors. Integration of the solvent extraction circuit to the conventional process route has a further disadvantage of capital cost, around 41% higher than the atmospheric leach option. This is owing to the additional equipment required to neutralise the bleed stream and additional zinc depletion SX circuit. Capital required for the Albion process is very similar to that of the atmospheric leach process. The additional capital for the ISAmill is offset by a 20% reduction in the residence time and hence cost of the leach reactors. The marginal reduction in agitation power also contributes.

<i>Cost as % of Atm leach total cost</i>	<b>Atm Leach</b>	<b>Press Leach</b>	<b>Press. L &amp; SX</b>	<b>Albion</b>
ZnS concentrate solids handling	1	1	1	5
Leach	16	28	28	14
Sulphur flotation	9	9	9	9
Sulphur melting	7	7	7	7
Purification	18	18	20	18
Bleed neutralisation			8	
Fe removal	10	10	12	10
SX			5	
Reagent make-up and supply	5	6	5	5
<b>DIRECT COSTS</b>	<b>67</b>	<b>79</b>	<b>94</b>	<b>67</b>
<b>INDIRECT COSTS</b>	<b>33</b>	<b>43</b>	<b>46</b>	<b>34</b>
<b>TOTAL COSTS</b>	<b>100</b>	<b>122</b>	<b>141</b>	<b>101</b>

**Table 4: Capital cost summary**

Buban et al (2000) compared the direct and atmospheric leach to each other. In their estimate, the pressure leach capital cost is between 1.08 and 1.25 times higher than the atmospheric leach. This study estimate the pressure leach capital cost at 1.75 times the atmospheric leach (leach sections only), higher than the estimate by Buban et al. They compared the cost of a single stage atmospheric and pressure leach processes whereas this study investigates two stage leach processes and includes a standby autoclave, which Buban et al have not considered. The assumptions made on the cost estimate of the proprietary equipment supplied by Outotec must also be noted and the potential impact on the results.

## CONCLUSION

A review of all zinc producing processes against the requirements of Skorpion Zinc firstly eliminated all the pyrometallurgical processes and the RLE process due to the production of sulphuric acid as by-product. The alkaline, chloride medium and oxidative leach processes in sulphide medium (excluding ferric leach) were eliminated because these have not been commercialised in any form and would require additional development work. This will add additional technical risk to the project and extend past the deadline to have processing capacity installed by 2017. The bio-leach processes have been discarded as they produce a dilute acid and the low PLS tenors from the bioleach is not suitable for direct electrowinning. A solvent extraction step would be required to upgrade the zinc tenors, increasing operating cost significantly.

Potential options identified for Skorpion Zinc for economic evaluation were the atmospheric leach, pressure leach and the Albion processes. The enhanced kinetics of dissolving sphalerite with ferric ions in sulphate solutions is well known and primarily influenced by temperature, particle size, ferric concentration and oxygen concentration, (Dreisinger et al, 1990; Harvey et al, 1993; Baldwin et al, 1995; Demopoulos et al, 1999; Souza et al, 2007). The various ferric leach processes developed aimed to benefit from these various parameters with temperature as one of the primary drivers. The capital and operating costs for the three options are summarised in Table 5, expressed as a percentage of the atmospheric leach option.

The option to consider inclusion of the solvent extraction circuit to reduce risk of 'off spec' zinc production cannot be justified. There is no benefit / reduction in capital cost if the SX is included and more importantly, it increases operating cost by ~40% against the option with the lowest operating cost.

<i>Cost as % of Atm Leach total cost</i>	<b>Atm Leach</b>	<b>Press Leach</b>	<b>Albion</b>
<b>Operating Cost</b>	<b>100.0</b>	<b>92.2</b>	<b>101.5</b>
<b>Capital Cost</b>	<b>100.0</b>	<b>122.4</b>	<b>101.0</b>

**Table 5: Cost comparison of three options**

The operating cost comparison between these options is highly sensitive to the process chemistry with regards to redox potential (ratio of ferric to ferrous), acidity of leach stages and the precipitation of iron during the leach process. The atmospheric and pressure leach options compare equally favourable. All three processes have high zinc recovery which is very dependent on variability of concentrate size distribution. The atmospheric leach and pressure leach are preferred over the Albion leach process as the latter has not been applied commercially. Even though the ultrafine grind is well established commercially, leaching of a fine grind in conventional stirred tank reactors has not been applied commercially on zinc concentrates and will increase risk and require further development work. The Albion process is therefore less likely to be considered further. However, a fine particle size distribution might be required by the atmospheric leach processes depending on the mineralogy and reaction kinetics. In such a case the ISAmill technology could be considered.

If the economics are considered for the pressure and atmospheric leach, at a zinc price of US\$2000 / t zinc produced and a life of 20 years, the Net Present Value of both options are equal. The pressure

leach appears to be more attractive due to the higher number of standalone processes commercialised and a lower sensitivity to the size distribution of the zinc concentrates. However, the atmospheric leach option cannot be discarded based on the findings of this study. The atmospheric leach process operating cost is highly sensitive to the leach parameters (residual ferric, ferrous and acid concentration) selected for the mass and energy balances. Atmospheric leach is relatively new and little information on the process is published. In addition, some uncertainty does exist on the concentrate particle size distribution required for the atmospheric leach process, as conflicting data is reported in literature. Comparative testwork by Buban et al (2000) indicates that a finer grind is required to obtain high recovery under atmospheric leach conditions, whilst Lahtinen et al (2005) reports that a concentrate particle size of ~90% passing 44  $\mu\text{m}$  is sufficient to obtain high recovery within 24-30 hrs.

This study therefore concludes that ferric leaching of sphalerite in a sulphate medium under atmospheric or pressure leach conditions are both suitable for Skorpion Zinc. These processes presents advantages over all other zinc processing options when elemental sulphur is preferred as the final department for sulphide sulphur. Both these processes can be integrated into the existing refinery and will be able to process concentrates with a wide composition range.

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