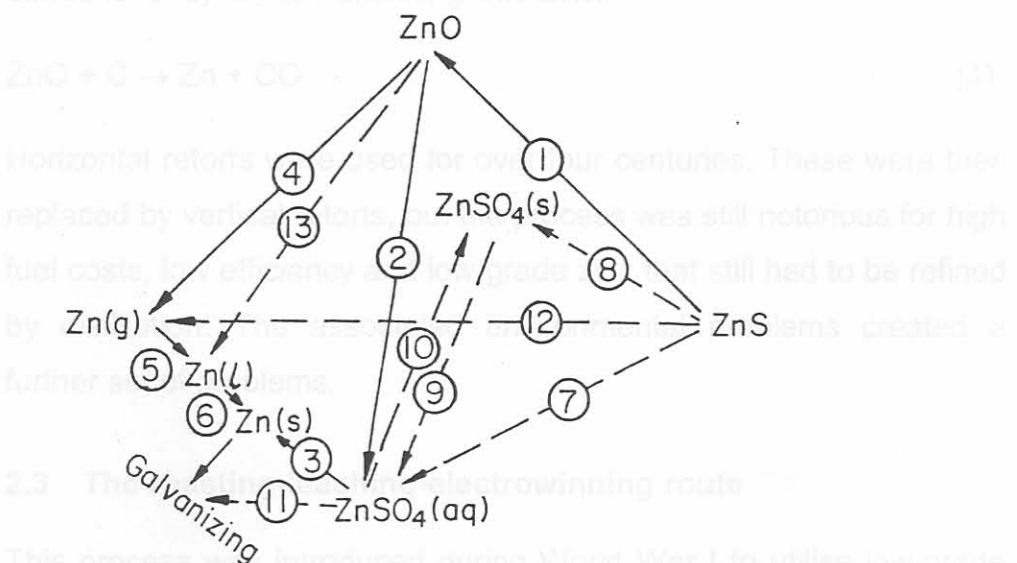


ZINC PROCESSING

2.1 Extraction of zinc from its ores



2.2 The retort processes

Habashi (1996) explains various processes for the treatment of sulphide concentrates of the common metals such as copper, zinc, nickel and lead. He states that these processes usually followed one pyrometallurgical route or another. In most of these processes, the sulphur content of the concentrate is usually released as SO_2 , and if the economic and market conditions are favourable, this is converted into H_2SO_4 . This is, however, not usually the case; large amounts of SO_2 are emitted to the atmosphere, causing environmental problems. Until a few years ago this was of no concern; a metallurgy book published in 1945, for example, never even mentioned what to do with SO_2 .

In these processes, zinc sulphide concentrate was roasted to oxide and SO_2 :



The oxide was then reduced to metal vapours in retorts and condensed rapidly to yield low-grade zinc:



Horizontal retorts were used for over four centuries. These were then replaced by vertical retorts, but the process was still notorious for high fuel costs, low efficiency and low-grade zinc that still had to be refined by distillation. The associated environmental problems created a further set of problems.

2.3 The roasting-leaching-electrowinning route

This process was introduced during World War I to utilise low-grade zinc concentrates that could not be economically treated by the retort

process. Acid obtained from the subsequent electrowinning step was recycled to leach the ZnO produced by the roasting step:



The process required extensive solution purification and was generally successful, because it yielded directly high-purity zinc. But it required sulphuric acid that had to be produced from the SO_2 produced in the roasting step, and a zinc ferrite was formed in the resulting residue.

Habashi (1999) notes that the problem with ferrite is its insolubility in the recycled (acid) electrolyte containing 25% H_2SO_4 . As a result, the early leaching process suffered from a low zinc recovery (85-93%); residues from this process contained as much as 20% Zn. Ferrites are soluble in hot concentrated H_2SO_4 , but under these conditions two additional problems could result:

- The impurity level (especially the iron content) will increase and extensive purification will be required before electrowinning.
- The high acidity must be neutralised to make electrowinning feasible.

Since this solution was costly, residues were treated by one of the following routes:

- Stockpiling until a better solution is found;
- treatment with coal in a rotary kiln (Waeltz process) to volatilise the zinc and recover it from the zinc oxide; or

- Treatment in a lead blast furnace to recover the zinc in the slag, which can be further processed by the fuming process to recover it from the zinc oxide fume as a fine powder.

Processes were developed to treat this material, but these created stockpiling problems because the final residue was more substantial than the original. Figure 3 gives a graphical representation of the process.

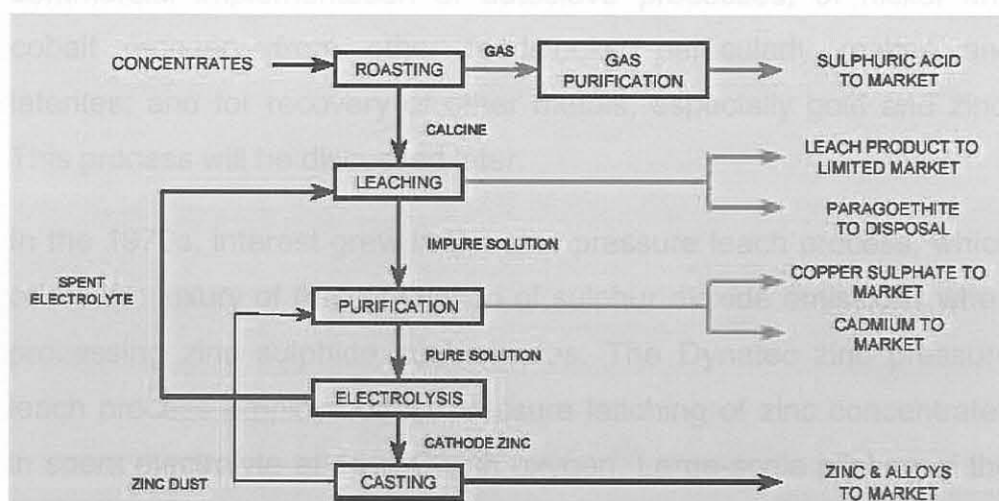


Figure 3: Roasting-leaching-electrowinning route for zinc (MIM Holdings 2002)

2.4 Pressure leaching process

Collins *et al.*, (2000) of the Dynatec Corporation gave a review on the Sheritt pressure leach process at the EPD 2000 Conference of The Minerals, Metals & Materials Society. He mentioned that the oxidative pressure leaching of base metal sulphides using continuous autoclaves was first successfully applied commercially in the early 1950s. The pioneers in this field were the Chemical Construction Corporation (Chemico), a subsidiary of American Cyanamid, and Sheritt Gordon Mines Limited, a Canadian copper and nickel mining company. The horizontal, multi-compartment autoclave was

developed at that time and continues to be the preferred equipment for pressure leaching processes.

The pioneering commercialisation of a pressure hydrometallurgical process for nickel production from pentlandite concentrate started in 1954 at Fort Saskatchewan, Alberta, Canada, site of the technologies division of Sherritt (now Dynatec, Metallurgical Technologies Division). This development led to continued improvement, especially in the commercial implementation of autoclave processes, of nickel and cobalt recovery from other feedstocks, particularly mattes and laterites, and for recovery of other metals, especially gold and zinc. This process will be discussed later.

In the 1970s, interest grew in the zinc pressure leach process, which offers the luxury of the elimination of sulphur dioxide emissions when processing zinc sulphide concentrates. The Dynatec zinc pressure leach process employs direct pressure leaching of zinc concentrates in spent electrolyte at 150 °C with oxygen. Large-scale piloting of the process took place toward the end of the 1970s, and the first commercial plant was started up in 1981. To date, Dynatec's zinc pressure leach process has been licensed at four refineries.

2.4.1 The Sherritt Zinc Process

Sherritt first proposed the direct leaching of zinc sulphide concentrates with the simultaneous extraction of elemental sulphur, as was mentioned above by Collins *et al.*, (2000) During the initial development work, experiments were carried out at temperatures below the melting point of sulphur. The outstanding features of the process – high zinc extraction, rejection of the iron in the insoluble form and production of sulphur in the non-polluting elemental form, all in a single leaching step – were reported by Gupta and Mukerjee

(1990). Keen interest was shown in the process by several firms during the sixties. In the seventies, the process was further developed and it was ascertained that in most applications leaching at a temperature above the melting point of sulphur gave the best results. Feasibility studies revealed that the idea of direct pressure leaching with electrolysis could have significant advantages over the conventional roasting-leaching-electrolysis method. A pilot plant, operated once again jointly with the Cominco Co. in 1977, led to the first industrial application of the process in Trail, when the basic process stages were integrated with the existing plant there.

The optimum process sequence for a completely new plant built on this process principle, or which is to replace an existing roast-and-leach plant, normally has two pressure-leaching stages. Zinc concentrate, mostly reduced by wet grinding to 90% below 44 μm , is leached with oxidation in two stages at a temperature of 150°C and at a pressure of 10 kg/cm^2 in which oxygen is used. A recirculating electrolytic solution, which can be used in both leaching stages, serves as a solvent. Approximately 80% of the zinc is dissolved in the first stage and 16-18% in the second. Some zinc oxide is added to the solution from the overflow weir of the thickener in the first stage, which has a pH of about 1.5 to 2.5, in order to neutralise residual acid and to hydrolyse residual iron that did not precipitate in the autoclave. After filtration, the solution is purified in the conventional manner and electrolysed to extract zinc, when copper-cadmium precipitate and cathodic zinc are also obtained.

The leaching residue of the first stage is pumped with the recirculating electrolysis solution into the autoclave of the second stage. The holding time in both leaching stages is usually less than two hours. After solid/liquid separation, the solution of the second stage is recirculated to the first. The resultant residue is then washed in counter

flow, elemental sulphur separated as required for extraction, and the iron oxide residue is either stored or processed to extract the precious metals and lead often contained in the residue.

Ozberk, *et al.* (1995 1) The oxidation pressure leaching of base metal sulphides using continuous autoclaves was first successfully applied commercially in the early 1950's. The pioneers in this field were the Chemical Construction Company, a subsidiary of American Cyanamid, and Sherritt Gordon Mines Limited (now Sherritt Inc.), a Canadian copper and nickel mining company.

Ozberk, *et al.* (1995 2) reports that since The third commercial application of the Sherritt zinc pressure leach process commenced operation at the Ruhr-Zink refinery in March 1991. Integration of pressure leaching with the existing roast-leach-electrowinning facility has increased zinc production capacity by at least 50 000 tonnes per year slab zinc.

According to Collins, *et al.* (1994), Hudson Bay was among the first companies to show an interest in commercialising the Sherritt Zinc Pressure Leach Process; however, three other zinc pressure leach plants were in operation prior to start-up of the pressure leach plant at Flin Flon. The process was first commercialised at the Trail, British Columbia, zinc refinery of Cominco Limited in early 1981. Subsequently, Kidd Creek Mines (now Falconbridge Limited, Kidd Creek Division), in Timmins, Ontario, and Ruhr-Zink GmbH (Datteln, Germany) commissioned plants in 1983 and 1991, respectively. In each case, the zinc production capacity of the existing refineries, using roast-leach-electrowin technology, was expanded without an increase in sulphur dioxide emissions and without a requirement for increased sulphuric acid production. In accordance with differences in

the method of iron rejection, the pressure leach step was customised to meet the requirements of the existing facilities.

Ozberk, *et al.* (1995 1) reported that the installation of three autoclaves with application of the Dynatec technology in 1993 at Hudson Bay Mining and Smelting had the advantage of eliminating the zinc roasting operation.

Gupta and Mukherjee (1990) reported that in the Cominco operation, zinc concentrate is leached with H_2SO_4 in the presence of O_2 at elevated temperature and pressure to produce a zinc sulphate solution, an iron-lead residue and molten elemental sulphur. The process employs a unique vertical sulphur separation autoclave to recover more than 90% of the sulphur in the molten state. After flash discharge of the slurry to atmospheric conditions, the remaining elemental sulphur is recovered by flotation, and the zinc sulphate solution undergoes purification and electrowinning to produce refined zinc metal. The iron-lead residue is treated in the smelter to recover lead and precious metals.

The process is based on the aqueous oxidation of zinc sulphide concentrates in dilute H_2SO_4 at 150°C and under oxygen pressure of 700 kPa:



The durability of the autoclaves is ensured by lining the inside of the vessel with acid-resistant bricks. The reaction is exothermic and yields elemental sulphur. No ferrites are formed, and therefore the residue can be disposed of directly and the solution can be purified in the usual way and electrolysed to yield pure metallic zinc and acid for

recycling to the leaching step. Figure 4 gives a graphical representation of the process.

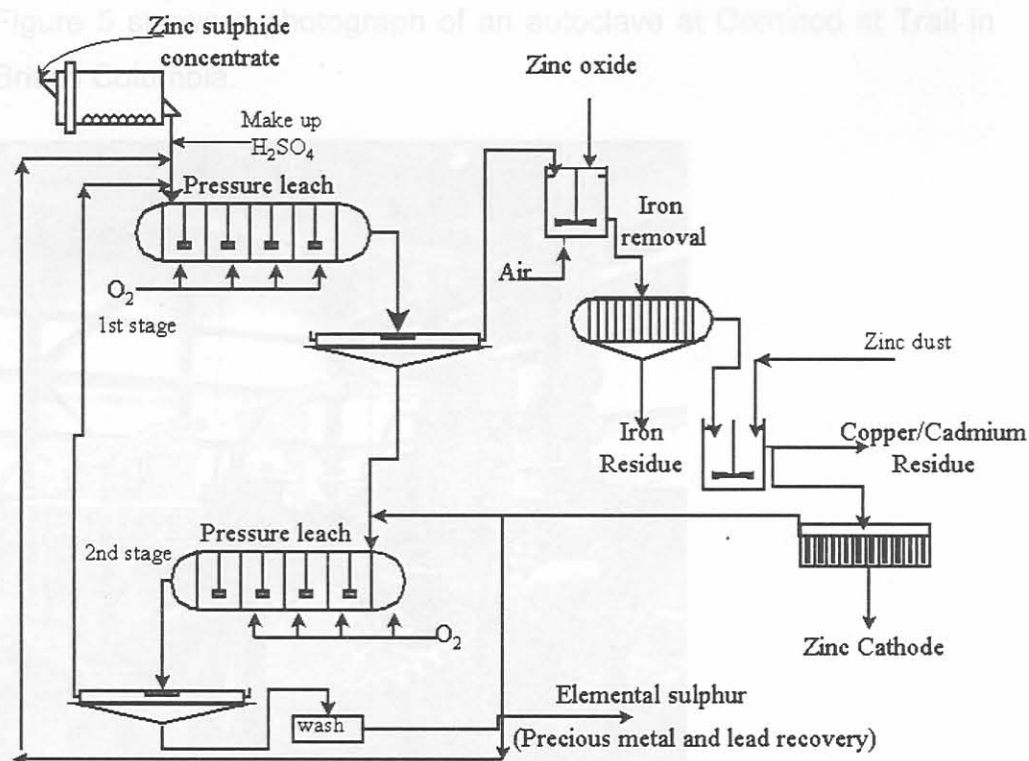


Figure 4: Pressure leaching of zinc sulphide concentrates to yield elemental sulphur

2.5 The Sherritt Zinc Integrated Process

Cominco Co., which in 1916 put up the first industrial plant to produce zinc by the roast-leach-electrolysis method, was also the first to introduce the direct pressure leaching of zinc concentrates with simultaneous production of elemental sulphur on an industrial scale. After Cominco had decided in favour of a general modernisation of the plant in Trail, it was obvious that expansion of the zinc capacity through pressure leaching would bring about significant economic and operational advantages. In particular, it would no longer be necessary to tie acid and fertiliser production to the production of zinc. An autoclave of 3,7 m in diameter and 15.2 m in length was installed with

a capacity of 190 t/d of zinc concentrate from the Sullivan mine that is known to contain lead as well.

Figure 5 shows a photograph of an autoclave at Cominco at Trail in British Columbia.

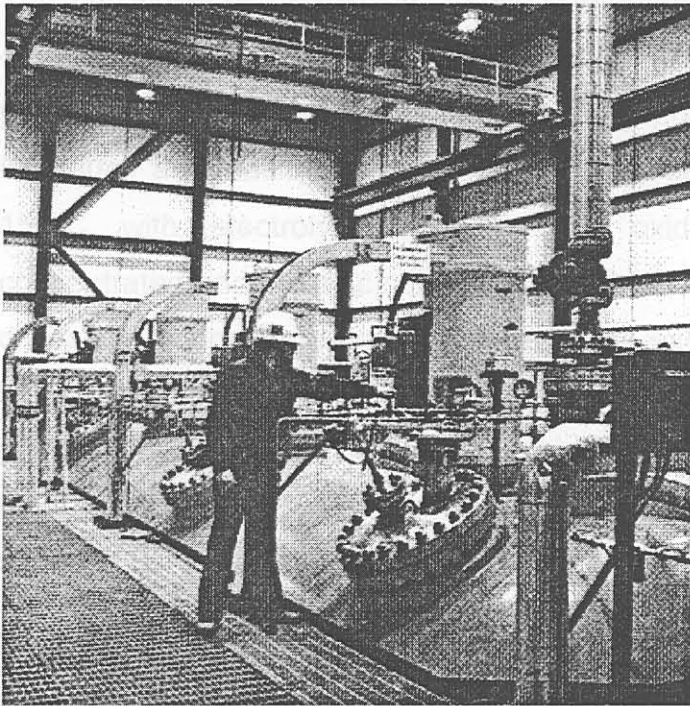


Figure 5: Photograph of an autoclave at Cominco, Trail, British Columbia (Sherrit Gordon)

During the pressure leaching of zinc, in which the sulphide sulphur is oxidised to elemental sulphur, the lead sulphide is also oxidised and converted to lead sulphate or lead jarosite ($\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$). The elemental sulphur formed is led into a special decanting vessel. Liquid elemental sulphur and a small residue of undissolved zinc sulphide, wetted by sulphur, are drawn off from the bottom of the vessel whilst the zinc sulphate solution, in which the oxidised lead and iron compounds are in suspension, is discharged continuously from above into a blow-off tank. The cooled suspension is subjected to flotation in order to separate the residual elemental sulphur that is not deposited in the decanting vessel. The suspension purified of sulphur is pumped

into the existing roasting-leaching plant, while pure elemental sulphur is obtained by hot filtration. The filter cake containing the remaining unleached sulphides is simply sent to the roasting plant as a smaller component.

The zinc works at Timmins in Ontario is intended to leach about 55 t/d of zinc, thereby fully utilising the capacity of the existing electrolysis plant. Here, the zinc concentrate needs no grinding; it is simply turned into slurry and leached in oxygen under pressure at a temperature of 150°C with electrolyte solution. The oxidised suspension is concentrated and the zinc solution is then treated with a small portion of roasted concentrate in order to neutralise excess acid. The vessel is also ventilated to oxidise traces of iron (II) before the solution is pumped to the existing roasting-leaching stage, since this does not have sufficient capacity for oxidation. The lower stream of the concentrator is fed to the existing jarosite washing circuit.

Further rapid introduction of the zinc pressure-leaching process by integration into already existing or completely new plants is at present blocked by the worldwide unfavourable zinc market.

2.6 Advantages of the Sheritt process

According to Habashi (1999), this process solves some very important problems of the hydrometallurgical zinc route.

- All the zinc goes into solution because no ferrites are formed;
- The process is independent of fertiliser manufacture because no sulphur dioxide is formed;
- Dissolution of willemite ($(\text{Zn,Mn})_2\text{SiO}_2$) and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) is viable.

- Acid dissolution of silicate minerals has been the basis of numerous process development studies for the extraction of metal values from ores or slags.

Veltman and Bolton (1980) stated that direct pressure leaching is an attractive alternative process for the future because of the following features:

- Capital costs are in the order of 25% lower than for the conventional roast-leach process.
- Gaseous emissions and the attendant environmental and hygiene problems are eliminated.
- Low-grade or bulk concentrates as well as high-grade concentrates can be accepted, since no ferrite is formed.
- Zinc and cadmium are produced in solutions amenable to conventional purification-electrowinning technology and at immediate high extraction rates.
- The process can be used to increase metal recoveries because a lower-grade concentrate can be processed economically.
- Easy integration into existing roast-leach-electrowin plants.
- Economy even in smaller modular units.
- Flexibility in acid production, since by-product elemental sulphur can either be stored or converted into sulphuric acid.
- Can be adapted to process a wide variety of unusual feeds or feed combinations.
- Has good turn-down capability.

- Has been successfully piloted, and will soon be applied commercially.

2.7 Ferric Ion as leaching agent

Dutrizac (1974) states that one great advantage of ferric ion leaching is the ease and variety of methods available for the generation of the lixiviant (solute). Acidic iron sulphate and iron chloride solutions are frequently produced as unwanted by-products of many commercial processes, for instance during the pickling of iron and steel. The leaching medium could also be prepared by the reaction of waste sulphuric or hydrochloric acids with scrap iron or with iron ores. In certain operations where large tonnages of acid are produced in regions remote from conventional sources of consumption, this method could be used to dispose of the acid and, at the same time, prepare a leaching medium suitable for the recovery of valuable metals.

As regards the economy of a ferric chloride leach operation, Smith, Brooks and May (1996) noted that a 1000 tonne per day plant was determined to have a low return on investment; however, depending on the size and type of mining operations employed and the FCL plant throughput, DCF-ROI projections of 20% to over 30% were calculated for 100% equity-financed "green field" mining, milling and FCL plant operations of 2000 t/day and higher.

The leaching of froth flotation concentrates in ferric chloride solutions was studied at different Fe^{3+} concentrations for different times at different temperatures with the influence of other species on the kinetics in mind. Considerable work has been done on the kinetics of ferric chloride leaching of sphalerite by Jin, Warren and Heinen (1985). Mandre and Sharma (1992) found that the maximum zinc

dissolution was obtained after 120 min using a 2 M FeCl_3 solution at 105°C . However, the addition of pyrite to the system enhanced the rate of zinc dissolution and reduced the consumption of ferric chloride. They attributed this phenomenon to possible galvanic interaction between pyrite and sphalerite. Another observation that they made in their precipitation studies of zinc was that the dissolved zinc could be recovered as zinc ammonium chloride rather than as zinc chloride. Warren *et al* (1985) gave an elaborate explanation of the reaction mechanism for the chloride leaching of sphalerite. Kołodziej and Adamski (1990) reported on the dissolution of sphalerite in aqueous hydrochloric acid under reducing conditions. Bobeck and Su (1985) reported on the dissolution of sphalerite in an acidic ferric chloride medium.

There are numerous metallurgical processes in which a product layer is formed on the reacting solid, zinc sulphide is no exception. The characteristics of the coating – e.g. whether it is porous or non-porous – will govern the kinetics of these reactions. If the reaction product forms a porous layer, the reagents will reach the interface more easily, and the rate will not be affected to the same extent as when the layer is non-porous and the reagent has to diffuse through the protective film before it reaches the interface. The kinetics of the two reactions will therefore differ markedly.

3.1.1.1 Criteria of porosity

Habashi (1969) further states that the porosity of a solid reaction product is determined by the ratio of the molecular volume of the product to that of the reactant:

$$\varepsilon = 1 - \left(\frac{M_p / \rho_p}{M_r / \rho_r} \right)$$