



Extending zinc production possibilities through solvent extraction

by D. Martín*, G. Díaz*, M.A. García*, and F. Sánchez

Synopsis

The Modified Zincex® Process, developed by Técnicas Reunidas, is highly flexible dealing with a wide range of pregnant leach solutions. No matter if those solutions are produced from primary or secondary raw materials, and/or are based on conventional leaching, pressure leaching, heap leaching or bio leaching the result is always high-purity zinc product. The zinc solvent extraction unit within the process is a very effective barrier for impurities and a buffer for the composition of the pregnant liquor. This unit achieves an extremely pure aqueous extract that can be converted into different final products. All of them are characterized by fulfilling the highest purity standards. Also, there is the possibility to adapt the global process to a wide range of pregnant liquor compositions and various production capacities up to a zinc production limit over 150 000 t/a with a single solvent extraction plant.

Introduction

Traditionally zinc production from zinc sulphide concentrates is based on the roasting, leaching and electrowinning (RLE) process¹. The concentrates containing around 50% Zn as zinc sulphide and about 30% sulphur are roasted to give zinc oxide calcine. The gaseous SO₂ outlet requires an annexed sulphuric acid plant. Zinc oxide calcines are leached with sulphuric acid solution generating a pregnant leach solution (PLS). In this process there is one single circuit between leaching and electrowinning (EW), therefore a high grade PLS is required and successful EW must carefully control impurities removal stages to avoid impurities passing to the pregnant electrolyte to achieve a high-grade zinc product.

Técnicas Reunidas, S.A. (TR) has developed, at commercial level, the 'Modified Zincex® Process' (MZP) where the solvent extraction (SX) unit behaves as a very effective barrier for impurities and a buffer for changes in the composition of the PLS. In this way not only zinc concentrates, but different raw materials can be processed to produce

special high-grade (SHG) zinc or other zinc compounds.

The Modified Zincex® Process description

The former Zincex® process^{2,3} was developed by TR in Spain and first introduced in commercial operation at the 8,000 t/a MQN plant in Bilbao (Spain) in 1976. The MQN plant treats secondary zinc materials and after proven success, another Zincex® plant with a capacity of 11,500 t/a was built in 1980 for Quimigal at Lisbon (Portugal). This plant treats high-chloride leach liquors from various sources.

The Modified Zincex® Process⁴⁻⁶ is a further developed and simplified version of the Zincex® Process, specifically adapted to treat solid oxidized materials or impure sulphate solutions. In 1997 a plant near Barcelona, Spain, was commissioned to recover zinc from 2,800 t/a of spent zinc batteries containing mercury and manganese as the main impurities⁹.

Zincex® processes have the ability to treat primary and/or secondary zinc materials¹⁰⁻¹³ for the recovery of zinc in circumstances where significant amounts of impurities are present. Solvent extraction is the key step used to concentrate and purify the zinc solution, which is then available for a number of products. Whilst the product can be slab zinc, it is equally possible to produce pure zinc sulphate and zinc oxide. In Table I flexibility and versatility of the MZP is briefly described.

A conceptual block diagram for the Modified Zincex® Process SX section, applied to different PLS to generate a zinc solution able to produce the desirable product, is shown in Figure 1. The process steps included in the

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Table I

Flexibility and versatility of the modified Zincex® process

PLS Sources	<ul style="list-style-type: none"> ➤ Primary ores (acid leaching, pressure leaching, bio-leaching, heap-leaching, etc.) ➤ Secondary raw materials (EAFD, Waelz oxides, galvanization ashes, tyre ashes, spent batteries, etc.)
Composition range	<ul style="list-style-type: none"> ➤ Zn: 5 or less to 160 g/l ➤ Metallic impurities: Cu, Cd, Co, Ni, As, Sb, etc. (g/l levels) ➤ Anionic impurities: Cl, F, etc. (g/l levels) ➤ Alkali and Alkali earth: Ca, Mg, Na, K, etc. (g/l levels)
Media	<ul style="list-style-type: none"> ➤ Sulphate ➤ Chloride ➤ Others
Products	<ul style="list-style-type: none"> ➤ Zn° SHG (by electrowinning) ➤ ZnSO₄ × H₂O ultra pure (by crystallization) ➤ ZnO ultra (by precipitation/calcinations), other Zn salts and solutions
Operation flexibility	<ul style="list-style-type: none"> ➤ All production capacity ➤ No shut-down problems & buffer for perturbances ➤ Suitability for other process (installed or not) combination

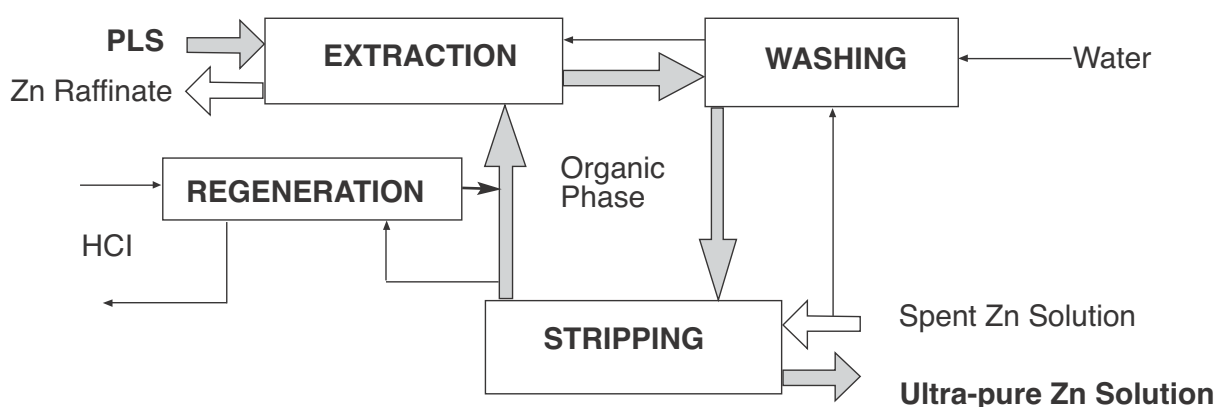
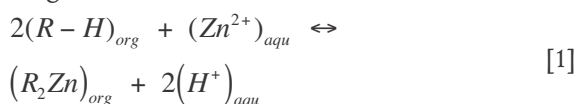


Figure 1—MZIP: Conceptual scheme of solvent extraction section

MZIP are extraction, washing, and stripping and organic phase regeneration. A solution of di-2-ethylhexyl phosphoric acid (DEHPA) as extractant reagent in kerosene (paraffin) base is used as the organic phase. This organic phase (RH) has a high affinity to extract the zinc at MZIP conditions according to the reaction.



Due to the process conditions applied by TR, impurities such as Co, Ni, Cd, Mg, Mn, Ca, etc. are not allowed to pass to the next process step. Under these conditions, the selectivity of the organic for the zinc is extremely high. Besides, in the washing stage the aqueous entrainment and the last residual co-extracted impurities are physically and chemically removed from the organic extract. Finally, in the stripping stage, an ultra-pure zinc sulphate solution is produced, able to be processed into the appropriate zinc compound (SHG-Zinc, ZnSO₄, ZnO). Additionally a bleed of the organic phase is treated with HCl solution, in the regeneration stage, to avoid the build up of co-extracted impurities (such as Fe) that are not stripped. A comparative diagram for impurities behaviour is presented in Figure 2, as a summary of the MZIP ability to deal with any kind of zinc PLS to generate a

commercial zinc product.

As can be observed Figure 2, and because of the physical and chemical separation between the PLS and the electrolyte, SX is a more effective barrier to impurities than the conventional RLE process. This is true for both steady and disturbed operation.

Range of applications for Modified Zincex Process

PLS quality and zinc product could be taken to define the range of application for MZIP. Several experimental investigations and industrial plant projects performed during the past 25 years have demonstrated the viability of the MZIP to treat any PLS (see Table II).

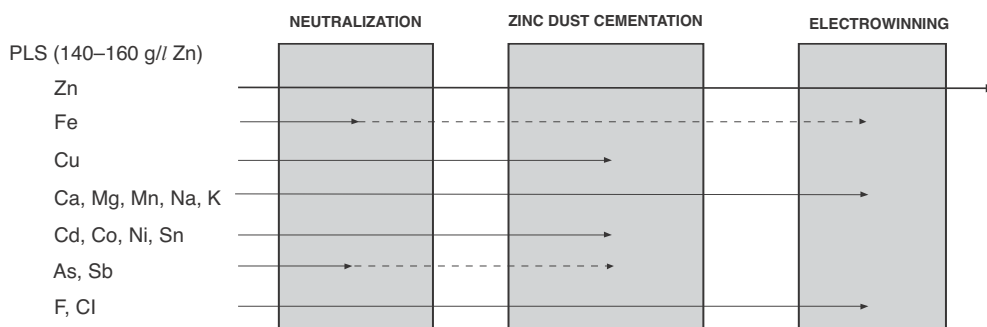
Zinc concentration in PLS

Low zinc concentration in PLS

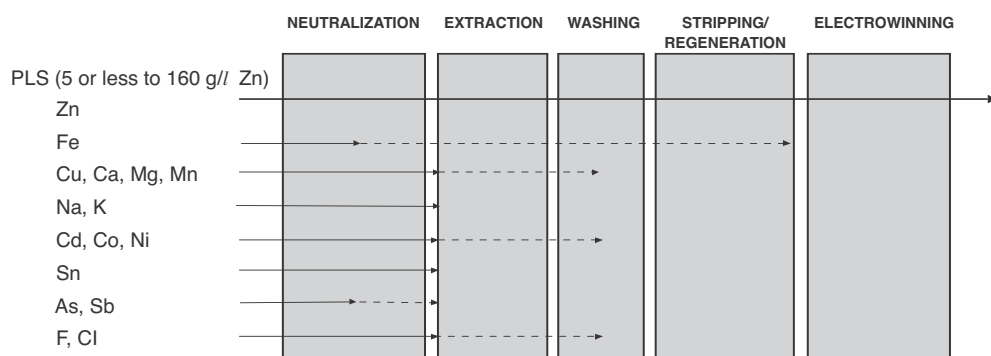
To date many primary zinc ores have not been treated due to their low zinc content that does not allow processing by the traditional RLE process. With the MZIP 11–15 it is possible to treat these raw materials because the MZIP solvent extraction circuit will produce an electrolyte that can be processed in any EW tankhouse. A general application is shown in Figure 3, where a zinc oxide ore is treated by means of the

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ROASTING-LEACHING-ELECTROWINNING



THE MODIFIED ZINCEX PROCESS



Note: Dotted line means ppm/ppb/ppt levels

Figure 2—Comparison between RLE and MZP. Concentrations and impurities

Primary	Zn	Main impurities	Project case
Oxidized ores from acid leaching	30	Cd, Cu, Ni, Co, Cl, F, Mg	Skorpion
Sulphide ores from Bio leaching	120	Cd, Cu, Cl, F, Mg	Confidential
Sulphide ores from Bio + Acid leaching	50	Cd, Cu, Ni, Co, Cl, F, Mg	Confidential
Sulphide ores from indirect bio-leaching	10	Cd, Cu, Ni, Co, Mg	RTM, S.A.
Sulphide ores from pressure leaching	150	Cd, Cu, Ni, Co, Cl, Mg	Confidential
Secondary	Zn	Main Impurities	Project case
EAFD from acid leaching	25	Cd, Cu, Cl	Elansa
Cu SX PLS Bleed from heap leaching	33	Cu, Ni, Co, Cl, Mg	Sanyati
Spent domestic batteries from acid leaching	20	Cd, Cu, Ni, Cl	Proces
Waelz O./Galv. ashes from acid leaching	32	Cd, Cu, Ni, Co, Cl, F	Comm. of EU

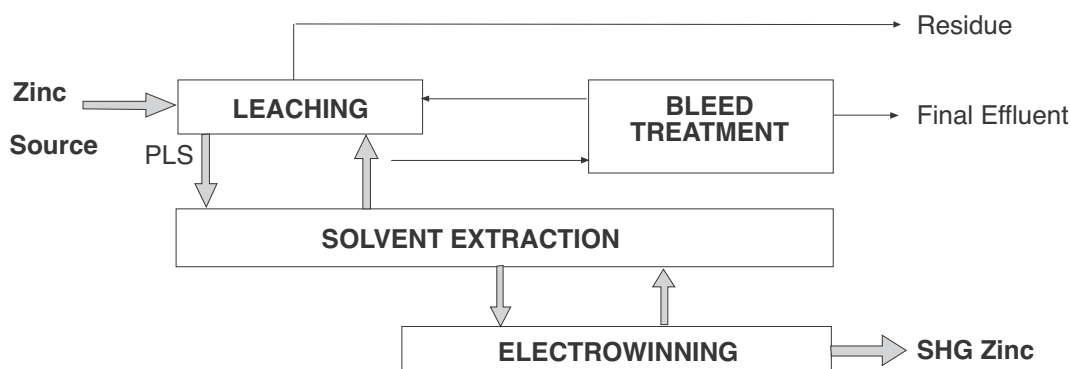


Figure 3—MZP applied on primary and secondary zinc materials

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proper leaching process, producing a PLS zinc concentration between 5–50 g/l Zn and Cu, Cd, Co, Ni, Fe, Ca and Mg as impurities, independent of the source.

A bleed of the raffinate is treated in a bleed-treatment unit, in order to avoid impurities building up in the system, and to then allow the EW unit to produce SHG zinc from the electrolyte.

High zinc concentration in PLS

Some zinc ore treatments (pressure, heap and bio leaching) are capable of producing high zinc concentrated PLS. In this way the associated impurity levels are too high and present difficulties for the traditional process route. Thus the benefits due to the reduction in equipment sizes in the leaching unit can be impaired by a major complexity in the purification unit. The use of the MZP for this PLS is technically and economically viable. Figure 4 shows an example of processing by bio leaching. In the bio leaching unit a PLS with 120 g/l Zn is produced and impurities such as Cu, Fe, Co, Ni, Cd, Ca, Mg are present in high levels. The SX unit, in the MZP conditions, produces an electrolyte without impurities that can be processed by EW to obtain SHG zinc ingots.

Impurities in PLS

Primary and secondary zinc raw materials contain different impurities that produce a negative effect in the traditional RLE zinc processing. These impurities are Sb, As, Cl, Co, Cu, F, Ge, Ni, Fe, Se, Te, Hg, Sn, Mn, Ca, K and Mg and the effect is produced mainly during the EW stage. While some of them are difficult to remove by cementation using RLE conventional process, others cannot be avoided (Cl, F, Mg, etc.) or make operation difficulties (Ca, Mn, etc.). The MZP is not conditioned by this fact, as these impurities are not allowed to pass to the electrolyte. It is possible to find two kinds of contaminated PLS, a lot of impurity compounds in the PLS

and a high concentration of impurities of some of them. Typical examples for these types of PLS are described below.

Variety of impurities

Secondary zinc sources such as Electric Arc Furnace Dust (EAFD), Waelz oxides, galvanizing A, tyre ashes, spent batteries, etc. are becoming, nowadays, more a zinc source than a residue. MZP applied on these raw materials^{4–10} has been demonstrated to be a viable solution to recover the zinc content. The MZP copes with the negative effect of the impurities being a fully effective barrier.

Electric Arc Furnace Dust (EAFD) can be processed by MZP (Figure 3) and this treatment has been successfully tested^{6,7}. Technical, environmental and economical feasibility has always been proven through several studies at all levels. PLS contain 30 g/l Zn, 25 g/l Cl, 0.9 g/l Cu, and produces an electrolyte with 90 g/l Zn suitable to produce SHG zinc by EW process.

High concentration of impurities

Hydrometallurgical processing of metals, such as Cu, Ni, etc. can require a bleed to avoid build up of impurities such as Zn. This results in losses of the desirable metal as well as the zinc content is not valued anymore. A profitable solution to avoid this is the use of MZP to recover the zinc content in the bleed that is a Zn PLS and at the same time returning a solution able to be recycled to the main process. In this way the value of the zinc is realized and the desirable metal is not lost from the PLS. The high level of impurities (for Zn processing) is not a problem for MZP while other processes to remove zinc from this impure solution means high costs and reagent consumption and without any zinc valorization. Application of the process on a Cu PLS in a conventional leaching, SX, and EW circuit is shown in Figure 5. The feasibility of treating PLS containing 1–2 g/l Cu, 16 g/l Mn,

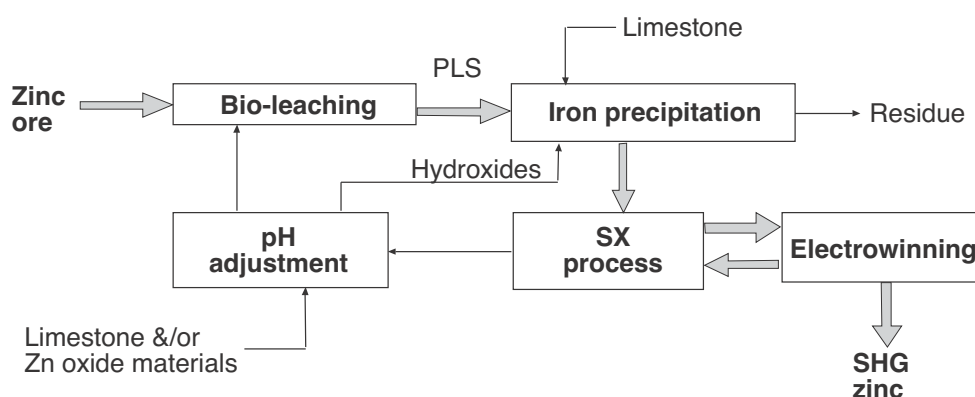


Figure 4—Example of MZP applied to zinc sulphide ores

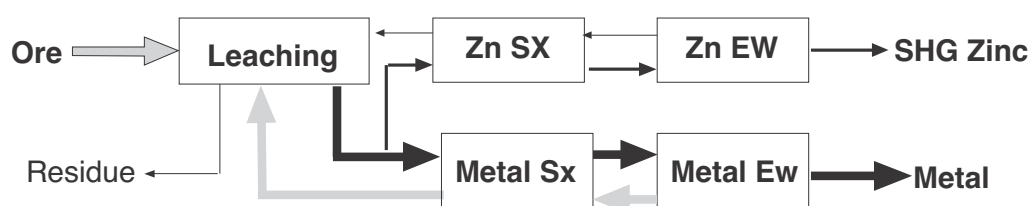


Figure 5—MZP applied on PLS bleeds of other metals production

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33 g/l Zn, 0.5 g/l Co, 2.4 g/l Mg, 0.1 g/l Ca, etc. has been demonstrated by Técnicas Reunidas.

Zinc product alternatives

MZP has the flexibility to produce zinc solutions able to be converted to any desired zinc product. This is possible due to the SX circuit that can be designed for every operation specifically to reach the desired zinc solution quality. Figure 6 shows a case of zinc sulphate salt production using MZP.

In Figure 7 we can see different alternatives for MZP applications regarding the zinc product.

Conclusions

In conclusion the statement can be made that the viability of the Modified Zincex® Process to deal with any kind of PLS and to produce different zinc products has been demonstrated. Irrespective of the raw material source, the zinc content in the PLS and the variety and quantity of impurities present, the MZP is the most suitable, efficient and reliable application. In this process the solvent extraction stage, using appropriate operation conditions, is able to produce ultra-pure zinc solutions that can be processed to obtain the desired final zinc product.

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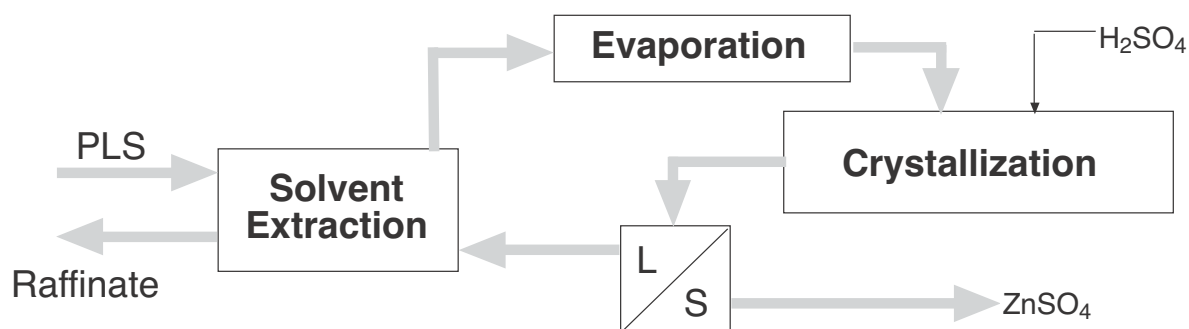


Figure 6—Zinc sulphate production from MZP

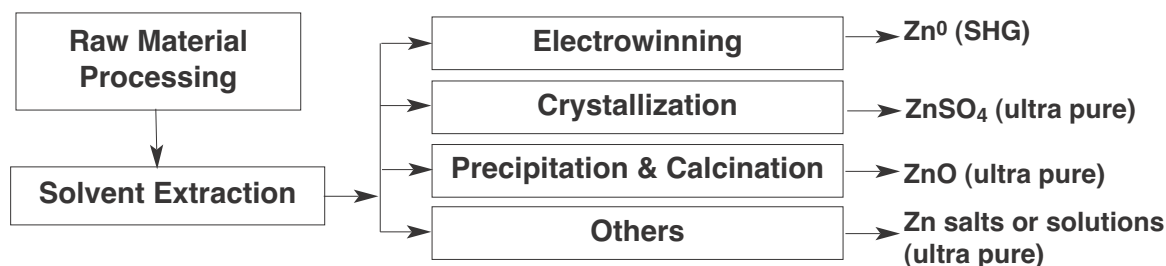


Figure 7—MZP zinc product alternatives

Eighth annual course on *The design of slurry pipeline systems**

Cape Town, 25 to 28 March, 2003

Paterson & Cooke Consulting Engineers will present the eighth annual course on the design of slurry pipeline systems in March 2003 at the Breakwater Lodge in Cape Town's Victoria & Alfred Waterfront.

The course was established in 1996 to provide guidance for the design of slurry pipeline systems for the mining and process industries. Slurry pipeline transportation is not adequately covered in most undergraduate engineering courses. Consequently, engineers and metallurgists are generally ill-equipped when faced with the task of designing a slurry transportation system or establishing why a system does not perform its required duty. The course aims to address this problem by giving delegates a sound understanding of slurry flow mechanisms and an appreciation of the design requirements for a successful slurry pipeline transportation system.

The course covers the following topics:

- flow behaviour and modelling of different types of slurries
- centrifugal and positive displacement pumps
- pump and pipeline wear
- instrumentation and laboratory techniques
- valves for slurry service
- hydraulic design and engineering considerations.

Formal design sessions will be introduced for the first time during the 2003 course. Delegates will be divided into four groups and tasked with designing a number of typical slurry pumping systems during five ninety minute sessions. Each design session will be led by a senior engineer from Paterson & Cooke Consulting Engineers.

A fully instrumented transparent test loop is used during the lectures to demonstrate various aspects of slurry pipeline flow. Visual observations of flow phenomena provide an insight into slurry behaviour and clarify theoretical concepts.

Delegates will be issued with a comprehensive set of printed reference notes, a CD containing the lecture slides and suggested solutions for the design tasks.

The course has proved to be extremely popular and is always fully booked. Delegates from Australia, Botswana, Brazil, Canada, Namibia, the Netherlands, the UK, the USA and Zimbabwe have attended the course.

The course will be held from 25 to 28 March 2003 at the Graduate School of Business, University of Cape Town, Breakwater Lodge, Victoria & Alfred Waterfront, Cape Town. *For more information please contact: *Ferial Perin*, Tel: +27 (021) 683 4734, Fax +27 (021) 683 4168 or e-mail *ferial@pcce.co.za* ♦

Downstream aluminium up and running*

Project Partners of the Downstream Aluminium Pilot Project happily launched the long-awaited project at a well-attended function at the ZCBF Community Park recently. The project, initiated by Hillside Aluminium and facilitated by the ZCBF is a fully operational foundry which aims to train potential entrepreneurs in all aspects of a small aluminium foundry's operation, thereby opening doors to formal or self employment.

The foundry is positioned to produce aluminium items for the local and international market thereby ensuring the self-sustainability of the project and allowing trainees to obtain hands-on experience in all aspects of a commercial foundry operation.

This project has been made possible through generous funding from Hillside Aluminium, Bayside Aluminium, BHP Billiton Development Trust and the Department of Economic Development and Tourism with technical assistance provided by the CSIR.

Funding from the Department of Trade and Industry has made it possible to launch Phase 2 of the Project which entails the establishment of an incubating facility for up to 10 entrepreneurs at a time, who will be able to utilize capital intensive equipment, machinery and support services in a secure environment, for the manufacture of sellable products. After a limited period of time (18 months to 2 years), their operations should have outgrown the incubator

and they will be encouraged to leave the incubator and set up their own businesses.

Last year, at an international aluminium industry conference it was made clear that South Africa could see an explosion in job creation if more downstream beneficiation could be achieved, particularly as it is much more labour intensive: a smelter requires one employee per 500 tons of aluminium produced while a downstream project like this one would require at least one employee per six tons. The conference also highlighted the cost advantages available in South Africa due to the lower cost of skills and duty-free export opportunities. With Richards Bay Industrial Development Zone already in the process of applying for an operator permit, all these benefits become distinctly realizable.

Speaking at the opening function, President and Chief Operating Officer of BHP Billiton Aluminium SA, Mahomed Seedat said: 'this is a project that is very close to my heart. I would love nothing better than to see the product produced by BHP Billiton Aluminium Smelters creating desperately needed jobs in South Africa. ♦

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