International Smelting Technology Symposium
(Incorporating the 6th Advances in Sulfide Smelting Symposium)

Edited by
Jerome P. Downey
Thomas P. Battle
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Preface

This book presents selected papers from the International Smelting Technology Symposium (incorporating the 6th Advances in Sulfide Smelting Symposium), which was held in conjunction with the 2012 TMS Annual Meeting in Orlando, Florida.

Originally, the 6th Advances in Sulfide Smelting Symposium was slated for the 2012 TMS program. However, the TMS Pyrometallurgical Committee decided to expand the scope of the symposium to include other smelting technologies. An organizing committee was formed and, in order to encourage growth through shared competencies and technological cross-fertilization between related fields, the organizers actively solicited papers from authors engaged in the analysis, development, and/or operation of high temperature processes that involve the production of ferrous and nonferrous metals, metalloids, and alloys. Thirty four papers are published from the Symposium, which comprised an interesting blend of presentations by experts from industry and the academe that described current practices, innovative technological advances, and promising research efforts.

Thus, the 2012 TMS International Smelting Technology Symposium provided a forum for papers that relate to advancements in all aspects of smelting technology, including the basic principles, technology, and current operating practice. In concert with the Symposium, the thirty four papers published in this book have been organized into five sections: Smelter Design, Construction, Commissioning and Operation; Current and Emerging Smelting Technologies; Feed Preparation and Recycling; Fundamentals: Thermodynamics, Phase Equilibria and Kinetics; and Pyrometallurgical Process Modeling, Control and Instrumentation. The organizers believe that the compendium will provide a useful and lasting resource of information for those interested in smelting technology.

Acknowledgements

The Lead Organizers gratefully acknowledge the support, advice and assistance provided by the entire organizing committee: Adrian Deneyes (Praxair, Inc.), William Imrie (Bechtel), Theo Lehner (Boliden Mineral AB), Phillip Mackey (PJ MackeyTech), Andreas Siegmund (Gas Control Technologies, LLC), and Tim J. Smith (SNC Lavalin). The TMS Staff and particularly Ms. Chris Wood are also acknowledged for their assistance in scheduling and executing the Symposium. Finally, Jerome Downey extends his personal thanks to Thomas Battle and Jesse White for their assistance in editing the manuscripts and their general support and guidance.

Jerome P. Downey, Thomas P. Battle, and Jesse F. White
December 2011
Jerome P. (Jerry) Downey is an Associate Professor and Goldcorp Distinguished Professor of Metallurgical and Materials Engineering at Montana Tech of the University of Montana. Dr. Downey is a registered professional engineer (Colorado and Montana) with a doctorate degree in Metallurgical and Materials Engineering from Colorado School of Mines. Prior to becoming a member of the Montana Tech faculty, Dr. Downey was Vice President at Hazen Research, Inc., where he directed the Thermal Processing Department. Dr. Downey's current research activities focus on the study of fundamental properties of slags, molten salts, and glasses; synthesis of ceramic materials for energy applications; and remediation of acid rock drainage. Dr. Downey has been a member of TMS since 1977, and he is the current Chair of the TMS Pyrometallurgy Committee. This is the third TMS conference proceedings that he has co-edited.

Thomas P. Battle is a native of Dearborn Heights, Michigan. He has undergraduate degrees in Materials Engineering and Astronomy from The University of Michigan, a Master's in Metallurgical Engineering from the Colorado School of Mines, and a doctorate in Materials and Metallurgical Engineering from Michigan. After a post-doc at Thames Polytechnic in Great Britain, he spent 18 years as a research engineer for DuPont Titanium Technologies. For the past three years he has been a Senior Metallurgist with Midrex Technologies in Pineville, North Carolina, where his research focus is on the extractive metallurgy of iron. This is the second conference proceedings for TMS that he has co-edited.
Jesse F. White is originally from Billings, Montana. He received a B.S. in Metallurgical Engineering from the South Dakota School of Mines, and an M.S. in Metallurgical Engineering from the Colorado School of Mines in 1995. He spent six years in the steel industry, and six years in the aluminum industry before finally joining Elkem in Kristiansand, Norway in 2007. His current research areas are physical chemistry of melts and slag-metal reactions pertaining to silicon refining.
International Smelting Technology Symposium
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Plenary Session
ALUMINOTHERMIC SMELTING: A VERSATILE PROCESS SERVING DEMANDING MARKETS

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Keywords: aluminothermic, master alloy, ferroalloy, thermite, thermit

Abstract

Aluminothermic ("thermite") smelting became commercial with the development of tonnage aluminum, and prospered producing metals and alloys with higher cleanliness, consistency and elemental control than competing technologies. We explore the scope of thermite smelting, and metallothermic smelting in general; the thermochemistry of the process; and its advantages and limitations as applied to industrial production. We review currently-produced products of thermite smelting in several forms and a wide range of heat sizes. As these products serve several industries, we relate the demands of those industries to the requirements imposed on the thermite process, leading to process dynamics and mechanisms to control/alter those dynamics. We review ways to lower the process costs by altering process stoichiometry, using other energy sources and utilizing less costly materials while considering effects on product quality and customer requirements. Finally, we examine overall emissions control and waste disposal.

Introduction

Aluminothermic smelting is the reduction of various oxides by aluminum to produce metals or alloys with varying levels of residual aluminum. One of the earliest uses of the process was the production of liquid iron to weld railroad rails, later modified in "thermite grenades" used to "spike" artillery pieces in World War II. Then during the 50's, 60's and 70's the growth of jet aircraft created a demand for new superalloys and titanium alloys, both requiring master alloys for efficient production. Aluminothermic smelting grew with the aerospace industry and with the expansion of microalloyed steels. It is very much a niche industry, dependent on the specialized demands of the specialty steel, superalloy and titanium industries. In this paper we introduce the characteristics of aluminothermic smelting, the scope of smelting operations, the markets served, and the environmental aspects of the process, as seen through the eyes of a company using aluminothermic smelting for over fifty years.

Aluminothermic smelting is inherently hazardous and must not be attempted by those unskilled in the art. Death, serious injury and property damage can result from mismanaged reactions.

Thermochemistry of Aluminothermic Smelting

The iron oxide-aluminum reaction that was the basis of thermite smelting is quite simple:

\[ \text{Fe}_2\text{O}_3 + 2\text{Al} = 2\text{Fe} + \text{Al}_2\text{O}_3 \]  

(1)
The reaction actually proceeds stepwise, as

$$9 \text{Fe}_2\text{O}_3 + 2\text{Al} = 6\text{Fe}_3\text{O}_4 + \text{Al}_2\text{O}_3 \quad (1a)$$

and

$$3\text{Fe}_2\text{O}_4 + 2\text{Al} = 9\text{FeO} + \text{Al}_2\text{O}_3 \quad (1b)$$

and

$$3\text{FeO} + 2\text{Al} = 3\text{Fe} + \text{Al}_2\text{O}_3 - \Delta G^o_T \quad (1c)$$

Reaction (1c) will control the yield of iron, since it is the most stable oxide in the above sequence. For reaction (1c) we can describe the equilibrium as:

$$K_p = \left( A_{\text{FeO}}^3 \cdot A_{\text{Al}_2\text{O}_3} \right) / \left( A_{\text{Fe}}^3 \cdot A_{\text{Al}}^2 \right) \quad (1d)$$

Since the $\text{Al}_2\text{O}_3$ is near pure, it can be assumed to have an activity of 1, as can the iron. This leads to:

$$\ln A_{\text{FeO}} = (\Delta G^o_T/3R) - 3/2 \ln A_{\text{Al}} \quad (1e)$$

Thus, higher yields are obtained by lowering temperatures and increasing aluminum levels in the metal phase. Lowering the activity of the metal (by alloying) also drives the reaction further to completion, as does lowering the activity of alumina in the slag (by adding fluxes). This is true for essentially all aluminothermic reactions we have examined to date. The production data indicate that the thermite reactions lead to results that closely confirm the thermodynamic predictions, within the uncertainty of the data. In actual master alloys, the alumina often is heavily fluxed, and the metal phase contains both the target metal and residual aluminum at levels that are well beyond the where Henrian behavior can be assumed.

Reaction (1) is accompanied by the release of 198 kcal of heat, sufficient to produce both liquid iron and liquid alumina. Similarly, $\text{V}_2\text{O}_3$ and $\text{V}_2\text{O}_5$, $\text{Nb}_2\text{O}_5$, $\text{MoO}_3$, $\text{Cr}_2\text{O}_3$, $\text{Ta}_2\text{O}_5$, $\text{Zr}_2\text{O}_5$ and many other oxides can be reduced to metals by exothermic reactions with aluminum. The available heat varies, of course, with the oxide and the oxidation state of the oxide. Of particular importance is the enthalpy per unit mass of the reactants (or “energy density”), as this determines the temperature the reactants can theoretically achieve. For the example in Equation 1, the heat per gram of reactants is 930 cal/gram. [While some may decry the use of enthalpies rather than free energies of reactions, in thermite reactions we are dealing only with condensed phases, so entropy changes are relatively insignificant. Using enthalpy (“heat”) simplifies the math and aids communications.]

Ignition is usually accomplished through “sparklers,” magnesium ribbons, electrical resistance wires, or packets of easily-ignited materials. These reactions are quite rapid, typically lasting from forty-five seconds to ninety seconds, so they might be considered close to adiabatic. As written, Equation 1 predicts reaction temperatures well above 2015 C, the melting point of alumina. This suggests the reaction will be very aggressive to containment vessels, and much of the oxide being reduced would not be recovered due to both dilution of the reductant (Al) in the product metal (Fe), and dissolution of the metal oxide ($\text{Fe}_2\text{O}_3$) in the liquid alumina. These losses are easily minimized by adding an excess of aluminum over stoichiometry and adding fluxes to lower the melting range of the alumina. These additions do not change the total energy available, but do increase the mass, thereby lowering the temperatures achieved in the reaction and potentially improving overall yields in the process. For the oxides mentioned above, the reaction enthalpy and energy density of the basic reactions are shown below. This list is certainly
not complete; there are many other metals and alloys produced by aluminothermic production. These are the most important ones commercially.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Enthalpy, kcal</th>
<th>Calories/gram</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3V_2O_3 + 10Al = 6V + 5Al_2O_3)</td>
<td>655</td>
<td>805</td>
</tr>
<tr>
<td>(3\text{Nb}_2O_5 + 10Al = 6\text{Nb} + 5\text{Al}_2O_3)</td>
<td>576</td>
<td>540</td>
</tr>
<tr>
<td>(\text{MoO}_3 + 2Al = \text{Mo} + \text{Al}_2O_3)</td>
<td>204</td>
<td>1080</td>
</tr>
<tr>
<td>(\text{Cr}_2O_3 + 2Al = 2\text{Cr} + \text{Al}_2O_3)</td>
<td>105</td>
<td>505</td>
</tr>
<tr>
<td>(3\text{Ta}_2O_5 + 10Al = 6\text{Ta} + 5\text{Al}_2O_3)</td>
<td>508</td>
<td>318</td>
</tr>
<tr>
<td>(3\text{ZrO}_2 + 4Al = 3\text{Zr} + 2\text{Al}_2O_3)</td>
<td>12</td>
<td>25</td>
</tr>
</tbody>
</table>

In the case of iron oxide reduction, there is excess enthalpy available. In the case of Equations 6 and 7, above, we have insufficient enthalpy to reach temperatures at which the alumina or the metal will be liquid, even if we add fluxes and no excess aluminum to the reaction. The solution is the use of "boosters," most commonly KClO₃ or NaClO₃.

\[\text{KClO}_3 + 2\text{Al} = 2\text{KCl} + \text{Al}_2O_3\] 299 1710 (8)

\[\text{NaClO}_3 + 2\text{Al} = 2\text{NaCl} + \text{Al}_2O_3\] 307 1915 (9)

These "boosters" significantly increase the available heat, but also tend to destabilize the reaction. They should be used in limited amounts and with due caution. Other options to increase the energy density include pre-heating of the charge (which can lead to premature ignition) and application of external heat sources, most commonly electric arc furnaces.

To lower the energy density, undersize revert from previous heats can be added to the blend, or non-reactive material such as alumina (high purity!) can be added. If available, lower oxides such as V₂O₃ can be used to replace higher oxides (V₂O₅), lowering both the energy density and the aluminum requirements for reduction. In the ferrovanadium industry it is quite common to combine electric arc furnace energy input with V₂O₃ to reduce production costs.

Controlling the energy available in a heat is important for several reasons. First and foremost, uncontrolled aluminothermic reactions can accelerate rapidly, spewing hot materials over a wide area and endangering both personnel and property. Excessive temperatures also can lead to significant loss of valuable oxides to the slag phase, as shown by Sattelberger and Löber, and to increased sublimation losses of molybdenum trioxide. In the case of RAI's water-cooled copper reaction vessels, excessive heat leads to accelerated erosion of vessel walls. RAI has determined safe and optimal energy ranges for all major alloys, and deviations are very carefully evaluated.

The Scope of Aluminothermic Smelting

By combining the above reactions in varying proportions and varying amounts of excess aluminum, a wide range of alloys can be produced. Reading Alloys makes almost a hundred different master alloys, with aluminum contents ranging from less than 1% to 60%, from simple
binary alloys like 35% Al-65% V to six- and seven-component alloys such as master alloys for Ti-17 and for Ti-5553 with minor additions. Many of these are custom formulated to meet individual customer requirements. The more common of these alloys are in Table 1, below.

Table 1. Nominal Compositions of Common Aluminothermic Master Alloys

<table>
<thead>
<tr>
<th>Composition</th>
<th>Composition</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>13Al-87V</td>
<td>5Al-95Nb</td>
<td>40Al-16Mo-13Sn-28Zr (6242)</td>
</tr>
<tr>
<td>15Al-85V</td>
<td>20Al-80Nb</td>
<td>30Al-30Mo-12Sn-22Zr (6246)</td>
</tr>
<tr>
<td>25Al-75V (C,N)</td>
<td>25Al-75Nb</td>
<td>25Al-25Cr-25Mo12Sn-12Zr (Ti-17)</td>
</tr>
<tr>
<td>35Al-65V</td>
<td>40Al-60Nb</td>
<td>28Al-28Mo-28V-16Cr (5553)</td>
</tr>
<tr>
<td>50Al-50V</td>
<td>40Fe-60Nb</td>
<td>25Al-50Mo-25V</td>
</tr>
<tr>
<td>60Al-40V</td>
<td>40Ni-60Nb</td>
<td>20Al-80Cr</td>
</tr>
<tr>
<td>40Fe-60V</td>
<td>35Al-65Mo</td>
<td>30Al-70Cr</td>
</tr>
<tr>
<td>40Ni-60V</td>
<td>45Al-55Mo</td>
<td>44Al-56Cr</td>
</tr>
<tr>
<td>20Al-69V-11Fe</td>
<td>15Al-85Ta</td>
<td>60Al-40Cr</td>
</tr>
<tr>
<td>40Al-40V-20Sn</td>
<td>35Al-30Sn-35Ti</td>
<td></td>
</tr>
</tbody>
</table>

In terms of scale of operations, RAI makes developmental heats with only two kilograms of total charge weight, and typical production heats yield an ingot weighing about 50 kg. Individual heats are small but RAI makes many of them, typically tens of thousands of heats per year. By contrast, in 2001 CBMM reported making aluminothermic heats of ferro-niobium with a charge weight over 29 metric tons, yielding ingots weighing 11 metric tons. The smelting process itself obviously is quite scalable, and some also have tried continuous smelting on a large scale. Many of the principles and techniques of aluminothermic smelting are applicable to other metallothermic reduction processes, such as calcio-thermic reduction of rare earth fluorides and chlorides. One early industrial process on which the author worked employed metallic calcium with neodymium fluorides to supply materials for the neodymium-iron-boron magnet market.

Aluminothermic smelting is most commonly done in refractory-lined vessels with emissions controls, often using the calcium aluminate slag from earlier heats as a significant portion of the vessel lining. At RAI we use this technique, but most of our smelting is done in water-cooled copper reaction vessels, as shown in Figure 1.

Figure 1. Water-cooled Copper Thermite Reaction Vessel in use.
Note ongoing reaction in background.
The combination of small heat sizes and water-cooled copper reaction vessels results in very rapid solidification, which minimizes any possible segregation in the alloys. The copper containment vessel also eliminated the possibility of contamination by refractory particles other than calcium-aluminates. The segmented copper vessels typically last for thousands of individual heats, and worn segments can easily be re-worked or replaced. At the end of their useful lives the worn-out vessels have value as copper scrap, as opposed to the disposal costs of spent refractory linings.

Reaction Kinetics

A well-controlled thermite reaction is similar to a fire in a sawdust pile. It spreads smoothly along a well-defined reaction front until all the available material is consumed. In our experience the reaction depends on vapor-phase penetration of the charge mass, so the permeability of the charge largely controls the rate of reaction. In contrast to most reactions, closer packing of the reactants slows the reaction rather than accelerates it. The particle size distribution of the components is the primary determinant of permeability, so consistency of the physical characteristics of raw materials is quite important. Changes in a key component’s particle size distribution can significantly accelerate or impede the reaction, and on occasion can lead to limited eruptions. The permeability of the charge can be modified by careful selection of fluxes and additives like “boosters” and heat sinks such as undersize revert alloy from prior heats, as well as changes to the particle size distribution of the oxide and aluminum. Blending of different lots of raw materials can effectively reduce variations in charge permeability, while vibratory or mechanical packing can reduce permeability heat-by-heat.

The heat released during the reaction will expand the gases normally present in the voids of the charge, and these expanding gases are easily expelled through the charge until the reaction propagation front covers the entire surface of the remaining charge. Then it is possible for pressure to be generated against what is effectively a liquid seal, with some “popping” or ejection of slag, metal and remaining charge materials. This phenomenon usually occurs towards the end of the reaction, and can be controlled by proper design of the reaction vessel.

In most smelting operations, the slag is used to purify the metal by absorbing undesirable materials. In aluminothermic smelting the slag can be a source of contaminants to the metal, because of the extremely reducing conditions present. Lime commonly contributes carbon, silicon and sulfur, while fluorspar can be the source of arsenic and antimony. Powdered aluminum contains significant levels of iron as a tramp element, but high-purity electrolytic refined aluminum has much lower iron levels but often contains elevated levels of silver, so “purer” isn’t necessarily better. “Sparklers” used for ignition can contribute small but significant amounts of iron to the alloy. In general, anything that goes into the charge can be expected to wind up in the metallic product, so selection of raw materials is very important to product quality. Unfortunately, increasing energy costs have led to “dead-burned” lime becoming almost impossible to find, and tramp elements picked up from low-grade fuels like shredded tires is commonplace. While the thermochemistry and dynamics of the process are well-established science, the search for suitable raw materials remains an art form.

Markets for Aluminothermic Products
The dominant market for aluminothermic smelting is ferroalloys for the steel industry, primarily ferrovanadium, ferromolybdenum and ferroniobium. Much smaller markets are master alloys for aerospace (titanium, superalloys and specialty steels) and feedstocks for refining to pure metals. The ferroalloy industry generally has wide tolerances on material composition, and a generous tolerance for iron and other elements commonly found in steels, such as manganese and silicon. This allows the ferroalloy industry to use less-costly raw materials, including commercial-grade oxides and secondary aluminum sources such as used beverage containers (UBC's). The aerospace industry, on the other hand, requires much tighter limits on material composition, tramp and trace elements, and particularly variation both within a lot and lot-to-lot. The aerospace industry also imposes strict requirements for raw material traceability. This limits the raw materials which can meet their requirements to higher-purity oxides, such as sublimed or precipitated MoO$_3$ (99+% MoO$_3$) rather than commercial grade MoO$_3$ (95% minimum MoO$_3$ content), and aluminum powder, granules or shot produced by a re-melting technique such as air atomization rather than by mechanical comminution.

Emissions Control and Waste Disposal

Thermite reactions typically involve only condensed phases, so emissions are more limited than in many other types of reactions. The thermal expansion of entrained gases (usually air) leads to a very small quantity of particulate material being expelled in each heat. At RAI high-efficiency wet scrubbers capture these particulates. The scrubbers use a self-contained water system which periodically is drained, the solids removed by filtration and the pH adjusted, and the water returned to the scrubbers for re-use. After numerous cycles the scrubber water is removed as a non-hazardous waste product. The filter cake produced from the scrubber water is sold to a recycler who processes it for valuable constituents (mostly fine alumina). The high-alumina slag generated in the reactions is by far the largest waste stream. It is roughly equal to the weight of metal produced, and is larger in terms of physical volume. This slag contains very small amounts of the original oxides (often less than 1%, depending on the oxide involved), and is sold for use as part of a slag conditioner for the steel industry. A small portion of the slag is used internally as part of our refractory systems.

The water used to cool the reaction vessels does not come in contact with the charge materials, and is discharged (with aeration) back into the pond from which it was drawn. Since the discharge water is slightly warmer than the incoming water, the pond is gradually warmed by a few degrees compared to similar ponds upstream. Local flora and fauna (including small-mouth bass) thrive in the slightly-warmed water.

References

(2) Sousa, C. A de F. “The Evolution of FeNb Manufacturing” ibid, 89-96
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Smelter Design, Construction, Commissioning and Operation
DESIGN AND COMMISSIONING OF THE AUSMELT TSL LEAD SMLTER AT YUNNAN TIN COMPANY LIMITED

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Abstract

A commercial lead smelter using Outotec Ausmelt TSL Technology has been successfully commissioned and put into operation at Yunnan Tin Company Ltd operations near Gejiu City, in Yunnan Province, China. The plant was commissioned in July 2010 after three years in the design and construction phase. The process uses a three stage batch process to produce lead bullion and zinc fume, and a slag that is low in metal values. The paper provides details of this lead smelting project, including the theoretical evaluation of the multi-stage process chemistry, engineering design, plant commissioning and the final operation. Comparison of the design targets and actual performance of the plant is emphasized. The fast ramp-up to full production of the largest Ausmelt TSL lead furnace built to date is highlighted.

Introduction

In 2002, Ausmelt and Yunnan Tin Company (YTC) successfully commissioned a smelter to modernise the Yunnan Tin smelter in Gejiu City, Yunnan Province, China. A single Ausmelt furnace was installed by YTC to process tin concentrate and revert materials, to produce YT Brand tin product. The advanced Ausmelt Technology furnace at YTC replaced seven existing reverberatory furnaces and provided a flexible, energy efficient and environmentally beneficial system to complement the world leading refinery facilities of YTC.

Building on the success of the tin project, YTC decided to expand and modernise a small lead smelter they also owned and operated near Gejiu. Outotec’s Ausmelt TSL technology was selected, when compared with other available nonferrous smelting technologies, due to its ability to process the available feed materials to produce 100,000 tonnes per annum of lead bullion, ~17,000 tonnes per annum of zinc oxide fume and ~50,000 tonnes per annum of waste slag. This process was also the design basis of an Ausmelt furnace at the Hindustan Zinc Limited Chanderiya smelter in Rajasthan, India[1].
The Project involved the design, construction and commissioning of the lead smelter, electrolytic refinery, sulphuric acid plant and all associated infrastructure on a greenfields site. YTC assembled a strong team comprising:

- Ausmelt Ltd (now Outotec) to supply the TSL Smelting Technology,
- China Nerin Engineering Co. Ltd (NERIN) to provide the Cansolv and sulphuric acid plants, and;
- China Nonferrous Engineering and Research Institute (ENFI) to provide electrolytic lead refinery technology and the balance of the plant engineering, procurement and construction management.

The Project design phase commenced in early 2007 and construction in 2008. The TSL furnace was heated up in July 2010 and the project moved into hot commissioning in August 2010.

Process Description

The process used was a three stage batch operation in a single furnace as depicted in Figure 1.

In the concentrate smelting stage, lead concentrates, lead rich fume (recycle), refinery reverts and fluxes of silica and limestone are smelted in the Ausmelt TSL furnace to produce crude lead bullion and a lead rich slag. Maintaining the smelting process temperature at 1150°C, lead bullion is intermittently tapped from the furnace and transferred to the refinery.

The slag reduction process begins when the furnace slag depth reaches 1.6 metres. This stage involves reducing the lead rich smelting slag initially with additional concentrate and then adding lump coal to recover a lead bullion product. Fume produced from this stage is recycled to the concentrate smelting stage. The bath operating temperature for the slag reduction stage is 1200°C.

After tapping the lead bullion product, the slag cleaning process commenced. Reductant coal is fed to produce a zinc/lead fume product and a waste slag product. The discard slag is tapped from the furnace, leaving a heel for the resumption of concentrate smelting in the next cycle. The bath operating temperature for the slag cleaning stage is 1250°C.
Concentrate Smelting Stage
The lead and iron sulphides present in the concentrates are oxidised with a controlled amount of excess air injected via the Ausmelt lance. The iron oxide combines with the SiO₂, CaO, Al₂O₃ and MgO components present in the feed mix and the coal ash to form a fluid slag containing ~35% lead as PbO. The addition of silica and limestone flux is necessary to ensure that the slag remains fluid in the later stages, where the PbO is reduced from the slag.

While the oxidation of sulphides releases energy, the process is not fully autogenous and supplementary energy is necessary. Fuel is injected through the Ausmelt lance to maintain the bath temperature at 1150°C throughout the smelting stage. Oxygen enrichment of the lance air to ~35% is employed to reduce the offgas volume and minimise fuel requirements.
A considerable amount of fume is generated during smelting due to the volatilisation of Pb, Zn, As and Sb species. This fume is collected and recycled to maximise the overall recovery of lead. Fume from the slag reduction process also has a high lead content and is recycled in the same circuit as the fume. The quantity of fume generated directly depends on the species present (metallic, sulphide, oxide) and the vapour pressure of those species at the furnace operating temperature. To minimise the lead fume recycle load, the following countermeasures are taken:

i. Maintaining a high oxygen potential to minimise the presence of lead sulphide, which has a significantly higher vapour pressure than lead metal or lead oxide.

ii. Minimising the operating temperature, thereby minimising the vapour pressure of the various lead species.

iii. Minimising the offgas volume by enriching the lance air with oxygen.

The reactions associated with smelting of the sulphide feed are principally:

\[
\begin{align*}
2\text{PbS}_\text{(s)} + 3\text{O}_\text{2(g)} & \rightarrow 2\text{PbO}_\text{(l)} + 2\text{SO}_\text{2(g)} \quad (1) \\
\text{PbS}_\text{(s)} + \text{O}_\text{2(g)} & \rightarrow \text{Pb}_\text{(l)} + \text{SO}_\text{2(g)} \quad (2) \\
\text{PbS}_\text{(s)} + 3\text{PbO}_\text{(l)} & \rightarrow 3\text{Pb}_\text{(l)} + 2\text{SO}_\text{2(g)} \quad (3) \\
\text{FeS}_\text{(s)} + 3/2\text{O}_\text{2(g)} & \rightarrow \text{FeO}_\text{(l)} + \text{SO}_\text{2(g)} \quad (4) \\
2\text{ZnS}_\text{(s)} + 3\text{O}_\text{2(g)} & \rightarrow 2\text{ZnO}_\text{(l)} + 2\text{SO}_\text{2(g)} \quad (5)
\end{align*}
\]

From Equations (1)-(5) it becomes clear that the total oxygen added to the bath must be manipulated to control the oxygen partial pressure to achieve the desired level of sulphide oxidation and lead metal production in the first stage. Control is achieved by the adjustment of lance air, oxygen and fuel added via the Ausmelt lance to the liquid slag bath. The level of PbO in the slag is controlled by the addition of PbS concentrate, air (oxygen), and/or coal to reduce PbO in slag and influence the overall bath oxidation condition.

During smelting the aim is to operate with a slag around 35% Pb (including all slag components), to allow for minimisation of fuming. At these conditions, PbO is a predominant phase and hence the slag had a low liquidus temperature. At the end of a smelting batch, before the slag reduction stage commences, the process requires an increase in bath temperature at a rate designed to maintain a fluid slag as lead is removed.

A typical slag system as designed for the processing of lead feed materials at YTC is shown in Figure 2. It provides an isothermal projection of the SiO$_2$-FeO-PbO system, depicting an operating window with the Fe/SiO$_2$ ratio of 1.2 anchoring the zone and the operating temperature of 1150°C.
Slag Reduction
When the slag level during the concentrate smelting in the TSL furnace reaches the desired level, the reduction process begins. The feed addition is stopped, and the lance operating conditions are adjusted. Also, additional lead concentrate and lump coal must be added to the furnace.

The lance air/fuel ratio is adjusted to maintain reducing conditions at the lance tip, and the fuel rate is adjusted to increase the temperature to 1200°C as the reduction process proceeds. It is necessary to increase the temperature to maintain the slag fluidity as lead oxide is reduced from the slag. The oxygen enrichment of lance air is about 30% during the slag reduction.

As the lead in slag approaches 5%, a final bullion tap takes place to recover the reduced lead metal.
The reduction of the predominantly PbO slag occurs in accordance with Equations 6 and 7 due to the addition of PbS and/or carbon (in the form of reductant coal). Figure 3 & Figure 4 depict the controlling factors of the reactions for this stage.

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PbS(s) + 2PbO(l) \rightarrow 3Pb(l) + SO_2(g) \quad (6)
\]

\[
PbO(l) + C(s) \rightarrow Pb(l) + CO(g) \quad (7)
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Figure 3: Theoretical relationships showing the role of PbS [2]

Figure 4: Theoretical relationships showing the role of PbS [2]