Operating Experience with the QSL-Plants in Germany and Korea

L. Deininger — Berzelius Stolberg GmbH, Stolberg/Germany
K. C. Choi — Korea Zinc Co., Onsan/Korea
A. Siegmund — Lurgi Metallurgie GmbH, Frankfurt/Germany

Abstract

The QSL plant in the existing "Berzelius" Stolberg GmbH lead smelter in Stolberg/Germany was commissioned in August, 1990. Following some modifications to the process and equipment which had become necessary in line with the implementation of this new technology, conclusive operating results are now available. These will be reported together with a short description of the plant design.

In May 1992, raw material feeding to the QSL reactor in the new lead smelter of Korea Zinc Co. in Onsan/Korea was started. As all the experience gained up to that point in time in the Stolberg plant had already been incorporated in this plant prior to start-up, it reached stable, satisfactory operating conditions in a short period of time. After an introductory description of the plant important operating results will be reported.

The operating experience gained in the two plants fully confirms the correctness of the inventors' creative ideas in the 70s. The QSL process meets all demands made on modern, ecologically compatible and energy-saving lead production technology. The paper ends with suggestions on how the QSL process will be optimized further in the future.

EPD Congress 1994
Edited by G. Warren
The Minerals, Metals & Materials Society, 1993

Introduction

The introduction of stringent environmental regulations for the industry by the authorities and rising operating costs in the standard process for the recovery of lead (sinter machine and shaft furnace), resulted in Lurgi looking for a new technology at the beginning of the seventies which would minimize air pollution and be more economical. In 1973 a continuous process for the treatment of metal sulphide concentrates with oxygen in one smelting unit was patented by Prof. Paul E. Queneau and Prof. Reinhardt Schuhmann. Based on this patent, Lurgi and Berzelius developed the QSL-process for the recovery of lead, to an industrial scale over the last two decades. The process is designed to treat all grades of lead concentrates as well as secondary materials, applying the bath smelting principle with submerged high-pressure injection of tonnage oxygen and fossil fuels. Two basically different pyrometallurgical reactions take place in the reactor: the autogenous roast-reaction smelting of raw materials containing sulphur and lead, and the carbothermic reduction of metal values from the fayalitic slag.

The reactor (figure 1) consists of a horizontal, slightly sloped cylinder, which is divided into an oxidation zone and a reduction zone and can be tilted by 90° about its longitudinal axis when operation is interrupted. The entire reactor is lined with high-quality chrome-magnesite refractories. Raw materials such as concentrates and secondary materials, fluxes, recirculated flue dust and, if required, solid fuel are agglomerated and charged through feed ports located in the roof of the oxidation zone without any further pretreatment. The agglomerated feed mixture falls into a molten bath consisting of slag and lead. Tonnage oxygen is blown into the melt through submerged, cooled injectors and the oxidation of the sulphides leads to the formation of primary lead bullion; slag with a lead oxide content of 25-35 % and sulphur dioxide-rich offgas. The exothermic reactions take place at 1100-1150° C.

Korea Zinc **LURGI**

QSL Reactor
(simplified)

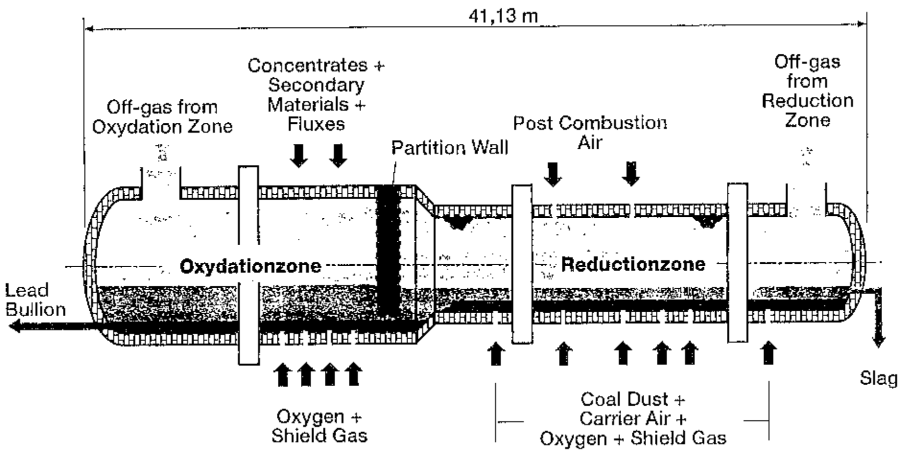


Figure 1

The lead bullion is discharged through a syphon, while the primary slag flows countercurrently to the lead and passes into the reduction zone. It is separated from the oxidation zone by a partition wall which has an underflow for the exchange of slag and metallic lead and an opening for the passage of the process gas. In the reduction zone a reductant, pulverized coal or coke, is injected into the molten bath through submerged, cooled injectors, together with carrier air and oxygen. The lead oxide is reduced by the reductant to metallic lead as the slag flows to the opposite end of the reactor. The carbothermic reduction takes places at 1200-1250° C. The metallic lead settles to the bottom of the reactor and flows back towards the oxidation zone to combine with the primary bullion. The low-lead final slag is removed at the end of the reduction zone via a slag tap .

Required postcombustion of the oxidation and reduction gases is accomplished with oxygen-enriched air or oxygen which is injected into the reactor gas atmosphere via lances. These lances are located in the roof of the reactor over its entire length.

The offgas with a high concentration of sulphur dioxide and some flue dust leaves the reactor at a temperature of approximately 1150-1200° C. It passes through a vertical uptake before entering a waste heat boiler for heat recovery and an electrostatic precipitator for dedusting. The precipitated flue dust can be recycled to the process or partially withdrawn to recover the cadmium contained in the dust. The offgas is finally passed through a wet gas cleaning step and a sulphuric acid plant.

If the raw materials contain a high amount of zinc, a separate uptake in the reduction zone may be installed for the recovery of zinc as zinc oxide fume. Under stronger reduction conditions, zinc is partially fumed off. The fumed metal is oxidized in the gas atmosphere and leaves the reactor through a vertical uptake. No gas opening is necessary in the partition wall in this instance. After the cooling of the offgas, the oxide dust, containing a mixture of zinc and lead oxide, is collected in a bag filter.

The advantages of the new process compared to the conventional operation are:

- direct recovery of metallic lead already during the oxidation of the sulphides
- lower amount of slag due to the direct recovery of metallic lead and hence, a lower amount of fluxes are required
- low offgas volume with high sulphur dioxide content resulting in comparatively small gas treatment equipment
- lower generation of materials to be recycled
- lower emissions
- high process flexibility
- recovery of the zinc content by fuming in the reduction zone and separate collection in a second offgas system for further treatment
- lower capital cost
- lower operating cost

Original Design of the QSL-Plants in Germany and Korea

In the second half of the eighties, the stringent German regulations for enviromental protection left Berzelius Binsfeldhammer in Stolberg/Germany with the options either to close down their lead smelter or to introduce a process which would meet the revised environmental standards. After the development of the QSL-technology to a semi-industrial scale, Metallgesellschaft AG decided in 1988 to replace the existing conventional lead smelter in Stolberg with the new process for 75,000 t/a of lead production.

At the end of 1988, Korea Zinc in Onsan/Republic of Korea signed a contract for a QSL-plant, rated with a lead production of 60,000 t/a.

Main Process Data

In the original design it was already intended for both plants to smelt secondary lead-bearing materials such as Pb/Ag-residues, Zn-residues, ashes, glasses, slags and battery paste together with concentrates. The ratios of concentrates to the amount of secondary materials in the raw material feed mixture and the composition of the main elements are indicated in Table 1.

Design Capacity and Feed Materials of the QSL Plants

QSL-Plants	Korea Zinc Onsan/Korea	Berzelius Stolberg/Germany
Production Capacity of tpa Lead Bullion	60 000	75 000
Reactor Size		
- total length in m	41.0	33.0
- dia. oxidation zone in m	4.5	3.5
- dia. reduction zone in m	4.0	3.0
Daily feed of Raw Material (dry) in tpd with 24h/d operation	550	500
Percentages of Concentrates and Residues in Raw Material Feed Mixture	53 % Concentrates 47 % Residues in Form of Pb/Ag-Residues, Zn-Residues, Pastes Au/Ag-Ores	63 % Concentrates 37 % Residues in Form of Pb/Ag-Residues Ashes, Glasses, Slags, Refinery Dusts
Composition of Raw Material Mixture		
- % Pb	35.0	45.0
- % Zn	10.0	5.0
- % Cu	0.6	0.7
- % As	0.3	0.3
- % Sb	0.3	0.4
- % Cd	0.3	0.05

Table 1

The size of a QSL-reactor is determined by the throughput of raw materials, the corresponding amount of slag produced and the amount of lead which has to be reduced. Tables 2 indicate the corresponding process and design figures for the QSL-plants in Stolberg as well as Korea.

Main Process Design Data of the QSL-Plants		
QSL-Plants	Korea Zinc Onsan/Korea	Berzelius Stolberg/Germany
Reactor Size		
- Total Length in m	41	33
- Oxidation Zone .. Length/Diameter in m	13 / 4.5	11 / 3.5
- Reduction Zone .. Length/Diameter in m	28 / 4.0	22 / 3.0
Feed in t/h (dry):		
- Raw Material	22.7	20.8
- Silica	-	0.004
- Limestone	2.7	0.3
- Recyc. Oxidation Fume	5.0	4.3
- Recyc. Leach Residue	1.3	-
- Recyc. Fumed Slag	-	-
- Coal Fines	2.8	1.9
Gases to Reactor in Nm3/h		
- Oxidation .. Tuyere Oxygen	7 300	4 700
- Reduction .. Tuyere Coal Dust in t/h	1.4	0.9
Lead Bullion in t/h	7.9	9.6
Slag in t/h	8.8	7.1
Final Slag - % Pb	2.0	2.5

Table 2

Testwork during the process development showed that high PbO levels in primary slags reduce the generation of lead fume with the PbS activity being inversely proportional to the square of the PbO activity in slag. On the other hand the PbO content in primary slag governs the slag fall -addition of fluxes- and the amount of reductant required. The original testwork, therefore, suggested a lead content in primary slag of 40 - 50 %, but practical operations at Berzelius/Stolberg and Korea Zinc proved a level of 25 - 35 % to be sustainable without increasing the flue dust production substantially.

Process Flow and Plant Layout of the Stolberg Plant

The smelter is designed for a throughput of lead-bearing materials of 150,000 t/a, these being mainly secondary materials. The ratio of concentrates to residues was intended to be approx. 63 : 37.

Figure 2 indicates the overall process concept for the Berzelius QSL-plant.

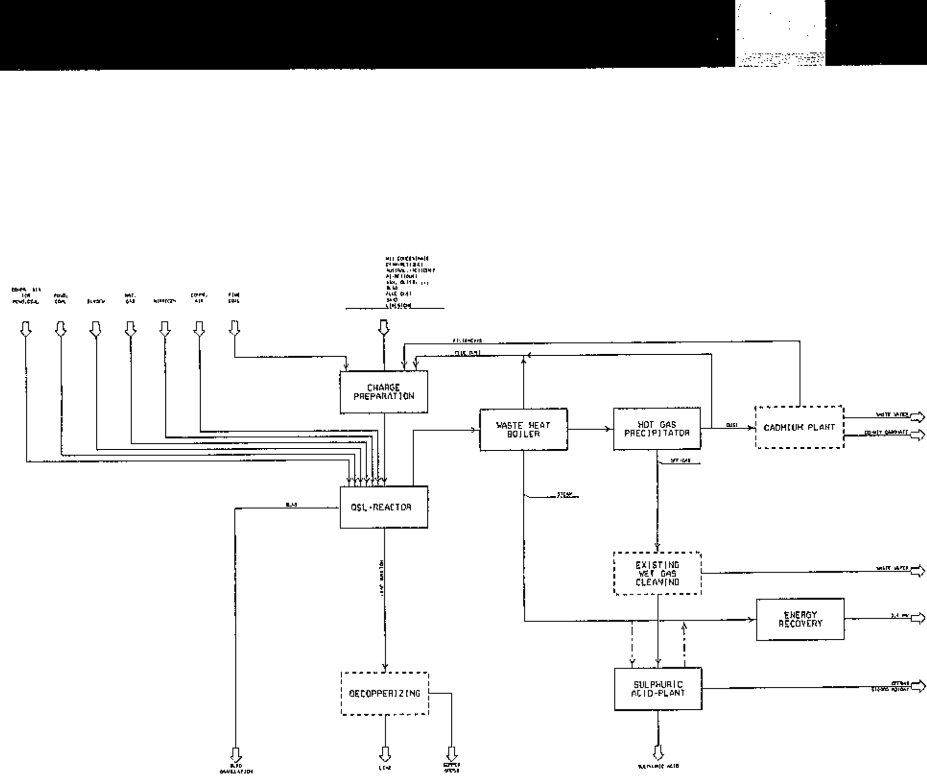


Figure 2: Process Flowsheet of the QSL-Plant at Berzelius in Stolberg/Germany

The QSL reactor replaced the conventional units, sinter plant and shaft furnace. The impure lead bullion produced in the QSL-reactor has to be treated subsequently in a pyrometallurgical refinery to marketable products.

Cadmium reports mainly to the flue dust from the oxidation zone and can be recovered as cadmium-carbonate by bleeding a certain amount of flue dust and the treatment in a subsequent leaching step.

A new sulphuric acid plant had to be erected for treatment of the sulphur dioxide containing process gas.

The excess heat from the reactor off-gases is recovered in a waste heat boiler and, together with the excess heat generated in the contact tower of the sulphuric acid plant, converted in a turbine into electric energy for plant use.

In the layout drawing (figure 3), the compact design of the QSL-plant becomes obvious. The reactor building has been erected parallel to the sinter plant to allow the connection of the existing feed preparation system, such as the proportioning system and the feed mixer for agglomeration. The pre-mixed feed material is transported to a new subsequent mixing drum, where coal fines and recirculated flue dust are added before entering the reactor.

The QSL-reactor has a total length of 33 m, a diameter of 3.5 m in the oxidation zone and 3 m in the reduction zone. The reactor was originally designed for a total installation of three pairs of shrouded injectors in the oxidation zone for the introduction of the oxygen required. Lead bullion is tapped through a syphon which is located at the end of the oxidation zone. The reduction zone has been designed for the installation of a total of 8 shrouded injectors for the injection of the reductant, in this case powdered coal. The final slag is discharged at the end of the reduction zone.

The process gas of the reactor is carried via a vertical radiation channel, through the convective pass of the waste heat boiler system, into an electrostatic precipitator. The off-gas then passes through a duct to the existing wet gas cleaning and the new sulphuric acid plant.

The coal proportioning system for the reduction zone consists of a coal silo, a pressure equalizing bin and four dosing vessels. From the silo, powdered coal or coke is periodically discharged into the pressure equalizing bin where the reductant is pressurized with nitrogen and then discharged to the dosing bins. Each dosing bin is equipped with a star feeder for mass flow control, and two outlets, which are used to provide continuous discharge of the reductant, being pneumatically transported to two reduction injectors.

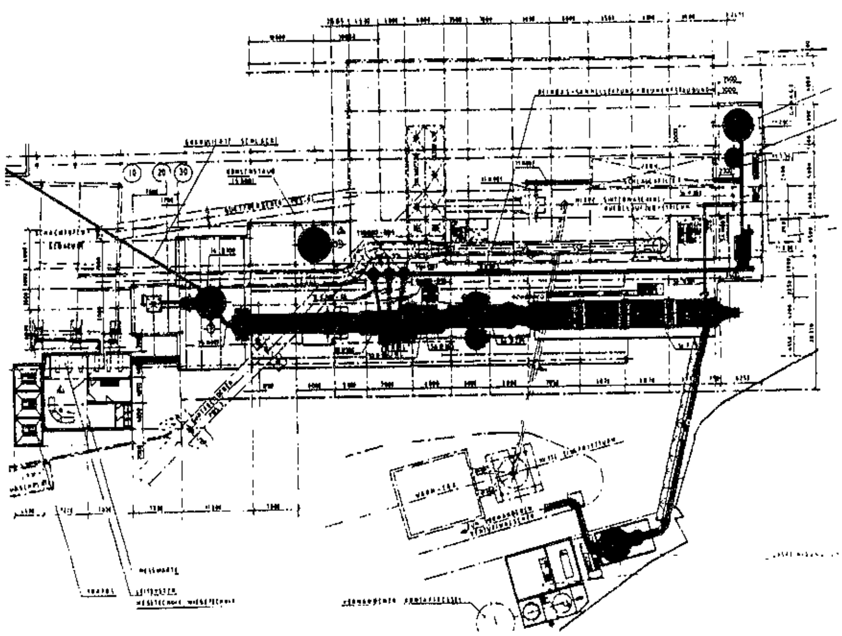


Figure 3: Arrangement of the QSL-Plant at Berzelius in Stolberg/Germany

<u>Process Flow and Plant Layout of the QSL-Plant Korea</u>

The QSL-plant in Onsan, Republic of Korea, is designed for the processing of feeding material with a residue content of approx 47 %. The overall process concept (figure 4) is similar to the Stolberg plant. Due to the comparatively high zinc load, zinc is recovered by fuming in the reduction zone. The fumes are drawn off together with the reduction offgas via a second offgas system, are collected in a baghouse and precipitated as mixed oxides for further hydrometallurgical treatment to recover the zinc.

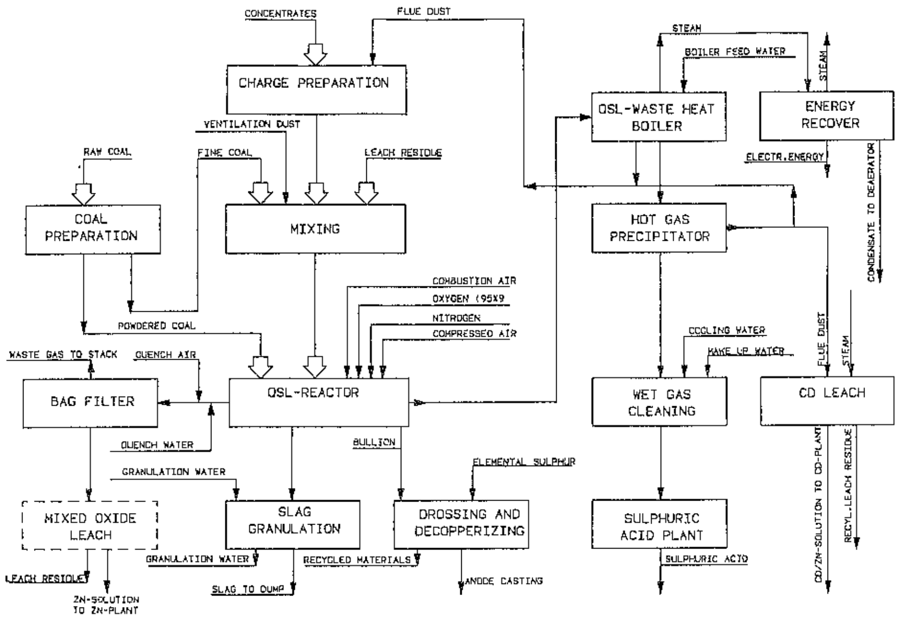


Figure 4: Process Flowsheet of the QSL-Plant at Korea Zinc in Onsan/Korea

The layout drawing (figure 5) shows the feed storage facilities, feed preparation, and the reactor building with slag treatment and offgas handling. The storage building is separated into a "dry" section where concentrates, fluxes etc. are stored, and a "wet" section for residue storage. The "dry" raw materials are unloaded from trucks in the unloading station and distributed by a tripper conveyor into individual boxes. "Wet" materials such as Pb/Ag-residues, are unloaded with a pay-loader and distributed by a crane into different storage boxes. Material reclaiming is done by two overhead cranes. "Dry" materials are transferred to the feed preparation area by a conveyor belt where they are stored in bins. Coal is unloaded pneumatically and transported into two silos before being crushed and ground in a coal milling plant. The "dry" materials from the bins are proportioned according to a preset amount and fed to a stationary mixer, while the "wet" materials are conveyed by a plate feeder and a weigh belt feeder directly to the mixer. The final mixture is then fed to the QSL-reactor via two feed bins.

The reactor has a total length of 41 m, a diameter of 4.5 m in the oxidation zone and 4 m in the reduction zone. Like the Stolberg reactor, it has been designed for the installation of three pairs of oxygen injectors in the oxidation zone and 8 injectors in the reduction zone.

Both waste gas systems are arranged at a 90° angle to the QSL reactor. The offgas from the oxidation zone with a high sulphur dioxide concentration is transferred to a sulphuric acid plant for the recovery of sulphuric acid.

The lead drossing kettles are located north of the reactor, alongside the waste gas system of the oxidation zone. The final slag is continuously discharged at the end of the reduction zone and treated in a subsequent slag fuming furnace or directly granulated, this taking place to the south of the reactor.

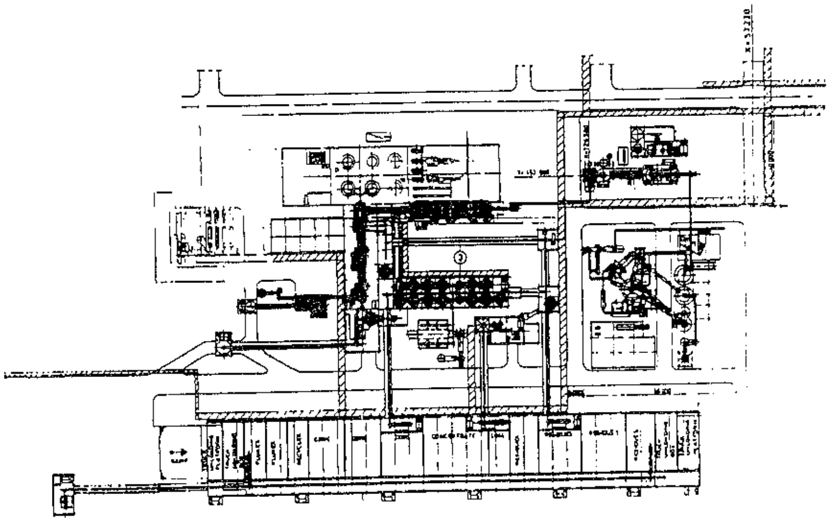


Figure 5: Arrangement of the QSL-Plant at Korea Zinc in Onsan/Korea

Operation of the QSL-Plant at Berzelius in Stolberg/Germany

Starting with initial tests in August 1990, the plant was officially inaugurated on November 11, 1990.

The operating experience gained since the start up has led to a number of modifications to the reactor and preceding or subsequent equipment which were implemented during a total of three plant shut downs.

Reactor

Compared to the initial concept, improvements have been introduced. This is shown in figure 6.

Oxidation Zone

In the original design three feedports were located directly above the oxidation injectors. This arrangement led to occasional blockages of the feed ports caused by splashing of melt from the injector. Consequently, the number of feed ports was reduced from 3 to 2 and located equidistant from the injectors. This modification took place in two steps (figure 6; modifications 1 and 2).

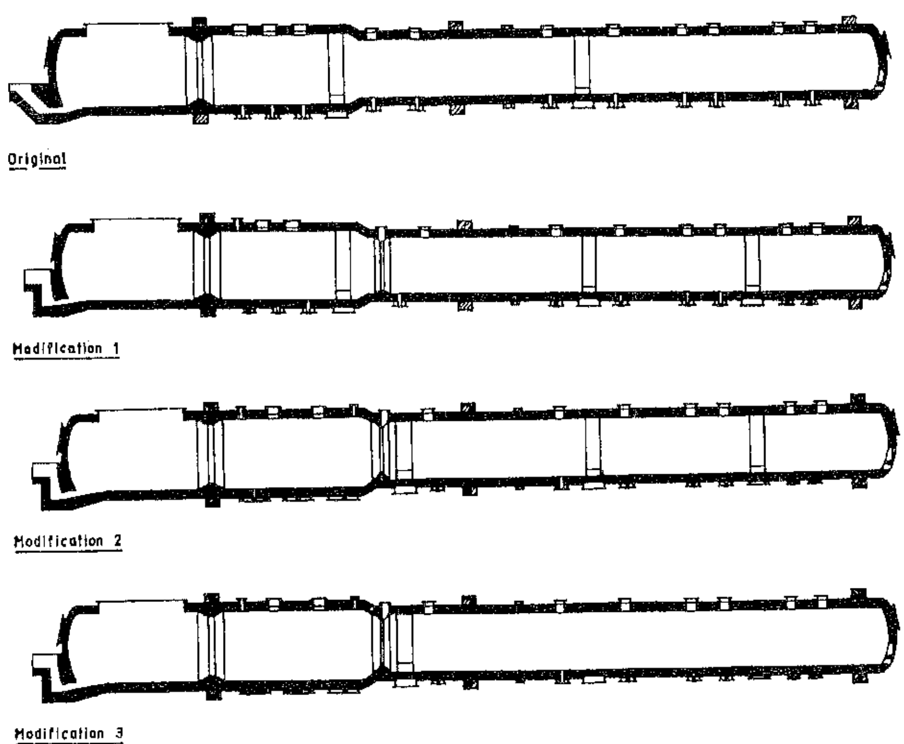


Figure 6: Original Design and Performed Modifications at the QSL-Reactor of Berzelius in Stolberg/Germany

<u>Submerged Injectors for Oxygen (S-Injectors) in the Oxidation Zone</u>

Oxygen is injected via a central pipe and its two surrounding annuli to oxidise the feed material. Shroud gas, a mixture of nitrogen and atomized water, is injected via an outer surrounding annulus to protect the injector tips from excessive burn-back. Natural gas can also be injected together with the shield gas for heating purposes. In the initial concept the injectors were cooled by nitrogen only, which resulted in instable burn-back rates of the injectors. With the introduction of a mixture of nitrogen and water as the cooling agent, the lifetime of the injectors was substantially increased and stable burn-back rates were obtained because stable mushrooms could be formed at the injector tip.

In parallel the construction of the brick arrangement adjacent to the injectors was modified. The wear rate of these bricks is high due to the aggressive and turbulent nature of the melt in this area and the exothermic chemical reactions. Provision had been made in the original design for the replacement of the bricks adjacent to the injector positions. A frame, in form of a flat arch, surrounds the injector bricks to prevent the remaining lining from collapsing during the replacement of the bricks. Experience has shown that the wear always begins in the joints of the bricks. The wear of the bricks spreads over an area which is approx. 10 times larger than the diameter of the injector. Based on examinations, an injector brick was introduced consisting of 3 chrome-magnesite based bricks glued into a sandwich structure to reduce the number of joints.

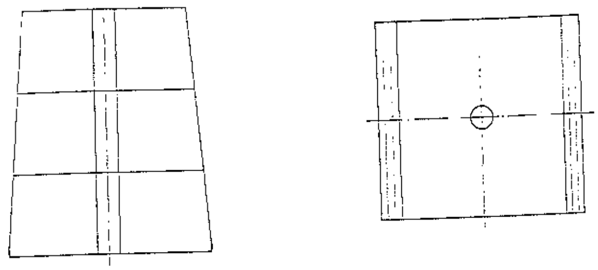


Figure 7: Injector Brick in Sandwich Structure

In addition, the cross-section of the flat arch was enlarged to provide a bigger area which can be replaced. Figure 8 shows a typical brick arrangement adjacent to an oxygen injector (S-injector) with a mushroom at the injector tip. The shown refractory lining was approx. 1 year in service.

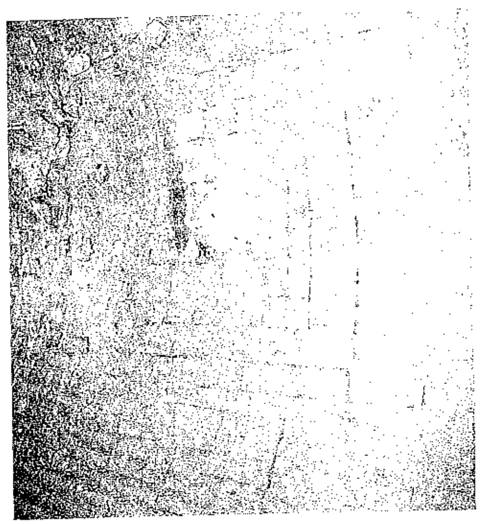


Figure 8: Typical Brick Arrangement Adjacent to an Oxygen Injector

All injectors manufactured from ferritic stainless steel, are sealed to the injector brick by cementing them into the refractory block prior to their installation.

Due to the modifications of the injectors themselves, the bricks adjacent to the injectors and an intensive cooling of the reactor shell in the injector area (figure 9), the lifetime of the S-injectors could be increased from short periods (in the start-up phase) to approx. 1000 h of real operation time.

Figure 9: Cooling of the Reactor Shell in the Oxidation Zone at the QSL-Plant in Stolberg/Germany

The total number of injector positions was reduced from 6 to 3 and located in the 0° vertical position (figure 6, modification 2).

Partition Wall

For modifications to the oxygen injectors with the enlarged injector brick area, an enlarged oxidation zone area was required. For this reason, the partition wall between the oxidation and the reduction zone had to be moved towards the reduction zone. To improve the lifetime of the partition wall, ground bricks were arranged in a ring structure (Figure 10).

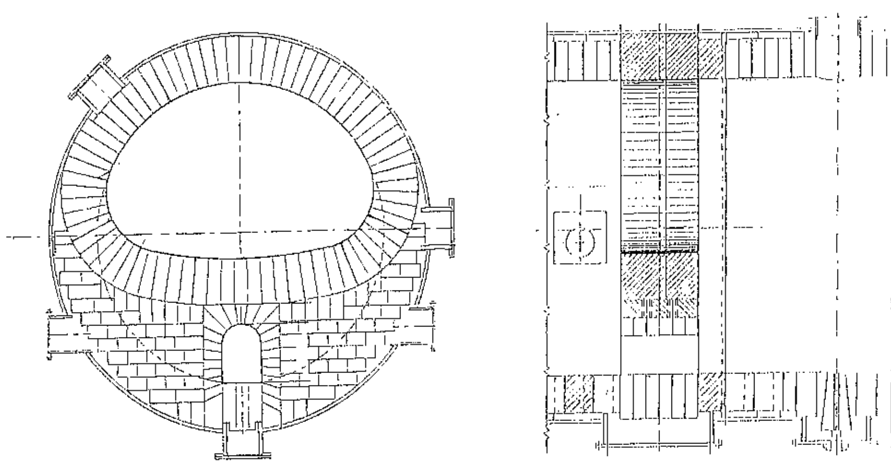


Figure 10: Partition Wall between Oxidation- and Reduction Zone at the QSL-Plant in Stolberg/Germany

Lead Syphon

To prevent blockages at the lead tap, the lead syphon was modified and built closer to the reactor shell (figure 6, modification 1). The built-up of accretions in the syphon area of the reactor and below the offgas channel was reduced by installing an insulating backlining to reduce heat losses. Furthermore, an oxy-fuel burner was installed at the end of the oxidation zone as a safety measure.

Reduction Zone

One result obtained from the start-up operation is that a lead bath above the injectors in the reduction zone is required to achieve a stable operation and the envisaged reduction results. In order to incorporate this concept in the existing reactor design, it was necessary to install a refractory dam ring upstream from the transition point of the reduction zone in the oxidation zone. This ensures that a certain level of lead is always maintained in the reduction zone. The installation was carried out in three steps for optimization reasons:

Figure 6:	modification 1	- a ring dam with a height of 150 mm
	modification 2	- a ring dam with a height of 300 mm
	modification 3	- a ring dam with a height of 350 mm

The overall reduction efficiency can be impaired if an oxidising post combustion jet impinges the slag layer. In the original design, the post combustion lances were located directly above the coal injectors so that the impingment of the post combustion jet in the splashed slag was relatively high. The post combustion lances are now offset from the coal injectors. To provide a better heat transfer to the melt, the post combustion lances operate with oxygen enriched air.

In the initial concept the reduction zone was to be divided into compartments. To eliminate back-mixing effects attributed to high bath turbulance, the reduction zone had been divided into three compartments by partition walls (figure 6, modification 1). After the optimising of the reduction parameters, it was found that the partition walls were not required and could be removed.

Submerged Injectors for Coal (K-injectors)

The injectors in the reduction zone are used for the injection of solid fuel. This is injected through a central ceramic pipe together with carrier air. Oxygen is injected through an annulus arranged concentrically around the central pipe which is surrounded by a further annulus through which shroud gas (nitrogen) is injected. The coal injectors are made out of the same grade of steel, have the same modified brickwork as the oxygen injectors and are also cemented into the refractory block prior to installation. A service life for the injectors of up to 2000 h of operation is obtained.

The last two injector positions, upstream of the slag tap were located in the vertical 0°-position (figure 6, modification 1).

Currently the reduction zone is operated with five coal injectors and one natural gas injector which is located next to the slag tap.

The reactor shell area adjacent to the injector flanges are cooled by a water cooling system

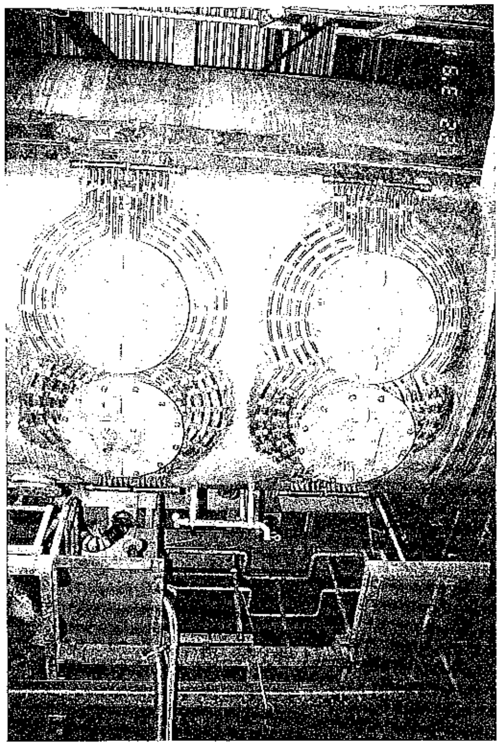


Figure 11: Cooling of the Reactor Shell in the Reduction Zone at the QSL-Plant in Stolberg/Germany

Waste Heat Boiler

For the efficient operation of the overall QSL-plant, a waste heat boiler was installed to remove heat from the offgas for energy recovery. The use of such a waste heat boiler system was new in a lead smelting process and, therefore, several design parameters were transfered from equivalent equipment in the zinc industry. After some minor modifications to the waste heat boiler had been performed, such as the improvement of the rapping device, it became obvious that the heat transfer area was not sufficient due to higher energy levels in the offgases than expected. Therefore, the heat transfer area was enlarged by the installation of two additional panels of about 100 m^2 into the radiation channel during the shut-down of the plant in May/June ´93.

An inclined membrane wall at the transition of the radiation channel to the convective pass was removed and substituted by a vertical wall because of the formation of sintered accretions which caused blockages in the transition, resulting in an interuption of the operation.

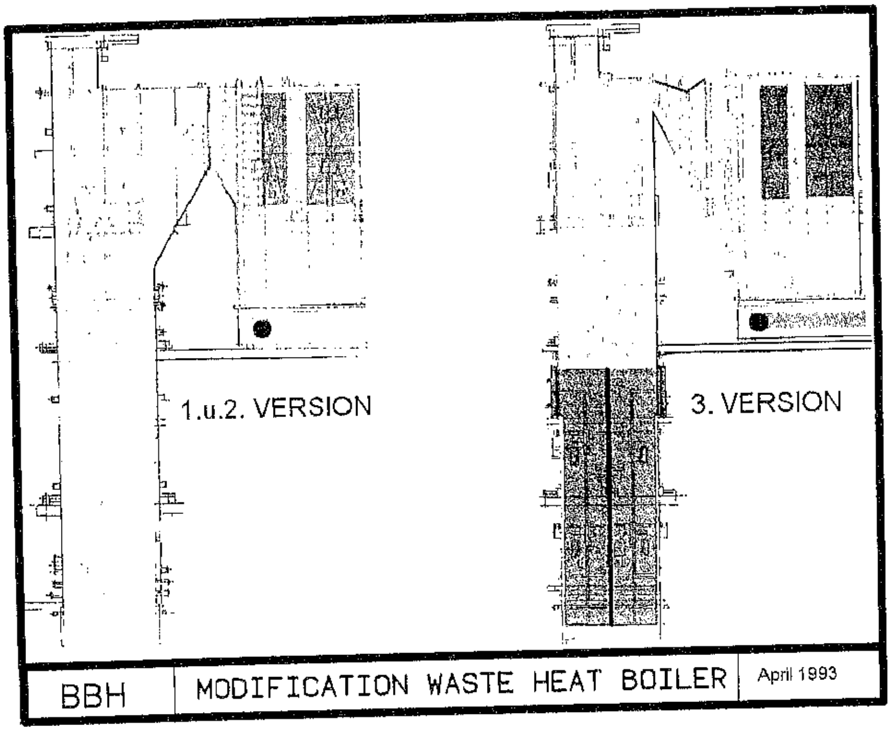


Figure 12: Performed Modifications at the Waste Heat Boiler of the QSL-Plant in Stolberg/Germany

Slag Treatment

It was initially planned to further treat the slag from the QSL-reactor in an electric furnace in order to decrease the residual metal content in the slag. Operation showed that this furnace-type requires too much energy and, therefore, alternatives were considered. A gas-operated forehearth was installed and replaced the electric furnace, to settle entrained metallic lead before the slag is granulated. With the optimized operation of the process, the slag can now be granulated directly at the slag tap of the reactor and, therefore, the forehearth was removed in May/June 1993.

Metallurgical Results

Since the operation mode was changed, maintaining a lead level between 250 - 350 mm in the reduction zone and a relatively thin slag layer of approx. 100 - 150 mm, the envisaged reduction results have been obtained under stable conditions. Moreover, back-mixing effects within the slag are minimized under these operating conditions.

The obtained stable reduction results may be attributed to the more intensive heat transfer in superheated lead, ion transport and different diffusion rates within the entire system as well as the overall reaction kinetics, and their influence on gasification of the coal or the reforming of natural gas. Required heat for the reduction reaction is provided by the superheated lead so that problems with the formation of massive, uncontrolled growth of accretion by frozen slag adjacent to the injectors no longer occur at operating temperature.

QSL STOLBERG
February 1993

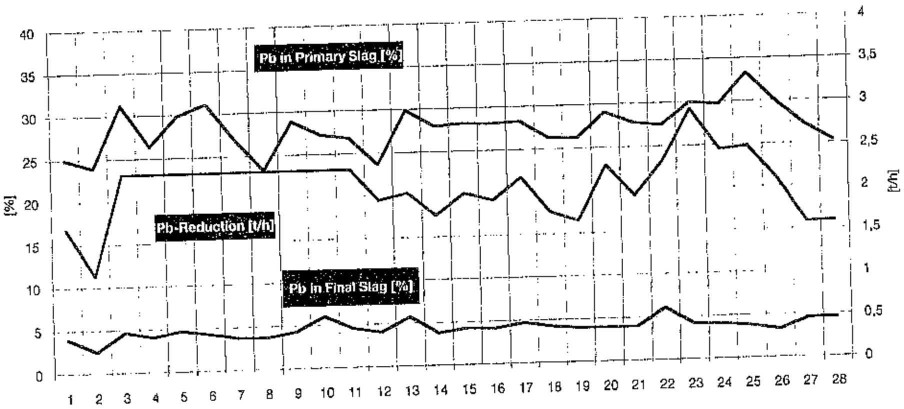


Figure 13: Reduction Results of the QSL-Plant at Berzelius in Stolberg/Germany

Until the last plant modification in May/June '93, the plant could only be operated below the designed capacity, due to the limitations of the waste heat boiler as mentioned above. After the restart of the plant in July '93, it was demonstrated within a short time that, with the enlargement of the heat transfer area in the waste heat boiler, the throughput of raw materials in the reactor could be significantly increased without deteriorating the envisaged operating results, mainly with regard to the reduction results. The reactor is presently operated with a ratio of concentrates to secondaries of approx. 1:1 and feed rates between 28 to 35 t/h. The lead content in the primary slag is adjusted at 25 - 30 %, resulting in a generation of flue dust of approx. 6 t/h. The total volume of offgas of 22,000 - 24,000 Nm^3/h behind the electrostatic precipitator has a sulphur dioxide content of approx. 8 - 10 % and is transferred to the sulphuric acid plant for the recovery of sulphuric acid.

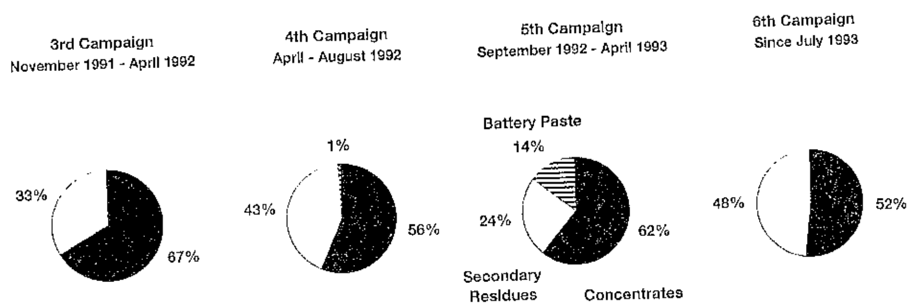


Figure 14: Fresh Feed Composition of the QSL-Plant at Berzelius in Stolberg/Germany

The slags produced are essentially iron silicate slags and, with reference to the percentage of the principal slag-forming constituents FeO, CaO, SiO_2 and Al_2O_3, are in the olivine range. The ratio of the CaO + MgO/ SiO_2 is on average 1.0-1.2. Due to the zinc content in the raw materials, the zinc content of the slag does not exceed 15 % even if the entire fresh zinc input is collected in the slag. The reduction potential in the reduction zone is adjusted so that no zinc is fumed. Otherwise zinc would be collected together with the dust from the oxidation zone due to the lack of a second offgas system, and recirculated back to the process, resulting in an accumulation of zinc in the slag. Above approx. 18 % zinc content, the slag becomes viscous and is more difficult to handle.

A comparison of energy consumption in the QSL-plant with the former mode of operation (sinter plant and shaft furnace), shows that only approx. 60 % of the energy is required for the QSL-plant. Even fuels containing sulphur can be employed because all offgases are treated in a sulphuric acid plant.

Energy Recovery

The hot process offgas from the QSL-reactor is cooled from approx. 1,200° C to 400° C in a waste heat boiler. Saturated steam with a temperature of approx. 250° C and a pressure of 47 bar is produced. This saturated steam is transferred to a superheater unit installed downstream from the contact vessel in the sulphuric acid plant. The steam in the superheater is heated to approx. 340° C with the excessive heat from the extremely exothermic reaction

$$SO_2 + \frac{1}{2} O_2 = SO_3$$

produced in the contact vessel. An auxiliary boiler with a separate superheater guarantees that the entire volume of steam is always available at a uniform temperature and pressure to operate a turbo-generator unit, even when steam generation from the operation fluctuates.

The turbo-generator unit is designed for a nominal output of 3.5 MW.

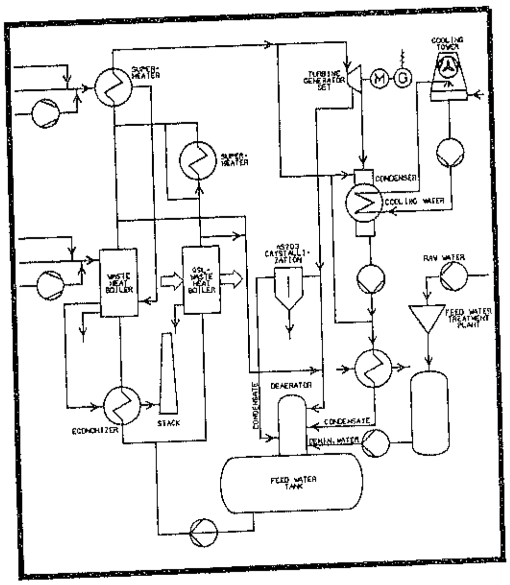


Figure 15: Waste Heat Recovery System at the QSL-Plant in Stolberg/Germany

According to the overall power generation concept, the turbo-generator can be operated independently. Consequently, in the case of a power failure, the QSL-plant can continue to be operated.

The supply of electric energy taken from the public grid could be reduced altogether from a former value of 4.5 MW to 0.5 - 1 MW. The energy gained by waste heat recovery averages 2.5 MWh per month.

Situation Regarding Emissions

For years, the degree of dust and heavy metal precipitation in the area of the plant has been measured by the means of a network of monitoring stations. In the immediate vicinity (4 km^2) of the smelter there are 16 examination areas, each of 0.25 km^2, where plant emissions are determined. In addition, there are 48 examination areas, each of 1 km^2, throughout the Stolberg area, and a further 13 areas, each of 1 km^2, over a wider area in the vicinity.

Based on measurements performed by the german authority the reduction of emissions from the QSL-plant compared to the former status, i.e. with the operation of the sinter machine and the blast furnace, is as follows

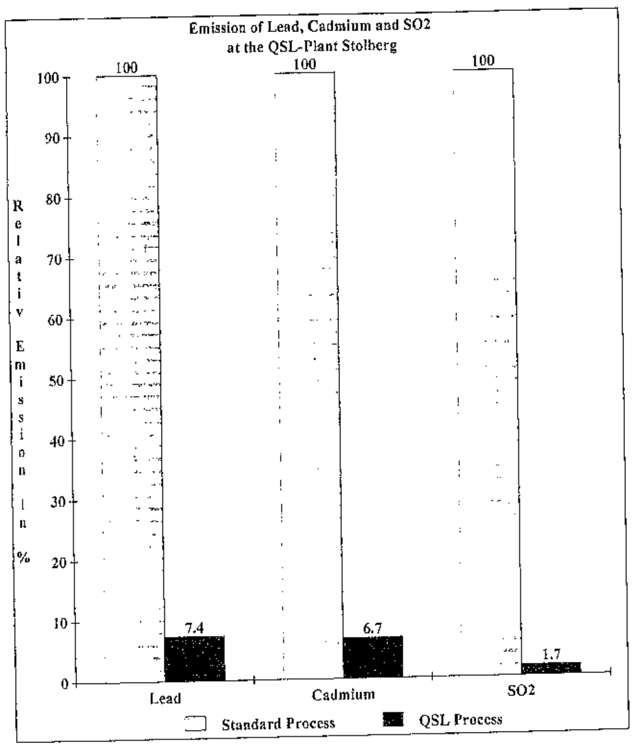


Figure 16

It was shown with the start-up of the new QSL technology that the high demands of the "TA-Luft" (German air pollution legislation) are attainable and, close to the plant boundary, the limits specified are significantly maintained.

Modifications Performed before Commissioning

The experience gained during the commissioning of the QSL-plant in Stolberg/Germany, resulted in some modifications carried out in advance of the plant at Korea Zinc being commissioned.

Figure 17: Original Design and Performed Modification at the QSL-Reactor in Onsan/Korea

A total of four additional S-injector flanges were installed to eliminate the problem of plugged feed ports caused by the splashing of melt. This arrangement allows the reactor to be operated with two or three feed ports always in service, while using 6 S-injectors located offset from the feed ports.

Two dam rings were incorporated in the reduction zone to provide a constant lead layer of between 250 - 350 mm over the whole length of the reduction zone and to achieve satisfactory and stable reduction rates.

Two additional partition walls were installed in the reduction zone for better control of the reduction itself and to decrease the amount of back-mixing.

The offgas opening in the partition wall between the oxidation zone and the reduction zone was closed completely to eliminate problems with the operation of a two fan system using two pressure control sensors and to improve the draft control.

An oxy-fuel burner was installed at both ends of the reactor to avoid the build-up of accretions and to keep the melt liquid.

In accordance with experience gained from the Stolberg plant, a water-cooled injector was introduced in the oxidation and reduction zone to improve the service life. In addition, the injectors were designed as movable injectors and can be shifted into the reactor according to the injector wear rate, up to a maximum length of 300 mm. In the case of the S-injectors, the ratio of oxygen to total gas volume per injector was also reduced by increasing the nitrogen shield gas volume. All injectors were equipped with an individual oxygen flow control to improve the overall operation.

The postcombustion lances in the oxidation zone were equipped with individual flow controls and an adjustable oxygen enrichment and/or pure oxygen flow operation, to improve the control of gas-postcombustion for a better heat-efficiency and to prevent uncontrolled lead oxidation. The postcombustion lances in the reduction zone were equipped with an individual flow control for the postcombustion air and with an adjustable oxygen enrichment of up to 40 % in the air, to improve postcombustion control for better heat-efficiency and to prevent a re-oxidation of lead which had already been reduced.

A water-injection system was installed in the radiation channel for peak off-gas temperature control if required, in order to avoid dust accretion build-ups in the waste heat boiler.

To guarantee the continuous operation of the coal injection in the reduction zone, the fluidization system of the coal dosing system was modified in order to pressurize the reductant up to the operating atmosphere by compressing the reductant without the formation of accretions and bridges.

Operating Performance

The commissioning of the plant began on May 10th, 1992, with the first material being charged into the reactor.

During the first operating period, some mechanical problems had to be solved, mainly in ancillary equipment upstream or downstream of the reactor, such as a leakage in the waste heat boiler system, the slag granulation system, etc.. Nevertheless, it was possible to demonstrate that good metallurgical results could be achieved in the plant.

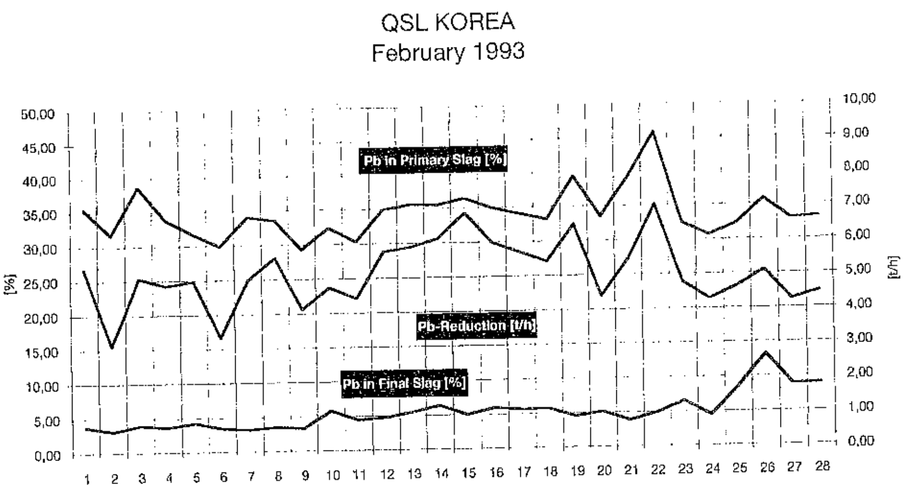


Figure 18: Reduction Results obtained at the QSL-Plant at Korea Zinc

During the month of August 1992, the plant already achieved its design capacity for lead bullion of 60,000 tpy. The reactor was operated mainly with concentrates as raw material and with feed rates of between 42 - 48 t/h. It was possible to adjust and maintain a lead content in the primary slag of about 30 - 35 %. This lead content was reduced to 2 - 5 % in the final slag tapped from the reduction zone. The total generated volume of offgas from the oxidation zone was between 30,000 to 32,000 Nm³/h, including false air from the transition reactor to the offgas channel, it contains approx. 9 - 11 % sulphur dioxide and carries between 7 to 8 t/h of flue dust.

On November 22nd, 1992, the plant was shut-down to replace the partition wall between the oxidation and reduction zone and to remove the two partition walls which had been installed in the reduction zone. After optimization of the operating parameters, it was found that stable and sufficient reduction rates could be achieved even without the partition walls in the reduction zone.

The incorporation of all the modifications prior to commissioning was an important measure to ensure the successful operation of the plant within such a short time after commissioning.

The arrangement of the installed S-injectors in relation to the feed ports eliminated splashing into the feed ports.

With the water-cooled, movable injector system an increased service life could be achieved from the beginning. After optimization by increasing the water flow rate up to 80 - 100 l/h to the injectors in the oxidation zone, the service life was substantially improved up to 1,600 operating hours resp. 67 operating days (table 3). The intensive cooling by the shield gas mixture is utilized to form a protective mushroom in the vicinity of the injector tip and the surrounding refractory. It is believed that an acceptable injector life can only be achieved when a stable mushroom is formed. On the other hand, acceptable reduction results could only be achieved as explained before in the presence of a certain lead bath height, which means a stable mushroom can only be formed if the distance of the injector tip from the lead/slag interface is not too high, otherwise the service life of the injectors is reduced (table 3). A possible explanation for this effect could be the degree of difficulty in forming a mushroom of solidified slag on the injector tip at high lead levels. Mushroom formation could be seen as a dynamic process involving the transport of slag to the injector tip, due to the turbulence caused by the gas plume above the injector and the remelting of the slag in the passage of superheated lead. The deeper the lead layer in the quiescent part, and hence, the lower the probability of slag being entrained in the stirred part of the bath above the injectors and dragged down to the vicinity of the injector. This decreases the growth rate of any mushroom being formed.

Actual Average Injector Service Life Korea Zinc

		S-Injectors		K-Injectors	
		In Deep Lead Bath (S2,S4,S6,S9)	In Shallow Lead Bath (S8,S10)	1992	1993
Overall Burn-Back Rate	mm/oper. hours	1.19	0.37	0.38	0.16
Service Life	oper. days	21	67	34	79

Table 3: Actual Service Life of the Injectors at the QSL-Plant at Korea Zinc in Onsan/Korea

The modified coal-dosing system resulted in a continuous flow of the reduction agent into the reactor. The cooling intensity of the injectors, dependent on the flow rate of the shield gas, has to be balanced so that the mushroom is large enough to afford reasonable protection to the injector tip, but not so large to provoke injector blockages by solid fuel. Currently, the achieved wear rates of the K-injectors are about 0.1 - 0.3 mm per operating hour, resulting in an effective, average injector service life of up to 4 months. However, this average is affected by the premature replacement of injectors in the course of preventive maintenance.

The individual control of the gas flow rates to the injectors, as well as the postcombustion lances provided a much higher flexibility in controlling the overall process with regard to the thermal and the material balance. Since the restart of the plant on January 5th, 1993, together with the operating parameters, optimized mainly with concentrates as new feed during the first five months after the commissioning of the plant, the amount of secondary materials has continuously increased, esp. Pb/Ag-residues. In July '93, the ratio of concentrates to secondary materials of the fresh material charged into the reactor was up to 55:45.

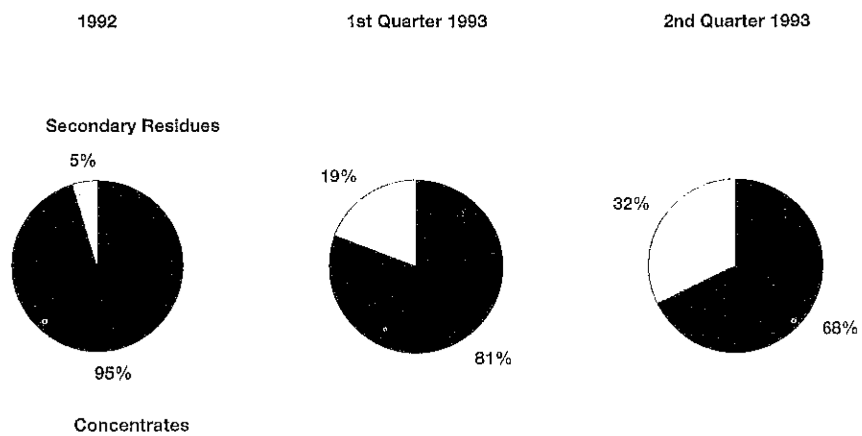
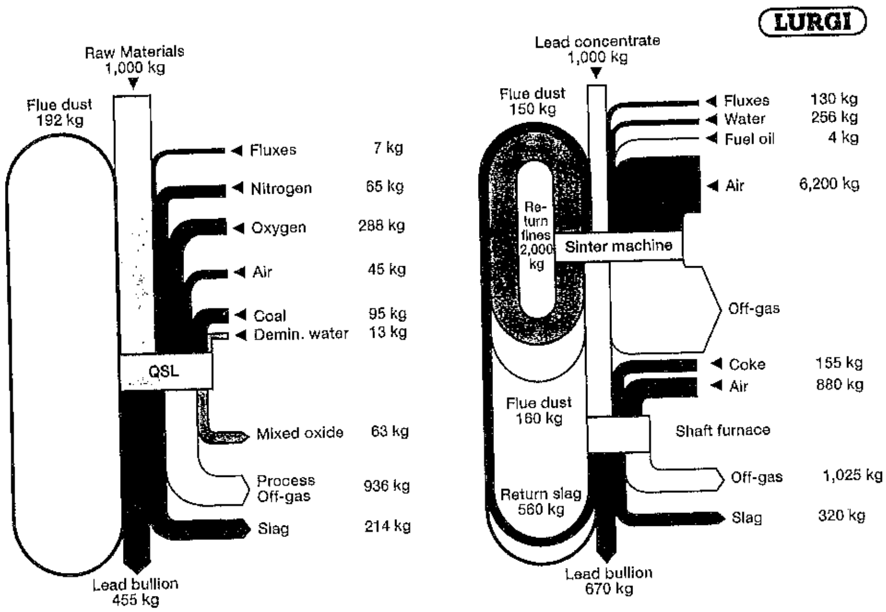


Figure 19: Fresh Feed Composition of the QSL-Plant at Korea Zinc in Onsan/Korea

In the process, copper and silver are collected mainly in the lead bullion and are recovered in subsequent refining steps. Similar to the Stolberg operation, the generated slags are essentially iron silicate slags and are, with reference to the principal slag-forming constituents only, in the olivine range. The adjusted basicity ($CaO + MgO/SiO_2$) is in the range between 0.6 - 0.8. Zinc is fumed in the reduction zone depending on the prevailing reduction potential, then collected in the mixed oxide dust, or leaves the reactor with the slag if not fumed. Depending on the reduction potential, most of the arsenic is reduced and partially dissolved in the secondary lead or fumed and collected together with the zinc in the mixed oxide dust. Cadmium is enriched in the flue dust of the oxidation zone. In order to control the cadmium content, a bleed of flue dust is performed periodically and cadmium is recovered by leaching and precipitation as cadmium carbonate.

The lead recovery rate obtained from the overall process is approx. 98 %.

A comparison between the operating results of the QSL-process and the standard process (sinter machine and blast furnace) indicates that the mass flows of recycled materials in the QSL-process have been drastically reduced. With the standard process (sinter machine/shaft furnace) the quantity of recirculated materials is approx. three times higher than the charged materials in order to obtain the lowest possible sulphur content in the sinter. In the Korean QSL-plant only approx. 19 % of the charge has to be recirculated. This results in fewer sources of emission. Moreover, in the QSL-process lower offgas volumes by the application of oxygen instead of air must be treated. As a consequence, this also results in a reduced amount of emitted mass flows. Even with the treatment of a raw material with a ratio of concentrates to high fuel requiring secondary materials of 55:45, the consumption of the solid fuel is lower in the QSL-process compared to the standard process operating only with concentrates. In addition, less expensive fuels and/or reductants can be applied, such as coal instead of coke. Most of the other consumption figures are lower in the QSL-process than in the standard process. Altogether, this results in a more economic operation with low environmental pollution.



Mass Flow in QSL-Lead Smelting Korea Zinc
Basis: 1000 kg Raw Material (55 % Concentrates, 45 % Secondary Materials) (46 % Pb)

Mass Flow in Conventional Lead Smelting
Basis: 1000 kg Concentrates (65 % Pb)

930170 M

Figure 20

Further Developments

For an even more economical operation of both QSL-plants, some investigations are still being carried out.

Service Life of the Refractory Lining

The service life of the main refractory lining in the QSL-plants in Stolberg and Korea is now longer than one year. Compared to the main brickwork, a higher wear rate of the refractories has been experienced in the partition wall, at the slag line and in the vicinity of the injectors.

The refractory wear in the partition wall always starts in the joints in the gas phase. After certain wear rates have been reached the attack affects single bricks which finally leads to the loss of that brick. The remainder of the brickwork is then no longer interlocked and will eventually cause the loss of the wall. To improve the service life of the bricklining of the partition wall, the design has been modified so that the partition wall is built with polished bricks without mortar to reduce the width of the joints. At the same time, a detailed examination to design a water and/or air-cooled partition wall is being performed. A totally different design of the partition wall area is also under investigation.

The wear rate at the slag line and in the bricks adjacent to the injectors is caused by erosion and the infiltration of slag into the bricks with the subsequent dissolution of the MgO-phase out of the bricks. To extend the lifetime of the bricks in these areas as well as the partition wall, different brick qualities are being tested in two test areas in the Stolberg reactor. These bricks have demonstrated an excellent resistance to high temperature, chemical attack, mechanical attack and thermal shock in lab-scale tests.

Service Life of the Injectors

Even though an acceptable and predictable service life of the S and K-injectors was achieved by introducing water-cooled and movable injectors, further investigations to improve the lifetime of the injectors are being carried out.

On a laboratory scale, several metallic and ceramic materials have been tested. Injectors have been constructed from the best proven materials from these tests in order to investigate how these materials behave under operating conditions.

Furthermore, investigations regarding different injector designs are being carried out in order to improve the cooling of the injectors by the gas media.

Slag Flow Phenomena

For a further optimization of the reduction of lead, fluid dynamics calculations on a computer model are being carried out to examine the flow phenomena of the slag at different depths of the lead and the slag layer in the reduction zone.

Conclusion

The QSL-process can meet the demands of modern, energy-saving, ecologically compatible, lead production technology. German and Korean QSL-plant operations show that QSL capital and operating costs are lower than those of the conventional sinter machine-blast furnace process. Stringent environmental standards can be met, and can be maintained on a permanent basis. The correctness of the inventors' creative ideas in the seventies has been confirmed.

The viability and flexibility of the overall process and of reactor design has been demonstrated in both plants. Lead bullion and low lead slag can be produced from a wide range of raw materials (concentrates and secondaries), as well as sulfuric acid from high sulfur dioxide content process off-gas. The service life of shell refractories and of submerged injectors is acceptable. Operating experience in the new plants has resulted in process modifications and there is potential for further improvements, as expected in the implementation of new technology.