OPERATING EXPERIENCE WITH QSL SUBMERGED BATH SMELTING

FOR PRODUCTION OF LEAD BULLION

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Abstract

A QSL demonstration plant was operated within the Berzelius Lead/Zinc smelter in Duisburg, Germany, from 1981 to 1986. During its operation a total of 100,000 tonnes of both high and low grade lead bearing feed materials (varying from 30-70% Pb in fresh feed) were treated. Since the completion of the demonstration plant phase four commercial plants have been designed and built. One of these plants, operated by Berzelius Stolberg in Germany, commenced operation at the end of August 1990. This paper concentrates on the experience gained in the Stolberg plant since startup.

Experience on a commercial scale has shown that the process concept is viable but that certain modifications were necessary to the original design which was based on the limited results obtained from the demonstration plant. Major progress has been made in improvement of submerged injector design and in the understanding of factors affecting the reduction of PbO slag.

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G. J. W. Kor, C. Bickert and M. G. Ranade
The Minerals, Metals & Materials Society, 1992

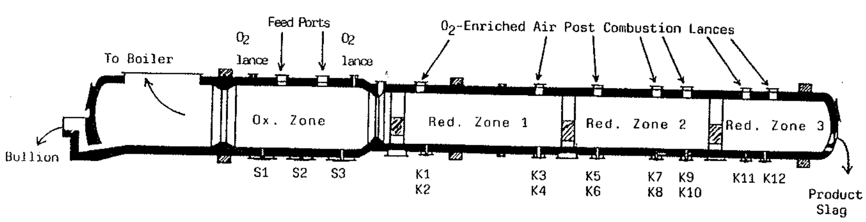
Introduction

The QSL process, named after the inventors Professors Queneau and Schuhmann and the process developer Lurgi AG, is a continuous direct lead smelting process. The entire process takes place in a single reactor as shown in figure 1. Four commercial scale units have been designed and built to date. The statements in this paper are based on experience made at the Berzelius plant located in Stolberg, Germany. This plant has been in operation since the end of August 1990.

The reactor, which is divided into an oxidation zone and three reduction zones, is a slightly sloped (0.5%) refractory-lined cylinder, which can be rotated through 90 degrees when operation is interrupted. Concentrates, residues, fluxes, recirculated flue dust and additional solid fuel are agglomerated and charged through feed ports located in the roof of the oxidation zone without any further treatment. The agglomerates fall into a melt consisting of primary slag and lead bullion. Industrial grade (min 96%) oxygen is blown into the melt through submerged gas-cooled injectors based on the Savard-Lee patents. Currently three oxidation injectors are employed in the Berzelius plant. The roasting reaction takes place at 1100-1150°C producing metallic lead, primary slag with a lead oxide content of 25-30%, and a sulphur dioxide-rich offgas containing the flue dust.

The lead bullion is discharged via a syphon, whereas the primary slag passes into the first reduction zone which is separated from the oxidation zone by a partition wall. Pulverized coke is injected into the reduction zones through submerged gas-cooled injectors, together with carrier air and oxygen. Currently five reduction injectors are employed in the Berzelius reactor, although up to eight injectors could be operated simultaneously in up to twelve different locations on the reactor shell. The lead is gradually reduced out of the slag as it flows to the opposite end of the reactor. The low-lead final slag is tapped at the end of the third reduction zone, whereas the lead settles to the bottom and flows back towards the oxidation zone to combine with the primary lead bullion.

Figure 1 - Overview of QSL Reactor Berzelius Stolberg



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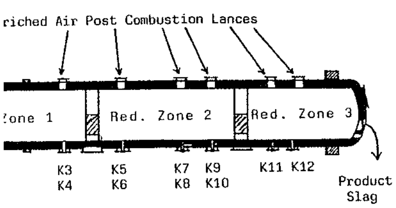


The offgas, which contains a high concentration of sulfur dioxide due to the use of tonnage oxygen, leaves the reactor through a vertical uptake. It passes a waste heat boiler for heat recovery and an electrostatic precipitator for dedusting before flowing to the sulfuric acid plant. The precipitated flue dust is recirculated to the feed mixing system.

Process Philosophy and its Effect on Reactor Geometry

The initial concept of the QSL process was to operate the reduction zone with as little metallic lead as possible, while retaining a lead sump above the injectors in the oxidation zone. The intention was to inject the reduction media directly into the slag bath, which would act as a molten slag gasifier. Although a lead layer covered the floor of the reduction zone in the demonstration plant, due to the fact that the reactor was not sloped and had a constant diameter over its entire length, this was not believed to have an influence on the rate of slag reduction. Therefore all four commercial plants were designed with a 0.5% slope and with a step in the reactor shell, the oxidation zone having a larger diameter than the reduction zone, while the reduction zone submerged injectors were angled 12 degrees from the vertical. This was to ensure that any lead reduced from the slag would drain from the reduction zone as quickly as possible and would not be reentrained into the slag by the submerged gas jets.

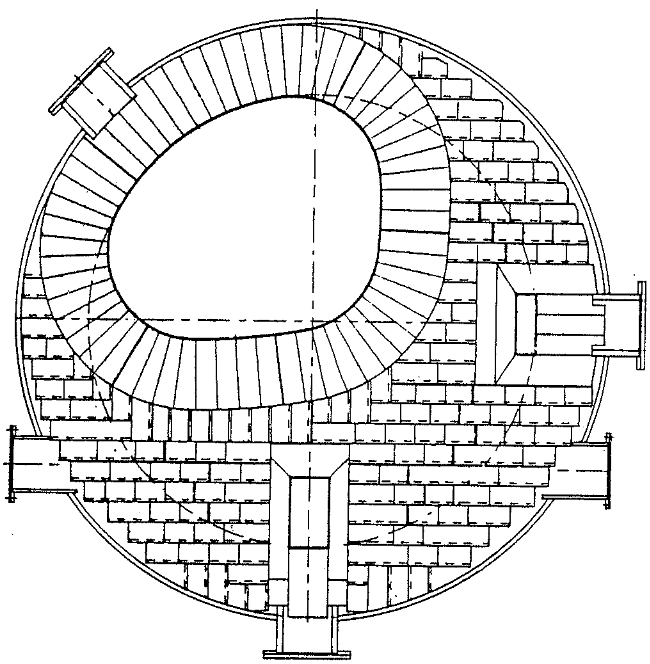
Experience has shown that this concept does not work as it was intended, especially when natural gas or lignite coke is used as the reductant. The cold reductant must be heated, together with the oxygen, carrier air and a limited amount of shroud gas, as quickly as possible on entry to the molten bath. It is believed that the heat transfer rate from the slag to the fuel is insufficient to facilitate gasification of the coke or reforming of the natural gas. As the slag is only about 100°C above its freezing point it is possible that a frozen slag layer coats some of the coke particles reducing the heat and mass transfer rates futher still. The problem has been further intensified by the fact that only relatively coarse coke has been used to date in the Berzelius plant, due to problems handling fine coke dust in the solids injection system.

It has also been shown that injection directly into a slag bath can lead to massive accretion formation on the reactor floor, which hinders lead flow out of the reduction zone, and complicates the plant operation generally.

It has been found both on the commercial Berzelius reactor and in laboratory scale (50kg) tests in Aachen University that the rate of gasification of coal or coke, or reforming of natural gas can be accelerated greatly if a molten lead layer covers the injector. It is now believed that a lead layer of approximately 250-300mm depth is necessary over the entire reduction zone if the desired reduction rates are to be achieved. In order to incorporate this concept into the existing reactor design, without it leading to excessive lead bath depths in the oxidation zone, it was necessary to install a 300mm high refractory ring dam (see figure 1) adjacent to the step in the shell diameter. This measure has proven successful not only in improving the reduction efficiency of the reactor, but also in simplifying the reactor operation as problems with massive accretion formation in the reduction zone no longer occur, the contact area of slag with the refractory lining being minimised due to the presence of the lead layer in between.

The reactor is divided into the oxidation zone and the three reduction zones by three refractory partition walls. These reduce back-mixing effects caused by the high bath turbulance. The partition walls have an underflow for the exchange of slag and metallic lead between each zone, and a gas opening for passage of the process offgases (figure 2).

Figure 2 - Partition Wall Design



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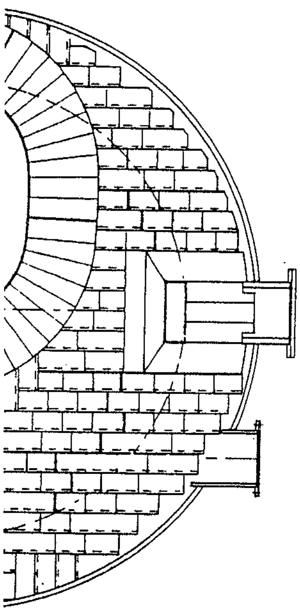

In the initial design the feed ports were located directly above the oxidation injectors. This led to major problems with feed port blockages caused by splashing from the injectors. Consequently, the oxidation injectors are now offset from the feed ports, in order to minimise the amount of splashing. They are placed such that their gas jets surround the fresh feed as it falls into the bath, thereby ensuring that there is sufficient heat and turbulence to melt and oxidise the feed immediately.

Oxygen or oxygen-enriched air is injected through lances in the roof of the reactor into the reactor gas atmosphere over the whole reactor length in order to optimise the heat balance of the process through post combustion of remaining combustibles.

Refractory

Various refractory materials were tested in the demonstration plant and as a result a special chrome-magnesite based brick (see table I) was adopted for the commercial plants. It is a direct-bonded chrome-magnesia brick, made from chrome ore and fused magnesia, with low silica content, good slag resistance, and very good thermal shock resistance.

Table I Refractory Brick Analysis

RADEX DB505B		
Chemical Analysis		
MgO	49	%
Cr2O3	26	%
Fe2O3	15	%
Al2O3	8	%
CaO	1	%
SiO2	0.8	%
Physical Data		
Bulk Density	3.32	g/cm3
Open Porosity	<18	%
Cold Crushing Strength	>30	N/mm2
Refractoriness under Load	>1700	ta(C)
	>1700	tb(C)
Specific Heat	0.85	kJ/kgK
Thermal Expansion	11	10-6K-1
Thermal Conductivity (600C)	2.0	W/mK
(1200C)	2.0	W/mK

Lifetimes of more than one year have been achieved with this material in the general reactor shell lining.

The wear rate of the bricks surrounding the injectors is much higher due to the aggressive and turbulent nature of the bath in their vicinity. Provision is made for straightforward replacement of the bricks in the areas adjacent to the injector positions, in the "rolled-out" position without having to empty the reactor. The brick arrangement is shown in figure 3. The injectors are cemented into a conical brick while the cone brick is surrounded by four "collar" bricks. Depending on the wear observed, either the cone brick alone, or the cone and collar bricks can be replaced with an injector. A brick frame surrounds the collar bricks in order to avoid collapse of the surrounding shell lining while replacing the injector bricks. The frame bricks form a flat arch in the injector vicinity.

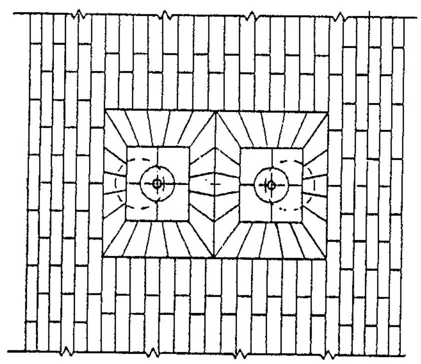

Figure 3 - Brickwork in Injector Vicinity

The lifetime of the partition walls is somewhat shorter than that of the shell lining because they are heated on both sides and there is little chance for heat transfer away to the shell. An original design with tongue-and-groove construction resulted in excessive wear at the brick joints. As a result a ground-and-glued construction has been adopted which, it is hoped, will extend the lifetime significantly.

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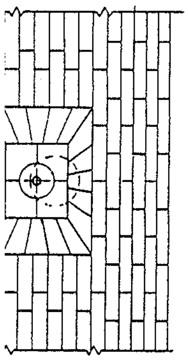

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Control of Oxidation and Reduction Zones

It is of utmost importance to control the flowrates of all media introduced to the process very closely as the following process parameters are determined by them:

* Heat balance and temperature profiles throughout the reactor

* Lead deportment between primary bullion and primary slag

* Degree of reduction

Oxidation Zone

Current practice is to aim to keep the PbO content of the oxidation zone slag at approximately 25-30% and the bath temperature approximately 1150°C. The more stable the composition of the oxidation zone slag, the easier it is to maintain a stable low PbO level in the final tapped slag. In normal operation the oxygen input to the bath through the oxidation injectors is interlocked with the total feed rate charged to the reactor. Should the feed composition remain constant, the oxygen rate, and hence the lead deportment in the oxidation zone is controlled automatically. However, some fluctuation in feed composition must be tolerated and this can be compensated for by adjustments to the specific oxygen rate. Regular oxidation zone slag analyses are used as the main control parameter for this purpose.

The bath temperature is controlled mainly via the variation of the amount of solid fuel added to the raw feed mixture, with short term alterations possible by addition of gaseous fuel through the submerged injectors. The relative change in bath temperature is monitored online via thermocouples installed in the floor of the reactor. The absolute bath temperature is measured regularly with a disposable thermocouple. Should the fuel input be altered, the specific oxygen rate must be adjusted accordingly.

In the Berzelius Stolberg plant the flue dust from the reduction zone passes into the oxidation zone where it combines with the dust from the oxidation zone bath and then passes into the waste heat boiler. The recycled flue dust is fed into the feed mixture automatically. Total dust rates are in the order of 20% of total mixed feed.

Reduction Zone

The main factors to be controlled in the reduction zone are the bath temperature and the reduction capacity. During its passage through the reduction zones the slag's temperature must be raised to about 1250°C and its lead oxide content lowered to 2%. In order to achieve this, the amount of reductant and the oxidant:reductant ratio are adjusted for each of the submerged reduction injectors. Slag samples are taken regularly from each of the reduction zones as are disposable thermocouple temperature measurements. The relative change in bath temperature is monitored via thermocouples installed in the floor of the reactor.

Reduction Mechanism

One advantage of the QSL process is its ability to produce a large amount of metallic lead directly from the lead-bearing feed materials in the oxidation zone. A certain amount of lead is unavoidably oxidised through to lead oxide, however, and passes in the slag into the reduction zone. The task of the reduction zone is to clean the slag of this lead and return the reduced lead to the lead syphon. This is necessary to make the process economic and to ensure that an environmentally acceptable discard slag is produced. It is currently achieved in a three stage process. The three reduction zones are separated from the oxidation zone and from each other by refractory partition walls. The partition walls restrict the amount of back-mixing of slag between the individual zones and thus aid the attainment of a steep concentration gradient along the reactor's length. Figure 4 shows an example of lead flows in slag and bullion through the individual zones, along with the lead concentration in the feed, dust and the various slags for the Berzelius reactor.

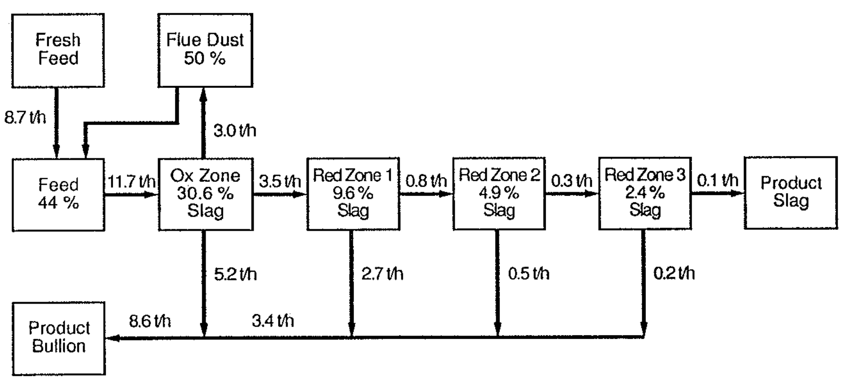

Figure 4 - Example of Lead Balance QSL Berzelius Stolberg

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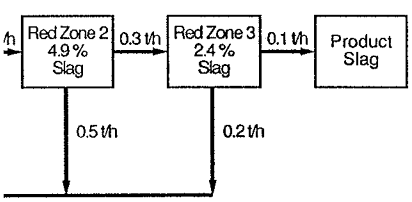

l Balance QSL Berzelius

Five reduction injectors are installed in the reduction zone of the Berzelius Stolberg reactor. Two are located in the first reduction zone, two in the second reduction zone and one in the final zone. Most experience to date has been obtained with lignite coke as the reductant, but test campaigns with natural gas have proven it to be of equal quality. Reducing agent, with carrier air if necessary, oxygen and shroud gas are injected into the bath from below. As mentioned previously, experience in the Berzelius reactor has highlighted the importance of the presence of a metallic lead layer at the tip of the submerged injector to achieve good slag reduction. The reduction reactions are believed to function along the lines illustrated schematically in figure 5.

Step 1: The oxygen, coke and air are heated quickly on introduction to the lead continuous layer, due to the high heat transfer properties of the molten lead, and the coke is gasified by the oxygen to form carbon monoxide. The oxidant:reductant ratio is adjusted automatically to obtain the desired gas mixture at the injector tip.

Step 2: The carbon monoxide rises into the slag continuous layer and reacts with the oxides in the slag to reduce iron, and form metallic phases, eg. lead and zinc, and carbon dioxide. The lead forms as small droplets and descends through the slag layer, finally reaching the lead continuous zone below. Any zinc fumed passes from the slag into the gas continuous zone.

Step 3: The zinc, the carbon dioxide and any unreacted carbon monoxide rise into the gas space above the slag layer. The zinc is totally, and the carbon monoxide partially, post combusted by the oxygen-enriched air injected through lances in the roof.

In table II the amounts of reductant used for each of the aforementioned reactions are shown for the Berzelius reactor.

Table II Example of Carbon Usage in the Reduction Zone

$PbO \rightarrow Pb$	30%
$ZnO \rightarrow Zn$	10%
$Fe^{3+} \rightarrow Fe^{2+}$	15%
Total Reduction	55%
Heating	45%

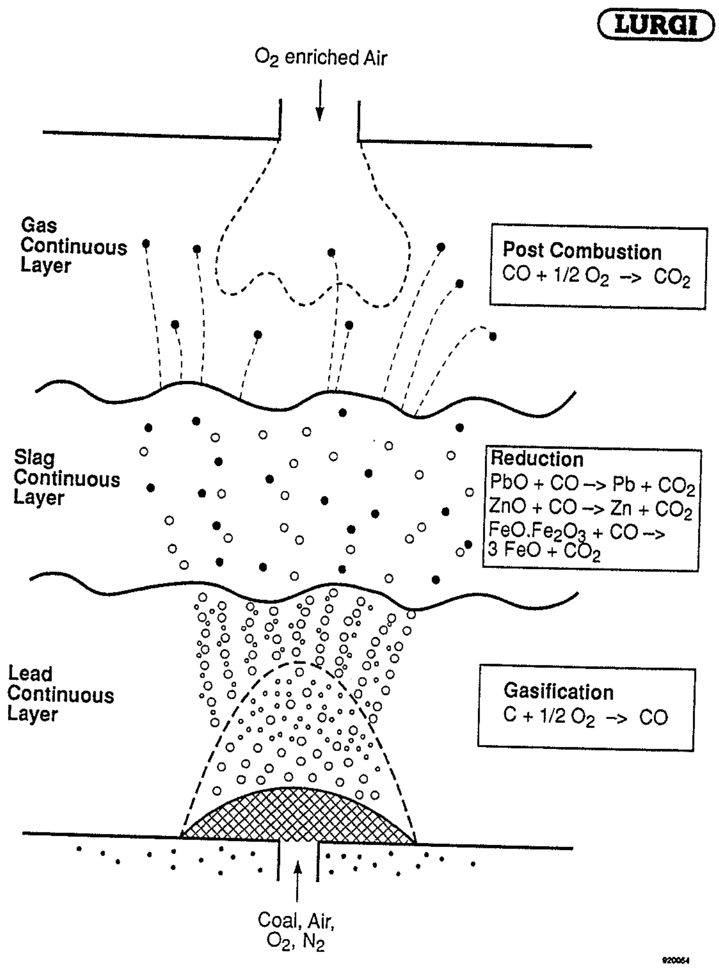

Figure 5 - Slag Reduction Mechanism

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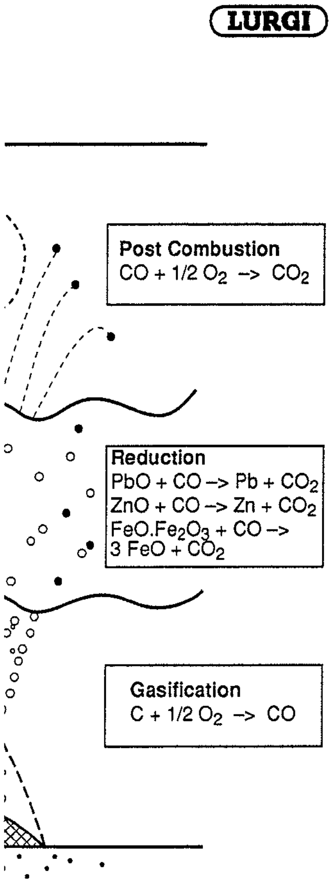

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Overall reduction efficiency can be impaired when an oxidising post combustion jet impinges into the slag layer. The post combustion jet should optimally be so adjusted that it can oxidise the gaseous species exiting the bath and transfer as much as possible of the resultant heat back to the bath, without allowing the reduced species in the slag to be reoxidised. However, if excessive air and oxygen rates are employed, reoxidation of reduced species can occur and the overall reduction capacity of the reduction zone can be decreased dramatically. This has occurred on occasions with individual lances and also at times throughout the entire reduction zone.

Figure 6 shows the lead content of the oxidation zone slag and the final tapped slag over a ten day period. Initially the total post combustion gas rate was approximately 2.5 times too high due to an error in the flowrate measurement. Subsequently the error was corrected and the flowrate reduced accordingly. This led to a significant improvement in the reduction efficiency of the reduction zone.

Figure 7 shows a similar albeit milder effect brought about by a post combustion lance installed in the reactor end wall immediately above the slag tap. Initially the lead content of the final slag varied between 2 and 10%. Once the lance was replaced with a burner operating under slightly reducing conditions (end of day 5) the lead content stabilised.

Submerged Injectors

Two basic types of submerged injectors are employed in the QSL process. The oxidation, or so-called S-injectors (Sauerstoff=Oxygen), are installed in the oxidation zone. Here oxygen is injected to oxidise the feed materials and shroud gas is used to protect the injector tips from excessive burn-back. The reduction, or so-called K-injectors (Kohle=Coal), are employed in the reduction zones. In this case reducing agent is injected in addition to the oxygen and the shroud gas.

S-Injectors

The development of the S-injector has produced a variety of cross-sections. The best proven design to date can be seen in figure 8. The actual dimensions of the channels vary from plant to plant depending on the local requirements. The data for the current injectors in the Berzelius plant and that of Korea Zinc can be seen in table III.

Oxygen is injected through the central bore and two of the surrounding rings of channels. It has been found that the impulse of the jet is reduced if it is split up into a number of channels with resultant decrease in the amount of splashing produced above the bath surface. This is especially important in the case of the S-injectors due to the vicinity of the feed ports. The small bore in the centre of the injector allows regular measurement of the injector length when the

Figure 8 - S-Injector Cross-Section

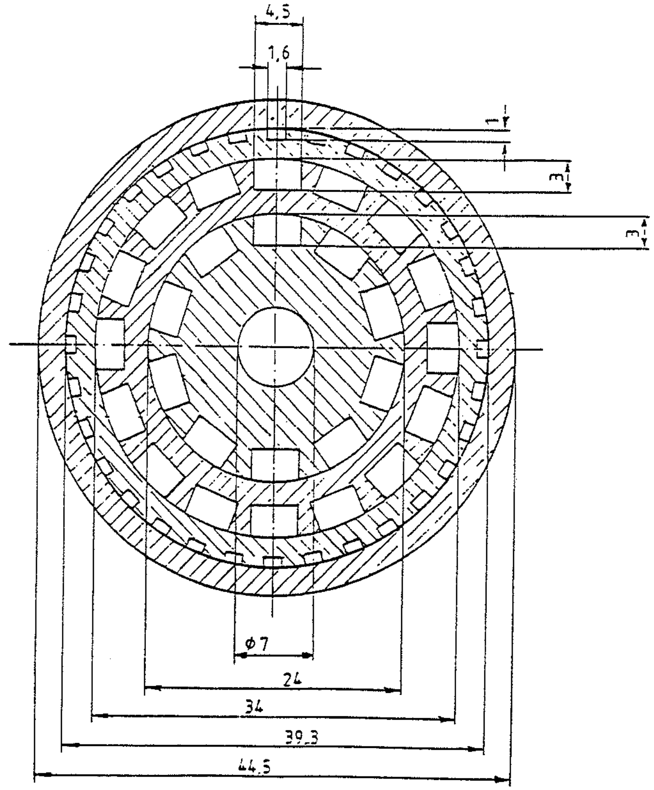
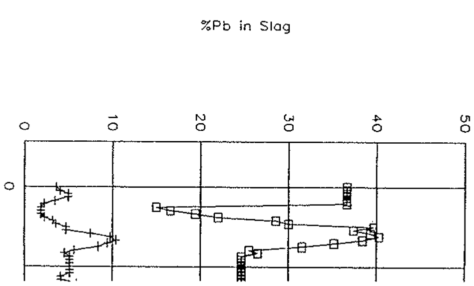


Table III - S-Injector Flowrate and Pressure Data

	X-Sectional Area mm^2	Nominal Flowrate Nm3/h or L/h	Nominal Pressure barg
Berzelius Stolberg			
Oxygen			
Total	242	1350	12
Central Bore	38.5		
Inner Ring	60		
Outer Ring	144		
Shroud			
Total	51	180-260	10-15
Water		20-30	
Hydrocarbon Gas		0-50	
Korea Zinc Corporation			
Oxygen			
Total	405	2000	12
Central Bore	38.5		
Inner Ring	145		
Outer Ring	232		
Shroud	51		
Total		180-260	10-15
Water		20-30	
Hydrocarbon Gas		0-50	



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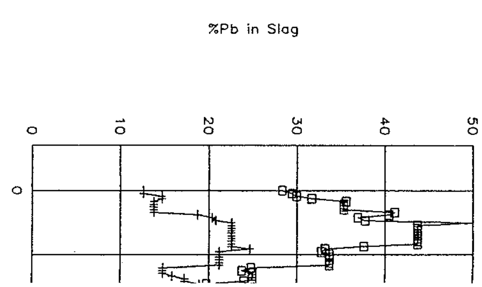

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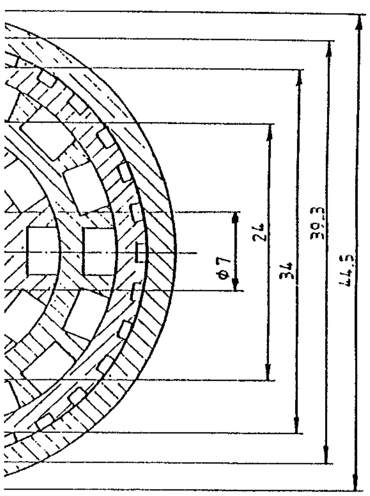

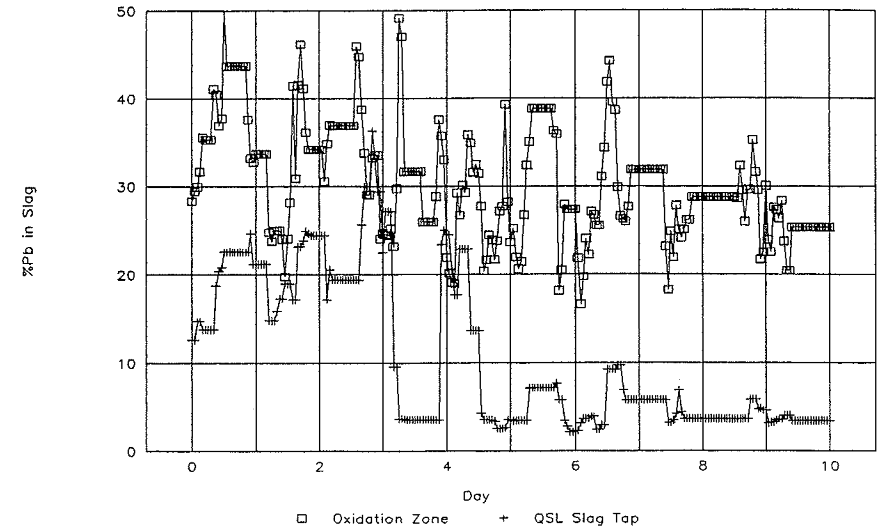

Figure 6 - Effect of Post Combustion Jet on Slag Composition.

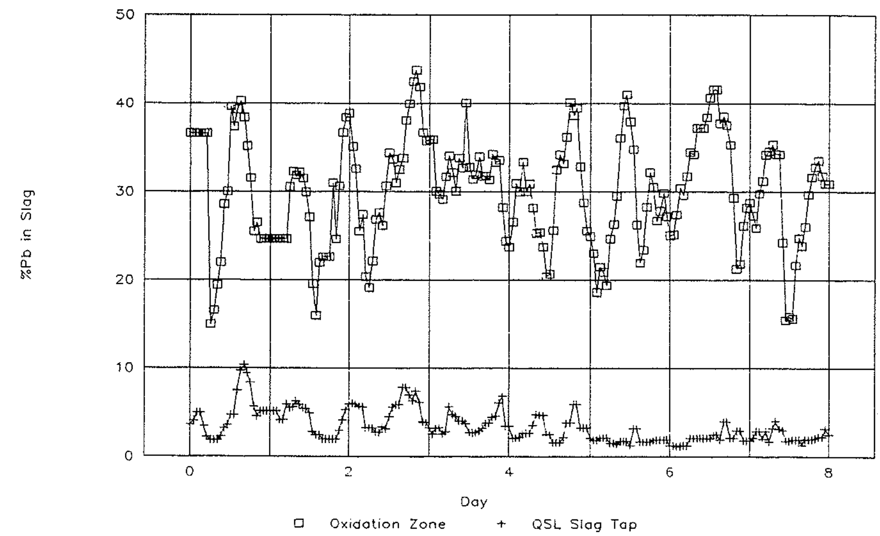

Figure 7 - Effect of Post Combustion Jet on Slag Composition.

reactor is in the standby position using a hooked wire. This is essential to keep a track on injector wear rates and in order to allow preventative maintenance to be carried out.

The oxygen is surrounded by a ring of channels through which shroud gas is injected. It has been found that the amount and type of shroud gas is of utmost importance for ensuring long injector lifetimes, especially considering the high oxygen flowrates through the centre of the injector. Currently a mixture of nitrogen, atomised water and hydrocarbon gas is used to obtain the cooling intensity required.

A schematic diagram of the control system for an S-injector is seen in figure 9. The oxygen rate required for the individual S-injectors is adjusted automatically using a specific oxygen rate based on the total feed rate. A nitrogen back up system ensures that a minimum pressure is maintained at all times on the oxygen channels even when the oxygen is shut off. This reduces the likelihood of run-back of liquid lead and/or slag into the injector. The shroud gas total pressure is held constant as are the flowrates of water and hydrocarbon gas. The nitrogen flowrate is adjusted automatically to make up the difference.

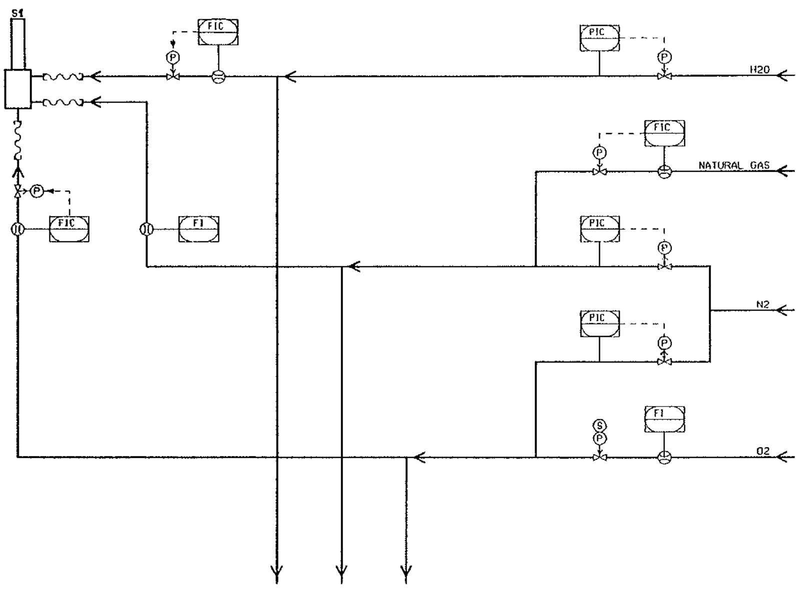

Figure 9 - S-Injector Control System

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Table IV

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surrounding refracto
This is especially i
due to the low visc
between the injector
refractory wear subs
fer between the cool
the formation of a p

S-Injector wear rate
achieved. This resu
useable length of 2
cooling brought abou
protective mushroom
surrounding refracto
can be seen in figur
and vary in diameter
injector life can on
is formed. Major e
reliability and life
placement still repr