

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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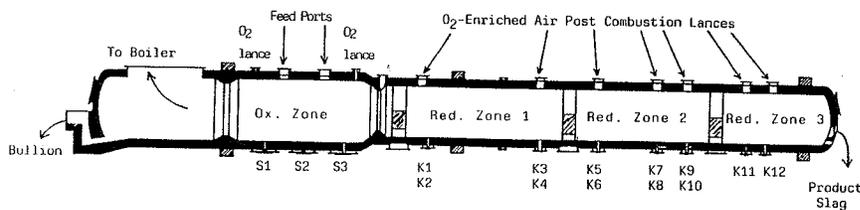
Introduction

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



The offgas, which contains lead, is used for the production of lead. It passes through a waste heat boiler, a dust precipitator, a sulphuric acid plant. The precipitator is a electrostatic precipitator. The sulphuric acid plant is a contact process. The dust is recycled back to the oxidation zone.

Process Philosophy and

The initial concept of the reactor was a zone with as little metal as possible. A sump above the injector injects the reduction melt as a molten slag. The length of the reduction zone in the reactor was not sloped, this was not for reduction. Therefore all zones had a 0.5% slope and with a diameter of 1.5m. Having a larger diameter zone submerged injector. This was to ensure that the slag from the reduction zone is reentrained into the slag.

Experience has shown that the reduction is slow, especially when the reductant is cold. The cold reductant, carrier air and oxygen, possible on entry to the reactor, transfer rate from the gas to the slag is only about 100°C at 1100°C. A frozen slag layer coats the reactor and mass transfer rate is intensified by the fact that the slag is only about 100°C at 1100°C. This is the fact to date in the Berzelius plant. The dust in the solids injector is recycled back to the oxidation zone.

It has also been shown that the lead to massive accretion on the reactor shell hinders lead flow out of the reactor. This is a problem in general operation.

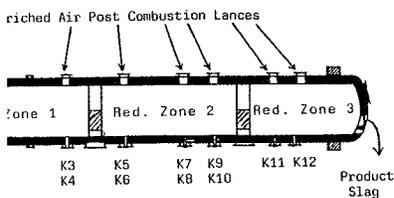
It has been found both at laboratory scale (50kg) and in the plant that the gasification of coal is accelerated greatly if the slag is now believed that a lead slag is necessary over the entire length of the reactor.

Professors Queneau and Berzeli AG, is a continuous direct process takes place in a single commercial scale units have been described in this paper are based on the Berzelius plant located in Stolberg, Germany. The end of August 1990.

The oxidation zone and three reduction zones are located in a refractory-lined cylinder, when operation is interrupted. The precipitated flue dust and additional slag are removed through feed ports located in the reactor for any further treatment. The injection of primary slag and lead and oxygen is blown into the melt based on the Savard-Lee process. The injectors are employed in the reduction zone which takes place at 1100-1150°C with a lead oxide content of 10-15% as containing the flue dust.

The primary slag which is separated from the reduced coke is injected into the reactor through gas-cooled injectors, together with the five reduction injectors are positioned through up to eight injectors at twelve different locations along the length of the reactor. The low-lead final slag is removed from the reduction zone, whereas the lead is removed towards the oxidation zone to

Berzelius Stolberg



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 further 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.

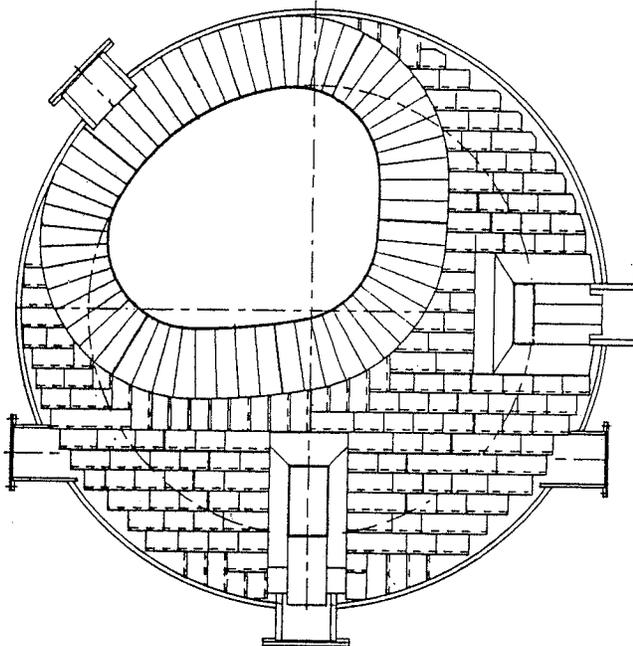
It has also been shown that injection directly into a slag bath can lead to massive accretion formation on the reactor floor, which hinders lead flow out of the reduction zone, and complicates the plant operation generally.

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 turbulence. 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



In the initial design the oxidation injectors. This was caused by splashing of the oxidation injectors are now controlled to minimise the amount of splash that surrounds the fresh feed. This ensures that there is sufficient time for the feed to be oxidized immediately.

Oxygen or oxygen-enriched air is injected into the reactor into the oxidation zone to provide the oxygen for the post combustion of remaining carbon.

Various refractory materials were evaluated and as a result a specific material was adopted for the construction of the partition walls. This material is magnesia brick, made from high purity silica content, good strength, and good thermal resistance.

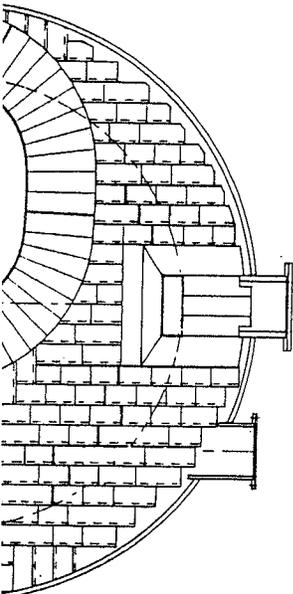
Table

RADEX DB
Chemical Analysis
MgO
Cr ₂ O ₃
Fe ₂ O ₃
Al ₂ O ₃
CaO
SiO ₂
Physical Data
Bulk Density
Open Porosity
Cold Strength
Refractoriness
Specific Gravity
Thermal Expansion
Thermal Conductivity

to incorporate this concept into it leading to excessive lead bath necessary to install a 300mm high adjacent to the step in the shell successful not only in improving the , but also in simplifying the massive accretion formation in the contact area of slag with the due to the presence of the lead

tion zone and the three reduction walls. These reduce back-mixing turbulence. The partition walls have g and metallic lead between each of the process offgases (figure

on Wall Design



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.

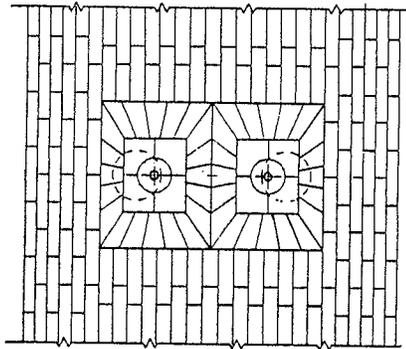


Figure 3 - Brickwork in Injector Vicinity

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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It is of utmost importance that the parameters are de

* Heat balance reactor

* Lead deposition slag

* Degree of

Oxidation Zone

Current practice is to use zone slag at approximately 1150°C. The slag, the easier to tap, is the slag. In the oxidation zone, the oxygen rate, is controlled automatically. The elements to the specification are used as

The bath temperature and amount of solid material alterations possible. The injectors. The reaction via thermocouples. The bath temperature should be adjusted according to the fuel.

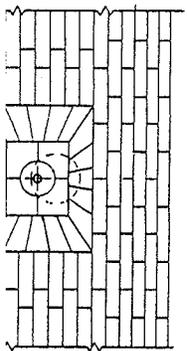
In the Berzelius zone, the oxidation zone. The recycled flux. Total dust rates

Reduction Zone

The main factors are temperature and reduction zones and its lead oxide

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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.

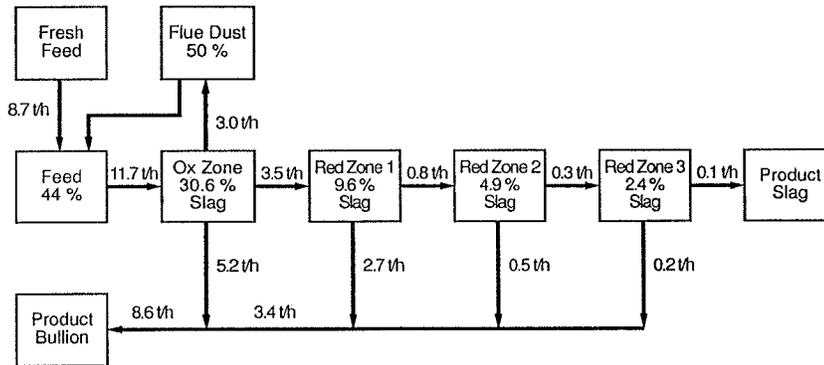


Figure 4 - Example of Lead Balance QSL Berzelius Stolberg

Five reduction in Berzelius Stolberg zone, two in the s experience to date tant, but test ca equal quality. Red and shroud gas ar previously, experi importance of the the submerged inje reactions are beli tically in figure

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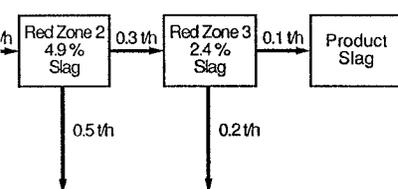
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ant:reductant ratio are adjusted injectors. Slag samples are taken zones as are disposable thermo- relative change in bath tempera- s installed in the floor of the

Mechanism

s its ability to produce a large n the lead-bearing feed materials unt of lead is unavoidably oxi- , and passes in the slag into the ction zone is to clean the slag of ad to the lead syphon. This is ic and to ensure that an environ- produced. It is currently achieved reduction zones are separated from er by refractory partition walls. unt of back-mixing of slag between e attainment of a steep concentra- ngth. Figure 4 shows an example of ough the individual zones, along feed, dust and the various slags



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 --> Pb	30%
ZnO --> Zn	10%
Fe3+ --> Fe2+	15%
<hr/>	
Total Reduction	55%
Heating	45%

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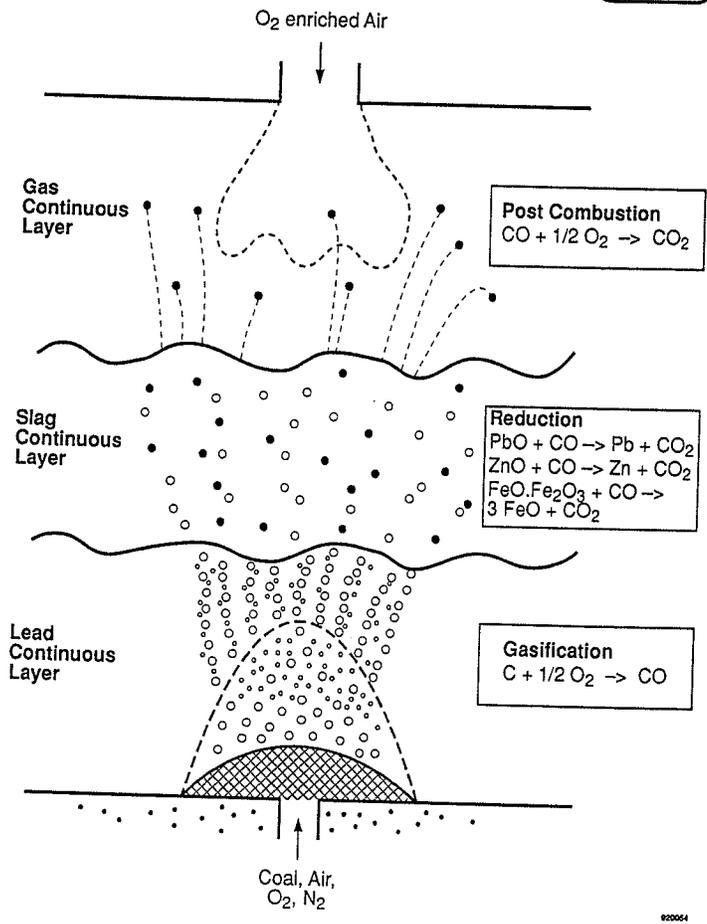


Figure 5 - Slag Reduction Mechanism

Overall reduction efficiency of combustion jet impingement should optimally be species exiting the burner resultant heat back to in the slag to be re-used. If rates are employed, re overall reduction can be dramatically improved. This has and also at times thro

Figure 6 shows the level of the final tapped slag over combustion gas rate with error in the flowrate reduced and the flowrate improvement in the red

Figure 7 shows a similar combustion lance installed in the slag tap. Initial between 2 and 10%. Once under slightly reduced and stabilised.

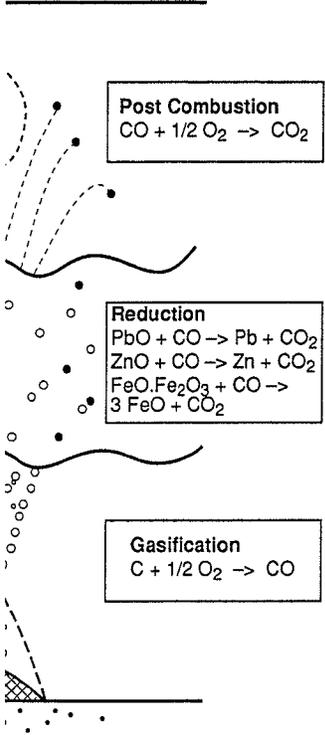
Two basic types of success. The oxidation, or installed in the oxidizer the feed materials and from excessive burn-b (Kohle=Coal), are employed reducing agent is injected gas.

S-Injectors

The development of the sections. The best practical dimensions of the on the local requirements Berzelius plant and the

Oxygen is injected through rings of channels. It is reduced if it is split decrease in the amount. This is especially important in the vicinity of the feed injector allows regula

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uction Mechanism

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

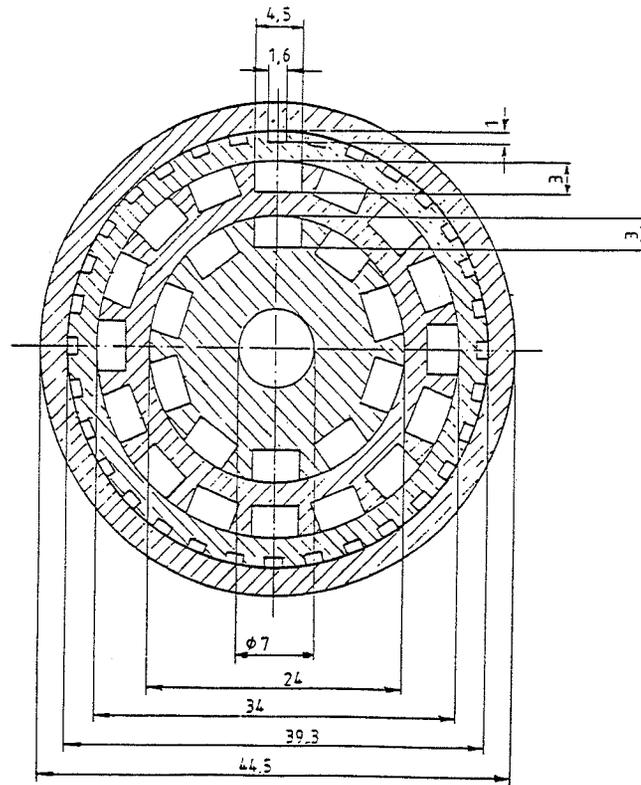
Two basic types of submerged injectors are employed in the QSL process. The oxidation, or so-called S-injectors (Sauerstoff=Oxygen), are installed in the oxidation zone. Here oxygen is injected to oxidise the feed materials and shroud gas is used to protect the injector tips from excessive burn-back.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



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Table III - S-Injector Flowrate and Pressure Data

	X-Sectional Area mm ²	Nominal Flowrate Nm ³ /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			
Total	51	180-260	10-15
Water		20-30	
Hydrocarbon Gas		0-50	

%Pb in Slag

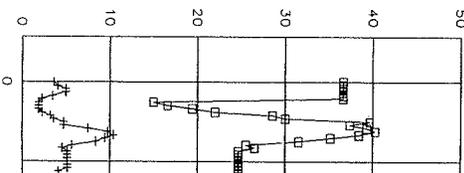


Figure 7 - Effi Comj

%Pb in Slag

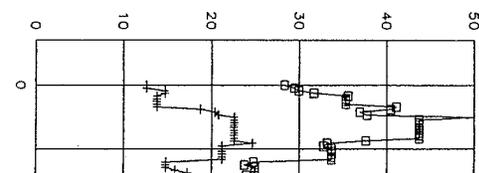


Figure 6 -

Korea Atomic Corporation		12	10-15
Oxygen	2000	405	180-260
Total		38.5	20-30
Central Bore		145	0-50
Inner Ring		232	
Outer Ring		51	
Shroud			
Total			
Water			
Hydrocarbon Gas			

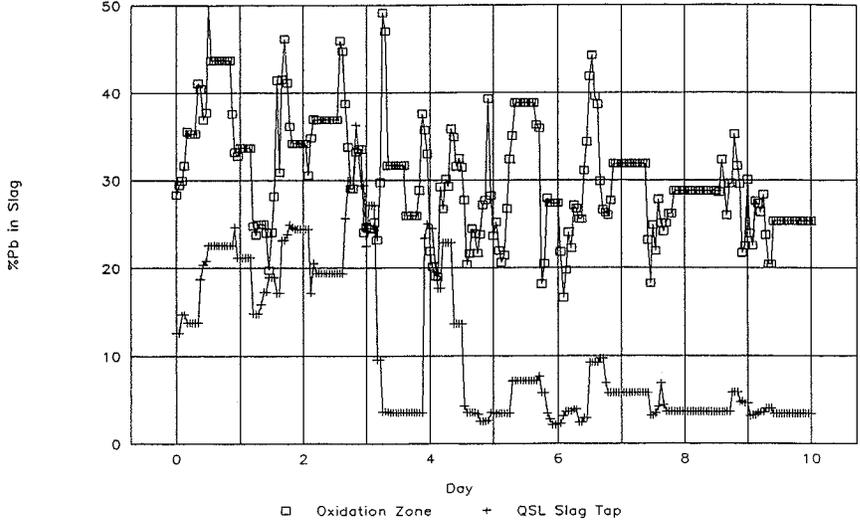
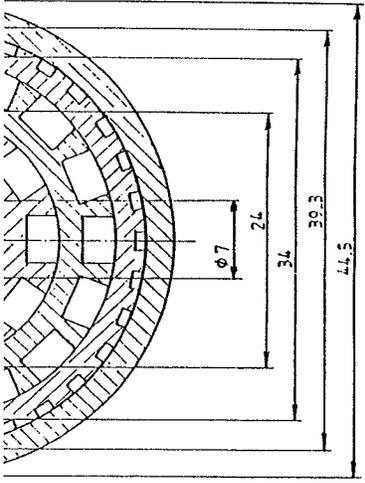


Figure 6 - Effect of Post Combustion Jet on Slag Composition.

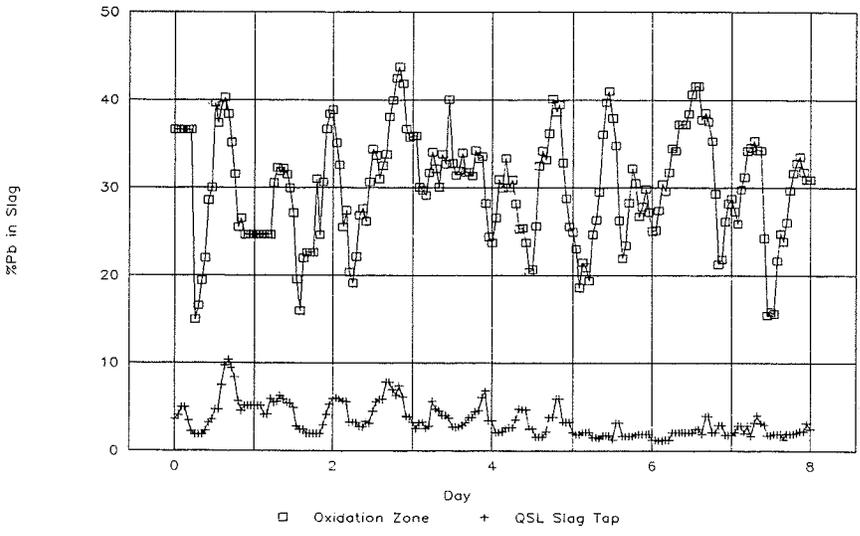


Figure 7 - Effect of Post Combustion Jet on Slag Composition.

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.

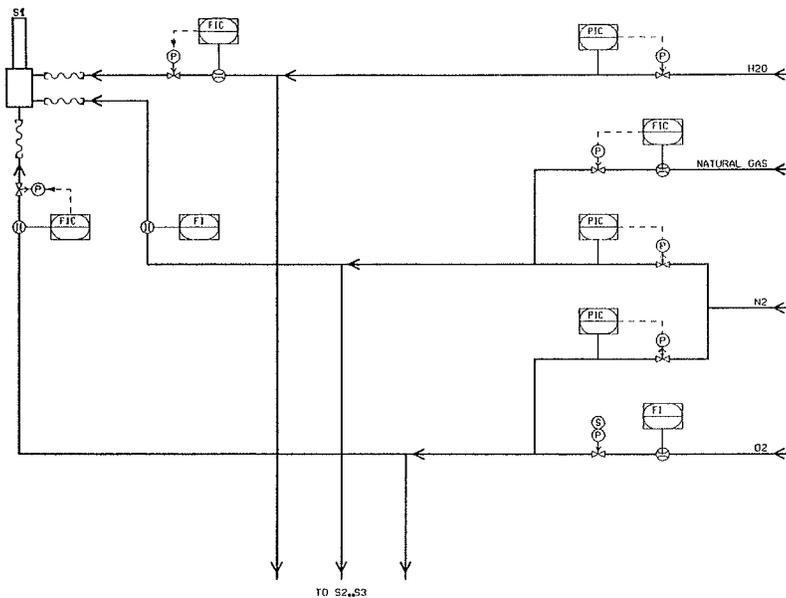


Figure 9 - S-Injector Control System

Experience has show ferritic stainless s the high solubility less steels are not the German standard of this steel is sho

Table IV

The injector is ceme in the reactor. This 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

using a hooked wire. This is to ensure uniform wear rates and in order to allow for easy removal.

The channels through which shroud gas flows are designed to ensure that the amount and type of shroud gas is sufficient for ensuring long injector lifetimes. The flow rates through the centre of the channels are controlled by nitrogen, atomised water and the cooling intensity required.

The control system for an S-injector is seen in figure 9. The control system for the individual S-injectors is designed to ensure that the oxygen rate based on the total oxygen rate ensures that a minimum pressure is maintained in the channels even when the oxygen flow is zero to avoid the possibility of run-back of liquid lead. The shroud gas total pressure is held constant by water and hydrocarbon gas. The control system is designed to make up the difference.

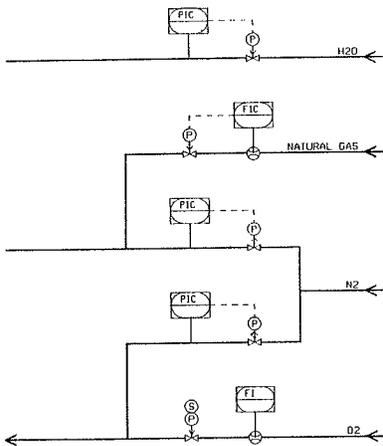


Figure 9 Control System

Experience has shown that the best lifetimes are obtained when a ferritic stainless steel is used for the injector pipes. Because of the high solubility of nickel in molten lead austenitic grade stainless steels are not suitable. The grade of steel currently in use is the German standard 1.4762, similar to the SAE 51446. The composition of this steel is shown in table IV.

Table IV Composition of Steel Used for Injector Pipes

Element	%
C	<= 0.12
Cr	23.0 - 26.0
Si	0.7 - 1.4
Al	1.2 - 1.7
Mn	1.0 Max
P	0.040 Max
S	0.030 Max
Ni	---

The injector is cemented into a refractory block prior to installation in the reactor. This ensures that the gap between the injector and the surrounding refractory is sealed as well as possible at all times. This is especially important in the case of superheated liquid lead due to the low viscosity. If the gap is not sealed lead can flow between the injector and brick, thus accelerating the injector and refractory wear substantially. The seal also improves the heat transfer between the cooled injector and the surrounding brick, which aids the formation of a protective "mushroom" around the injector tip.

S-Injector wear rates of about 0.3mm per operating hour are currently achieved. This results in effective injector lifetimes (given a useable length of 200mm) of up to 4 operating weeks. The intense cooling brought about by the shroud gas mixture is utilised to form a protective mushroom in the vicinity of the injector tip and the surrounding refractory. A photograph of a typical S-Injector mushroom can be seen in figure 10. The mushrooms are typically of cow pat shape and vary in diameter from 300 to 500mm. It is believed that extended injector life can only be obtained when a stable mushroom of this type is formed. Major efforts are being concentrated on improving the reliability and lifetimes of the injectors further as injector replacement still represents a major operating cost.

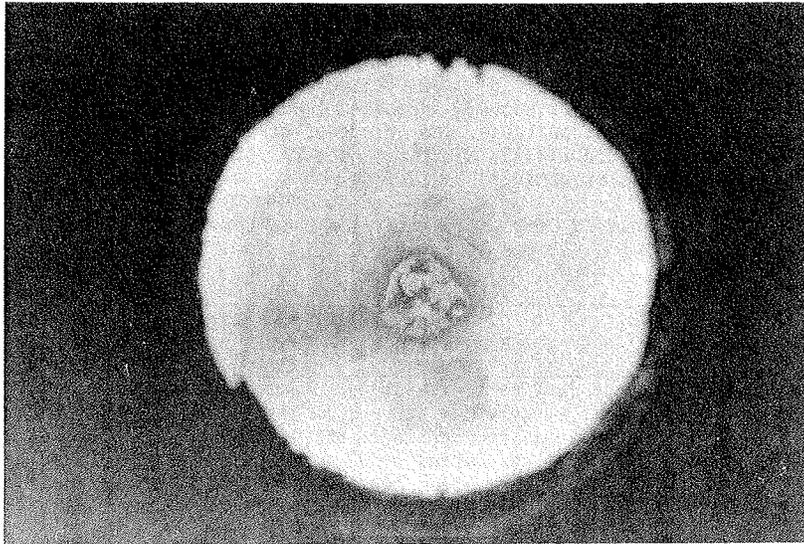


Figure 10 - Typical "Mushroom" on Injector Tip

Although it would be preferable to use more hydrocarbon gas in the shroud gas to intensify the injector cooling, it has been found that once a mushroom forms, a certain amount of shroud gas is forced back through the gap between the injector and the refractory brick towards the reactor shell, even when the gap is minimised using a cement seal. The resultant reducing atmosphere between the refractory lining and the steel shell can lead to refractory attack. The "vagabond" gas can also reemerge in the gas space above the bath surface, where it combusts, leading to unnecessary overheating of the offgas. Therefore hydrocarbon gas in the shroud mixture is kept to a minimum, normally being used just for short-term bath temperature corrections.

K-Injectors

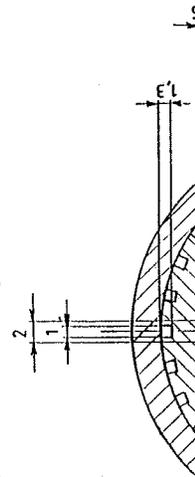
The best proven K-injector design to date can be seen in figure 11. The actual dimensions of the channels also vary from plant to plant depending on the local requirements. The data for the current injectors in the Berzelius plant and that of Korea Zinc can be seen in table V.

Solid fuel is injected through the central bore of the injector along with carrier air. Due to the abrasive nature of the solid fuel, it is necessary to install a ceramic pipe in the innermost steel pipe. The ceramic pipe and surrounding steel pipe can be removed from the injector when the reactor is in the standby position. This allows measurement of the injector length and replacement of the entire coal pipe should it block.

Table V - K-Injector Flowrate and Pressure Data

	X-Sectional Area mm ²	Nominal Flowrate Nm ³ /h, L/h or kg/h	Nominal Pressure bar/g
Berzelius Stolberg			

Figure 11 - K-Injector Cross-Section



Oxygen is injected through a ring of channels arranged concentrically around the central pipe.

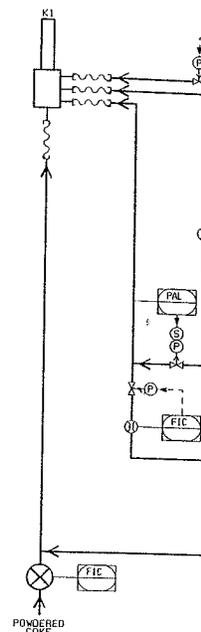
The oxygen channels are surrounded by a further ring of channels through which shroud gas is injected. A mixture of nitrogen, atomised water and hydrocarbon gas is again used to obtain the cooling intensity required to protect the injector tip.

A schematic diagram of the control system for a K-injector is seen in figure 12. The solid fuel flowrate for each K-injector is set by the operator and the carrier air pressure maintained constant to ensure that run back cannot occur. The oxygen rate required to achieve the desired oxidant:reductant ratio is calculated automatically for each injector by the control system, based on the solid and gaseous fuel rates and the rates of oxygen and carrier air. The oxygen flow is adjusted correspondingly. Individual nitrogen backup lines ensure that the oxygen channels do not run back should the oxygen pressure fall below a minimum value. The total shroud gas pressure is held constant as is the total flowrate of hydrocarbon to all K-injectors. The water flowrate to the individual injectors is held constant and the nitrogen flowrate adjusted automatically to make up the difference. The distribution of the nitrogen and hydrocarbon to the individual injectors is determined by the resistance at the individual injector tips.

As with the S-injectors, experience has shown that the best lifetimes are obtained with ferritic stainless steel injector pipes. The same grade of steel is used as with the S-injectors.

The K-Injectors are also cemented into a refractory block prior to installation in the reactor.

K-Injector wear rates of about 0.2-0.3mm per operating hour are currently achieved. This results in effective injector lifetimes (given a useable length of 200mm) of up to 6 operating weeks. Mushroom formation is also observed on the K-injector tips. Controlled mushroom formation is made more difficult however, due to the injection of solid fuel through the mushroom. If the mushroom is too large the solid particles can blind the pores and lead to blockage of the injector. If the fuel is coarse, as in the case of the Berzelius reactor, or contaminated with foreign matter, the situation is worsened. This means that the cooling intensity has to be balanced so that the mushroom is large enough to afford reasonable protection to the injector tip, but not so great as to provoke injector blockages. As with the S-injectors, major effort is being expended on extending the lifetimes of the K-injectors and making them more reliable.



Fifteen months of operation have shown the viability of the design. It is possible to operate over a wide range of conditions as sulphuric acid is not a problem. The lifetime of the injectors is being extended for further improvement.

Experience has shown that the reduction zone of a reactor design has a long operating philosophy.

Injector wear rates and the reliability of the design are being treated on extended costs.

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by a further ring of channels
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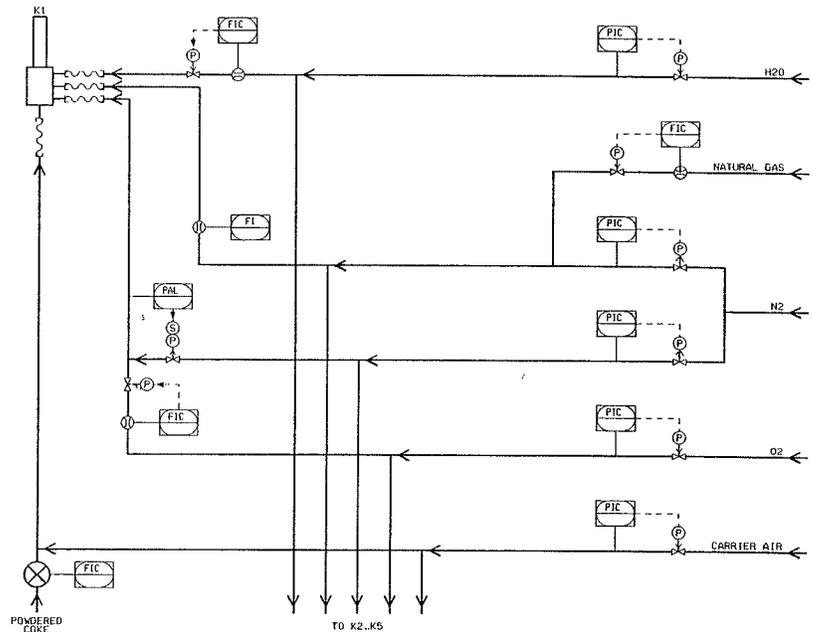


Figure 12 - K-Injector Control System

Summary

Fifteen months operation of the Berzelius Stolberg QSL plant have shown the viability of the overall process concept and the reactor design. It is possible to produce lead bullion and low lead slags from a wide range of feed materials (concentrates and secondaries) as well as sulphuric acid from the cooled, dedusted SO₂-rich offgases. The lifetime of the shell refractory is acceptable but there is potential for further improvements.

Experience has shown that a lead layer along the entire length of the reduction zone aids the slag reduction process significantly. The reactor design has been modified to facilitate this major change in operating philosophy.

Injector wear rates are still one of the major problems affecting the reliability of the process. Major efforts are continuing to be concentrated on extending injector lifetimes in order to reduce operating costs.