The COP KIN® System Part II: Performance and benefits – a world wide overview

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ABSTRACT

In 1989 Inco installed the first porous plugs and an oxygen lance in a Peirce Smith Converter shell. Since 1994 there has been increasing interest in porous plugs in the copper industry. Today gas stirring systems are used from Canada to Chile and also in Europe, Africa, Asia and Australia. For copper production alone, the RHI group has installed more than 100 single porous plug elements in different furnaces. On some selected examples the performance and benefits of these systems are shown and also the newest purging system - the COP KIN® System - will be introduced.

INTRODUCTION

The use of gas stirring systems through the bottom of a furnace in metals industries with different type of plugs - porous plugs, multi hole plugs or single pipe plugs - is now more than 30 years old. The first application was in refining treatment ladles in the steel industry. The next important step was the development of injection plugs into BOF converters also for the steel industry.

Today in the steel industry bottom gas injection is widely used and there is no question about the usefulness of injection plugs e.g. in ladles, converters or electric arc furnaces. In the late ´80s Inco Ltd., Canada (1,2) ran the first full-scale furnace using porous plugs in the copper industry and in 1990 the Reynolds Metals Company, Alabama operated five smelting and six holding furnaces equipped with multiple porous plugs (3,4). The RHI group has installed more than 100 single stirring elements in different furnaces in the copper industry, a worldwide acceptance has not yet occurred.

In the recent past no one supplier would warranty the engineering, hardware and start-up know-how for a completely proven gas stirring system and the risk was fully with the smelter. This was the primary reason that in April 2002 "RHI Non Ferrous Metals Engineering GmbH" based in Leoben, Austria was founded.

Our newest standardised gas stirring system "COP KIN®" is RHI's commitment to provide a complete system, which can be easily adapted to the needs of each customer. To discuss the effects of the COP KIN® System in more detail the application in an anode furnace was chosen as an example.

The two main components of the gas purging system are the plug and the gas control station.

PLUGS

In the non ferrous industry three different designs of plugs are in use:

- Porous plugs
- Multi hole plugs
- O_2-plugs

Porous plugs

For gas stirring systems one must make the distinction between changeable and non-changeable systems. A changeable arrangement is shown in Figure 1. It consists of the porous plug itself, surrounded by an insert and a well block. The changeable porous plug is fixed by a specially designed closing system in combination with a holding ring.

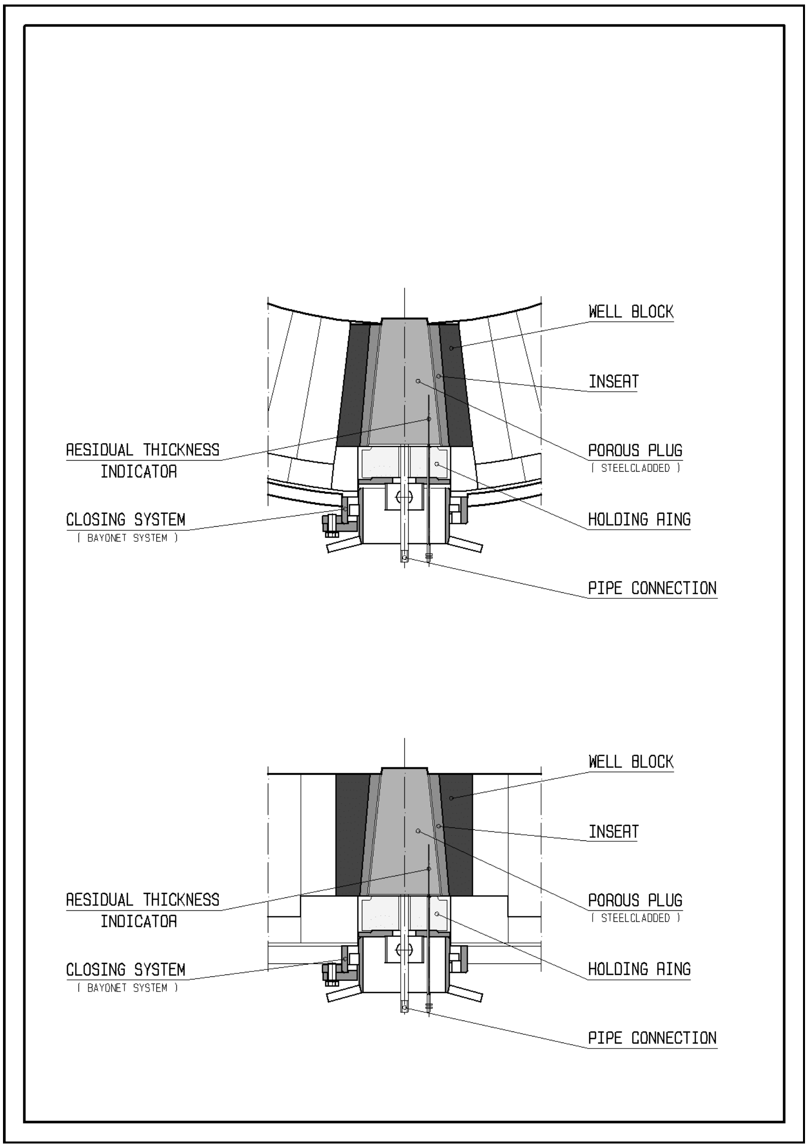

Figure 1 - Changeable Porous Plug Arrangement

The porous plugs are made out of pure magnesia, magnesia-chrome, alumina-chrome or other patented material with a prescribed permeability and with a maximum length of 450 mm. They are enclosed in stainless steel casing and the latest generation of plugs include a residual thickness indicator and three thermocouples. The thermocouples and the residual thickness indicator are connected to the gas-control-station and thus it is possible to monitor the wear of the plug at all times. The insert between the plug and the well block which is used only in a changeable system is similar to a safety lining to protect the well block when the plug is to be changed. The well block and the insert are both produced from a highly refractory material to guarantee compatibility with the rest of the lining.

The bayonet closing system in combination with a PLF-extraction device is a development of RHI Non Ferrous Metals Engineering GmbH and allows a change of single plugs in a very short time (between 10 minutes to three hours).

It is known from longstanding experience that the wear of porous plugs using inert gas only (normally nitrogen) is similar to the wear of the surrounding bricks. It is also known that the wear is higher using air as a reaction gas for example during the oxidation period in an anode furnace. The ratio of the oxygen and nitrogen in the purging gas will produce a related plug wear rate - using pure nitrogen the wear is equal to the surrounding refractory lining wear, whereas using pure air the wear is ~30 % higher. The use of plug injected air during copper oxidation will result in an increased reaction rate and therefore requires a changeable system.

Non-changeable systems are often used in environments where high plug wear rates are not expected e.g. in stationary furnaces (for scrap smelting), in converters or in slag cleaning furnaces using relatively pure nitrogen. In stationary furnaces and also in slag cleaning furnaces there are technically no possibilities to change plugs during operation. In such an application the use of an inert gas is essential. Today in the non-ferrous industry gas stirring systems with porous plugs are in use in:

- Melting furnaces (Al)
- Holding furnaces (Al, Cu)
- Anode furnaces (Cu)
- Peirce Smith Converters (Cu)
- Casting furnaces (Al)
- Ladles (Non ferrous alloys)
- Launders (Al, Cu)

using nitrogen, argon, air, nitrogen/air, nitrogen/hydrogen, argon/chlorine or nitrogen/argon.

Multi hole plugs

As shown in Figure 2 a multi hole plug consists of a fired refractory brick which is encased in stainless steel and which includes a certain number of single pipes. The number of the pipes and also the inner diameter depends on the application. The desire to operate systems with process gas is the reason for the use of MHP´s (multi hole plugs).

To operate porous plugs with natural gas during the reduction step is not possible due to the cracking of natural gas above 550°C. This will occur also in MHP´s but if the gas pressure is high enough the cracked carbon does not block the plug. In theory using the MHP´s it is also possible to replace the tuyeres in an anode furnace. Tests, using MHP's in the copper industry are in progress.

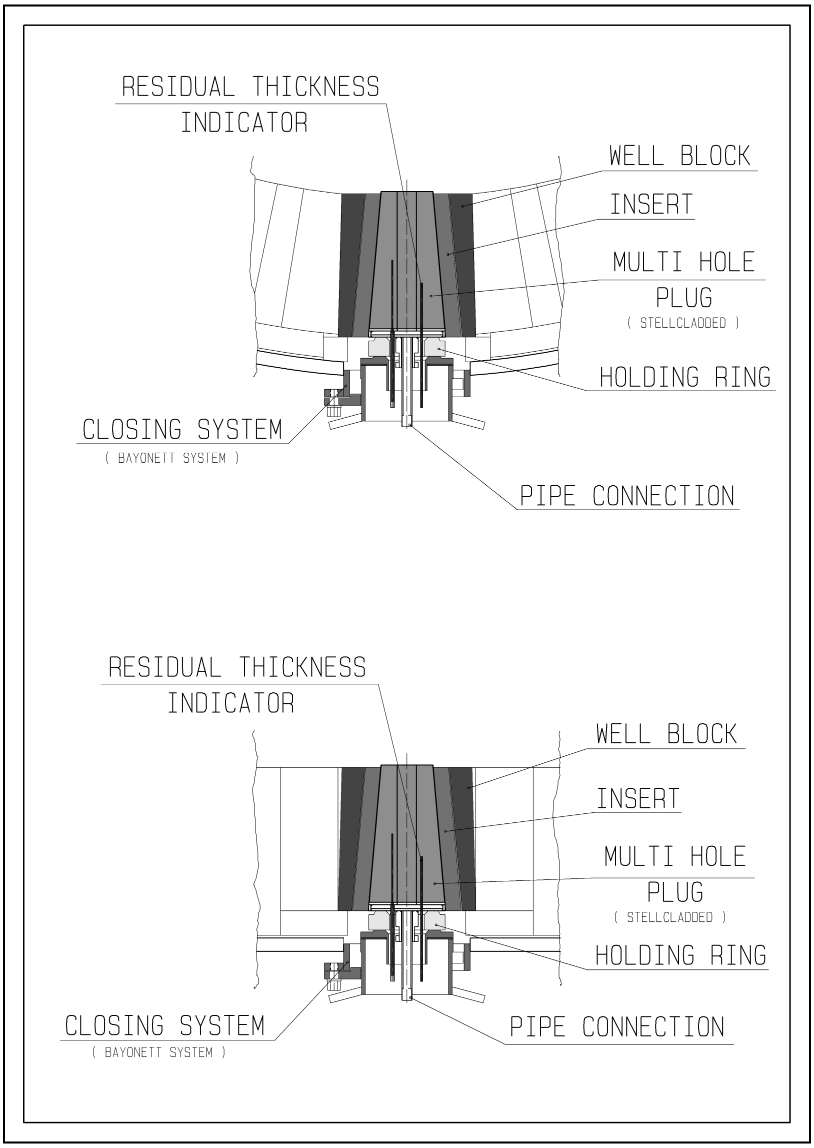

Figure 2 - Multi Hole Plug

O_2-plugs

To introduce pure oxygen into a metal bath, so called O_2-plugs, as shown in Figure 3, are used. A double shell pipe is located in the centre of a fired refractory brick. Pure oxygen is inject through the inner pipe and a protecting gas (nitrogen, argon or natural gas) is introduced through the surrounding gap. To minimise the wear of such a plug it is necessary to always operate in a “jetting” mode. Therefore the gas outlet pressure is quite high (between 10 to 20 bar).

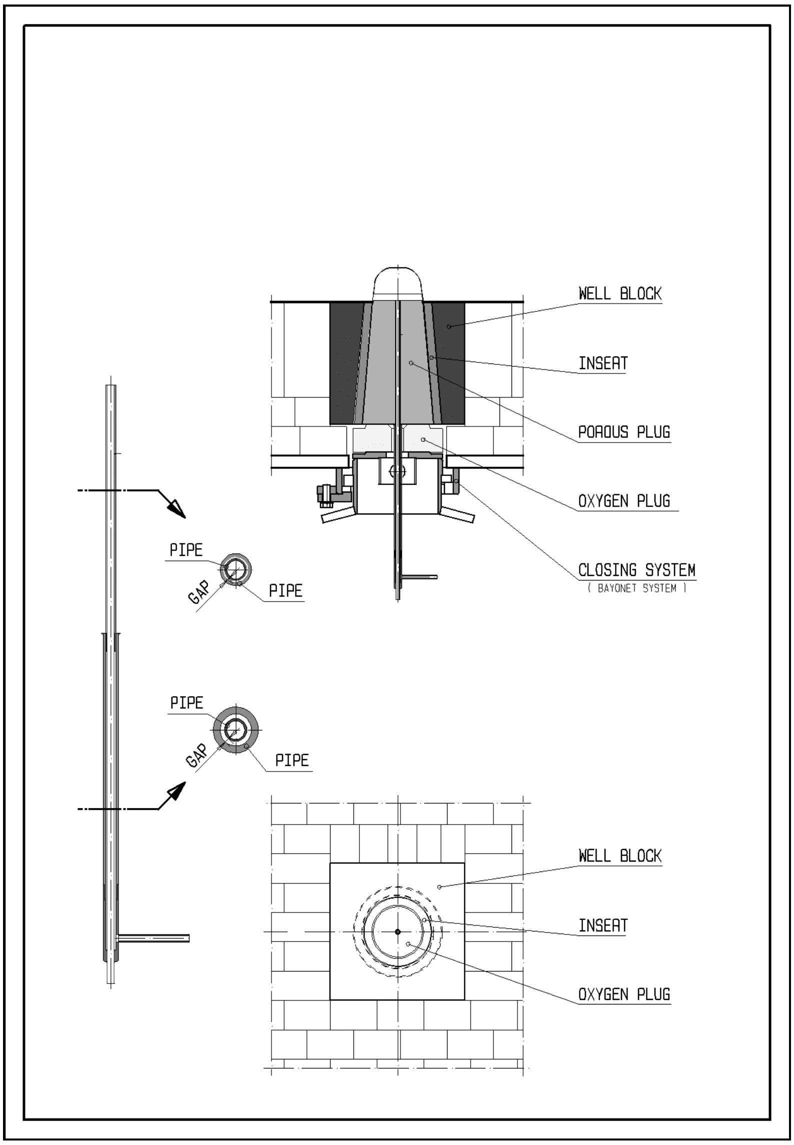

Figure 3 - O_2-plug

COP-KIN SYSTEM

Gas Control Station

The gas control station is the heart of a COP KIN® System. In Figure 4, a six-line gas station is shown. This example has two gas inlets (for air and nitrogen), a gas mixing station and six outgoing pipes for six porous plugs. The remaining plug thickness indicators are also installed in this control panel. Our experience has shown that controlling a constant mass flow with a varying bath depth of molten metal is of the utmost importance to run the stirring system effectively. The gas pressure must be carefully monitored in "real time" by the panel and adjusted to allow for a consistent stirring action. A minimum pressure of 6 bar for the inlet gas is required to provide the panel the flexibility to keep the mass flow constant.

Furthermore the package of a COP KIN® System consists of:

- Furnace Design Engineering
- Plug Refractory Hardware
- Control Station Software
- On-Line Start Service

Furnace Design Engineering

After the required processing requirements of the furnace has been established a design is developed to ascertain the exact type of plug required, the optimal number of plugs and, most importantly in our opinion, the placement of the plugs in the base of the furnace. In an anode furnace, for example, four different criteria should be taken into consideration depending on the process:

- an optimised gas bubble distribution in the bath
- an effective stirring action
- a controlled movement of the slag to the skimming mouth
- a maximised surface contact between slag and metal

For this engineering work the CFD (computational fluid dynamics) software FLUENT® is used.

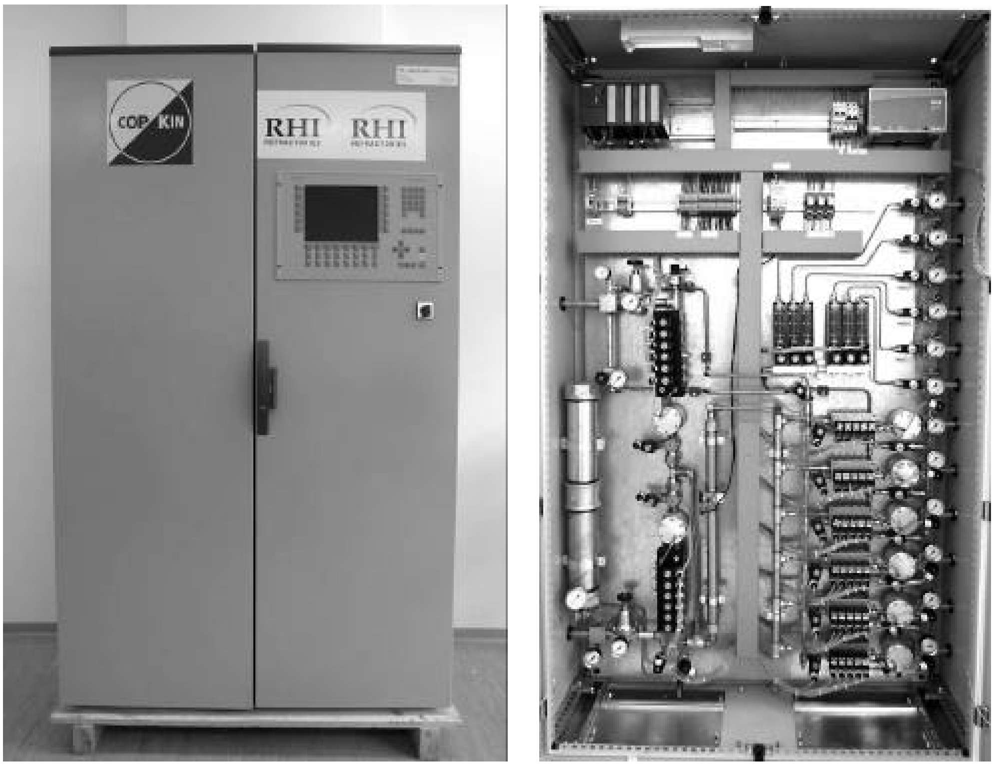

Figure 4 - Gas Control Station for two different Inlet Gases and 6 Single Plugs

Plug Refractory Hardware

In addition to the gas control station and the plug sets (plug, insert brick and wellblock) the complete gas injection system comprises a bayonet closure system, the gas supply pipes between gas control station and furnace, a plug removal device and surrounding refractory magnesia-chrome bricks.

The bayonet closing system together with a PLF-extraction device guarantees a quick change of plugs in hot conditions. The last generation of plugs are equipped with a residual thickness indicator and three thermocouples to indicate the rate of wear of each plug. Therefore three pipes for each plug are necessary, one for the gas, one for the residual thickness indicator and one for the three thermocouples.

Control Panel Software

The software controls each plug individually to achieve a constant mass flow rate. This software is run on the anode furnace computer system on site and allows for constant monitoring and adjustment of the gas flow rates as required in the oxidation/reduction or skimming phases of the process. Depending on the particular requirement different gas mixes and different flow rates per single plug can be programmed. Several safety and emergency devices are also installed. For example, if an inlet gas line is blocked for some reason the control station will switch to the back-up second incoming gas line immediately and an alarm will be given.

On-Line Start-Up Service

The plug system package provided by RHI includes the provision of experienced engineers during installation and start up to the point where the customer is confident to run the system in a proper way. Electronic digital communication is available with a direct line to RHI's "COP KIN®" database in Radenthein, Austria where software "tweaks" in the program can be downloaded immediately and online help is also possible.

As mentioned previously the application in an anode furnace was chosen as an example for the use of the COP KIN® System:

ANODE FURNACE OPERATION

The main objective of an anode furnace is to reduce impurity contents from about 200 ppm sulphur (or up to 0.6%S if the blister copper is produced by a continuous converting route e.g. by the Mitsubishi Process) and 2000 ppm oxygen to 20 ppm sulphur and 1200 ppm oxygen. At 1180°C the partial pressure of SO_2 at equilibrium is calculated to be 0.05 atm based on 200 ppm S and 2000 ppm O_2 (7,8). Theoretically, the equilibrium atmosphere above the copper melt in an anode furnace contains little sulphur dioxide, but in fact, the copper melt is not in equilibrium with the atmosphere above it. Consequently, during the oxidation step it is necessary to over-oxidise the melt in order to reduce its sulphur content to the desired concentration. This over-oxidation has two undesirable effects. It drives copper into the slag as copper oxide, and it also results in a higher concentration of dissolved oxygen in molten copper which has to be reduced in the following reduction step to approximately 1200 ppm oxygen.

Based on the objectives and on the process for fire refining the COP KIN® System has achieved the following metallurgical benefits:

<u>Homogenisation of the Bath Temperature</u>

Due to the agitation effect of the gas bubbles the convection in the bath is increased and a uniform bath temperature is achieved throughout the depth of the bath.

<u>Less Slag Overheating</u>

The optimised stirring efficiency and increased heat transfer ensures that it is not necessary to overheat the slag to provide the required bath temperature for consistent metal temperature. The COP KIN® System significantly reduces the fuel and energy consumption as well as the refractory wear in the slag zone.

Prevention of Build-Up

In the course of time build-up can form in the cooler regions of the vessel reducing the capacity of anode furnaces, especially in stationary furnaces for scrap smelting and the larger capacity (over 4.6m.dia. furnaces). The effective stirring action is particularly useful in eliminating the so-called “dead” zones in the fluid flow behaviour of molten copper. The full capacity of the furnace is ensured for the whole campaign of the vessel.

Slag Removal

COP KIN® Systems have been designed to allow for efficient slag removal in anode vessels. By controlling each plug separately the gas flow rates of plugs are programmed differently based on the metallurgical tasks. During slag skimming, controlled movement of the slag to the skimming door can be achieved and therefore less need for physical work combined with a better separation of slag and metal can be attained as an additional advantage.

Removal of Undesirable Elements - Problems with As, Sb

In addition to sulphur and oxygen there are also other impurities which must be eliminated from or considerably reduced (5,6) in blister copper (i.e. lead, zinc, tin, arsenic or antimony). Arsenic especially needs more attention. On the one hand a certain amount of arsenic is necessary to prevent Sb^{5+} which causes floating slimes in the electrorefining tankhouse electrolyte. Excess arsenic, on the other hand, cannot be tolerated.

The more effective mixing of the copper with a customised slag can aid in the removal of these contaminating metals. Lead, for example, is best removed by interfacing the blister copper in an oxidising atmosphere with a silica–rich acid slag.

Process Time Reduction

The agitation of the bath results in a very uniform oxygen distribution within the charged blister copper. Removal of the sulphur can occur before tuyere air injection is initiated since the amount of dissolved sulphur and oxygen is determined as a function of the atmospheric SO_2-partial pressure above the bath (see Figure 5). The SO_2-partial pressure in a gas bubble is zero and the rising column of bubbles will act to lower the content of dissolved sulphur and oxygen. In other words the desulphurisation starts earlier and can be completed (20 to 100 ppm S) with less dissolved oxygen in the bath. As an average value a 30% decrease in desulphurisation time could be attained and, just as importantly, with a lower final oxygen level (6000 ppm instead of 9000 ppm for example).

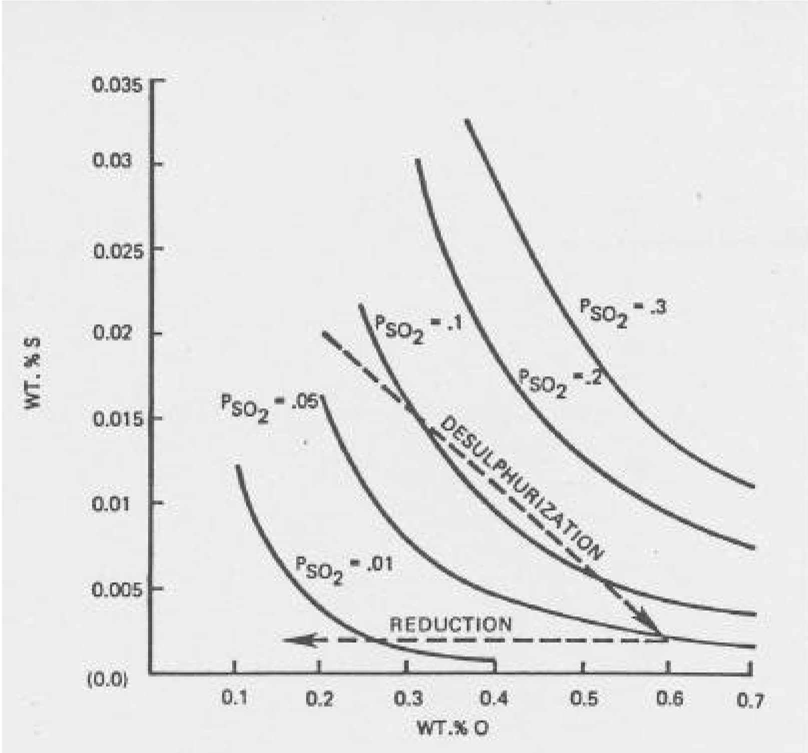

Figure 5 - Equilibrium of dissolved sulphur and oxygen in molten copper at 1100°C

Lower final Oxygen Content

A lower oxygen content of cast anodes should be regarded as having additional benefits. One of the most important factors often overlooked in the anode production area of the smelter is the fact that the current density distribution in the refinery tankhouse is strongly influenced by the quality of the cast anodes. Both the geometry of and the surface defects on the anodes, the distribution of impurities, the metallurgical composition between air and mould side affects the passivation behaviour of the anodes and the quality of the electrocrystallisation. Generally speaking a lower oxygen content in the neighborhood of 1200 ppm in anodes increases the current density and improves the production efficiency of the refinery tankhouse.

More uniform Oxygen Content during the Entire Casting Stage

A uniform oxygen content of the cast anode is more important than the absolute value. Due to the mixing and agitation effect of the gas bubbles a uniform oxygen level is achieved during the entire casting period and the oxygen variation from one charge to the next one is minimised.

SAMPLES

The advantages of the COP KIN® System are strongly influenced by the individual smelter process parameters, therefore it is necessary to discuss the requirements of each system separately. The reference list shown in Table I tabulates the operational units. To distinguish between the new COP KIN® System and older gas stirring systems the COP KIN® System users are written in *italic*.

To highlight the benefits of a gas stirring system some non-confidential figures are given.

2001 Andrzej Warczok and Gabrial Riveros (9), both from the University of Chile, Santiago, investigated the economic effect of the use of porous plugs in fire refining. At Disputada Minera, Chagres they compared two anode vessels, one of them was equipped with a gas stirring system. Following assumptions were given:

- time for desulphurisation can be shortened from 90 min to 50 min.
- time of slag skimming can be reduced from 20 min to 10 min
- time of deoxidation can be reduced from 100 to 50 min in the case of application of a new RHI technology based on addition of charcoal.

Finally, the average cycle time can be reduced by ~150 min from 550 min to 400 min. It corresponds to the increase of furnace productivity from 470 t to 580 t of copper per day. The decrease of fuel oil (ENAP-6) was stated at 200 l/cycle.

C. Acuna et al. (10) describe a study where the effect of the bottom stirring by nitrogen gas injection through porous plugs for the treatment of the crude copper in the range of 400-150 ppm sulphur, 3000-2000 ppm arsenic and 14000-7000 ppm oxygen content was investigated. The conclusion was that the process cycle time might be shortened by 45%.

Sang-Su Lee et al. (11) reported about the application of a porous plug system in anode vessels treating copper from a Mitsubishi continuous copper converter. The fuel consumption and the build-up inside the furnace were decreased by the higher heat transfer due to the stirring effect of the nitrogen through the porous plugs. Sang-Su Lee reported also that in principle it should be possible to reduce the desulphurisation time from more than 5 hours to ~3.5 hours. However, education of the operators would be required to avoid overoxidation of the copper before reduction was initiated

Table I – Customers using a Gas Stirring System

Country Customer	Vessels	Plugs	Remark	Start Up
Australia				
WMC, Olympic Dam	1	1	AF	2001
	2	14	AF	2003/4
MIM, Mt. ISA	2	12	AF	2003/4
Austria				
Montanwerke Brixlegg	1	4	HF	2003
Canada				
INCO Ltd., Ontario	1	9	Reactor	1990
	3	18	2AF, 2MPV	1990
Falconbridge Copper	2	8	AF	2001
Chile				
Disputada Minera, Chagres	2	8	AF	2000
Enami, Ventanas	1	4	HF	2002
China				
Jinchuan	2	12	AF	2003
Finland				
Outokumpu OY, Harjavalta	1	3	AF	2001
Germany				
Norddeutsche Affinerie	2	8	AF	2002
South Korea				
LG-Nikko Inc.	1	4	AF	2002
Sweden				
Boliden, Rönnskar	1	3	AF	2000
	1	6	AF	2003
U.S.A.				
Kennecott Copper, Utah	2	10	AF	1994
Phelps Dodge, Arizona	1	3	Scrap Smelting	1992

SUMMARY

Nitrogen stirring of molten copper through porous pugs is an established technology which has been proven to increase the productivity of anode refining vessels. The "COP KIN" System offers immediate access to these benefits and a substantial return on investment.

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