MET KIN® - A Gas Purging System for Metallurgical Smelting Furnaces

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Abstract

There are different reasons for purging a metal bath. The operations are varied, for example the purging gas can be used as a reactive gas being part of the metallurgical process or as an inert gas using the rising gas bubbles for agitation only.

The effects of gas purging are discussed in more detail for the anode furnace and the converter. For an optimised arrangement of numbers and position of all single plugs in the furnace, mathematical modelling- the CFD Computational Fluid Dynamics method - is used.

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 purging plugs in the copper industry. For copper production alone, the RHI group has installed more than 100 single porous plug elements in different furnaces.

Gas stirring systems are used from Canada to Chile and also in Europe, Africa, Asia and Australia. On some selected examples the performance and benefits of these systems are shown and also the newest purging system - the MET KIN System - will be introduced.

1 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 in the steel industry. The next very important step was the development of injection plugs into BOF converters also for the steel industry. In the late ´80s INCO, Canada ran the first full-scale furnace using porous plugs in the copper industry and in the aluminium industry in 1990 the Reynolds Metals Company, Alabama operated five smelting and six holding furnaces equipped with multiple porous plugs [1-4].

Even though reasons for using a bottom gas purging system could be different depending on the furnace and process and on the gas used (inert gas or process gas) in general there are three main reasons to use such a system:

a) Thermal and analytical homogenisation of the molten bath

- ✓ reduction of fuel and auxiliary material consumption
- ✓ decreased slag overheating
- ✓ decreased refractory wear
- ✓ uniform chemical purity

b) Increased surface layer between slag and metal bath

- ✓ decreased boundary layer
- ✓ increased diffusion controlled reaction
- ✓ increased metal recovery
- ✓ decreased highly oxidised slag

c) Inert gas bubbles in the molten bath

- ✓ decreased partial pressure for SO_2
- ✓ decreased partial pressure for H_2O
- ✓ decreased partial pressure for CO
- ✓ system reaches equilibrium more quickly

Of course the advantages listed are dependent on the process.

Today in the steel industry bottom gas purging is widely used and there is no uncertainty about plugs e.g. in ladles, converters or electric arc furnaces. In the non ferrous industry more and more plants are using such a technique now but a world-wide growth has not yet occurred.

There are several reasons why the non ferrous industry does not use stirring systems to an adequate extent. 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.

2 MET KIN®, COP KIN® and AL KIN®

Looking at the principles of the above-mentioned effects of inert gas purging one can see the following:

The thermal distribution is caused by convection and most of the chemical reactions are controlled by diffusion. Both are influenced positively meaning that the kinetics are increased. To influence the kinetics of the metallurgical reactions was the idea behind the name

*MET*allurgical *KIN*etics.

Especially for the aluminium industry and for the copper industry we have established two more trademarks:

AL KIN and COP KIN (see figure 1).

Figure 1: Registered mark for MET KIN, COP KIN and AL KIN

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

- Porous plugs
- Multi hole plugs
- O_2-plugs

2.1 Porous plugs

For purging systems you can distinguish between changeable and non-changeable systems.

A changeable arrangement is shown in figure 2. 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.

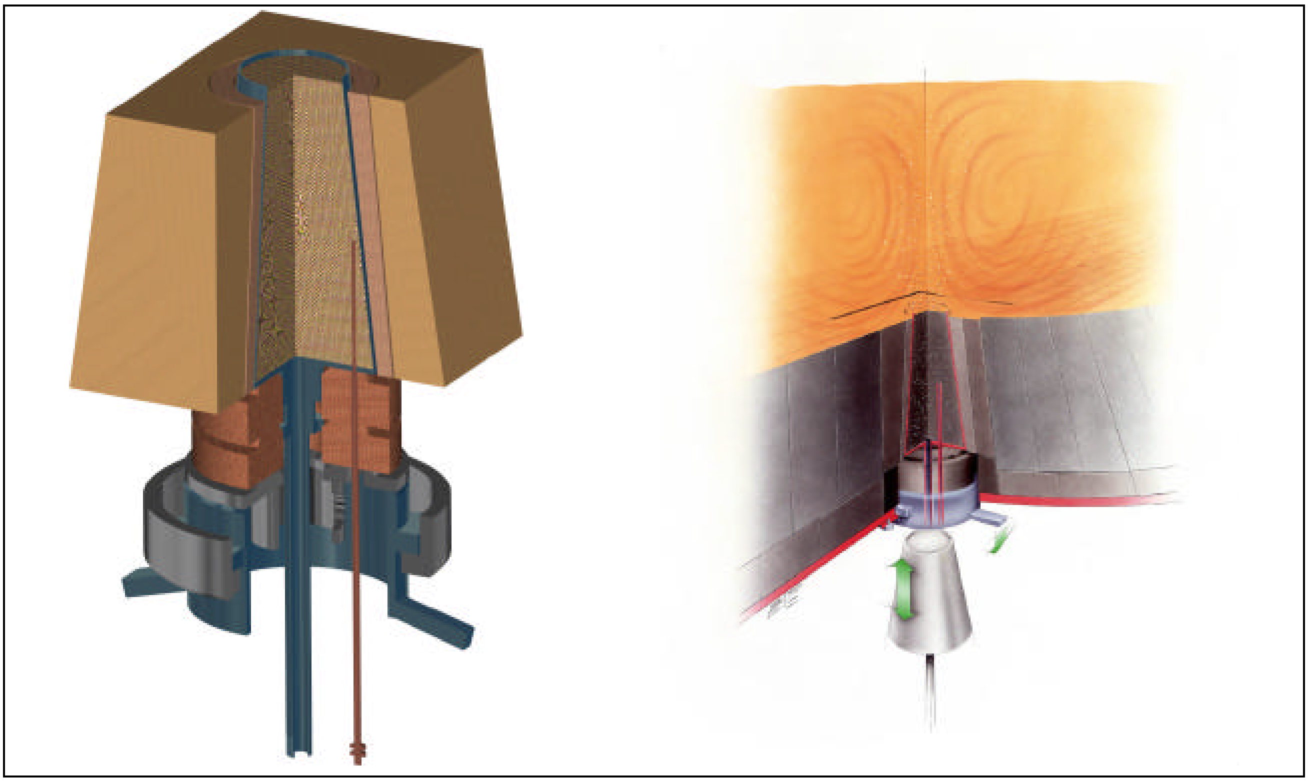

Figure 2: Changeable porous plug arrangement

The porous plugs are made out of pure magnesia, magnesia-chrome, alumina-chromite or other patented material with a certain porosity and with a maximum length of 450 mm. They are covered with stainless steel 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 so is it possible to control 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 like 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 fire resistant material to guarantee a perfect connection to 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). To have the possibility to change plugs in such a short time leads to a higher performance of purging systems because now is it possible to also use reaction gas.

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 when changeable systems are not required e.g. in stationary furnaces (for scrap smelting), in converters or in slag cleaning furnaces. 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 purging gas is essential. In converters a changeable system is not required because the normal tuyere zone repair could also be used to change the porous plugs.

Today in the non ferrous industry gas purging 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 as purging gas.

2.2 Multi hole plugs

As shown in figure 3 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 in an anode furnace 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.

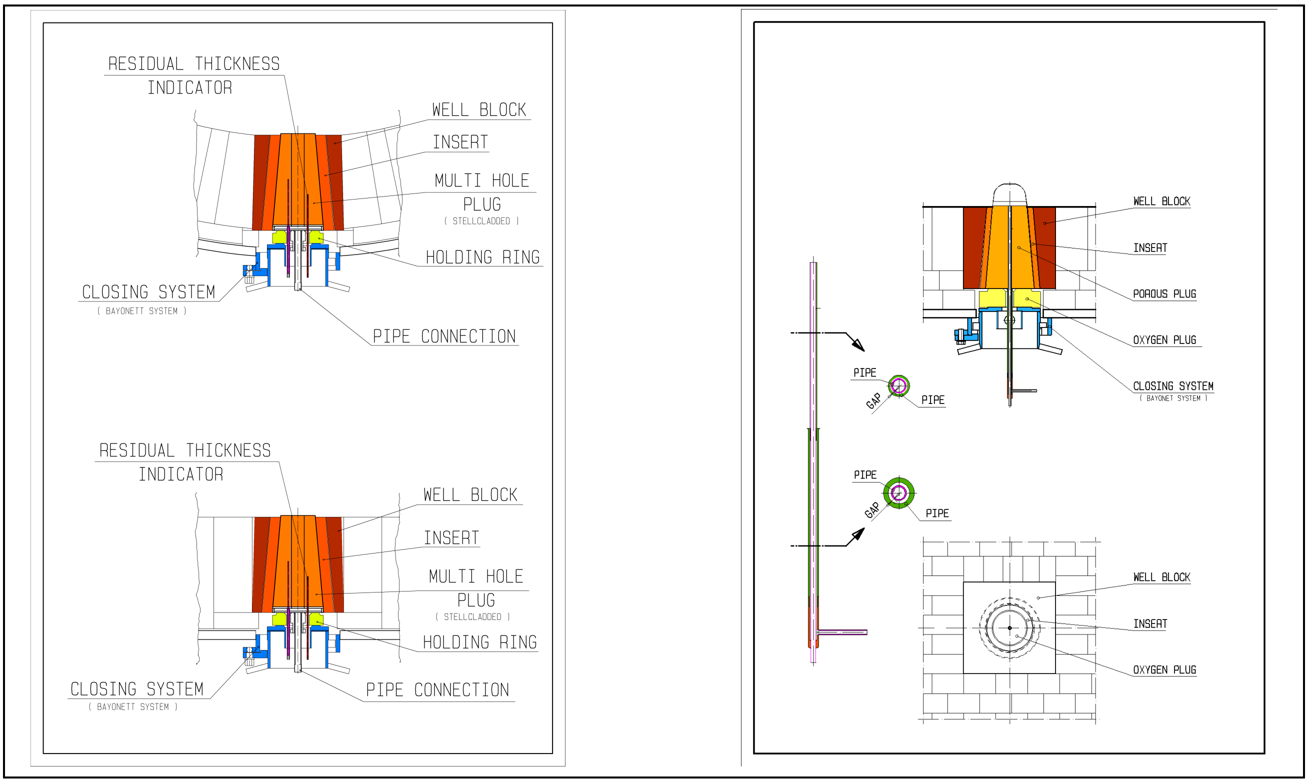

Figure 3: Left: Multi hole plug, right: O_2-plug

2.3 O_2-plugs

To purge pure oxygen in 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 pinject through the inner pipe and a protecting gas (nitrogen, argon or natural gas) is purged through the surrounding gap. To minimise the wear of such a plug it is necessary to operate in a "jetting" mode all the time to prevent a so called back attack. Therefore the gas outlet pressure is quite high (between 10 to 20 bar). These O_2-plugs are for example the standard plugs in QSL-reactors in the lead industry.

3 Examples

To discuss the effects of the COP KIN® System in more detail two examples are given now.

3.1 Anode furnace

3.1.1 Targets

The main objective of an anode furnace is to reduce impurity contents from about 200 ppm sulphur (the sulphur content is much higher when the blister copper is produced by a direct smelting route e.g. by the Mitsubishi Process) and 2000 ppm oxygen to 20 ppm sulphur and 1000 ppm oxygen. At 1100°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 [5,6]. 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 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 1000 ppm oxygen.

Based on the objectives and on the process for fire refining the COP KIN® System should achieve following targets:

✓ Homogenisation of the bath temperature

Due to the agitation effect of the purged gas bubbles the convection in the bath is increased and a uniform bath temperature is adjust for the whole process.

✓ Less slag overheating

Caused by a higher convection and an increased heat transfer it is not necessary to overheat the slag as much as before. That's why the COP KIN® System reduce the fuel and energy consumption as well as the refractory wear in the slag zone.

✓ Prevention of coatings

In the course of time a lot of coatings could reduce the capacity of anode furnaces, especially in stationary furnaces for scrap smelting and huge drum furnaces. The agitation effect of the gas bubbles is once more the reason why so called death zones in the fluid flow behaviour of the melt could be avoid. The full capacity of the furnace is available during the whole lifetime.

✓ Easier slag work

With the COP KIN® System it's possible to control the flow rate of each plug separately that means that the flow rates of all single plugs are programmed differently based on the metallurgical tasks. During slag skimming a certain movement of the slag to the slag skimming door could be achieved and therefor an easier slag work combined with a better separation of slag and metal could be pointed out as an additional advantage.

✓ Removal of undesirable elements - problems with As, Sb

Beside sulphur and oxygen there are also other impurities which should be taken into consideration e.g. lead, zinc, tin, arsenic or antimony. Especially arsenic needs more attention. On one hand a certain amount of arsenic is necessary to prevent five valid antimony which causes floating slimes in the tankhouse [10] on the other hand especially in South America the amount of arsenic is very high and causes a lot of health problems [7].

✓ Process time reduction

During the oxidation period two effects are important. At first due to the agitation the mixing in the bath is much higher and the oxygen distribution is better. The second point is, that the amount of dissolved sulphur and oxygen is a function of the atmospheric SO_2-partialpressure above the bath (see figure 4). The SO_2-partialpressure in an upcoming gas bubble is zero at the beginning and this leads partial under each gas bubble to lower content of dissolved sulphur and oxygen. In other words the desulphurisation starts earlier and for a total desulphurisation (between 20 and 100 ppm) less solved oxygen in the bath is required. As an average value a 30 % decrease in desulphirasation time could be given and of course a lower oxygen level (6000 ppm instead of 9000 ppm for example) reduce also the period of reduction.

✓ Lower final oxygen content

If the reduction of process time is not of importance a lower oxygen content is achieved in the same time. The current efficiency in a tankhouse is influenced by a lot of parameters. One of the most important one is the current density distribution which is strongly influenced by the geometry of electrodes, the bubbles and blisters on anodes, the distribution of impurities - difference between air and mould side (e.g. oxygen), the passivation behaviour of the anodes and the electro crystallisation. General speaking a lower oxygen content in anodes increase the current efficiency in a tankhouse.

✓ More uniform oxygen content during the entire casting stage

Below a certain oxygen content a uniform content 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 hole casting period and the oxygen variation from one charge to the next one is minimised.

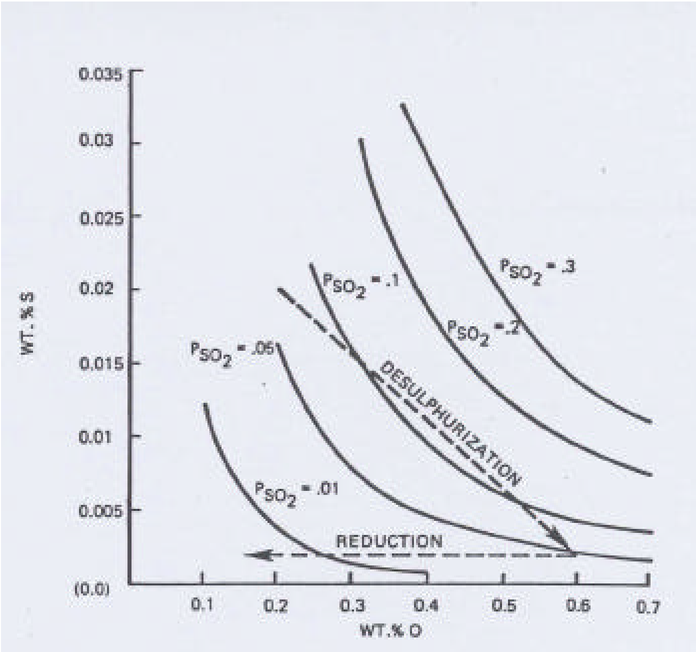

Figure 4: Equilibrium of dissolved sulphur and oxygen in molten copper at 1100°C

3.1.2 Examples

As mentioned before the advantages of the COP KIN® System are strongly influenced by the process therefore is it necessary to discuss the use and targets of each system separately. In spite of that few figures are given:

In [8] two Anodes Refining Furnaces; Ø 13´ x 23´; 140 t /cycle; one equipped with purging elements and the second one without were compared.

The results have shown that using porous plugs and nitrogen as purging gas

- time of copper oxidation can be shortened from 90 min to 50 min
- time of slag skimming can be reduced from 20 min to 10 min
- time of copper reduction can be reduced from 100 to 50 min in the case of application of a new RHI technology based on additional of charcoal
- the decrease of oxidation and slag skimming time 40 min results in decrease of oil consumption 200 l/ cycle

C. Acuna et al. [7] 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%.

The reduction of desulphurisation time is higher the higher the sulphur content in the blister. Mr Sang-Su Lee [9] reported that using the COP KIN® System after a Mitshubishi converting furnace it was possible to reduce the oxidation period from 5 to 3 hours. But Mr. Lee have described also the fact that using purging elements will change some principles of the process and therefor a proper process control and well educated operators are important.

3.2 Peirce Smith Converter

In the early part of the 20th century the Peirce Smith Converter was developed. Today, nearly 100 years later, the Peirce Smith Converter remains the dominant copper converting technology. To covert matte with a copper content between 47 to 70 % into blister (96 – 99.5 % Cu) in principle five steps have to be done.

- Charging
- Iron slagging
- Slag tapping
- Converting
- Discharging

Using the COP KIN® System in a PS Converter will effect the process as follows:

- Charging:

  Normally in the time when the first ladle of matte is filled into the converter to the start of iron blowing the converter is not used as a metallurgical reactor. The possibility to inject air through porous plugs will start the iron slagging immediately and the converter is in operation from the very beginning (for example 8 to 10 plugs are used with a flow rate of 200 l/min/plug).
- Iron slagging:

The effect during iron slagging is not easily recognisable although the death zone opposite the tuyeres will be agitated and all above mentioned principles are of course valid in the converter process.

- Slag tapping:

  As mentioned before with the COP KIN® System it's possible to control the flow rate of each plug separately and so a certain movement of the slag to the charging door could be achieved. This results in an easier slag work combined with a better separation of slag and white metal.

- Converting:

  In the second period of the converting process - the copper blowing – white metal is converted to blister copper (3.1, 3.2).

$$2Cu_2S(m) + 3O_2 \Leftrightarrow 2Cu_2O(l) + 2SO_2(g) \tag{3.1}$$

$$2Cu_2O(l) + Cu_2S(m) \Leftrightarrow 6Cu(l) + SO_2(g) \tag{3.2}$$

  In the end of the copper blow a lot of copper oxides - and so a copper oxide rich slag - occur. To use nitrogen as a purging gas should start the desulpurisation earlier due to the decreased partial pressure of SO_2 in the bath, should increase the oxygen efficiency due to a better agitation, should increase the surface area between slag and blister copper and end of the day should therefor decrease the amount of slag.

- Discharging:

  To discharge a PS Converter with e.g. 300 t of blister/cycle takes also at least one hour. Using nitrogen as a purging gas the converter could be used as metallurgical reactor once more and the sulphur content could be reduced to lower levels. If at the same time a stirring system is installed in the anode furnace these two systems could work hand in hand and an optimised process could be operate.

First trials using a COP KIN® System in a PS Converter are carried out at the moment at BOLIDEN, Sweden. During the first trial two porous plugs were installed to test the wear behaviour of porous plugs in a converter. Both plugs were operated with nitrogen and air without any problems and after 12 weeks the plugs were removed during a planed shut down. Compared to the surrounding bricks the wear was hardly visible. During the second test four plugs were installed and the result concerning wear out of the first test was confirmed. To investigate the metallurgical effects eight plugs will be installed in week 27.

The goal at BOLIDEN is to reduce the amount of high copper oxide rich slag.

4 COP KIN® System

To buy and install just single purging plugs is not enough. At least as important as the plugs are a proper gas control station and the engineering work for each application. The RHI Non Ferrous Metals Engineering Group offer a complete solution, the so called COP KIN® System. The main parts of this system are:

- Engineering
- Hardware
- Software
- Service

Engineering:

After a definition of need and targets of a gas stirring system the right type, the right number and the right position of plugs has to be calculated. For an anode furnace – as example - four different effects should be taken into consideration depending on the process, the situation on site (gas supply, gas pressure and so on) and the required goals:

- an optimised gas bubble distribution in the bath
- an optimised agitation effect
- an optimised movement of the slag to the slag skimming door
- an maximised surface between slag and metal

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

Hardware:

Beside the plug sets (plug, insert and wellblock) also a closing system (bayonet system), the pipes between gas control station ad furnace, a gas control station, a pulling out device and surrounding bricks are included in the hole package.

The bayonet closing system together with a PLF-pulling out device guarantees a quick change of plugs in hot condition. The last generation of plugs are equipped with a residual thickness indicator and three thermocouples to control the wear of each plug. Therefore three pipes per plug are necessary – one for the purging gas, one for the residual thickness indicator and one for the three thermocouples.

The gas control station is the heart of a COP KIN® System. In figure 5 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. One can also see six instruments for the thickness indicators. Out of experience it's of importance to run the system with a certain gas flow and the gas pressure should be variable. That's why a minimum pressure of 6 bar for the inlet gas is required.

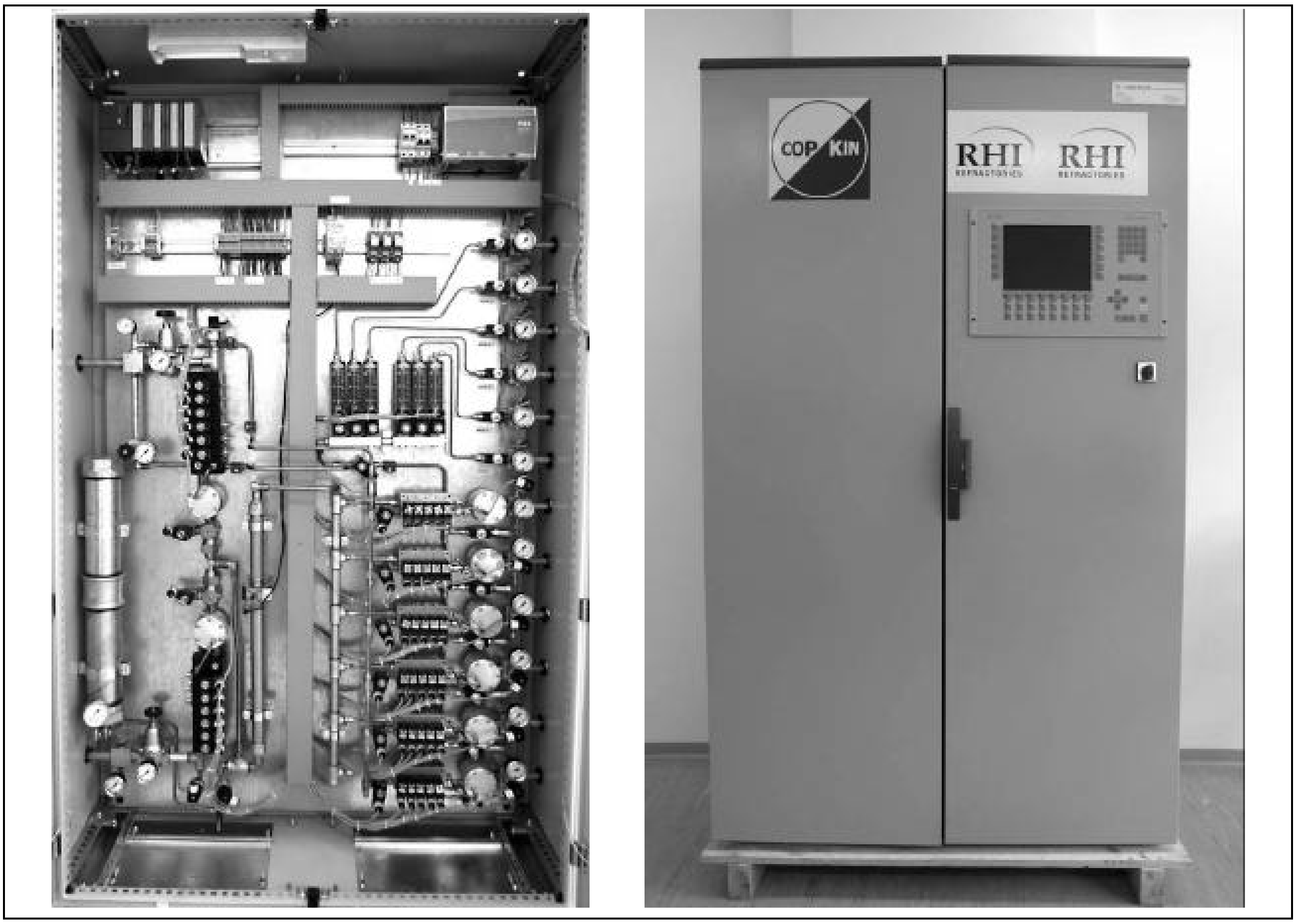

Figure 5: Gas control station for two different inlet gases and 6 single plugs

Software:

The software controls each plug individually to achieve a constant 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.

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.

5 Summery

Stirring of molten metals through porous pugs using different gases is an established technology which has been proven to increase the productivity of metallurgical processes. The MET KIN®-, COP KIN®- and AL KIN® System offer immediate access to these benefits and a substantial return on investment.

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