

SLAG CLEANING OF OUTOKUMPU DIRECT-TO-BLISTER FLASH SMELTING SLAGS

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ABSTRACT

Outokumpu Direct-to-Blister Flash Smelting is currently in operation in two smelters, a third one is under construction and a fourth one is in the design phase. The two smelters in operation are Głogow 2 smelter of KGHM Polska Miedz S.A. in Poland and Olympic Dam smelter of BHP Billiton in Australia. The Outokumpu Direct-to-Blister smelter of Konkola Copper Mines Plc. in Zambia is under construction and the new smelter of Głogow 1 is under design and waiting for final go-ahead decision. Additionally, Garfield smelter of Kennecott Utah Copper Corp. makes blister copper out of matte in a Flash Converter. A similar operation is under construction for Yanggu Xiangguang Copper Co. in China.

The slag cleaning process, which is needed to clean the slag of Direct-to-Blister Flash Smelting Furnace, has different requirements depending on the feed to flash furnace. These differences are discussed in the paper.

The differences of the processes and produced slag are discussed as well as the metallurgical requirements for slag cleaning. The Direct-to-Blister process, where the blister copper is produced directly from concentrate in one step, requires at least a partial treatment of the slag in an electric slag cleaning furnace. The existing impurities determine the specific requirements of the actual cleaning process. The different processes are discussed in the paper.

The newest developments of Outokumpu Technology Oy for electric slag cleaning furnace design are presented as well as the characteristics, which the furnace shape gives to the process.

THE DEVELOPMENT HISTORY OF BLISTER FLASH SMELTING

The history of making blister copper in an Outokumpu Flash Smelting Furnace dates back to the late 1960's, when Outokumpu first piloted the Outokumpu Direct-to-Blister (ODB) process. Throughout the early 1970's testing was continued first as Outokumpu's internal technology development project and later also in cooperation with Polish and Zairean customers.

Table 1. – Important milestones in Blister Flash Smelting

Year	Milestone	Type
1969	First successful pilot scale tests	Direct-to-Blister
1974	Pilot tests with KGHM's concentrates	Direct-to-Blister
1978	Start-up of Głogow 2 smelter in Poland	Direct-to-Blister
1984	Development of Flash Converting	Flash Converting
1988	Start-up of Olympic Dam smelter in Australia	Direct-to-Blister
1995	Start-up of Kennecott smelter in the USA	Flash Converting
1999	Start-up of Olympic Dam furnace #2	Direct-to-Blister
(2007)	Start-up of Yanggu smelter in China	Flash Converting
(2008)	Start-up of KCM smelter in Zambia	Direct-to-Blister
	Start-up of Głogow 1 smelter in Poland	Direct-to-Blister

It had been obvious also earlier that with Flash Smelting it was possible to raise the matte grade higher and higher to white metal and finally reach blister copper instead of matte. It was also known that the resulting slag would be high in copper and, therefore, copper circulation via slag would be a decisive factor in evaluating the economical feasibility of Direct-to-Blister smelting. Through pilot scale testing it was possible to verify the technical suitability of Flash Smelting for Direct-to-Blister smelting and to accumulate detailed information on the distributions of copper and impurity elements between blister and slag in different process conditions, with different raw materials and with different slag compositions.

Also the furnace structure was an important area of development. Oxidized blister copper is much more challenging to the refractory lining and to the cooling system of the furnace and, thus, major development had to be done in order to make the Direct-to-Blister process technically viable. These same difficulties are now being faced by the new converting processes, which are currently struggling to reach furnace campaigns of some months.

In the course of the development work, several test campaigns were conducted using both lean chalcopyrite type concentrates and richer chalcosite-bornite type concentrates. All copper concentrate types were shown to be metallurgically and technically suitable

for Direct-to-Blister smelting, the only main difference being the amount of slag produced. With rich concentrates it was obvious that Direct-to-Blister smelting is a feasible option economically. With lean concentrates on the other hand the amount of slag becomes large. Therefore, the capacity of the slag treatment facilities also has to be large and the amount of copper returned from slag treatment is large. It was clearly recognized that in order to make Direct-to-Blister smelting feasible for leaner, chalcopyrite type concentrates, more efficient slag cleaning methods and also different options for slag chemistry needed to be developed.

The development of Direct-to-Blister smelting for rich concentrates i.e. low-iron concentrates was continued and it resulted in the construction of KGHM Polska Miedz' Głogow 2 smelter in Poland. Głogow 2 smelter was commissioned in 1978 and has been producing copper successfully and economically for more than 26 years. The capacity of the Głogow 2 smelter has been gradually increased from the original 65 000 tpa to the present 200 000 tpa of copper.

The second industrial scale application of the Outokumpu Direct-to-Blister process for rich concentrates was constructed by WMC in Olympic Dam, Australia. The smelter was commissioned in 1988 with a capacity of 55 000 tpa of copper. By the late 1990's the capacity had been increased to 85 000 tpa, when WMC decided to build a completely new Direct-to-Blister smelter at Olympic Dam. The new smelter started operation in 1999 with a capacity of 200 000 tpa and has been operating successfully since start-up.

Since 1984 Outokumpu and Kennecott had been together developing a new application for Blister Flash Smelting. This application used solid copper matte instead of concentrate as feed material and it was named Kennecott-Outokumpu Flash Converting. Basically, all the lessons Outokumpu had learned from Outokumpu Direct-to-Blister process could be used because of the metallurgical similarity of the two processes. Chemically and mineralogically copper matte and rich copper concentrates are almost identical. Copper matte, actually, is much easier to smelt in Flash Converting, because most impurities have already been removed in the Flash Smelting stage and the quality of matte is much more constant than the quality of concentrates.

In 1992 Kennecott made the decision to expand their smelter by using Flash Smelting and Flash Converting, as the previous Noranda reactors were not able to meet environmental standards. The new smelter was started up in 1995 with a capacity of 280 000 tpa of copper. Since the beginning the Flash Converting process itself has been operating very smoothly and it quickly demonstrated its ability to reach design capacity, but only after replacing the bottleneck of the Sumitomo anode casting shop, the whole smelter was able to reach design capacity on a yearly level in 1998. Today the bottleneck is a shortage of concentrate and the Flash Converter actually would be able to treat plenty of more matte than is currently available at the Kennecott smelter.

Latest Developments in Blister Flash Smelting

During the last ten years Outokumpu, together with its Flash Smelting and Flash Converting licensees, has focused on the development of equipment and operating procedures to further improve the efficiency of the Flash processes. Accurate, but still robust, equipment for controlled feeding of concentrate and matte have been developed along with new and improved concentrate burners. Furnace design and cooling technology has been a very important area of development to improve efficiency and reach longer and longer furnace campaigns.

The Flash Converter of Kennecott recently finished a campaign, which lasted more than 5 years and during the shutdown it was found that the campaign could have been stretched even longer. The Direct-to-Blister furnace at Olympic Dam is stretching for a campaign of 6 years and also Głogow 2 smelter is demonstrating longer and longer campaign lives. Due to the special nature of the concentrate in Głogow 2, the campaign lives have been somewhat shorter, but still reaching 3 years.

The latest boom, which has started in the copper industry as a result of the rising concentrate treatment and refining charges, has also resulted in a new boom for Blister Flash Smelting. In the spring of 2005 Yanggu Xianguang Copper decided to construct a new smelter employing Flash Smelting and Flash Converting. In the first stage this smelter will produce 200,000 tons of copper per year and a subsequent expansion to 400,000 tons per year has been taken into account already in the design phase. The start-up of the smelter is planned to take place in 2007.

Almost at the same time with Yanggu, KGHM Polska Miedz made the decision to start the basic engineering for a new Direct-to-Blister smelter, which would replace the older Głogow 1 and partly also Legnica smelters. The final investment decision is yet to be made, but according to plans this smelter would produce 350,000 tons of copper per year with a single Flash Smelting Furnace. With this production level, the new Głogow 1 furnace will be the biggest copper-making furnace in the world, provided of course that Yanggu is not quicker with their Flash Converter expansion to 400,000 tons.

In January 2006, Konkola Copper Mines (KCM) decided to modernize and expand their smelter in Zambia to 300,000 tons of copper per year and they decided to employ Direct-to-Blister Flash Smelting for this. The KCM smelter is scheduled to start production in 2008. In addition to Flash Smelting, Outokumpu Technology will deliver the slag cleaning process and equipment to KCM.

This means that within a period of 10 months, decisions on three new Blister Flash Furnaces with a combined capacity of 850,000 tons of copper per year were made. This will more than double the Blister Flash Smelting capacity in the world. After these projects have been completed, more than 10 % of the world copper production will come from Blister Flash Furnaces.

SLAG CHEMISTRY OF BLISTER FLASH SMELTING

Especially from a slag chemistry point-of-view, Flash Converting is the easier form of Blister Flash Smelting, because the gangue material contained in the concentrate have already been removed in the smelting stage. Therefore, there are no additional limiting factors in choosing the slag system. When smelting blister copper directly from concentrates, i.e. Direct-to-Blister smelting, one has to take into account also the gangue minerals contained in the concentrate, such as silica, calcia, magnesia and alumina. These materials will end up in the slag and, therefore, they will greatly limit the options for choosing the most feasible slag system.

Table 2. shows the slag compositions, which would come as a result of smelting certain concentrate mixtures. The concentrate mixtures represent compositions, which are currently being used or are being planned for Direct-to-Blister smelting. The concentrate mixture analyses and the slag analyses clearly show that different types of concentrates are suitable for Direct-to-Blister smelting and they also show how the slag composition is totally dependent on the concentrate mixture.

Table 2. – Examples of slag compositions from different concentrates when smelted directly to blister copper.

	Smelter 1	Smelter 2	Smelter 3	Smelter 4	
Flux type	Calcium oxide	Calcium oxide	Silica	Silica	
Concentrate mixture analysis (excluding slag concentrate)					
Cu	27,9	37,7	43,1	36,5	%
Fe	3,3	14,2	20,1	18,9	%
Cu/Fe	8,4	2,7	2,1	1,9	-
S	10,8	22,1	25,5	30,9	%
Cu/S	2,6	1,7	1,7	1,2	-
SiO ₂	16,6	13,9	5,2	8,7	%
CaO	7,8	0,5	0,3	0,1	%
MgO	4,2	1,1	0,1	0,1	%
Al ₂ O ₃	5,7	3,2	0,6	2,3	%
FSF slag analysis					
Cu	14,3	17,0	24,0	24,0	%
Fe	6,4	23,9	36,0	34,5	%
S	0,05	0,2	0,20	0,20	%
SiO ₂	31,4	23,6	18,0	17,0	%
CaO	14,0	5,0	0,3	0,2	%
MgO	6,2	1,9	0,1	0,2	%
Al ₂ O ₃	9,4	5,4	1,4	4,1	%
Fe/(SiO ₂ +CaO)	0,1	0,8	2,0	2,0	-

One benefit of Direct-to-Blister smelting is the fact that practically all the iron in the concentrate is absorbed by the slag. This iron effectively dilutes the gangue minerals coming with the concentrate, thus, making it possible to smelt also concentrates with exceptional gangue mineral contents. Typical examples are smelters 1 and 2 in Table 2. The concentrates have very high levels of silica, calcia, magnesia and alumina and only very little iron. With Direct-to-Blister smelting, all the iron can be used to dilute the gangue minerals and the smelting can still be carried out economically.

All the concentrates used for Direct-to-Blister smelting contain silica levels that are too high for using a pure calcium ferrite slag. Therefore, the slag systems are silica-based with varying additions of calcia and other gangue minerals. In smelters 1 and 2, the high silica level, or more importantly low iron-to-silica ratio necessitates the use of calcia as flux, because there is not enough iron in the concentrate to flux the silica. In smelters 3 and 4 the contents of other gangue minerals, besides silica, are very low and, therefore, an almost pure iron silicate slag can be used.

The complex nature of some of the Direct-to-Blister slags makes it very difficult to present the slag compositions and the thermodynamic behavior of the slags in simple diagrams. The ternary phase diagram $\text{SiO}_2 - \text{CaO} - \text{Fe}_2\text{O}_3$ (Figure 1.) gives some indication of the liquidus temperatures and the components, which first precipitate from the slags. These simple diagrams, however, do not take into account the fluxing effect of monovalent copper, often also referred to as Cu_2O .

Without the effect of Cu_2O , the precipitation of magnetite in the area marked in the diagram would start in temperatures above 1400 °C. Test work, industrial practice and more comprehensive thermodynamic calculations, however, have clearly shown that these typical Direct-to-Blister slags remain completely in the liquid state down to temperatures below 1300 °C. The thermodynamic evaluations for specific slags and specific process conditions can nowadays be carried out very accurately using thermodynamic databases and calculation software.

CaO-SiO₂-Fe₂O₃

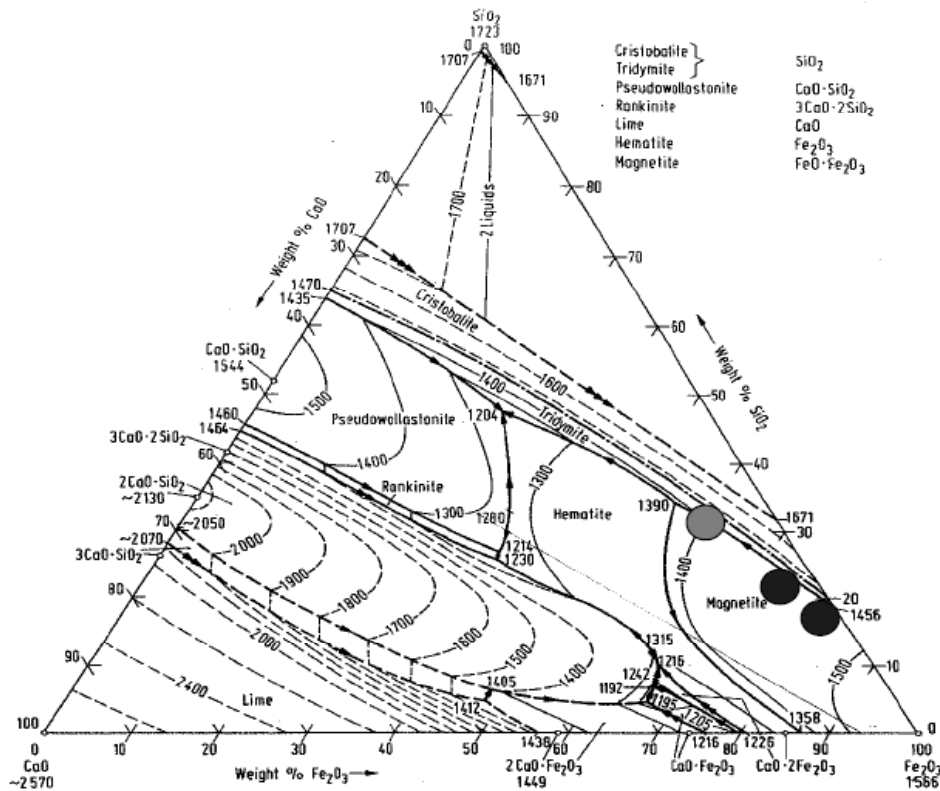
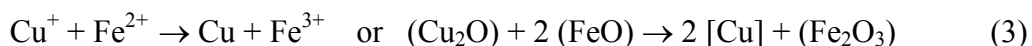
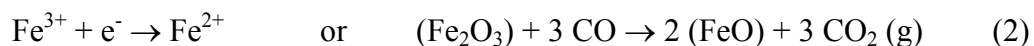
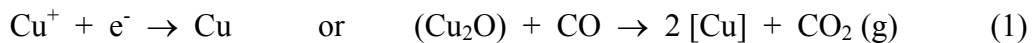


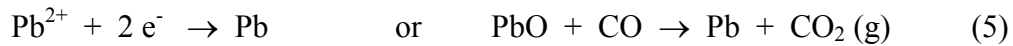
Figure 1. – Liquidus projection of the ternary phase diagram CaO – SiO₂ – Fe₂O₃ [1]
 The marked areas represent actual Direct-to-Blister slags.
 Please note that the diagram does not take into account the
 fluxing effect of monovalent copper (or Cu₂O).

CHEMISTRY OF SLAG REDUCTION

The purpose of electric furnace slag cleaning is to reduce oxidized copper to metallic copper and trivalent iron to divalent iron and to settle the metallic copper droplets from the slag. The simplified reactions taking place are:



As the oxygen potential of the slag decreases further, also further reduction reactions take place, such as:



During the reduction of a blister smelting slag, the trivalent iron is reduced from the slag simultaneously with the copper. This is an important factor, because the copper in the slag or Cu_2O is an important fluxing agent. Now as the copper in the slag decreases, the trivalent iron and thus magnetite decreases and magnetite precipitation is avoided.

Kinetically the reduction reactions require that electrons or CO gas gets into contact with the oxidized copper and iron ions and enables the reduction reactions to take place. Industrial practice as well as theoretical evaluations has shown the importance of mass transfer in electric furnace slag cleaning. Mixing of the slag intensifies the reduction reactions. The reactions are most intense when FSF slag is being tapped into the electric furnace as the jet of incoming slag causes mixing in the slag bath. Also the electrodes cause mixing in the slag because the slag around the electrodes is hotter and because of MHD (magnetohydrodynamic) flows.

The mixing caused by the inflowing slag is shown in Figure 2, which presents results from CFD calculations. The lighter gray areas show higher slag velocities and the scale is in m/s. The incoming slag jet hits the surface and penetrates through the 1 m thick slag layer. The momentum of the slag jet is distributed in all directions and the mixing effect extends also to a distance of approximately two meters from the entry point. The CFD calculation does take into account also the MHD flows and other flows around the electrodes, but as the figure shows, these flows are completely insignificant compared to the flows caused by the slag jet entering the furnace.

The CFD calculations also clearly show that the flows created by the incoming slag jet are completely dissipated inside the slag bath and no channeling of the flow can be detected. Claims have been made that a major part of the slag would flow directly from the entry point to the slag taphole of a round electric furnace, but in the light of industrial studies and CFD calculations, this is a false assumption. The slag flow is completely dissipated and mixing of the slag is quite efficient. The round furnace makes use of practically the entire bath volume and, therefore, the distance from entry point to slag taphole is not a significant parameter in designing a slag cleaning furnace.

If an electric furnace is operated as a batch process, most of the reduction reactions and also most of the settling occur during the filling of the furnace. After the inflow of slag is stopped, there is little flow or turbulence in the slag bath and the reactions proceed very slowly. The only mass transfer occurring in the bath is the flows caused by the electrodes, the mixing caused by settling droplets and rising gas bubbles and diffusion.

This gives time for the copper droplets to settle and the slag copper content slowly approaches its final copper content.

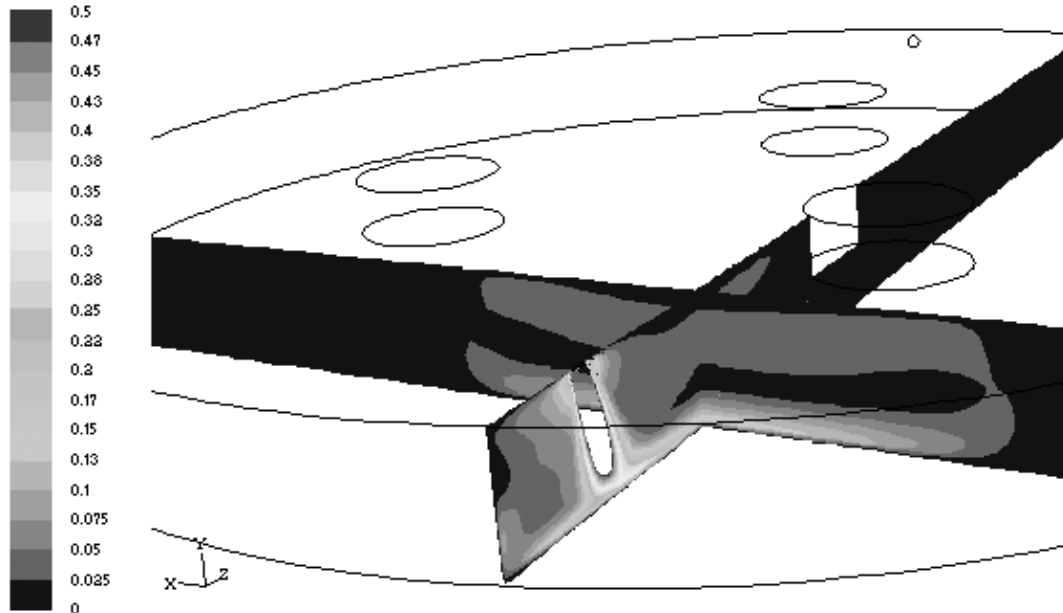


Figure 2. – Slag flow velocities in m/s inside a slag bath with a depth of 1 m
Light and gray areas show higher velocity.

Both industrial and modeling studies done by Outokumpu Technology clearly indicate that reduction and settling of the copper in the slag is greatly enhanced by mixing of the slag bath. The nucleation of the blister copper droplets from the slag creates microscopic droplets, which are too small to ever settle from the slag in normal industrial practice. Mixing is, therefore, required to allow the droplets to coalesce, form larger droplets and then settle through the slag bath.

FURNACE CONSTRUCTION

In the course of history, the construction of the electrical slag cleaning furnace has changed considerably. The reasons are the increase of the furnace size, more demanding process conditions, including high temperature and more aggressive slags. The stricter environmental regulations also require more sophisticated gas handling systems.

Especially the development of furnace cooling technology has allowed the change of furnace construction resulting in longer campaign lives. The cleaning of the slag from the blister production is more demanding than the cleaning of the slag of matte production. Therefore, these improvements are especially critical for the success of Blister Flash Smelting processes.

Furnace Bottom

In the past and even today in many matte smelters, electric furnace bottom construction was insulated. Today, air-cooling is more often applied. The requirements of the bottom cooling are determined by the aggressiveness of the process. Blister copper, in particular, has a strong tendency to infiltrate into the brick lining and this tendency is even stronger if the blister copper contains certain minor elements. Figure 3. shows the technical solution used in many smelters for the cooling of the modern slag-cleaning furnace. This construction consists of air-boxes through which the cooling air flows. This bottom cooling system is especially suitable for blister smelting.

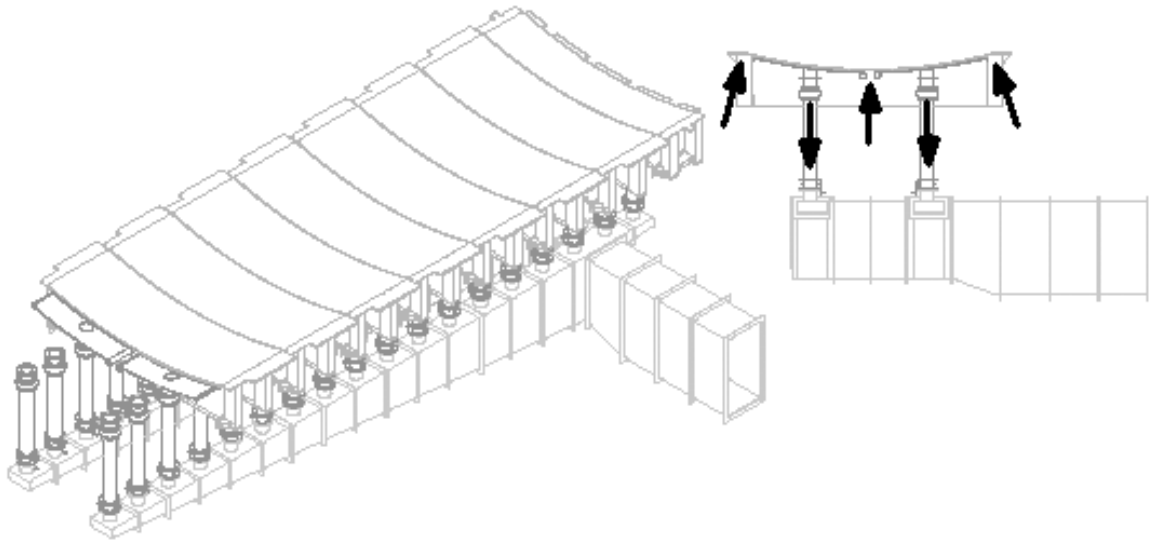


Figure 3. – Technical solution for the cooling of a furnace bottom. Cooling air flows into the air box through the openings indicated with arrows and out of the air box through the ducts also indicated with arrows.

Furnace Shell

The traditional construction of the furnace shell has a water spray cooling. Spray cooling, however, cannot provide adequate cooling for the walls in the most critical areas. The modern cooling calls for the use of cooling elements especially in the bath area. In blister copper processing, this need for efficient cooling is even more essential than in matte processing. Figure 4. shows an example, where the lower part is cooled by vertical SIC (Steel Implanted in Copper) elements and the upper part has a spray cooling. The SIC elements have been specifically developed for blister furnaces and they can withstand contact with molten blister copper much better than normal copper cooling elements. The upper part of the furnace wall can also be cooled by using horizontal cooling elements to give increased campaign life and safety.

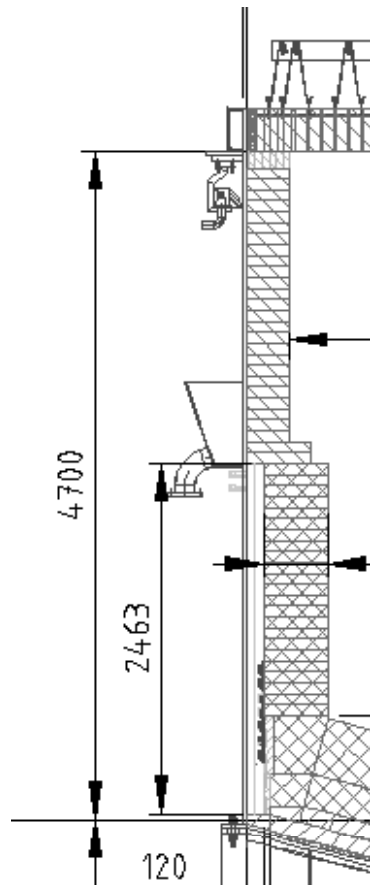


Figure 4 – Cooling of the wall of a modern electric furnace with cooling elements in the bath area and spray cooling on the upper part of the shell.

Furnace Roof and Its Support

The traditional roof construction of an electric furnace was an arch type roof resting on the furnace shell and without cooling. To extend the life of the roof, the furnace was kept at significant under-pressure in order to cool the roof with ingress air. Today most furnaces have a suspended flat roof hanging from horizontal beams. Still today in many furnaces the roof rests on the furnace shell increasing the risk of deformation of the shell even though a more stable structure would be to support the roof from vertical beams outside the furnace shell.

The suspended flat roof makes it possible to use copper cooling elements for roof cooling. This eliminates the need for cooling the roof with ingress air, thus, making the gas treatment of the electric furnace smaller and less expensive. The cooling elements best suited for electric furnace roof cooling are of BIC (Brick Implanted in Copper) type. The roof area to be cooled is designed based on the heat load and requirements of the

slag cleaning process. Figure 5. shows an example, where cooling elements cool practically the whole surface area of the roof.

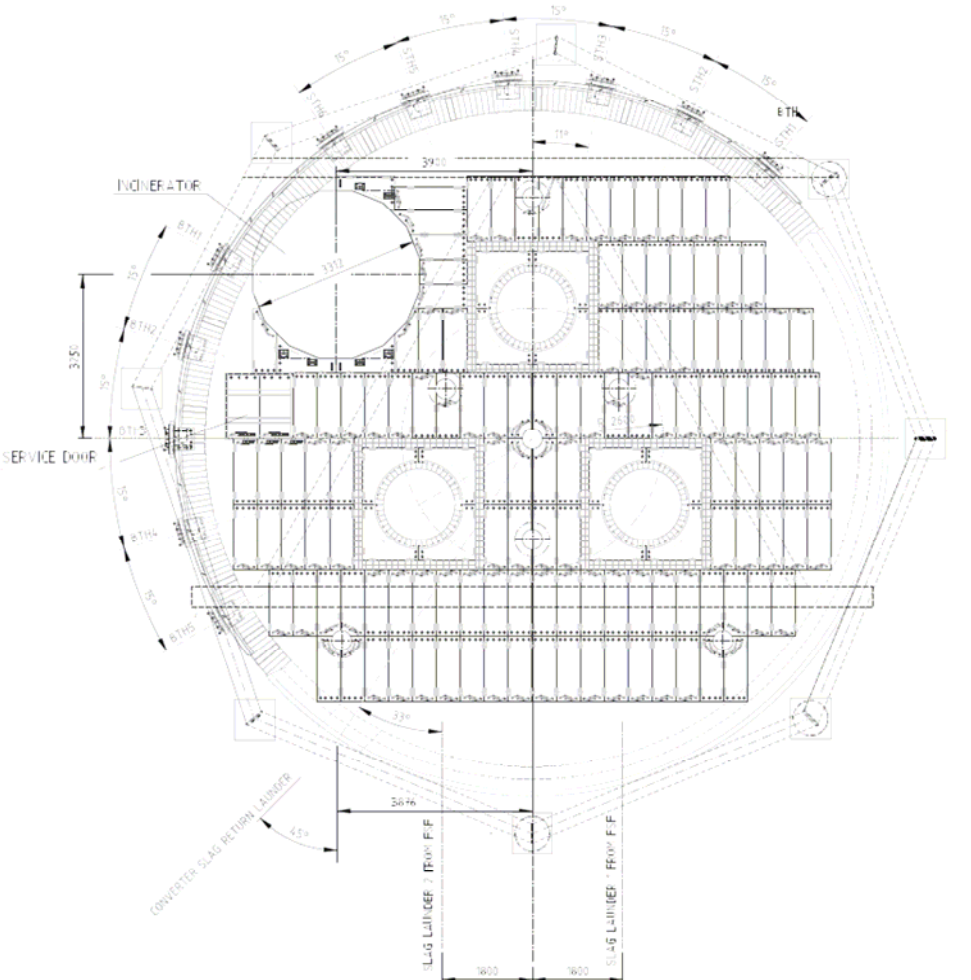


Figure 5. – Electric furnace roof cooling with cooling elements covering practically the entire surface area of the roof.

Placing copper cooling in the roof and especially near the electrodes carries the risk of arcing between the electrodes and cooling elements. The cooling elements are always connected to the earth potential and, therefore, special attention must be paid in designing the electric furnace roof. The cooling elements must be isolated from the electrodes. For this purpose, Outokumpu Technology uses layers of refractory brick between the electrodes and cooling elements as shown in figure 6.

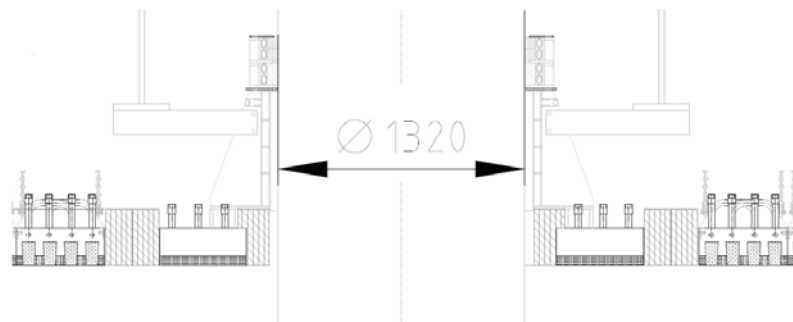


Figure 6. – Electrical insulation of cooling elements from electrodes.

Gas Handling

In the past it was often possible to exhaust the electric furnace gas directly into the atmosphere through a simple gas duct. Today, however, environmental requirements necessitate the application of gas cleaning. The electric furnace gas is rich in CO, which must first be burned in an incinerator. After this, the gas can be cooled using either dilution air or an evaporative cooler followed by dust removal. Incinerator and gas duct design must take into account the characteristics of the gas and the dust in order to avoid clogging of the duct. Therefore, expertise and experience in the slag cleaning process and in the design of the equipment is crucial in designing the gas handling system of an electric furnace.

CONCLUSIONS

During the last 30 years Blister Flash Smelting, i.e. Direct-to-Blister smelting and Flash Converting, has evolved into a major technology in copper smelting. Within the next few years the share of copper produced via Blister Flash Smelting will exceed 10 % of world production. One of the most decisive factors influencing the economical viability of Blister Flash Smelting is the slag cleaning.

Slag cleaning in an electric furnace is a well-established method for recovering metals values from slags. This, however, does not mean that this method is outdated. Continuous development is being done on the chemistry of slag cleaning and on the equipment. Outokumpu Technology has developed state-of-the-art technical solutions to the structure of electric furnaces and to the slag cleaning process as a whole. Modern calculation methods along with more traditional test work are actively employed in the development. As a result, slag cleaning furnaces have longer and longer campaign lives and even the metal recoveries are being continuously improved.

REFERENCES

1. Allibert et al., Slag Atlas, Verlag Stahleisen GmbH, Düsseldorf, Germany, 1995.