

# Arsenic Removal from Blister Copper by Soda Injection into Melts

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## ABSTRACT

Soda injection into blister is one of the most important operations in copper refining processing. The aim of this work is to determine optimal parameters of a technology for arsenic removal from anode copper by use of soda ( $\text{Na}_2\text{CO}_3$ ) injected into molten copper bath by submerged tuyeres. Results of the work reveal that the rate of reaction between soda and arsenic is very high and form sodium arsenate  $\text{Na}_3\text{AsO}_4$ . These findings have been used to work out a table, which gives an amount of soda to be used in process as a function of refined copper quantity and arsenic content. The second part of this work is to demonstrate the use of nitrogen as a carrier gas for soda injected into blister for arsenic removal. An application of neutral gases in this process is beneficial, and results in energy conservation.

## Introduction

In the conventional copper-making processes, most of the arsenic is removed during these many stage processes by evaporation and slagging. In contrary, the modern processes are capable of smelting and converting copper concentrates in a single reactor, and the overall process is much shorter. The decreased in the processing time results in lower removal of arsenic. The Outokumpu flash one-step process has been operated in Poland since 1978 and steadily increasing concentration of As in blister copper steadily increases during the last years and nowadays can be as high as 1.2 pct. The reason of it is that arsenic content in Polish concentrates is steadily increased, and arsenic rich slags are reverted into materials stream within smelters. This creates very serious problem, which has been solved by implementation, a submerged injection process. Sodium carbonate and calcium hydroxide were used as fluxes in this process.

During the last two decades injection fluxes into metals have become a very important tool in metallurgical processes. Thanks to this technique, the reactions become very rapid and provide higher yields in comparison with conventional processes. Elimination of arsenic from molten copper by soda injection was described for the first time by Eddy [1] and Hillenbrand et al. [2]. Zhao and Themelis [3] and Stapurewicz and Themelis [4] investigated the kinetics of the arsenic and antimony elimination process by soda. There has been a report on industrial tests by Jiao et al. [5].

The importance of this technique is obvious, if the following factors are discussed:

- It is believed that mass transfer is controlled by the reaction rate in the most of the metallurgical processes. The rate of mass transport can be described by the equation:

$$J = S \cdot D \cdot \frac{dC}{dx} \quad (1)$$

J- is amount of a substance passing perpendicularly through unit area during time unit,  
S-is surface area across which mass transport occurred,  
D-is diffusion coefficient,

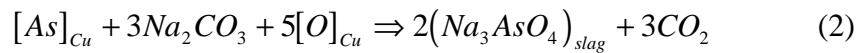
$\frac{dC}{dx}$  - is concentration gradient.

This equation clearly shows that mass transport rate can be increased by:

- increase of surface area,
- increase of concentration gradient.

The injected soda is melted immediately due to small size of its particles. Reactions start instantly after the injection of the soda into the bath and, hence, the yield is very high. As the reactions involved are take place on molten flax/molten bath interface, so refractory lining is not attacked so vigorously, an therefore their life would be prolonged. In addition is far easier to control temperature, oxygen potential, heat transfer and rate of reactions in the injecting processes. When the flux reach the top, the reaction between formed slag and arsenic take place through the slag-metal interface.

The first part of this study was to investigate industrial scale removal of arsenic from blister copper with the reaction of the molten metal with air and sodium carbonate. Removal of arsenic from the blister copper is one of the major problems in copper refining process. Technology currently used in Poland consists of soda injection into melt, with air used as a carrier gas. The injection into the bath is immediately followed with reaction between soda and arsenic. And it is believed that the slag consisting of sodium arsenate was formed according to the reaction [6]:



It was found that the oxygen content in the copper after the process is usually higher and it is caused by oxygen dissolution in the copper according to the reaction:



Next, this oxygen has to be removed in deoxidising stage of the process, and therefore some additional amount of hydrocarbons is required for it. The paper is to demonstrate that the use a neutral gas instead of air results in considerable energy saving

### **Injection of sodium carbonate into molten copper in industrial furnace.**

Very fine  $Na_2CO_3$  with compressed air used as a carrier gas was applied for injection into molten copper contained in rotary refining furnace at Glogow copper smelter as can be seen in Figure 1.

The trajectories of the particles and the carrier gas are very important factor, as they influences of the contacting pattern of the particles with the copper and gas phase. There were a number of performed works performed on cold models of injections [7,8], and only few with molten metals at elevated temperature [9]. In industrial practice, most pneumatic injection devices operate with

medium flow rates, which insure their jet performance unless coagulation of these particles occurs. In such case jets can be separated by bubbles, and it might result in clogging of tuyere. During the experimental work a several tuyere cloggings were experienced. It can be assumed that fine soda particles flow with the same velocity as the carrier gas. And because of high surface tension of the copper, these particles do not penetration of these particles into the melt, however they are melted nearly instantaneously, due to their small size and low melting point. The time for the reaction when particles travel with gas carrier through the melt is quite short, however, it is expected that the flux layers are generally thin, and therefore the reaction rate is not process controlling. As density of soda is lower than that of molten copper, the formed slag rises with the plume and reaches the surface of molten copper. Therefore the refining process can be split up into two consecutive steps.

- Process of arsenic removal by soda rising through the copper bath.
- Process of arsenic removal by soda floating on the copper surface.

## Results of the industrial tests

The copper for refining in the anode furnace was partly from production of the Outokumpu direct-to blister process, but majority of the copper was from converting of Cu-Fe-Pb alloys in Hoboken's converters. Copper contained: Pb-0.1-0.3 wt pct; As-0.4-0.9 wt pct; S-0.01-0.05wt pct, and O-0.5-1.16 wt pct. Air flow rate was 1200 m<sup>3</sup>/h per tuyere and air pressure was varied between 0.15-0.25 MPa. Soda with air was injected only through one of two tuyeres, and only air was injected through the another.

Charges of 200-320 Mg of the blister copper were used for experiments. Soda charges of 0.5-0.8 Mg were injected into copper at various rates, and analysis of [As]<sub>Cu</sub> content in copper and the formed slag followed each injection. Then next charge of the soda was injected and the operation was repeated as long as the arsenic content in the copper decreased below 0.1 wt pct. The slag was skimmed off from the furnace after single injection or after 2-3 injections. The quality of the slag ranged from fluid to very lumpy one, and no reason was found for such behaviour. Results revealed that the ratio of the injected soda to removed arsenic was almost constant regardless of the soda injection rate, and corresponds to stoichiometric formation of Na<sub>3</sub>AsO<sub>4</sub>. These results enabled development an equation for soda quantity needed in arsenic removal process:

$$Soda[kg] = 21.2 \bullet ([\% As]_{Cu}^{Initial} - [\% As]_{Cu}^{Final}) \bullet Q_{Cu}[Mg] \quad (4)$$

where: Q<sub>Cu</sub> is quantity of refined copper in anode furnace expressed in Mg.

The above correlation was used for construction of a table, which is used for estimating the amount of soda required for arsenic removal to assumed final arsenic content.

At the end of the arsenic removal same quantities of calcium hydroxide were added to form calcium arsenates, which are more stable than sodium arsenate, and prevents As to be reverted from slag to copper during the reducing stage. This procedure proved to be necessary because of the difficulties in skimming the whole slag before the reducing stage.

Figure 2 illustrates validity of this equation for refining campaign during three consecutive months at the G ogów (Poland) smelter. As can be seen there is a very good agreement between quantity of soda used and those computed with equation (4).

### **An application of neutral gases in arsenic removal process.**

As it has already been mentioned slag formed in industrial conditions ( $P_{CO_2} \ll 1$  bar), should consist almost entirely of sodium arsenate according to the equation (2). This reaction indicates that there is no need to use air as a carrier gas, if blister copper contains dissolved oxygen. Furthermore, if nitrogen or another neutral gas is used, arsenic and oxygen could be removed simultaneously. It can be found from the stoichiometry of the reaction (2) that for every 100 g of arsenic removed from the copper also 53 g of the oxygen is also driven out from the refined copper during the process of sodium arsenate formation. It provides also another advantage because refractory lining of the anode furnace does not corrode so vigorously when there is less oxidised copper. Therefore, laboratory experiments were carried out to investigate arsenic removal process in case when nitrogen is used as a carrier gas.

### **Laboratory experiments**

The Cu-As-O mixture was prepared by melting 850 g of electrolytic copper at 1523K in an alumina crucible of 50 mm ID and 150 mm height with predetermined amounts of  $Cu_2O$  and Cu-As master alloy to obtain the desired composition. Initial compositions of the samples were assumed to be 0.4, 0.8, 1.2 wt pct of arsenic and 1.0 wt pct of oxygen.

Figure 3 shows schematically the experimental apparatus used for the arsenic and oxygen removal experiments. An amount of 850 g of prepared Cu-As-O mixture was placed in alumina crucible. The crucible was then placed in the hot zone of a crucilite furnace. Nitrogen carrier gas was introduced into melt through a lance made of an alumina tube of 6 mm ID and 8 mm OD that was immersed into the molten copper. Pure and dried soda was used as the fluxing and slag-forming agent. In all experiments, the overall amount of injected soda was about 10% more than of the amount required to form  $Na_3AsO_4$  from arsenic contained in the refined copper. The molten copper was then sampled periodically with a silica tube of 3 mm. inner diameter. The sample was quenched in water or liquid nitrogen and then analysed for arsenic and oxygen. The nitrogen gas flow rate was established on 15 l/h or 20 l/h. The lance tip was positioned in the melt at 10 mm from the crucible bottom. The soda injection rate was 13.3, 26.7 or 33 g/h.

### **Results of laboratory experiments**

The effects of nitrogen flow rate for different oxygen and arsenic contents in samples on the arsenic and oxygen removal process are listed in Table 1-3.

An elimination rate of the arsenic from copper was defined as:

$$a = \frac{[As]_{Cu}^0 - [As]_{Cu}^t}{[As]_{Cu}^0} \cdot 100\% \quad (5)$$

Where:  $[As]_{Cu}^0$  -is initial concentration of arsenic in copper,  
 $[As]_{Cu}^t$  -is concentration of arsenic in copper after time "t".

A change of the arsenic elimination rate, determined during injecting experiments is presented in Figure 4.

As it can be seen in Fig 5 that there is a clear tendency for the oxygen content of the copper to decrease as the arsenic is removed. This decrease is roughly equal to 53 % of eliminated arsenic as can be predicted from equation (2).

## Conclusions

There are several advantages of the injection technique over the surface addition treatment, which can be summarised as follows:

1. The injecting technology shorten refining process in comparison with surface addition of soda by about 10%, however, potentially it can be done far more effectively, if blockages of pneumatic installation for soda transport to tuyeres can be eliminated.
2. Oil and gas consumption decreased by about 25%.
3. Soda consumption decreased by about 33% in comparison with the surface addition technique.
4. Refractory consumption seemed to be much smaller, however the final results would be revealed in much longer time.
5. Flue dusts quantity decreased considerably.
6. Under industrial conditions, the principal reaction product can be assumed to be  $Na_3AsO_4$ .
7. The laboratory tests demonstrate usefulness of neutral gases in some fire refining processes of copper. Replacement of the air with nitrogen which is a by-product in many copper smelters should result in a considerably energy savings and decrease of processing time. It is expected that the life of anode furnace refractory lining could be prolonged because of lower oxygen content in the copper and shorter process itself.
8. The rate of arsenic removal was found to be independent of initial arsenic and oxygen contents in copper within experimental error.

## Acknowledgement

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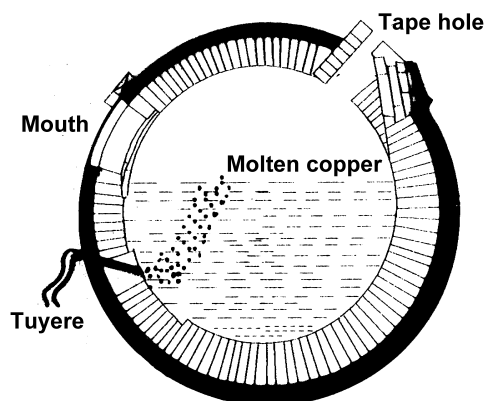


Figure 1. Rotary refining furnace.

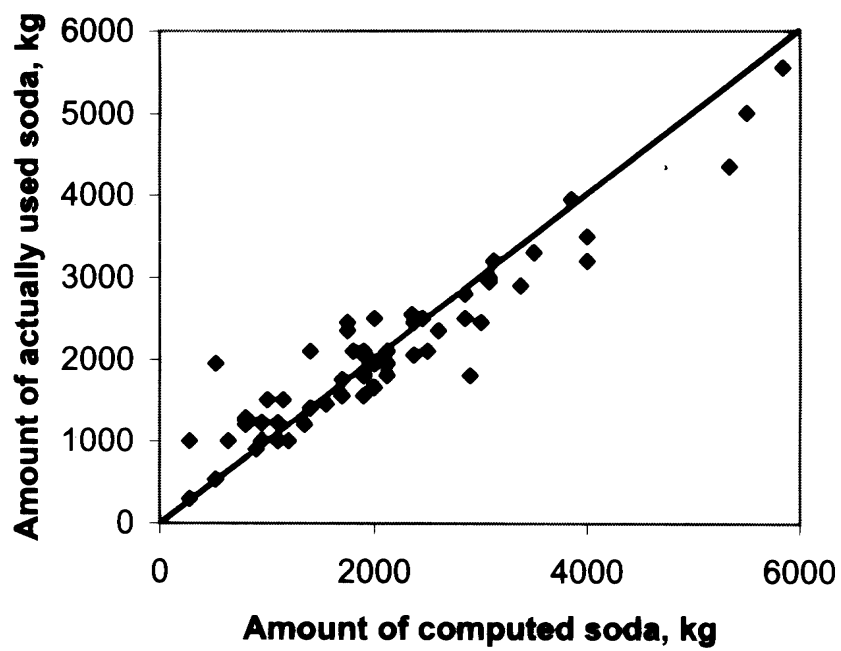


Figure 2. Comparison of used soda versus those computed by equation (4).

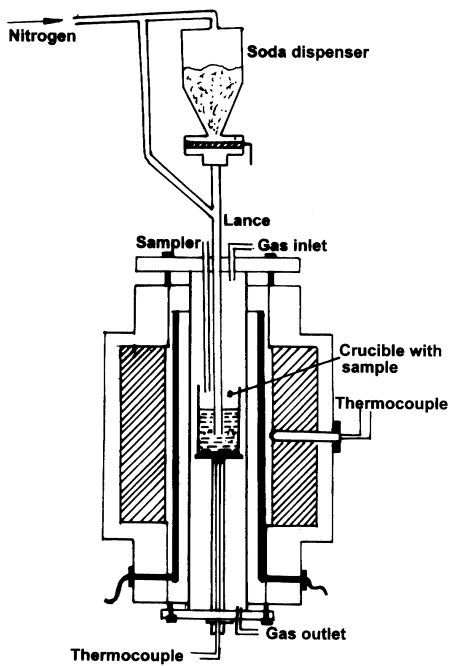


Figure 3. Schematic diagram of experimental setup.

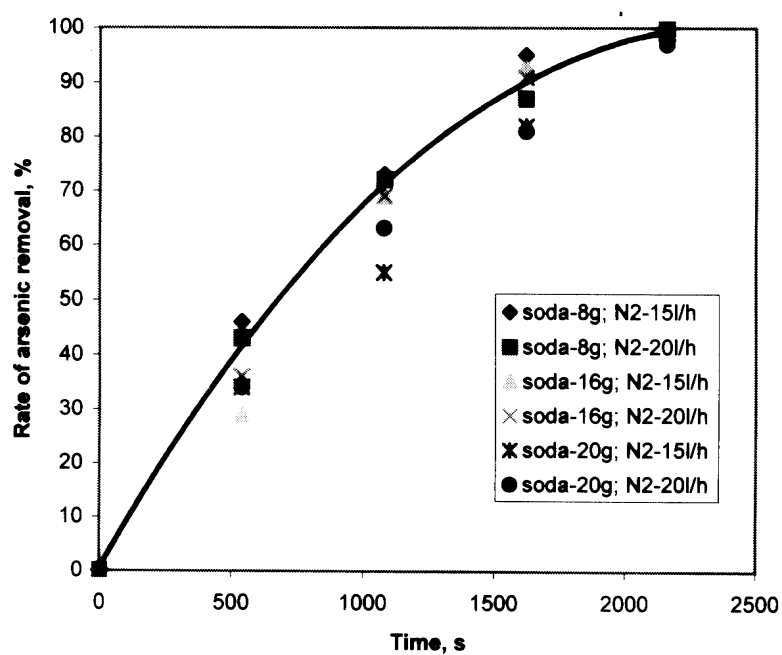


Figure 4. Rate of arsenic elimination at 1523 K.

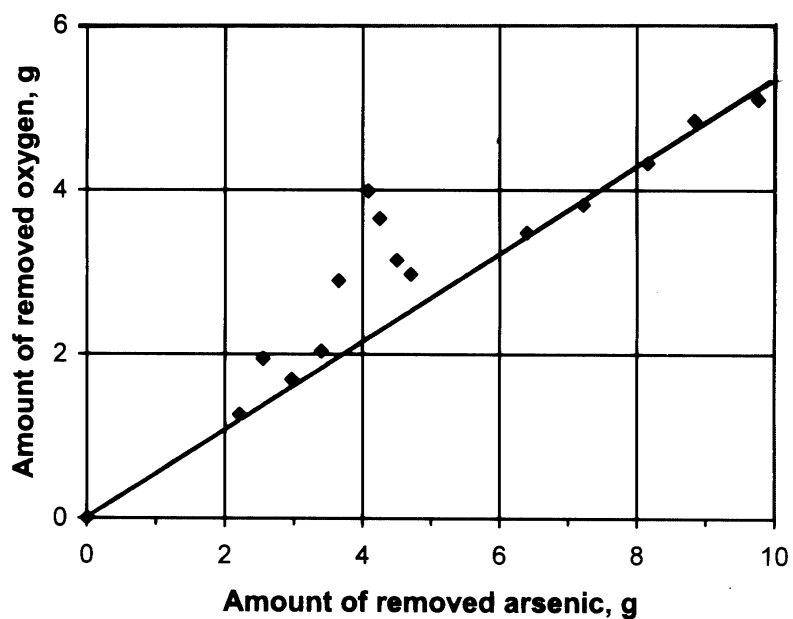


Figure 5. Correlation between arsenic and oxygen removed from copper.

Table 1. Experimental results for  $[\text{As}]_{\text{Cu}}$  and  $[\text{O}]_{\text{Cu}}$  removal. Charge of 8 g of  $\text{Na}_2\text{CO}_3$  was injected into 850 g of copper at 1523K.



Time of the process, s	N <sub>2</sub> flow rate = 15l/h		N <sub>2</sub> flow rate = 20l/h	
	[%O] <sub>Cu</sub>	[%As] <sub>Cu</sub>	[%O] <sub>Cu</sub>	[%As] <sub>Cu</sub>
0	0.70	0.389	0.64	0.366
540	0.96	0.208	1.02	0.209
1080	0.87	0.105	0.42	0.104
1620	0.43	0.021	0.50	0.048
2160	0.69	0.006	0.73	0.001

Table 2. Experimental results for [As]<sub>Cu</sub> and [O]<sub>Cu</sub> removal. Charge of 16 g of Na<sub>2</sub>CO<sub>3</sub> was injected into 850g of copper at 1523K.

Time of the process, s	N <sub>2</sub> flow rate = 15l/h		N <sub>2</sub> flow rate = 20l/h	
	[%O] <sub>Cu</sub>	[%As] <sub>Cu</sub>	[%O] <sub>Cu</sub>	[%As] <sub>Cu</sub>
0	0.31	0.759	0.78	0.788
540	0.67	0.538	0.78	0.502
1080	0.44	0.237	0.63	0.246
1620	0.20	0.054	0.44	0.074
2160	0.30	0.006	0.35	0.004

Table 3. Experimental results for [As]<sub>Cu</sub> and [O]<sub>Cu</sub> removal. Charge of 20 g of Na<sub>2</sub>CO<sub>3</sub> was injected into 850g of copper at 1523 K

Time of the process, s	N <sub>2</sub> flow rate = 15l/h		N <sub>2</sub> flow rate = 20l/h	
	[%O] <sub>Cu</sub>	[%As] <sub>Cu</sub>	[%O] <sub>Cu</sub>	[%As] <sub>Cu</sub>
0	0.82	0.1.04	0.93	1.19
540	0.62	0.69	0.69	0.79
1080	0.49	0.49	0.52	0.44
1620	0.37	0.19	0.42	0.23
2160	0.25	0.005	0.33	0.04