

## HYDRO - PYROMETALLURGICAL TREATMENT OF COPPER CONVERTER FLUE DUST

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### ABSTRACT

*The aim of this study is to investigate the possibility of pyrometallurgical recovery of lead and bismuth from preliminary desulfated copper converter flue dust into a metal phase, by carbothermal reduction in a soda ash smelt.*

*Hydrometallurgical treatment of flue dust is actually caustic leaching and it aims to remove the sulfate sulfur. The desulfation degree of the converter flue dust, using 35 g NaOH per 100 g dust, is 80 % and the total impurities concentration in the Na<sub>2</sub>SO<sub>4</sub> solution is below 50 mg l<sup>-1</sup>.*

*The solid product from the hydrometallurgical step was subjected to pyrometallurgical treatment in a soda ash smelt. The effect of temperature, reducing agent type and amount, soda type and amount, on metal yield as well as the distribution of Pb, Bi, Cd, Ag and Cu among the process products, have been determined. It was found that with the increase of temperature, reducer and soda amounts the metal yield increased, but the copper and silver concentrations in the metal phase also increased.*

*The laboratory experiments showed that it is possible to recover Pb and Bi in a separate product at a temperature of 900°C. The optimum established parameters for carbothermal reduction of desulfated copper converter flue dust are: temperature 900°C, soda amount 50 % of the dust mass, reducer amount 10 % of the dust mass and process duration 30 min. The recovery rates of lead and bismuth at these conditions are 80 % and 65 %, respectively. The obtained alloy consists of 74.87 % Pb, 12.96 % Bi, 0.22 % Cd and 11.63 % Cu.*

*Semi industrial experiments should be carried out to clarify the optimal process parameters, since the furnace type and the method of charge heating will also influence the distribution of the metals among the products of smelting.*

*Keywords: copper converter flue dust, desulfation, carbothermal reduction.*

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### INTRODUCTION

The converter dusts are valuable feedstocks, due to their high copper content, as well as the presence in them of other valuable metals like silver, lead, bismuth, zinc and others.

If copper dust is directly returned to the flash smelting furnace, the content of the impurities (arsenic, bismuth, and zinc) in the feed materials will be raised greatly and the processing capability of furnace will be reduced. The process of copper electro-refining and the

quality of electric copper will be affected greatly by the circulating accumulation of the impurities, such as bismuth, antimony, arsenic, and iron [1].

The removal of impurities is critical in the copper metallurgy for the production of high quality copper, but it is also of great importance from an environmental aspect. Due to the constant increase in impurities in copper ore over the years, an even more critical situation can be reasonably expected in the future. It is essential to keep impurities below the levels accepted by national and international standards for the copper industry, and

to decrease the total emission of harmful components. Currently, the majority of smelters around the world face this problem [2].

Therefore, it is necessary to separate copper dust from the copper smelting system and reclaim valuable metals.

The choice of a suitable technology for processing of the dust depends exclusively on their chemical and mineralogical composition. The hydrometallurgical methods for treatment of the dusts can be divided into two main groups – acidic and alkaline methods. The reagent used most frequently by the acidic methods is sulfuric acid, and by the alkaline methods – sodium hydroxide [3 - 6].

So far, the two-stage methods of processing of the dusts on the basis of aqueous extraction and sulfuric-acid treatment of the residue after the first stage, have found the widest industrial application. In the case of water and acid dissolution, the copper, zinc, cadmium and iron sulfates, and the arsenic oxides pass into the solution. The lead, bismuth and silver compounds, present in the dust, remain in the insoluble residue. The alkaline methods have not found any industrial application till the present day.

The latest trend in the sulfuric-acid methods is their combination with the processes of copper solvent extraction, followed by electrowinning and obtaining of high-quality cathodes.

The aim of this study is to investigate the possibility of pyrometallurgical recovery of lead and bismuth from preliminary desulfated copper converter flue dust into a metal phase, by carbothermal reduction in a soda ash smelt.

## EXPERIMENTAL

The object of this research is the converter dust, which is a white powder with very low bulk density and low fluidity. The chemical composition of this material is presented in Table 1.

A mineralogical study of the dust was carried out by X-ray diffraction. According to the diffractogram of the material (Fig. 1), the possible phases in it are:  $\text{PbSO}_4$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{Cu}_2\text{SO}_4$ ,  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ ,  $\text{CdSO}_4$ ,  $\text{CdPbO}_3$ ,

$\text{Bi}_6\text{O}_6(\text{SO}_4)_3$ ,  $\text{CdBi}_{38}\text{O}_{58}$ ,  $\text{Pb}_5\text{Bi}_8\text{O}_{17}$ . A characteristic feature of converter flue dust is the high concentration of sulfate ions - 37 %.

The treatment of converter flue dust is carried out in two stages – hydrometallurgical for removal of sulfate sulfur and carbothermal reduction of desulfated dust in a soda ash smelt.

Desulfation of the converter flue dust was realized at room temperature under continuous stirring with an alkaline reagent. All metals concentration in the solutions were analyzed by atomic absorption analysis. Measurement of pH was made with a Mettler Toledo pH meter. Pyrometallurgical experiments were conducted into a graphite crucible in an electric furnace, as the charge consists of dust, a reducing agent and soda. Chemical composition of the obtained alloys is analyzed by a handheld XRF spectrometer Brucker S1 TITAN.

## RESULTS AND DISCUSSION

### Hydrometallurgical stage - Desulfation of the converter flue dust

Copper and lead in converter flue dusts are mainly in the sulfate form. The presence of sulfates makes difficult their pyrometallurgical treatment. For this reason, the first stage of the proposed technology is desulfation of the dust. The purposes of such treatment are:

- Maximum removal of sulfate sulfur;
- Minimum dissolution of metals into the solution of sodium sulfate.

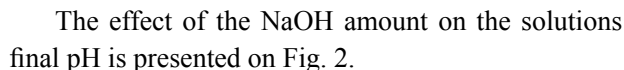
The realization of the first purpose will lead to an effective pyrometallurgical processing of flue dust as well as to minimized sulfur dioxide emissions.

The realization of the second purpose provides obtaining of pure sodium sulfate, which is a commercial product.

Sodium base has been selected as the reagent for desulfation. The tests for converter flue dust desulfation were conducted with 100 g l<sup>-1</sup> NaOH at ambient temperature for a period of 30 min. The reactions of the converter dust components are hydrolysis of the sulfate compounds:

Table 1. Chemical composition of converter flue dust, %.

Cu	Ag	Cd	Pb	Bi	As
14	0,0440	1,76	21,08	3,82	0,32



of NaOH amount and reaches 100 % at 0,4 g NaOH per g converter dust. The full desulfation also leads to rise of the impurities concentrations in the  $\text{Na}_2\text{SO}_4$  solution.

The desulfation degree of the converter flue dust, using 0,35 g NaOH per g dust, was 80 % and the total impurities concentration in the  $\text{Na}_2\text{SO}_4$  solution was below 50 mg l<sup>-1</sup>. In this case, the chemical composition of the desulfated convertor dust is presented in Table 2. The main products of the process are a residue with reduced sulfur (sulfate) content and a solution of sodium sulfate.

NaOH, g.g <sup>-1</sup> convertor dust	pH
0.20	7.0
0.30	9.1
0.33	10.2
0.35	11.8
0.40	12.2

Fig. 2. Effect of the NaOH amount on the pH of Na<sub>2</sub>SO<sub>4</sub> solution (at ambient temperature, 30 min).

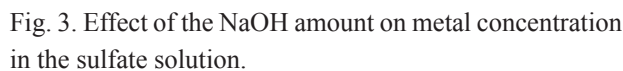


Table 2. Chemical composition of the desulfated converter dust.

Cu	Fe	Bi	Cd	Pb	Zn	Ag	As
17,84	0,96	4,87	2,24	23,2	8,16	0,06	0,21

### Pyrometallurgical stage - carbothermal reduction of desulfated converter flue dust

The main aim of the pyrometallurgical treatment is to recover lead and bismuth from the preliminary desulfated copper converter flue dust into metal phase and to concentrate copper and silver in a matte-slag phase. The factors that determine the process are – temperature, reaction time, amount and type of the soda and the reducer. All pyrometallurgical experiments were carried out with 80 % desulfated converter dust in soda ash smelt in an electric furnace.

#### Effect of temperature

Experimental melts for determination of temperature effect were carried out, maintaining the following parameters constant:

- Soda type -  $K_2CO_3$ - $Na_2CO_3$ ;
- Soda: converter flue dust ratio - 1;
- Reducer amount - 10 % of dust weight;
- Reducer type - charcoal;
- Process duration - 30 min.

The results, shown in the graphs (Fig. 4), support the hypothesis that lead and bismuth compounds predominantly are reduced at temperature of 900°C. The

recovery degrees of lead and bismuth into the metal phase are respectively 83 % and 72 %. The chemical composition of the obtained alloy at these conditions is presented in Table 3.

#### Effect of soda: converter flue dust ratio

The role of the soda melt is to fix the remaining sulfur in the desulfated dust and to prevent the allocation of arsenic in the vapor phase. The results for the melts (Fig. 5), carried out at temperature of 900°C, anthracite coal amount of 10 % of the dust mass and process duration of 30 min, showed that the increasing of soda consumption, leads to significant increasing of the metallic phase extraction. At soda: dust ratio of 1, the resulting metal alloy is 40 % by mass of the initial converter dust.

The chemical analysis of the metal phase, depending on the soda:dust ratio is shown in the Table 4. At higher consumption of soda, the metallic phase yield is higher. As seen in the table, the concentration of copper in the metallic phase decreased with the increasing of soda consumption. The concentrations of lead, bismuth and silver recovery in the metal phase also increased by increasing the consumption of soda, while the extraction rate of copper and cadmium remained practically constant.

Table 3. Chemical composition of the obtained alloys, %.

Ag	Cu	As	Sb	Cd	Pb	Bi	Zn
-	2,538	-	-	0,433	76,338	17,653	-

Table 4. Chemical compositions of the obtained alloys, depending on soda amount, %.

Soda:dust ratio	Cu	Ag	Cd	Pb	Bi
0,25	13,98	-	0,14	72,32	12,51
0,5	11,68	0,13	0,22	74,87	12,96
1	7,82	0,10	0,22	77,95	13,73

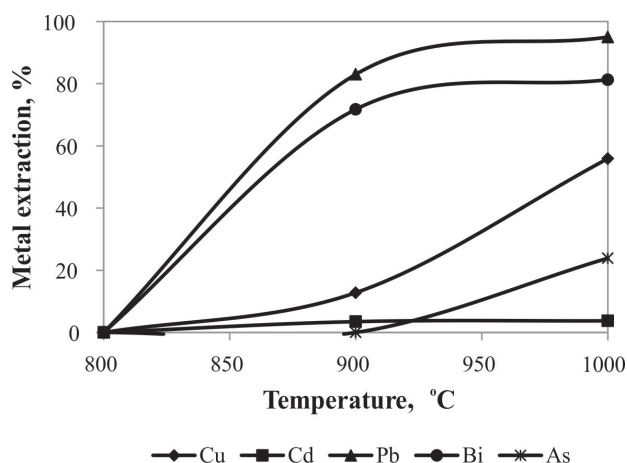


Fig. 4. Metal extraction dependence on the temperature.

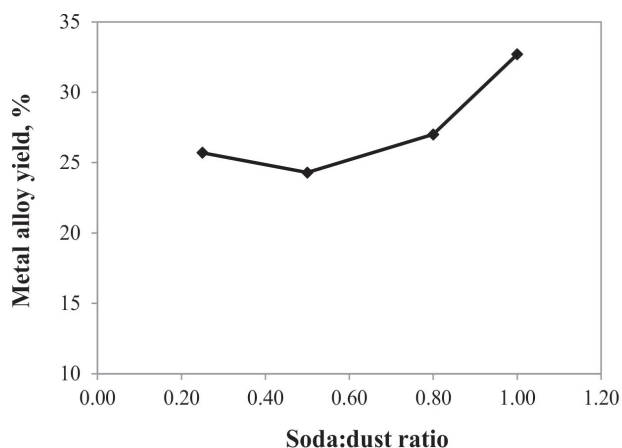


Fig. 5. Metal alloy yield dependence on soda:dust ratio.

#### Effect of reducer amount

The experiments were conducted at reducing agent consumption of 10 %, 6 % and 4 % by mass of the dust, at constant soda amount (25 % of dust mass), 30 min duration and temperature of 900°C.

The results of the experimental melts (Fig. 6) showed, that with the increase of reducer amount, the extraction degree of the metallic phase increases.

#### Effect of reduction duration

The experiments have been conducted at different reduction durations - 20, 30 and 45 min. The results obtained are presented in the Fig. 7. It is observed that with the increase of reduction time, the yield of metallic phase increases, but after the reduction duration 30 minutes the yield remains constant.

Based on the experiments, a material balance on a melt carried out under the following conditions has

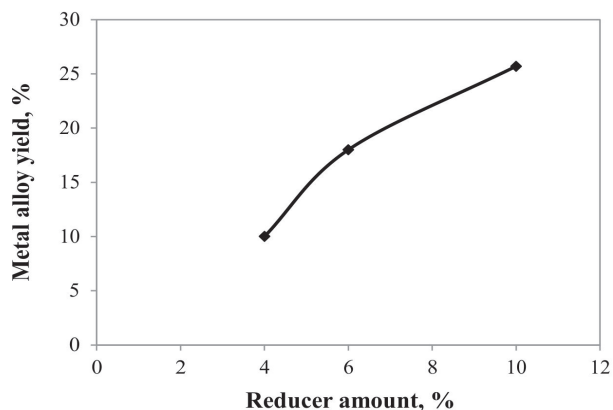


Fig. 6. Metal alloy yield dependence on reducer amount.

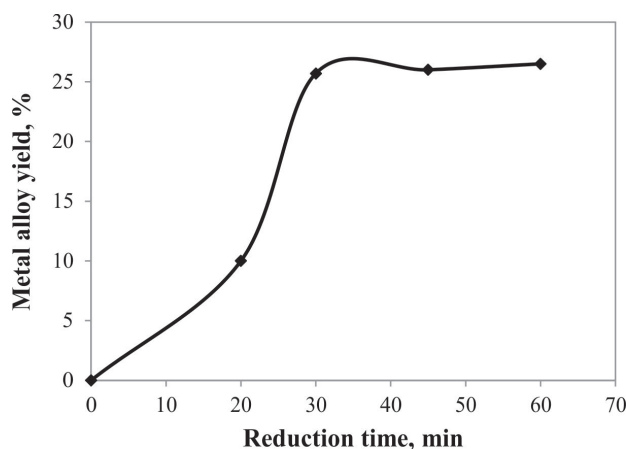


Fig. 7. Metal alloy yield dependence on reduction duration.

been calculated:

- Soda: dust - 0.5;
- Reducer amount - 10 % of dust weight;
- Reduction duration - 30 min.

As a result of the pyrometallurgical treatment of desulfated converter dust under the specified conditions, a metal alloy which is 15,07 % of the initial converter dust mass was obtained. Almost the same mass has the matte-slag melt (Fig. 8). The high proportion of gas-dust mixture (over 60 %) is noteworthy.

Contrary to our expectation, more than 90 % of the arsenic and cadmium, as well as 80 % of the copper, pass into the gas phase (Fig. 9). The copper and silver concentration into the metallic phase is also high. The obtained results do not match with those reported in [7], according to which the carbonate melt can be enriched in arsenic up to 30 %, and until the arsenic content in it is less than 18 %, it does not evaporate into the gas phase.

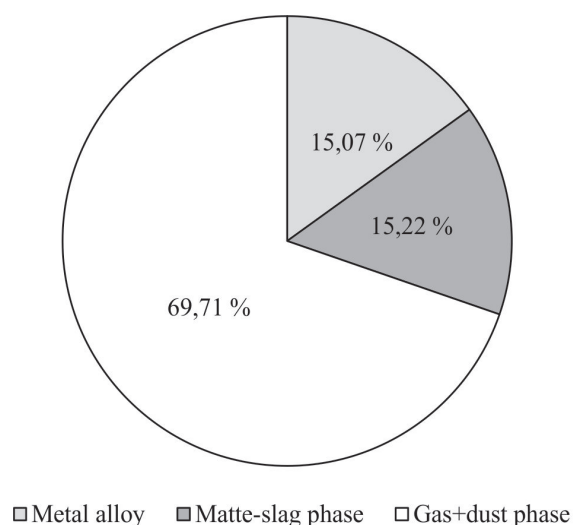


Fig. 8. Material balance of the melt.

## CONCLUSIONS

The presented research offers one version of a technology for extraction of lead and bismuth from copper converter flue dust in a separate metallic phase, which consists of two stage - a hydrometallurgical, and a pyrometallurgical treatment.

The first stage of the proposed technology is dust desulfation by a sodium hydroxide solution. The consumption of NaOH should be such that the final solution pH should be around 12, wherein the desulfation degree is 80% and the total impurities concentration in the resulting  $\text{Na}_2\text{SO}_4$  solution, is below  $50 \text{ mg l}^{-1}$ .

The second stage is the carbothermal reduction of the desulfated converter flue dust. Pyrometallurgical experiments showed that the lead and bismuth predominantly concentrate into a metal phase, at temperature up to  $900^\circ\text{C}$ . At this temperature, the removal of 80 % of the Pb and 65 % of the Bi content in the converter flue dust is possible. This significantly reduces the circulation of harmful impurities in the copper smelting system.

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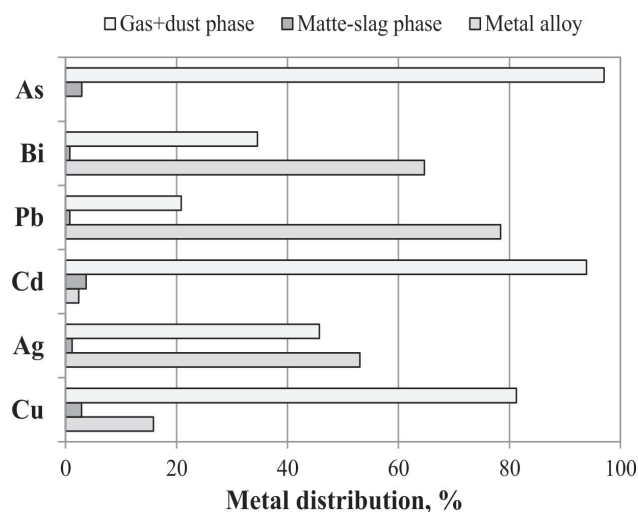


Fig. 9. Metal distributions between the melt products.

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