



Research article

Investigating the possibility of removing lead (Pb) from copper melt during the smelting process in Sarcheshmeh copper complex

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Keywords

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Thermal refining
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Harmful elements
Lead (Pb)
Flux agents

Abstract

This research focused on optimizing the removal process of the harmful element lead (Pb) in various stages of copper production (flash smelting, copper converting, and thermal refining). The present study used a factorial design of experiments to investigate the effects of various parameters, including reheating and the use of various slag-forming agents, including CaO, MgO, SiO₂, Na₂CO₃, and Na₂SO₄, on the removal rate of this harmful element. Initially, thermodynamic calculations showed that increasing the temperature does not significantly accelerate Pb removal, and the use of slag-forming agents for this purpose is essential. In the flash furnace, the results showed that adding Na₂SO₄ has the greatest effect on reducing the amount of Pb in the matte, followed by MgO. Microstructural studies of blister copper and converter furnace slag indicated that although a portion of Pb can be removed through the slag, the remaining amounts of this element in blister copper are still significant. Therefore, relying on reheating or slag-forming agents alone is not sufficient at this stage. In the matte blowing stage, the presence of slag-forming agents SiO₂ and Na₂SO₄ helped reduce Pb by forming stable compounds in the slag, and therefore, the use of this combination was introduced as an effective method for separating Pb due to the creation of favorable chemical reactions and the formation of sodium Pb silicate. In the anode furnace, SiO₂ had the greatest effect on Pb removal, and the simultaneous presence of CaO-MgO-Na₂CO₃ and MgO-Na₂SO₄-SiO₂ also produced very good results. Experimental studies and statistical analyses showed that the anode furnace is the best stage for removing the element Pb before electrolytic refining due to the process conditions. The optimal levels of slag-forming agents were also determined in this stage. The results showed that in the presence of slag-forming agents CaO-MgO-Na₂CO₃ and MgO-Na₂SO₄-SiO₂, very good results in terms of lead reduction (more than 79%) were achieved. Overall, this research provided valuable information on how to remove the element Pb from copper in various stages of production and can be used to optimize copper production processes and improve the quality of the final product.

1. INTRODUCTION

The passivation of the copper anode during the electrorefining process is a widespread challenge in this stage [1–4]. This phenomenon

depends on several physical and chemical factors, including the nature of the anode slime, the chemical composition of the anode and electrolyte solution, the applied electric current density, the electrolyte temperature, and the

chemical composition of the non-conductive layers formed on the anode surface [4–7]. Reducing the applied electric current density, and consequently reducing the production of pure copper, increasing power consumption, and reducing cathode quality due to increased floating slime are among the consequences of copper anode passivation [7,8]. To prevent such problems, it is necessary to prevent the formation of anode slime or to remove impurities that cause these slimes [9].

Commercial copper anodes typically contain significant amounts of certain impurities, particularly arsenic, bismuth, antimony, nickel, iron, Pb, selenium, tellurium, sulfur, as well as precious metals such as gold and silver [10,11]. Although the overall concentration of these impurities within the anode may be less than one weight percent, even these small amounts of certain impurities can significantly affect the anode behavior and the copper electrorefining process [12]. Arsenic, antimony, and bismuth, along with oxygen, are impurities that play a significant role in anode passivation and anode slime formation [8,11,13,14]. On the other hand, Pb is one of the elements that is abundantly found in copper sulfide ores and does not have a significant effect on the electrical or thermal conductivity of copper and its alloys. However, the presence of Pb in copper increases the volume of anode slime during the electrorefining process [15], and for this reason, many studies have been conducted to remove Pb during the copper smelting process [16–19].

The injection of clean concentrate into converters is also commonly used to improve efficiency and as a suitable solution for removing more impurities. This method is only valid if a clean concentrate (free of trace amounts of lead, bismuth, arsenic, and antimony) can be injected into the system, and faces serious limitations [20]. In the meantime, the use of slag-forming agents has also been accepted as a main solution. For example, Heo et al. [21] investigated the distribution coefficient of Pb between slag and molten copper at a temperature of 1473 K. They found that by increasing the Al_2O_3 content in the slag, the activity of FeO decreases, and this leads to better dissolution of Pb in the slag [34]. In another study, the effect of the weight percentage of copper in the matte on the distribution coefficient of impurities between slag and matte was investigated. The results of this study also showed that with increasing copper content in the matte, the distribution coefficient between slag and matte for copper, zinc, and lead increases [22].

Despite the research carried out to remove the element Pb, it should be noted that a small amount of Pb still remains in the copper anode, which can cause problems in the electrolytic refining stage. One of the possible solutions to minimize the harmful effects of this harmful element is to remove it during the smelting and production of copper anodes and prevent it from entering the copper electrorefining process. Therefore, this research attempts to investigate the optimal conditions for removing the element Pb during the various stages of thermal refining of copper by performing a factorial design of experiments. For this purpose, the effect of the presence of various slag-forming agents such as CaO, MgO, SiO_2 , Na_2CO_3 , and Na_2SO_4 on the removal rate of this harmful element was investigated.

2. MATERIALS AND METHODS

2.1. Sampling

Sampling of concentrate, flash furnace dust, matte, and slag from the furnace was performed at 5-hour intervals. Concentrate destined for the smelting unit of the Sarcheshmeh Copper Complex is fed into concentrate storage tanks by a conveyor belt, which also controls the rate of transfer to the cooler and then to the flash furnace burner. It should be noted that sampling of the concentrate entering the flash furnace is only feasible from the belt feeding the aforementioned tanks. Additionally, concentrate entering the storage tanks enters the flash furnace approximately three hours later. As soon as the concentrate enters the flash furnace, dust from the concentrate becomes part of the melting boilers; however, the formation of matte and slag requires at least one hour. Consequently, sampling of concentrate, flash dust, matte, and slag exiting the flash furnace was performed according to Table 1 at 5-hour intervals.

Table 1. Name, code, and sampling time of the concentrate entering the flash furnace, boiler dust, and outlet matte

No.	Sample name	Sample code	Sampling time (h)
1	Concentrate entering the flash	C0	Time origin (zero)
2	Concentrate entering the flash	C1	1
3	Concentrate entering the flash	C2	2
4	Concentrate entering the flash	C3	3
5	Concentrate entering the flash	C4	4
6	Concentrate entering the flash	C5	5

7	Dust entering the boiler	G1	3
8	Dust entering the boiler	G2	4
9	Dust entering the boiler	G3	5
10	Dust entering the boiler	G4	6
11	Dust entering the boiler	G5	7
12	Matte output from the flash	M1	4
13	Matte output from the flash	M2	5
14	Matte output from the flash	M3	6
15	Matte output from the flash	M4	7
16	Matte output from the flash	M5	8
17	Slag output from the flash	S1	4
18	Slag output from the flash	S2	5
19	Slag output from the flash	S3	6
21	Slag output from the flash	S4	7
21	Slag output from the flash	S5	8

From the four stages described above, a total of 21 samples were prepared and subjected to compositional analysis to examine the changes and distribution of impurity elements at each stage. To capture a reliable range of variations, multiple samples were considered. Using the data from this study, a mass-balance calculation was performed to determine the contributions of impurity elements in the dust and in the exhaust gas from the smelting plant (acid plant feed gas). Sampling was conducted separately for the converter and the anode in accordance with Table 2.

Table 2. Name, code, and stage of samples prepared from the smelting furnaces of the Sarcheshmeh Copper Complex

No.	Sample name	Sample code
1	Converter melt at the beginning of the slag blowing stage	Matte
2	Converter slag at the beginning of the slag blowing stage	Matte Slag
3	White metal	WM
4	Anode furnace melt at the beginning of the oxidation stage	Anode
5	Anode furnace slag at the beginning of the oxidation stage	Anode Slag
6	Sample without slag-forming agent at 1250 °C	Just Heat

Table 4. Parameters and levels selected in the second stage of experimental design (factorial)

Factor	Levels		
	First	Second	Third
Optimal slag-forming agent 1	20% less than stoichiometry	stoichiometry	20% more than stoichiometry
Optimal slag-forming agent2	20% less than stoichiometry	stoichiometry	20% more than stoichiometry

Tables 5 to 7 present the parameters and their levels for the first-stage (screening) experimental

2.2. Experimental Design (DOE)

The effect of adding alloying elements on the solubility of impurity elements in the matte exiting the flash furnace was studied through remelting (Just Heat) and slag-making experiments by incorporating the relevant chemical compositions into the slag.

To study the effect of adding different compounds to the slag-forming agent, the slag-making process was conducted with the melt held stationary in the furnace at a temperature of 1250 °C. In addition, the effect of increasing the melt temperature to 1300 °C was also investigated. It should be noted that, in all cases, the impurity-element removal experiment was repeated only once in the Just Heat mode, while in other modes (adding slag-forming materials), the experiments were repeated twice. The slag-forming agents selected in this study were CaO, Na₂CO₃, SiO₂, Na₂SO₄, and MgO.

In DOE, slag-forming additives were treated as the factors, and the percentage of impurity elements as the response. Given the large number of potential slag-forming agents, the initial stage employed screening to optimize the chosen slag-forming agent and to examine the levels of their variation. This was conducted at two levels: presence or absence of the slag-forming agent (Table 3).

Table 3. Parameters and levels selected in the first stage of experimental design (screening)

Factors	Levels		Amount of compound at second level (high level)
	First	Second	
CaO	0	1	0.12
Na ₂ CO ₃	0	1	0.24
SiO ₂	0	1	0.0059
Na ₂ SO ₄	0	1	0.33
MgO	0	1	0.088

Following the screening, to identify the optimal slag-forming agent, the second stage employed a full factorial design at three levels (Table 4).

design for the matte, white metal, and anodic copper samples, respectively.

Table 5. Partial factorial experiment design for Matte samples (screening)

Run	Factor 1	Factor 2	Factor3	Factor4	Factor 5
	A: CaO	B: MgO	C: Na ₂ CO ₃	D: Na ₂ SO ₄	E: SiO ₂
Matte1	1	1	0	1	0
Matte2	0	1	1	1	0
Matte3	1	1	1	1	1
Matte4	1	1	0	0	1
Matte5	1	0	1	1	0
Matte6	1	0	1	0	1
Matte7	0	1	0	0	0
Matte8	1	0	0	1	1
Matte9	0	0	0	1	0
Matte10	1	0	0	0	0
Matte11	0	1	1	0	1
Matte12	0	0	0	0	1
Matte13	0	0	1	1	1
Matte14	0	0	1	0	0
Matte15	0	1	0	1	1
Matte16	1	1	1	0	0

Table 6. Partial factorial experiment design for white metal samples (screening)

Run	Factor 1	Factor 2	Factor3	Factor 4	Factor5
	A: CaO	B: MgO	C: Na ₂ CO ₃	D: SiO ₂	E: Na ₂ SO ₄
WM1	0	0	0	0	1
WM2	0	0	1	0	0
WM3	1	1	1	1	1
WM4	1	1	1	0	0
WM5	1	1	0	1	0
WM6	1	0	0	0	0
WM7	0	1	0	1	1
WM8	0	0	0	1	0
WM9	1	0	1	0	1
WM10	1	0	1	1	0
WM11	0	0	1	1	1
WM12	0	1	1	0	1
WM13	0	1	1	1	0
WM14	1	1	0	0	1
WM15	0	1	0	0	0
WM16	1	0	0	1	1

Table 8. Chemical composition of the concentrate consumed in the Sarcheshmeh Copper Complex smelting plant (wt.%)

Cu	Fe	S	SiO ₂	Al ₂ O ₃	MgO	K ₂ O	CaO	Na ₂ O	Pb	As	Sb
18.8	21.8	26.8	10.1	3.8	0.6	0.8	1.6	0.35	0.09	0.06	0.03

Table 7. Partial factorial experiment design for anodic copper samples (screening)

Run	Factor 1	Factor 2	Factor3	Factor 4	Factor5
	A: CaO	B: MgO	C: Na ₂ CO ₃	D: SiO ₂	E: Na ₂ SO ₄
Anode1	1	1	0	1	0
Anode2	0	0	1	1	1
Anode3	0	1	0	1	1
Anode4	1	0	0	0	0
Anode5	0	1	1	1	0
Anode6	1	0	1	1	0
Anode7	0	0	1	0	0
Anode8	1	1	1	1	1
Anode9	1	1	0	0	1
Anode10	1	0	1	0	1
Anode11	1	0	0	1	1
Anode12	0	1	0	0	0
Anode13	0	0	0	0	1
Anode14	0	1	1	0	1
Anode15	0	0	0	1	0
Anode16	1	1	1	0	0

2.3. Chemical-Composition Analysis Of Impurities

The weight percentages of impurity elements were measured by inductively coupled plasma (ICP) analysis. The instrument used was a Varian 715-ES ICP, capable of detecting elements at sub-ppm levels.

3. RESULTS AND DISCUSSION

3.1. Flash-Furnace

Table 8 shows the chemical composition of feed concentrate in the Sarcheshmeh copper complex. As seen, the amount of Pb in the concentrate is 0.09 wt.%. Also, the amount and distribution of Pb in the matte production stage in the flash furnace, as well as the chemical composition of dust, matte, and flash furnace slag, are presented in Table 9. The results show that 59% of the input Pb is accumulated in the exhaust gas, 32% is retained in the matte, and 9% is found in the slag. Additionally, the cooling of the furnace exhaust gas in the heat-recovery boilers causes the majority of lead exiting the furnace to settle in the dust phase.

Table 9. Circulation of impurity elements in the flash furnace of Sarcheshmeh Copper Complex (wt.%)

Element	In matte	In slag	In exhaust gas	
			In gas phase	In solid phase (dust)
Pb	32	9	21	38

Table 10 shows the results of experiments on the effect of adding various compounds to molten and matte copper slag. As presented, Na_2SO_4 has the strongest effect. Following Na_2SO_4 , MgO also produced a substantial reduction in Pb content in the matte exiting the flash furnace, decreasing it from 2094 ppm to 1830 ppm. Other added slag-forming compounds also contributed to reducing the lead content to a lesser extent.

Table 10. Changes in the concentration of impurity elements in flash-furnace matte and slag due to the addition of slag-forming compounds

Additive to slag	Melt	Pb (ppm)
No additive	Matte	2094
	Slag	518
CaO	Matte	1910
	Slag	641
Na_2CO_3	Matte	2001
	Slag	550
Na_2SO_4	Matte	1743
	Slag	795
MgO	Matte	1830
	Slag	710

3.2. Converter-furnace

3.2.1. In the matte blowing stage (slag blowing)

Table 11 presents the Pb content detected in products from experiments designed to evaluate the effect of slag-forming agent addition to converter matte. The Just Heat test results indicate that approximately 53% of the Pb is removed from the melt. Notably, Figure 1 shows that the incorporation of slag-forming agents enhances Pb removal from the melt, achieving approximately 77% and 75% Pb removal with the slag-forming agents Na_2SO_4 and MgO , respectively.

The results of the ANOVA analysis to investigate the effect of slag-forming agents on Pb reduction in the molten matte are presented in Table 12. Figure 2 illustrates the influence of the presence of different slag-forming agents on Pb removal from the molten matte (as derived from the ANOVA results). The statistical analysis indicates that the simultaneous presence of two slag-forming agents, Na_2SO_4 and SiO_2 , has the greatest effect on Pb content in the melt. However, as shown in Figure 3, this combined

effect on the response is positive, and among the slag-forming agents tested, SiO_2 and MgO have the largest individual influence on lead presence in the melt. As illustrated in Figs. 2 and 3, MgO emerges as the slag-forming agent that significantly reduces lead content in the melt when considered alone.

Table 11. Amount of lead identified in samples from tests designed to remove lead in the matte blowing stage in the converter, achieved through reheating and the addition of various slag-forming agents to the slag

Run Order	Experiment set	Pb	
0	Base matte	8370	
0-1	Just Heat	3086	
1	Na_2SO_4	1922	1985
2	Na_2SO_4 - Na_2CO_3 -CaO	2830	2857
3	Na_2SO_4 - SiO_2 -CaO	3348	3385
4	Na_2SO_4 - SiO_2 -MgO	3069	3048
5	Na_2SO_4 - Na_2CO_3 - SiO_2 - MgO- CaO	3537	3520
6	Na_2CO_3 - SiO_2 -MgO	2879	2860
7	SiO_2	2820	2858
8	Na_2CO_3 -MgO-CaO	2856	2840
9	CaO	3862	3750
10	Na_2SO_4 -MgO-CaO	1934	1918
11	Na_2CO_3	3185	3200
12	Na_2SO_4 - Na_2CO_3 - SiO_2 - MgO	3170	3158
13	SiO_2 -MgO-CaO	2381	2370
14	MgO	2030	1940
15	Na_2SO_4 - Na_2CO_3 -MgO	2330	2344
16	Na_2CO_3 - SiO_2 -CaO	2527	2510

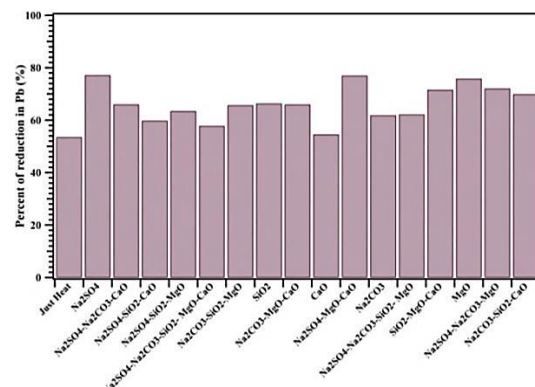
**Fig. 1. Percentage of Pb removed from the melt in the presence of various slag-forming agents in converter furnace matte slag formation.**

Table 12. ANOVA results examining the effects of individual slag-forming agents and their simultaneous presence on the residual Pb content in the converter matte

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	15	9880153	658677	10153.02	0.000
Linear	5	2789091	557818	8598.35	0.000
CaO	1	441330	441330	6802.78	0.000
MgO	1	901153	901153	13890.61	0.000
SiO ₂	1	943938	943938	14550.10	0.000
Na ₂ CO ₃	1	484620	484620	7470.06	0.000
Na ₂ SO ₄	1	18050	18050	278.23	0.000
2-Way Interactions	10	7091062	709106	10930.35	0.000
CaO*MgO	1	146611	146611	2259.90	0.000
CaO*SiO ₂	1	578888	578888	8923.13	0.000
CaO*Na ₂ CO ₃	1	288420	288420	4445.78	0.000
CaO*Na ₂ SO ₄	1	26681	26681	411.26	0.000
MgO*SiO ₂	1	873842	873842	13469.63	0.000
MgO*Na ₂ CO ₃	1	733866	733866	11312.00	0.000
MgO*Na ₂ SO ₄	1	436178	436178	6723.36	0.000
SiO ₂ *Na ₂ CO ₃	1	127008	127008	1957.73	0.000
SiO ₂ *Na ₂ SO ₄	1	3684255	3684255	56790.06	0.000
Na ₂ CO ₃ *Na ₂ SO ₄	1	195313	195313	3010.60	0.000
Error	16	1038	65	-	-
Total	31	9881191	-	-	-

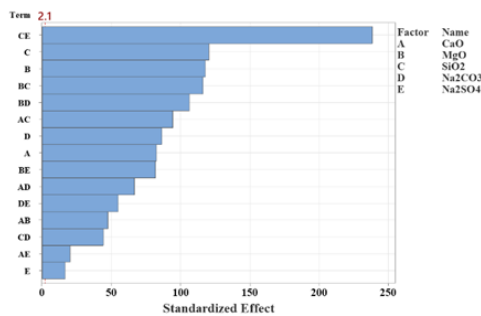


Fig. 2. Standardized effects illustrating how the presence of different slag-forming agents in the slag from the matte blowing stage of the converter influences the removal of Pb.

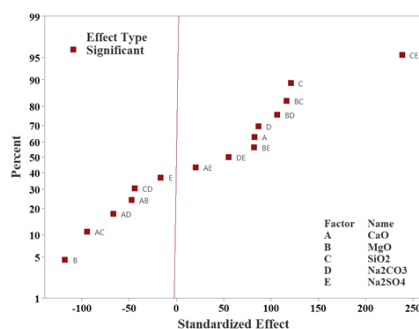
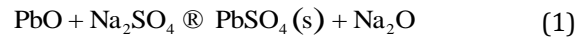


Fig. 3. The type of positive/negative effects of experimental-Design parameters on Pb removal.

In the experiments, the combined use of slag-forming agents SiO₂ and Na₂SO₄ in the converter furnace is observed to reduce Pb content in the molten matte through chemical reactions that form stable slag compounds. The proposed mechanisms are outlined below.

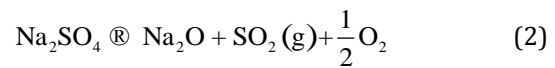
(i) Na₂SO₄ reacts with PbO to form stable lead sulfate-containing species:



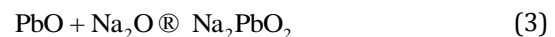
Lead sulfates are thermodynamically stable at converter temperatures and preferentially partition into the slag.

(ii) Thermal decomposition of Na₂SO₄ at high temperatures followed by reaction with PbO:

- Partial decomposition of Na₂SO₄ at elevated temperatures:



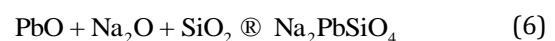
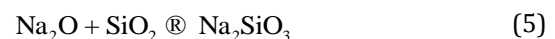
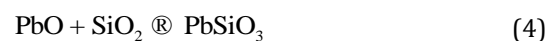
- Subsequent reaction of Na₂O with PbO to form lead-containing slag phases:



Na₂O acts as a basic slag former and promotes incorporation of Pb into slag phases.

(iii) SiO₂-PbO-Na₂O interactions forming lead- and sodium-containing silicates:

- Acidic slag-forming SiO₂ reacts with PbO in the presence of Na₂O to form silicate compounds:



Silicate phases are thermodynamically stable with high melting points and readily partition into the slag.

3.2.2. In the copper (white metal) blowing stage

Table 13 presents results from tests investigating the effect of adding different slag-forming agents on the removal of Pb from molten white metal. As seen, the heating process alone removes only about 11% of the Pb in the melt, which is lower than the removal observed in tests conducted with slag-forming agents. On the other hand, among the slag-forming agents tested, Na₂CO₃, MgO, and SiO₂ rank first to third, respectively, in their effectiveness at removing Pb from the melt. In contrast, CaO shows the Pb ability to remove lead. Figure 4 provides a visual comparison of lead removal from molten white metal in the presence of the different slag-forming compounds.

Table 13. Amount of lead identified in samples from tests designed to remove lead in the copper (white metal) blowing stage in the converter through reheating and adding various slag-forming agents to the slag

Run Order	Experiment set	Pb	
0	White Metal	3950	
0-1	Just Heat	3510	
1	CaO	2956	2995
2	MgO- SiO ₂ - Na ₂ SO ₄	2576	2573
3	CaO-MgO- Na ₂ CO ₃	2290	2287
4	MgO- Na ₂ CO ₃ - SiO ₂	2580	2575
5	Na ₂ CO ₃	2008	2012
6	CaO-MgO- Na ₂ SO ₄	2491	2420
7	CaO- SiO ₂ - Na ₂ SO ₄	2386	2375
8	CaO-MgO- SiO ₂	2585	2570
9	CaO- Na ₂ CO ₃ - SiO ₂	3223	3210
10	MgO- Na ₂ CO ₃ - Na ₂ SO ₄	2897	2890
11	MgO	2048	2010
12	SiO ₂	2282	2251
13	CaO-MgO- Na ₂ CO ₃ - SiO ₂ - Na ₂ SO ₄	2508	2510
14	Na ₂ CO ₃ - SiO ₂ - Na ₂ SO ₄	3310	3303
15	Na ₂ SO ₄	2331	2340
16	CaO- Na ₂ CO ₃ - Na ₂ SO ₄	3699	3687

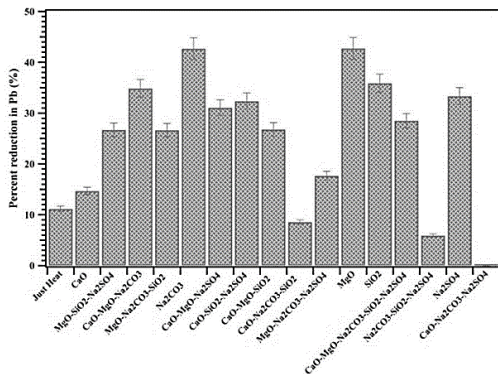


Fig. 4. Percent of lead removed from white metal melt in the presence of various slag-forming agents in copper slag-making (WM) in a converter furnace.

Table 14 presents the ANOVA results for the data in Table 13. Based on the p-values reported in this table, all factors and interactions considered in this analysis are statistically significant. Also, Figure 5 shows the effect of the presence of the various factors on Pb removal from the white metal, as derived from the ANOVA results. Figure 6 illustrates the standardized effects of the slag-forming factors on Pb removal, enabling direct comparison of their respective influences. As seen, the two factors Na₂CO₃ and MgO exert the strongest opposing influences on Pb removal: Na₂CO₃ has a positive effect (increasing lead removal), while MgO has a

negative effect (reducing lead removal) on the average residual lead in the melt. Other potential binary interactions that may significantly affect the residual lead include MgO–CaO and Na₂CO₃–Na₂SO₄. The interpretation suggested by the analysis is:

MgO–CaO: predicted to decrease the residual lead content.

Na₂CO₃–Na₂SO₄: predicted to increase the residual lead content.

Table 14. ANOVA analysis to investigate slag formers and the effect of their simultaneous presence on the amount of residual lead in WM

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	15	6634842	442323	1434.37	0.000
Linear	5	2928410	585682	1899.25	0.000
CaO	1	552826	552826	1792.71	0.000
MgO	1	649230	649230	2105.33	0.000
Na ₂ CO ₃	1	1051250	1051250	3409.00	0.000
SiO ₂	1	66248	66248	214.83	0.000
Na ₂ SO ₄	1	608856	608856	1974.40	0.000
2-Way Interactions	10	3706431	370643	1201.92	0.000
CaO*MgO	1	839160	839160	2721.23	0.000
CaO*Na ₂ CO ₃	1	8712	8712	28.25	0.000
CaO*SiO ₂	1	597324	597324	1937.01	0.000
CaO*Na ₂ SO ₄	1	631126	631126	2046.62	0.000
MgO*Na ₂ CO ₃	1	334562	334562	1084.92	0.000
MgO*SiO ₂	1	21632	21632	70.15	0.000
MgO*Na ₂ SO ₄	1	10296	10296	33.39	0.000
SiO ₂ *Na ₂ CO ₃	1	64980	64980	210.72	0.000
Na ₂ CO ₃ *Na ₂ SO ₄	1	727218	727218	2358.23	0.000
SiO ₂ *Na ₂ SO ₄	1	471420	471420	1528.72	0.000
Error	16	4934	308	-	-
Total	31	6639776	-	-	-

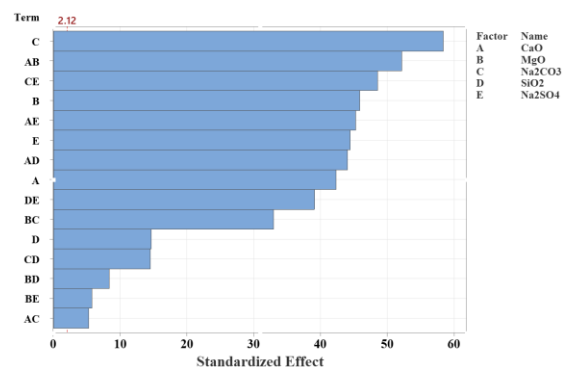


Fig. 5. Standardized effect of the presence of different forms of slag-forming agents on the slag from the copper stage (WM) in the converter on the removal of Pb impurity element.

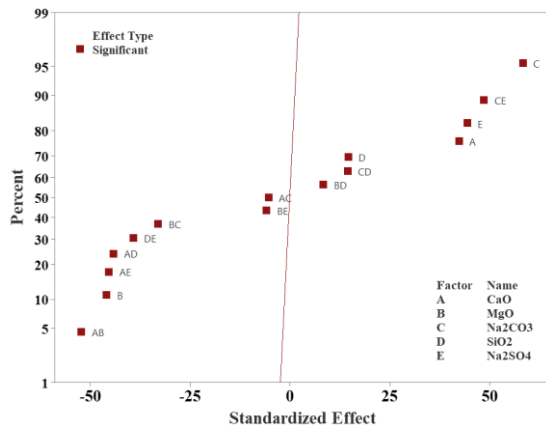


Fig. 6. Type of positive/negative effect of the parameters investigated in the experimental design on the removal of the harmful element lead from molten copper (WM) in the copper blowing stage.

3.3. Anodic-Furnace

Table 15 presents the Pb content measured after slagging tests on anodic copper. In the test designed to assess the effect of reheating the melt, approximately 12.5% of the Pb is reduced during this process. Consistent with prior results on Pb removal, the addition of slagging agents significantly decreases the Pb content in the melt. The percentage reduction of Pb from the anodic copper melt across different tests is shown in Figure 7. Notably, among the main slagging agents, SiO₂ exhibits the greatest effect, reducing Pb content by more than 66%. Furthermore, in tests employing multiple slag-forming agents simultaneously, the results indicate very favorable Pb-reduction performance (greater than 79%) in the presence of CaO–MgO–Na₂CO₃ and MgO–Na₂SO₄–SiO₂ systems.

The ANOVA results, aimed at evaluating the interactive effects of slag-forming agents on Pb reduction, are reported in Table 16. The main effects are depicted in Figure 8, while their effect on the average antimony content in the melt is shown in Figure 9. The presented data indicate that the binary combination CaO+Na₂SO₄ has the largest influence on changing Pb content in anodic copper, although this effect does not translate into a reduction in the average Pb content. Additionally, Na₂CO₃ emerges as the most effective slag-forming agent among those tested for reducing Pb present in the melt.

Table 15. The amount of Pb detected in samples from tests designed to remove Pb in the anode furnace slag stage through reheating and adding various slag-forming agents to the slag.

Run Order	Experiment set	Pb	
0	Anode	560	
0-1	Just Heat	490	
1	SiO ₂	169	158
2	CaO- Na ₂ CO ₃ - SiO ₂	181	168
3	CaO- Na ₂ SO ₄ - SiO ₂	106	95
4	MgO- Na ₂ SO ₄ - SiO ₂	119	109
5	CaO-MgO- Na ₂ SO ₄ - Na ₂ CO ₃ - SiO ₂	379	389
6	MgO- Na ₂ SO ₄ - Na ₂ CO ₃	178	168
7	Na ₂ SO ₄	173	165
8	CaO-MgO- Na ₂ CO ₃	105	93
9	Na ₂ SO ₄ - Na ₂ CO ₃ - SiO ₂	229	209
10	CaO	181	155
11	CaO-MgO- SiO ₂	159	140
12	Na ₂ CO ₃	385	372
13	CaO-MgO- Na ₂ SO ₄	212	204
14	MgO	225	185
15	MgO- Na ₂ CO ₃ - SiO ₂	435	485
16	CaO- Na ₂ SO ₄ - Na ₂ CO ₃	205	217

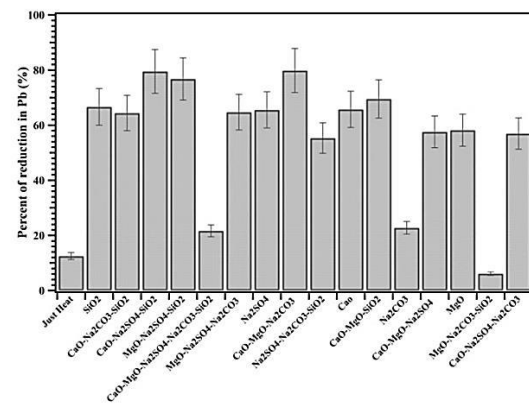


Fig. 7. Percentage of Pb removed from anodic copper melt in the presence of various slag-forming agents.

Table 16. ANOVA analysis to investigate the effect of slag agents and the effect of their simultaneous presence on the amount of residual Pb in anodic copper

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	15	635027	42335	11014.01	0.000
Linear	5	232682	46536	12107.01	0.000
CaO	1	29343	29343	7633.83	0.000
MgO	1	27671	27671	7199.03	0.000
Na ₂ SO ₄	1	14835	14835	3859.52	0.000
Na ₂ CO ₃	1	141379	141379	36781.54	0.000
SiO ₂	1	19454	19454	5061.15	0.000
2-Way Interactions	10	402345	40235	10467.51	0.000

CaO*MgO	1	657	657	170.93	0.000
CaO* Na ₂ SO ₄	1	150015	150015	39028.30	0.000
CaO* Na ₂ CO ₃	1	24035	24035	6253.08	0.000
CaO* SiO ₂	1	63	63	16.46	0.001
MgO* Na ₂ SO ₄	1	270	270	70.32	0.000
MgO* Na ₂ CO ₃	1	11438	11438	2975.81	0.000
MgO* SiO ₂	1	115560	115560	30064.46	0.000
Na ₂ SO ₄ * Na ₂ CO ₃	1	1024	1024	266.35	0.000
Na ₂ SO ₄ * SiO ₂	1	1047	1047	272.27	0.000
Na ₂ CO ₃ * SiO ₂	1	98235	98235	25557.15	0.000
Error	16	61	4	-	-
Total	31	635088	-	-	-

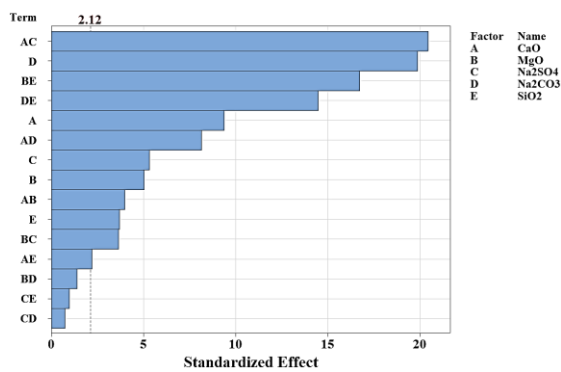


Fig. 8. Standardized effect of the presence of different forms of slag-forming agents in anode furnace slag on the removal of harmful element Pb.

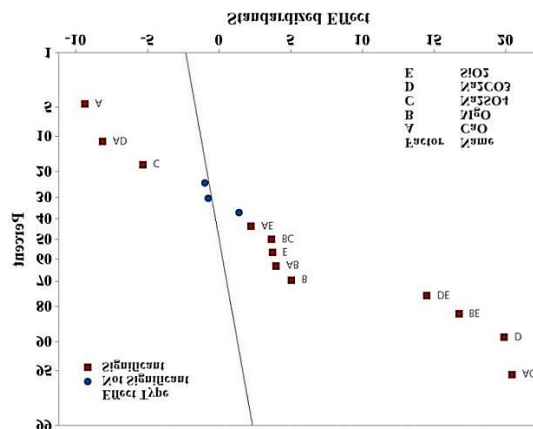


Fig. 9. The type of positive/negative effect of the parameters investigated in the experimental design on the removal of the harmful element Pb from the anodic copper melt.

The slag-forming agent Na₂CO₃ decomposes upon addition and exposure to high temperature, yielding Na₂O and CO₂. The formed Na₂O subsequently reacts with PbO and SiO₂ to produce stable sodium Pb silicate compounds, such as Na₂PbSiO₄, through the Reaction. (6)

On the other hand, SiO₂, as an acidic slag former, can react with PbO and Na₂O to form Pb- and Na-containing silicate phases through Reactions (4) and (5), respectively.

3.4. Optimizing Pb Removal Process

Since the removal of the Pb impurity in the anode furnace resulted in a reduction of this element to very low levels, the optimal stage for lead removal was also identified as the anodic copper production stage. Considering the high removal percentage observed in the initial experiments and the prediction made by the ANOVA statistical analysis, the slag-forming combination of CaO and Na₂CO₃ was studied.

Table 17 shows the residual Pb content in the different slag melts in the slag optimization experiments. The lowest lead content (below 100 ppm) in these experiments was related to the samples in which both slag-forming agents were at their highest levels.

Table 17. Residual Pb content in anodic copper melt in slag-forming composition optimization experiments

RunOrder	CaO	Na ₂ CO ₃	Pb
1	1	1	168
2	3	1	120
3	2	1	130
4	1	2	165
5	1	2	160
6	3	2	110
7	1	3	125
8	3	2	103
9	3	3	90
10	3	1	116
11	3	1	124
12	3	3	92
13	3	3	98
14	2	2	133
15	1	3	118
16	2	2	128
17	1	1	180
18	3	2	113
19	2	1	142
20	2	2	148
21	2	3	125
22	2	1	138
23	1	2	154
24	2	3	139
25	1	1	155
26	1	3	132
27	2	3	119

The results of the ANOVA analysis of the data from this part of the study are presented in Table 18. The results of this analysis showed that both

slag-forming agents and their dual interaction had a significant effect on the change in the amount of molten lead, and among these factors (as shown in Figs. 10 and 11), CaO had the greatest effect on the removal of molten lead. Figure 11 shows that increasing the amount of both slag-forming agents is accompanied by a decrease in the average amount of Pb in the melt, while high levels of slag-forming agents (20% more than the stoichiometric amount) showed the lowest average amount of lead.

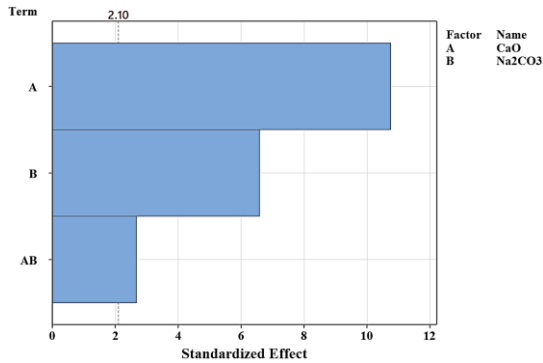


Fig. 10. Comparison of the effect of slag formers Na₂CO₃ and SiO₂, individually and together, in removing Pb from anodic copper melt.

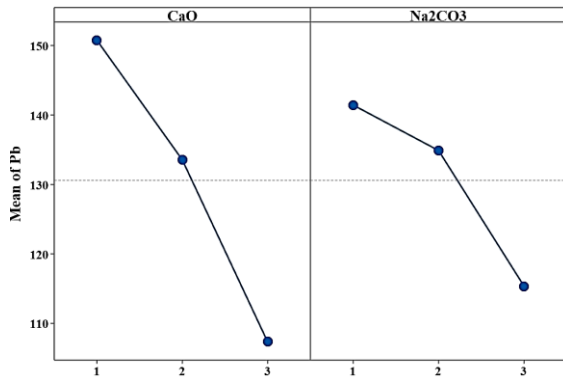


Fig. 11. Changes in the average amount of Pb present in the anodic copper melt due to the addition of different amounts of two slag formers, Na₂CO₃ and CaO.

Table 18. ANOVA analysis of optimization of Na₂CO₃-CaO slag in lead removal from anodic copper melt

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	8	12932.0	1616.50	26.63	0.000
Linear	4	11936.4	2984.11	49.16	0.000
CaO	2	8614.9	4307.44	70.96	0.000
Na ₂ CO ₃	2	3221.6	1660.78	27.36	0.000
2-Way Interactions	4	995.6	248.89	4.10	0.016
CaO*Na ₂ CO ₃	4	995.6	248.89	4.10	0.016
Error	18	1092.7	60.70	-	-
Total	26	14024.7	-	-	-

4. CONCLUSIONS

In this study, the removal of the harmful element Pb in the copper smelting and production process was optimized. For this purpose, the influence of various slag-forming agents, including CaO, MgO, SiO₂, Na₂CO₃, and Na₂SO₄, was explored across different stages of the production process, including flash, converter, and anode furnaces. A factorial experimental design was employed to investigate the factors and treatment methods. Among the results, the following can be highlighted:

- The results of reheating tests at different stages of the process showed that, although increasing the temperature can be effective in some cases, it cannot reduce the amounts of Pb to the required level. Therefore, the use of slag-forming agents was prioritized at all stages for removing Pb.
- Sodium sulfate (Na₂SO₄) exhibited the strongest effect, followed by magnesium oxide (MgO) to decrease in Pb content from matte in the flash furnace. Specifically, Na₂SO₄ reduced the Pb content in matte exiting the flash furnace from 2094 ppm to a substantially lower value, with MgO also producing a notable reduction to 1830 ppm. Other added agents contributed to lowering the Pb concentration to a lesser extent.
- In experiments conducted to remove Pb during the matte blowing stage in the converter, the combination of slag-forming agents SiO₂ and Na₂SO₄ in the converter furnace was observed to promote Pb removal through favorable chemical reactions and the formation of stable slag compounds. Silicate species, owing to their thermodynamic stability and high melting points, readily enter the slag and are ultimately separated from the metal phase. Consequently, using SiO₂ in combination with Na₂SO₄ is considered an effective strategy for separating and removing Pb from molten copper, facilitated by the possible formation of stable compounds in the slag, such as sodium Pb silicate.
- Among the slag agents used to remove Pb in the copper blowing stage, Na₂CO₃, MgO, and SiO₂ ranked first to third in terms of success in removing this troublesome element from the melt, respectively. On the other hand, CaO showed the least ability to remove this harmful element.
- In the anode furnace stage, among the main slag formers, SiO₂ had the greatest effect (more than 66%) in reducing the lead

content of molten copper anode. On the other hand, in tests in which several slag formers were used simultaneously, the results presented showed that in the presence of slag formers CaO-MgO-Na₂CO₃ and MgO-Na₂SO₄-SiO₂, very good results in terms of lead reduction (more than 79%) could be seen.

- The results of the optimization test for the Pb removal process also showed that increasing the amount of both slag-forming agents CaO and Na₂CO₃ is associated with a decrease in the average lead content in the melt, and among them, high levels of slag-forming agents (20% more than the stoichiometric value) showed the lowest average lead content.

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