

THE EFFECT OF IRON AND OXIDIZING FLUX ADDITION ON THE FIRE ASSAY OF LOW GRADE PYRITIC REFRACTORY GOLD ORES

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Abstract

In this study, experiments were conducted to understand the effects of different quantities of additional iron and oxidizing flux (Na_2O_2) on the direct fire assay of low grade pyritic refractory gold ores instead of performing any pre-treatment like roasting before fire assay. A portion of the pyritic ore was primarily roasted using a rotary kiln to remove sulphur content for the comparison of the results obtained from direct fire assay of the pyritic ore. Then, fire assay process was performed to the roasted ore and gold and silver content in the ore was determined. Unroasted ore specimens were fused by using fluxes and PbO , which accumulates the precious metals, with various quantities of iron. Correlation between the quantity of additional iron and the recovery of gold-silver were investigated. Various quantities of Na_2O_2 , as an oxidizing flux, were added to the smelting charge with iron additions, from which the highest gold and silver recoveries were obtained from previous experiments. From the results, it was clear that the increase in additional iron and Na_2O_2 quantities was the reason for the increase in the recovered amounts of lead, gold and silver during the process.

Keywords: Fire Assay, Refractory Gold Ore, Pyrite, Cupellation

1. Introduction

Fire assay is the oldest and most

commonly used method for the determination of gold, silver and the platinum group metals content of auriferous

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ores and concentrates. According to Bachmann, this technique has been in use since 4th millennium B.C [1].

This method has three stages including smelting of ores with various fluxes (CaCO_3 , Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, etc.) and PbO , isolation of the precious metals from metallic lead phase and finally analysis of the precious metals obtained.

Refractory and native gold ores are main types of gold containing auriferous ores. The term, refractory gold ores, refers to sulfide and arsenide ores comprising gold [2]. However, the term, native gold ores, indicates other gold ore types such as gold present in silicate and dolomite minerals.

Avoiding a lead-containing matte formation is a necessity for the fire assay of pyritic refractory gold ores. Otherwise a considerable amount of lead combines with the sulfur, collected in the matte phase. Thus the precious metals are collected in the matte phase instead of metallic lead phase [3]. Removal of sulfur content of pyritic ores by roasting is the common method which has been reported by various researchers [2-5]. Also oxidation kinetics and mechanisms of arsenic sulfides and partially pyrite mineral were comprehensively carried out by N. Štrbac et. al. in 2009. The research indicated highly evaporative behavior of As_2O_3 between 260 °C and 330 °C and the oxidation tendency of pyrite mineral (FeS_2) between 584 °C and 745 °C [6]. However, the presence of the SO_x (sometimes As_xO_y) gases has hazardous effects for the operator and the environment and this presence is also corrosive for the equipments. As an alternative method for the pretreatment of ores before fire assay, an oxidizing flux [3]

or iron [5,7] is added on the smelting stage of pyritic refractory ores in order to reduce lead from the matte phase. Iron addition to the smelting charge technique was previously investigated by Petrovic et. al. [5].

In this study, experiments were conducted to optimize the fire assay for Au and Ag analysis of low grade pyritic refractory gold ores. The use of both iron and oxidizing flux additions was comprehensively investigated. Parameters such as suitable temperature, iron and flux addition quantities were aimed to be determined. Atomic absorption spectrometry (AAS), inductively coupled plasma spectrometry (ICP), X-ray fluorescence (XRF), X-ray diffraction (XRD) and electron probe microanalysis (EPMA) techniques were used to characterize the pyritic refractory ore samples and the end products.

Experiments were primarily conducted to determine the Au and Ag content of the ore after roasting at 950 °C. Roasted ore was smelted with fluxes, lead oxide and reductants and metal and slag phases were obtained as a result of smelting. The precious metal content of metallic lead button, which mainly consists of lead, was isolated from the button by using cupellation. Precious metal-containing bead was respectively digested in HNO_3 and aqua regia solutions ($\text{HNO}_3/\text{HCl}:1/3$, mol). Gold and silver quantities in the solutions were measured by using AAS and ICP techniques as the amount present in the original samples.

In the second step, specimens were smelted with flux, lead oxide and various quantities of iron nails at 1100 °C and 1200 °C in order to directly analyze Au and Ag content of unroasted ore. Lead (buttons), matte and slag phases were obtained.

Cupellation process was performed to the lead buttons in order to isolate gold-silver-containing beads. Thus, the beads were digested in HNO_3 and residues in aqua regia respectively. Gold and silver amounts in the solutions were measured by using AAS and ICP techniques. Correlation between the quantity of additional iron and the recovery of gold and silver at various temperatures were investigated.

Last experiments were conducted to enhance measured Au-Ag amounts with Na_2O_2 addition to flux, at $1100\text{ }^\circ\text{C}$ on the iron addition of 20 and 60 g. (points the highest Au and Ag amounts were obtained).

The results which were obtained after roasting and direct fire assay of ore samples were compared.

2. Theoretical Background

In this method, finely ground ore is mixed with glass fluxes (CaCO_3 , Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, SiO_2 , etc.), litharge (PbO) and a carbon source such as charcoal or flour. The mixture is placed in a ceramic crucible and smelted at $900 - 1100\text{ }^\circ\text{C}$, approximately for an hour. A lead button, which collects all gold and other precious metals, forms at the bottom of crucible as a result of the reduction of PbO . The lead button is separated from the slag [2-5,7, 8].

The isolation of the precious metals from the lead button, which is known as cupellation, is performed by using MgO or CaO cupels absorbing oxidized lead at a temperature above the melting point ($888\text{ }^\circ\text{C}$) of PbO . The operation temperature for the cupellation process is between $900 - 1000\text{ }^\circ\text{C}$ [2-5]. Thus, a bead of precious

metals is obtained at the bottom of the cupel. Obtained bead is dissolved by using HNO_3 to separate silver and various analysis techniques are used to determine the amounts of the precious metals remaining in the bead [2].

The sulphur content of sulfide minerals (pyrite, chalcopyrite, argentite, etc.) leads to the formation of the matte phase. It is an undesired phase because it dissolves the precious metals during smelting [3, 5]. A considerable amount of used lead combines with the sulphur from the matte. PbS-FeS phase diagram is given in Figure 1.

In fire assay, added iron combines with sulphur in the matte phase. Thus, lead returns to the metallic state again. Iron addition is a suitable method for obtaining reliable results from traditional fire assay procedure [5, 7].

3. Experimental

Turkey Eastern Anatolia, Keban Region gold-silver-containing pyritic ores were used for experiments. According to X-ray diffraction results (XRD, PANalytical PW3040/60) shown in Figure 2, these ores comprise magnetite, quartz and a slight amount of gypsum. Quantitative determination of ore content was performed by using an X-ray fluorescence analyzer (XRF, Thermo SCIENTIFIC, NITON XL3t). An atomic absorption spectrometer (AAS, Perkin Elmer Analyst 800) and an inductively coupled plasma spectrometer (ICP, JY 138 ULTRACE) were used to determine both gold-silver quantities of the raw ore, which were below the detection limits of used XRF, and for the characterization of results. Table 1 shows

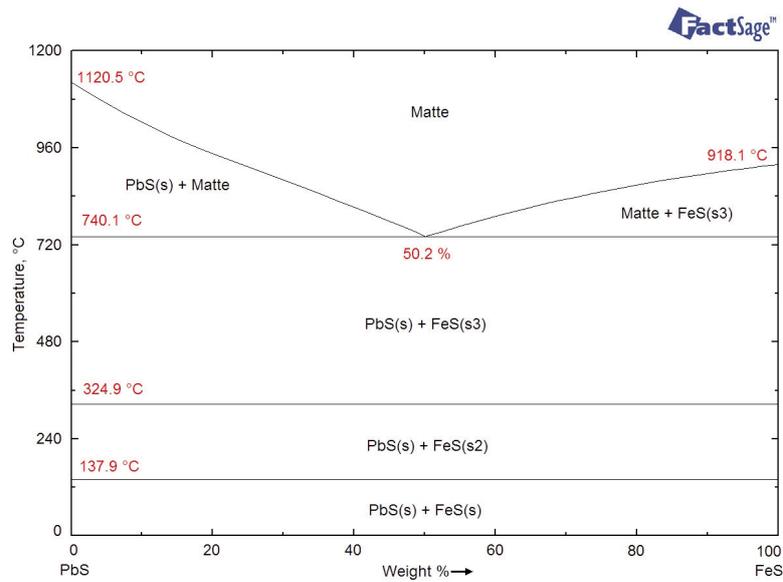


Fig. 1. PbS-FeS phase diagram

analysis of the raw ore.

Raw ore samples were crushed and ground by using a jaw crusher, a roller crusher and a continuous vibratory cup mill. 95 % of raw ore passed through a 100 mesh (150 μm) sieve. Finally, ground ore was

homogenized.

Experiments were conducted in three stages including smelting of ores using fluxes, separation of gold-silver-containing beads from the lead buttons and finally determination of amounts of gold and silver

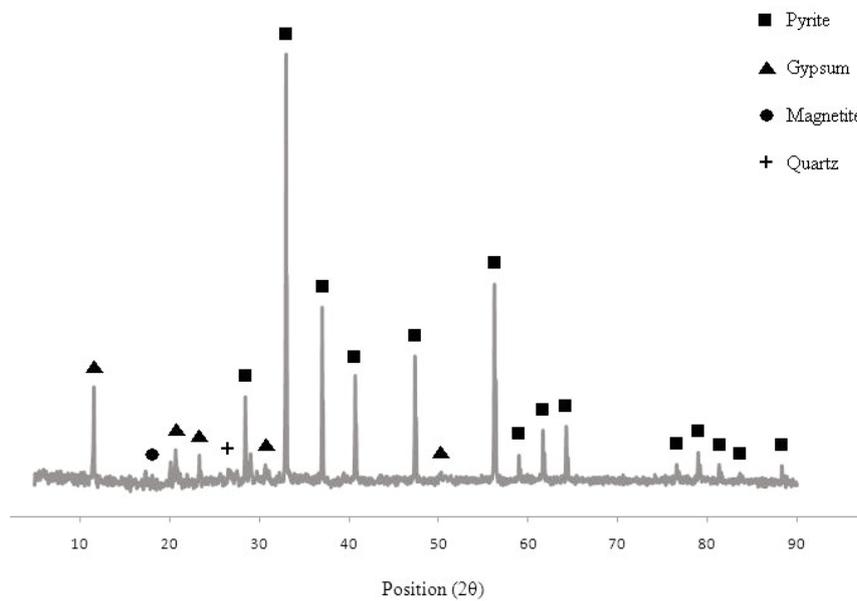


Fig. 2. XRD pattern of the raw ore

in the beads using AAS and ICP. The flowchart of fire assay process is given in Figure 3.

Table 1. Quantitative analysis results of the raw ore

Component	Analysis Method	Weight (%)
Fe	XRF, AAS, ICP	30.99
S	XRF	28.8
Si	XRF, AAS, ICP	4.26
Ca	XRF	2.94
Al	XRF	1.37
P	XRF	0.5
As	XRF	0.1
Cl	XRF	0.09
Mn	XRF	0.08
Ti	XRF	0.05
Cu	XRF, AAS, ICP	0.04
Cr	XRF	0.03
Pb	XRF	0.03
Sr	XRF	0.02
Balance	XRF	30.71
Au	AAS, ICP	N/A
Ag	AAS, ICP	0.0025

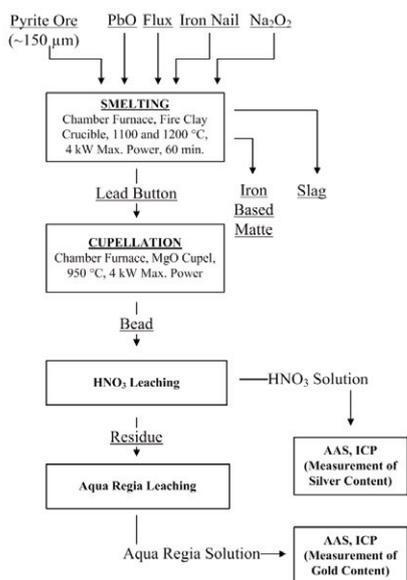


Fig. 3. Flowchart of fire assay process

Experiments were primarily conducted to determine the Au and Ag content of the raw ore after roasting. Samples were roasted by using a rotary kiln to remove sulphur content at 950 °C for 60 minutes. Roasted ore was smelted with fluxes, lead oxide and reductants, metal and slag phases were obtained as a result of smelting. The precious metal content of metal button, which mainly consists of lead, was isolated from the button by using cupellation. Precious metal-containing bead was respectively digested in HNO₃ and aqua regia solutions (HNO₃/HCl:1/3, mol). Gold and silver amounts in the solutions were measured by using AAS and ICP techniques as present in the original ore samples.

The second experiment set was conducted to understand the influence of additional iron on the direct fire assay of ore samples instead of applying roasting. After ore sample was dried at 105 °C for 120 minutes, mixtures were prepared containing 50 g of the raw ore and a constant quantity of flux materials. Amounts of used flux materials and lead oxide are given in Table 2. Various quantities of iron nails with 98.5 % iron content were added to the mixtures with varying amounts from 0 to 60 g. Then prepared specimens were placed in pre-heated fire clay crucibles and smelted at 1100 °C and 1200 °C for 60

Table 2. Amounts of used flux materials and lead oxide

Materials	Weight (g.)
PbO	150
Na ₂ CO ₃	100
Na ₂ B ₄ O ₇ ·10H ₂ O	25
SiO ₂	50
Iron	From 0 to 60

minutes. All fusion processes took place in a chamber furnace.

Cupellation was applied to the lead buttons, which were obtained from the previous smelting processes, in order to isolate gold-silver-containing beads. Cupellation processes took place in a chamber furnace at 950 °C. MgO cupels were used. Beads were digested in HNO₃ to separate silver. After the filtering the HNO₃ solutions, remaining gold residues were dissolved in aqua regia. Finally, gold and silver contents of solutions were measured by using AAS and ICP.

Final experiments were conducted to enhance measured Au-Ag amounts with Na₂O₂ addition (between 10 g. and 30 g.) to flux, at 1100 °C on the iron addition of 20 g. and 60 g. (The highest gold recoveries).

Another important feature for the experiments conducted with the iron and oxidizing flux addition is that any reductant material was not used unlike the experiments conducted for the fire assay of roasted ore. Because, sulphur present in the samples, behaves as a reductant as well.

4. Results and Discussion

The Au content of roasted ore is determined as 1.18 ppm and Ag content is 16.85 ppm.

According to the results, the highest gold concentration (0.76 ppm) was determined on the iron addition of 20 g at 1100 °C. The second highest concentration (0.60 ppm) was on the iron addition of 60 g at 1100 °C. Although the highest Au recovery was expected to be obtained on the iron addition of 60 g., it was obtained in the sample with 20 g. iron addition. We assumed the eutectic point, shown in Figure 1, is the reason of this case. The highest Ag concentration was 17.57 ppm (1200 °C, 50 g iron). The change of obtained lead phase, gold and silver recoveries with the increase of iron addition are shown in Figure 4, 5 and 6 respectively.

In the light of previous results, experiments were conducted to enhance measured Au-Ag amounts with Na₂O₂ additions (between 10 g. and 30 g.) to the flux, at 1100 °C, with the iron additions of 20 g. and 60 g.

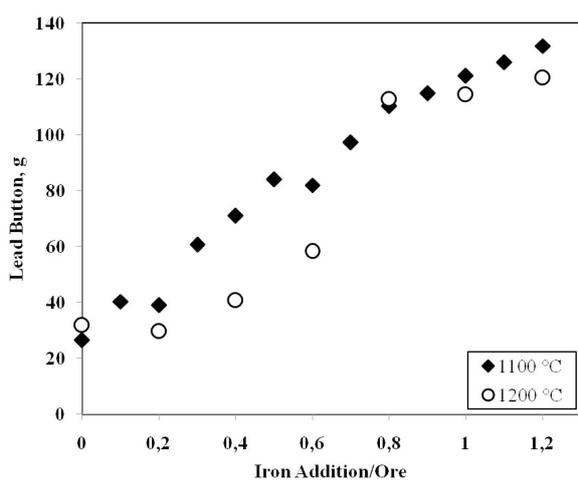


Fig. 4. The change of obtained lead phase with the increase of iron addition

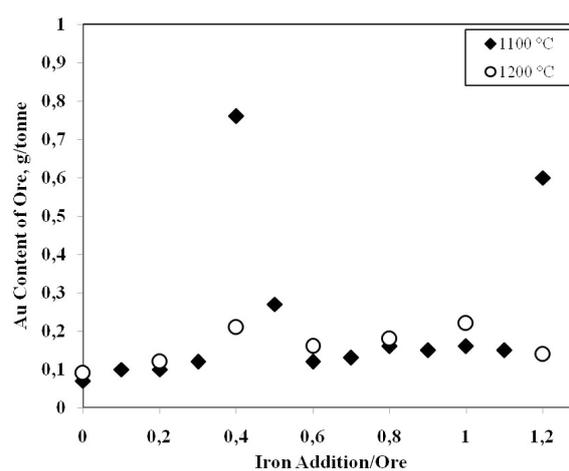


Fig. 5. The change of gold recovery with the increase of iron addition

The highest Au amount, 1.24 ppm, was obtained on the Na_2O_2 addition of 20 g and the iron addition of 60 g. during conducted experiments. Although the highest Ag concentration (17.3 ppm) was obtained on the Na_2O_2 addition of 30 g and the iron addition of 60 g., Ag recoveries were observed to be similar to each other on the Na_2O_2 additions of 15, 20, 25 and 30 g.

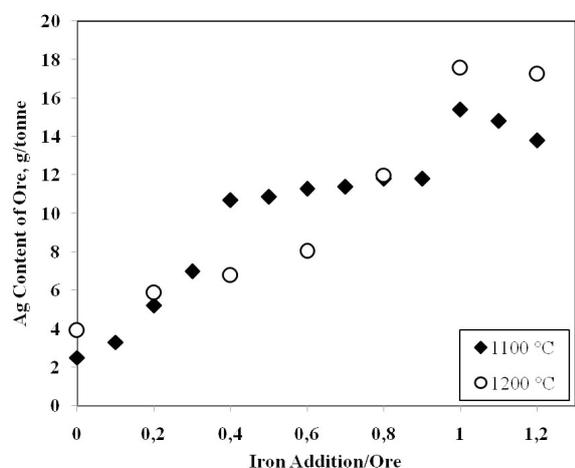


Fig. 6. The change of silver recovery with the increase of iron addition

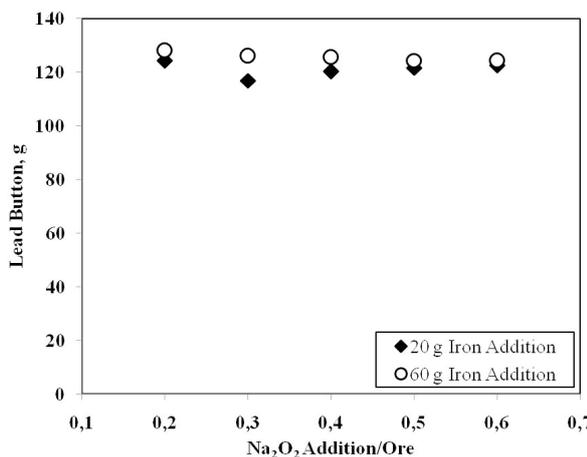


Fig. 7. The change of obtained lead phase with the increase of Na_2O_2 addition on the Iron Addition of 20 g. and 60 g.

The change of obtained lead phase with the increase of Na_2O_2 amount in the charge is given in Figure 7.

Au and Ag recoveries are shown in Figure 8 and Figure 9 respectively.

Furthermore, the change of Au concentration with the HNO_3 leaching of the Au-Ag containing beads is shown in Figure 10 and Figure 11.

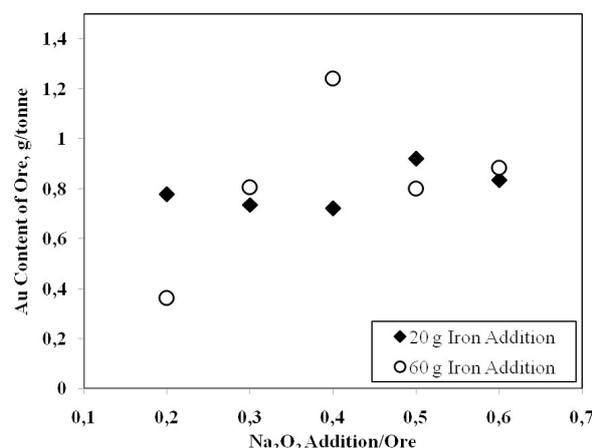


Fig. 8. The change of gold recovery with the increase of Na_2O_2 addition on the iron addition of 20 g. and 60 g.

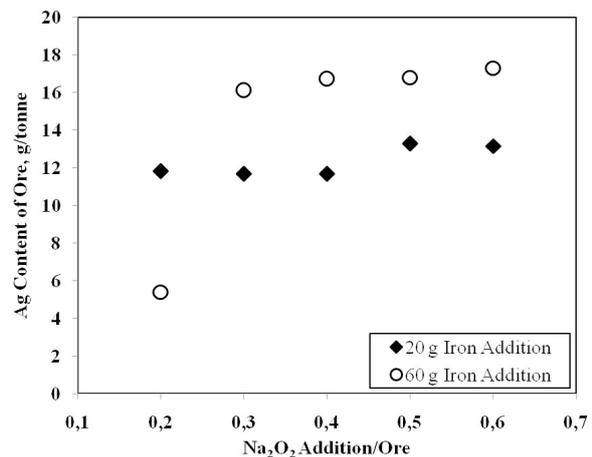


Fig. 9. The change of silver recovery with the increase of Na_2O_2 addition on the iron addition of 20 g. and 60 g.

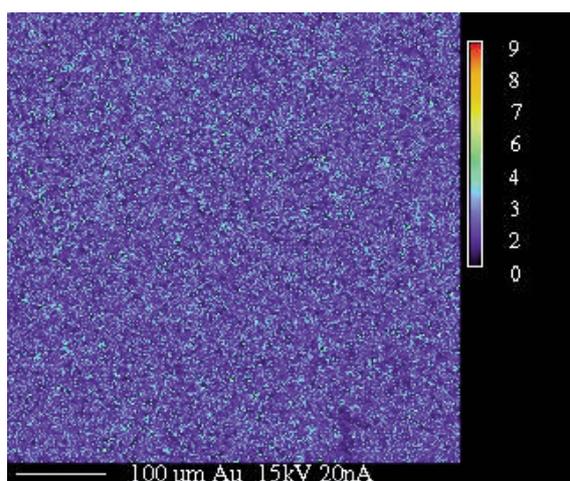


Fig. 10. Au distribution of Au-Ag containing bead obtained by electron probe microanalysis.

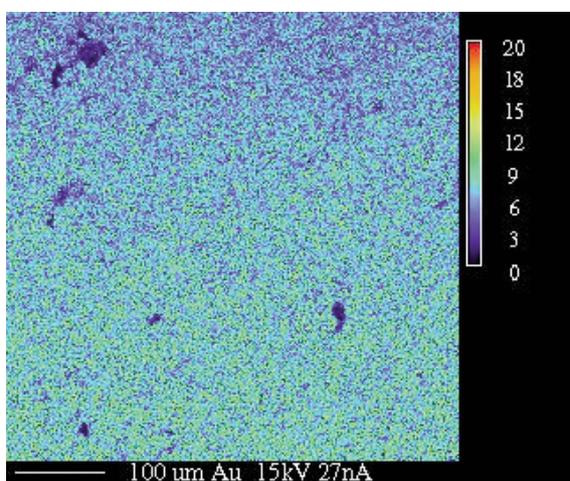


Fig. 11. Au distribution of leached Au-Ag containing bead obtained by electron probe microanalysis.

5. Conclusion

A fire assay process, which can be employed to the direct analysis of low grade pyritic gold ores, was carried out. Thus, pyritic ores can be analyzed by not applying any pre-treatment to remove the sulphur content.

During conducted experiments, obtained lead phase, Au and Ag amounts increased

with the addition of iron to flux. The highest Au recoveries were reached on the points 0.4 (iron addition/ore) and 1.2 (iron addition/ore) at 1100 °C as respectively 0.76 and 0.60 ppm. The eutectic point between FeS and PbS results in high Au content recovery on the point 0.4. But obtained those amounts are not adequate when they are compared with the result reached on the fire assay of roasted ore. Therefore, various amounts of Na₂O₂ were added as an oxidizing flux to flux mixtures prepared for 0.4 and 1.2 (iron addition/ore).

The highest Au amount, 1.24 ppm, was obtained on 0.4 (Na₂O₂/ore) and 1.2 (iron addition/ore) at 1100 °C. Although the highest Ag concentration (17.3 ppm) was obtained on 0.6 (Na₂O₂/ore) and 1.2 (iron addition/ore), Ag recoveries were observed to be similar to each other on the points 0.3, 0.4, 0.5 and 0.6 (Na₂O₂/ore) and 1.2 (iron addition/ore) at 1100 °C. All results are duplicated to verify.

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