Effects of Flux Materials on the Fire Assay of Oxide Gold Ores

Haluk Ozden Basaran[1], Ahmet Turan[1,2], Onuralp Yucel[1]*
[1]Istanbul Technical University; Chemical Metallurgical Faculty, Department of Metallurgical and Materials Engineering; Maslak, Istanbul, 34469, Turkey
[2]Yalova University, Yalova Community College, 77100, Yalova, Turkey

Abstract: Fire assay is the most accurate and widely used method for the determination of gold, silver and the PGM contents of ores and other solid materials. The technique has three steps; first step is the smelting of charge mixtures which consist of ground ore samples, acidic and basic fluxes, lead oxide and a carbon source. Isolation of precious metals which are collected in metallic lead phase as a result of the reduction of PbO is the second step and it is called cupellation. Obtained precious metals are analyzed by using wet analysis methods such as AAS (Atomic absorption spectrometry) and ICP (Inductively coupled plasma spectrometry) at the last stage. The aim of this study is the investigation of the effects of the acidic flux materials for the fire assay of oxide gold ores. Acidic fluxes, sodium borax decahydrate (Borax, $Na_2B_4O_7\cdot 10H_2O$) and quartz (SiO_2), were individually and together added to the charge mixtures which contain oxide gold ore samples, sodium carbonate (Na_2CO_3) and lead oxide with flour as a carbon source. Acidic flux additions were performed in different amounts. Smelting stage of the experiments was conducted at 1100 °C in fire clay crucibles for a reaction time of 60 minutes by using a chamber furnace. After the cupellation step in the chamber furnace, gold containing beads were obtained. The beads were digested in nitric acid (HNO_3) and aqua regia respectively to analyze the gold contents by using AAS and ICP.

Key words: Fire Assay, Cupellation, Flux Material, Oxide Gold Ore

1. Introduction

Fire assay is a traditional analysis method which is widely used because it provides very accurate results on gold, silver and the PGM analysis of ores and concentrates. Its basic principles were exhibited in the Agricola's book named 'De Re Metallica' in 1556 and it was reported that the technique is in use since the years B.C. [1, 2].

In the method, ore is firstly ground and mixed with a charge which consists of $NaCO_3$, $Na_2B_4O_7.10H_2O$, PbO, SiO_2 and a carbon source such as flour. The charge is smelted in a ceramic crucible and the precious metals are collected in the metallic lead phase which is reduced from PbO by carbon based reductants [1, 3-7].

After obtained metallic lead phase is separated from the slag phase, the precious metals are isolated from the metallic lead phase by using a technique named 'cupellation'. The process 'cupellation' is performed in a crucible called 'cupel' which is absorbed oxidized lead at about 950 ˚C. As a result of the process, a bead which consists of the precious metals remains at the bottom of the cupel. Silver is isolated from the bead by using HNO_3 leaching. After the leaching, the precious metals which still remain in the bead are analyzed using different techniques [1, 3-8].

The main importance of the fire assay technique is that the method provides the precious metals analysis results more accurate than the chemical analysis methods. Because chemical analysis of gold ores causes to dissolve gangue minerals and so gold nuggets are surrounded by the contaminations in the leaching step of the chemical analysis. In this manner, interferences occur on the chemical analysis conducted with AAS and ICP techniques. On the other hand, fire assay includes the steps which are the isolation of the precious metals from gangue minerals and then the analysis of the isolated precious metals. The previous studies also indicate that it can be successfully employed for the analysis of sulphur and arsenic containing ores, which are classified as refractory ores. The term ‘refractory’ refers to the following phenomenon; these kinds of ores have very refractor behavior and resistance against digesting in acids. So, this resistance makes the fire assay method the most remarkable solution for analysis. Also previous studies prove that the composition of slag and matte phases has an important role in the smelting stage of fire assay. Because, gold and silver collecting rates in metallic lead are affected from the composition of these phases [1, 3-5].

The aim of the study is the investigation of the effects of the acidic flux addition on the fire assay of oxide gold ores. The ores were smelted with the different types and the quantities of the flux materials in the smelting stage of the process and the effects of conducted experiments on gold recovery were comprehensively carried out.

2. Experimental

Turkey, Eastern Anatolian Region, low grade and carbonate gold ores were used in the study. Raw ore samples were firstly ground by using a vibratory cup mill. Ground ore was homogenized and average grain size was calculated as 238 µm using sieve analysis results. The experiments were performed with a charge mixture containing ground raw ore, lead oxide (PbO) as collector, flour as carbon source and various flux materials such as sodium carbonate (Na_2CO_3), sodium borax decahydrate (Borax, $Na_2B_4O_7{\cdot}10H_2O$) and quartz (SiO_2) in the smelting stage. All materials which were used in charge mixtures are in technical grade.

XRD (X-Rays Diffraction Spectrometer) pattern of the raw ore is shown in Figure 1 and the quantitative analysis results of the raw ore which is determined by using XRF (X-Rays Fluorescence Spectrometer), AAS and ICP are given in Table 1. According to quantitative analysis results, raw ore mainly comprises very high level of $CaCO_3$ and SiO_2, however gold content was determined as below the limit of detection.

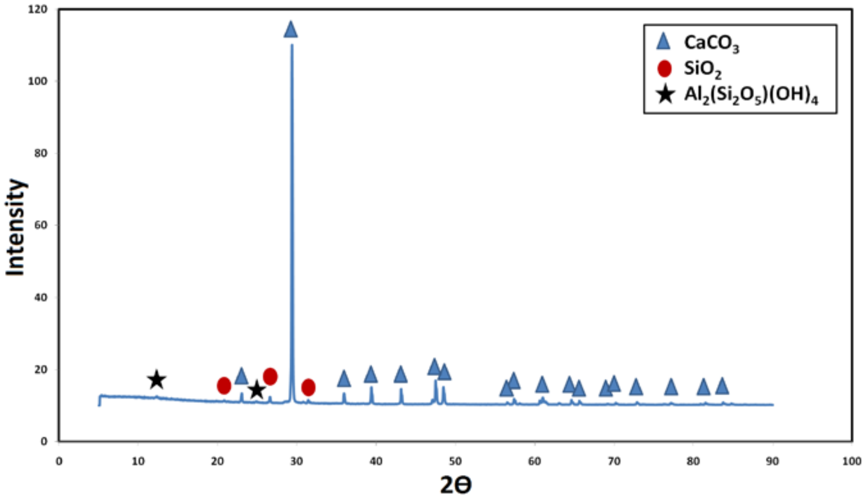

Fig. 1 XRD pattern of the raw ore

Table 1 Quantitative analysis results of the raw ore

Component	Quantity (%)	Component	Quantity (%)
$CaCO_3$	79.38	Zn	0.13
SiO_2	10.03	S	0.08
Fe_2O_3	2.79	Pb	0.06
Al_2O_3	3.63	Mn	0.03
Cu	0.17	As	0.02
P	0.16	Cr	0.01

In this study, optimum addition amounts of the acidic flux materials (Borax and SiO_2) to the smelting charge were tried to determine for the fire assay of oxide gold ores. For this purpose, sodium borax decahydrate and quartz were individually and together added to the charge mixtures in various amounts. The relationship between the added flux materials and obtained lead and precious metal amounts were compared. The flowchart of the conducted experiments is given in Figure 2.

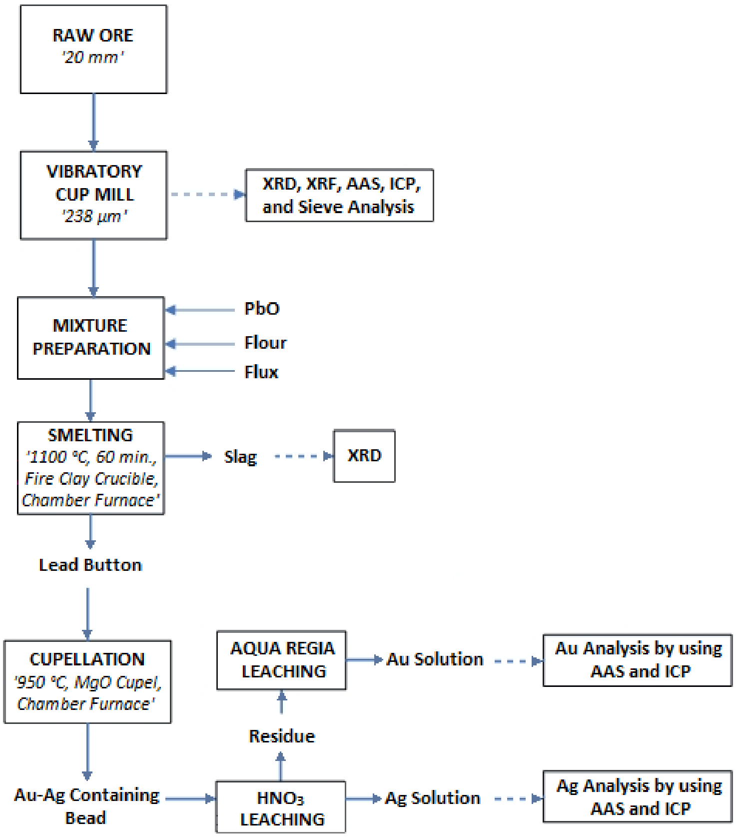

Fig. 2 The flowchart of the conducted experiments

In the first experimental set, ore samples were mixed with flour, lead oxide, sodium carbonate and different quantities of borax. The mixtures were smelted at 1100 °C which is adequate temperature to occur the required reactions and to smelt the slag phase. Table 2 shows the content of the charge mixtures. Smelting process was performed using fire clay crucible in a chamber furnace for 60 minutes process duration which is enough time to finish the reactions. The amounts of the components in the charge mixtures (apart from the acidic fluxes), process temperature and duration were determined in the light of conducted previous studies [1, 3-5]. After smelting step, obtained metal and slag phases mechanically separated from each other. Slag phases were ground and characterized by XRD, XRF and wet analysis techniques. The precious metals were isolated from the metallic phase by cupellation method. HNO_3 and aqua regia (HNO_3/HCl: 1/3, mol) leaching processes were performed respectively and gold content of the samples were measured as present in the raw ore by using ICP and AAS.

Table 2. Content of charge mixtures for the experiments conducted with borax addition

Component	Quantity (g)
Ore	30
PbO	90
Na_2CO_3	30
$Na_2B_4O_7{\cdot}10H_2O$	0-10-20-30-40-50-60
Flour	6.5

In the second experimental set, ore samples were mixed with flour, lead oxide, sodium carbonate and different quantities of quartz instead of sodium borax decahydrate. Quartz is another acidic flux material like sodium borax decahydrate. The content of prepared mixtures is given in Table 3. After smelting stage, same operations and analysis techniques were applied to the obtained phases as the first experimental set.

Table 3. Content of charge mixtures for the experiments conducted with quartz addition

Component	Quantity (g)
Ore	30
PbO	90
Na_2CO_3	30
SiO_2	0-10-20-30-40-50-60
Flour	6.5

To investigate the effect of the use of borax and quartz together in the charge mixture, a last experimental set was designed and the content of the charge mixtures is shown in Table 4. Borax/quartz ratios were selected as 1 in all experiments. Same operation and analysis steps were applied to the obtained slag, metallic phases and the precious metals.

Table 4. Content of charge mixtures for the experiments conducted with borax and quartz additions

Component	Quantity (g)
Ore	30
PbO	90
Na_2CO_3	30
$Na_2B_4O_7{\cdot}10H_2O$*	0-5-10-15-20-25-30
SiO_2*	0-5-10-15-20-25-30
Flour	6.5

** $Na_2B_4O_7{\cdot}10H_2O$ / SiO_2 : 1/1 in all experiments*

3. Results and Discussion

Charge mixtures which comprise ore samples, PbO, flour and sodium carbonate were prepared. Borax and quartz were added to the charge individually and together in different amounts.

All experiments were conducted in a chamber furnace at 1100 °C for 60 minutes. In the smelting stage, reductive smelting operations were conducted in fire clay crucibles. As a result of reductive smelting stage, slag and metallic lead phases were obtained. The relationship between the addition of acidic fluxes (Borax and quartz) to the charge mixtures and the weight of obtained metallic lead phases can be seen in Figure 3.

Cupellation process was applied to the metallic lead phases to isolate the precious metals from the metallic phases. The process was performed in the chamber furnace which was previously employed for the smelting operations. MgO based cupels were used for the process and process temperature was 950 °C. Gold and silver containing beads were obtained as a result of the process and the relationship between the acidic fluxes and the weight of the beads is given in Figure 4.

The beads were leached using HNO_3 and the silver content of the beads removed. Residues which remain after HNO_3 leaching were leached by using aqua regia. Aqua regia solutions were analyzed by using ICP and AAS techniques to determine the gold contents of the aqua regia solutions. The gold content which was measured for every experiment was calculated as present in the original ore samples. The change of measured gold contents with different amounts of acidic fluxes are shown in Figure 5.

Figures 6, 7 and 8 show the change of the phase structure of slag phases, obtained after smelting stage, through XRD patterns. The change of the amounts of metallic lead phases, obtained beads and measured gold values with the change of the addition of acidic fluxes can be seen in Table 5.

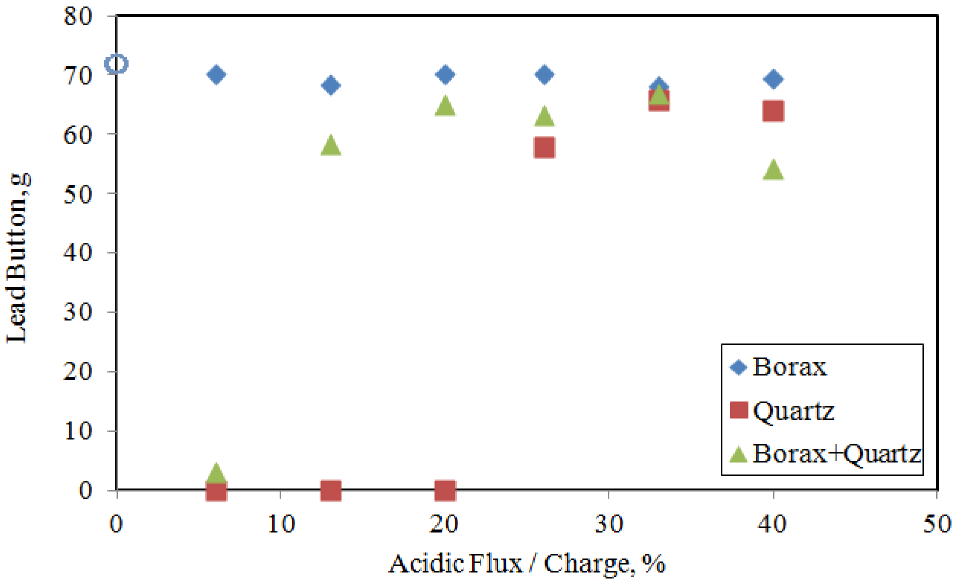

Fig. 3 The change of metallic lead phase (Lead button) weight with the increase in acidic flux addition

The results demonstrate that the amount of obtained lead phase is nearly constant for borax addition for all percentage, while it increases after 26% quartz (in comparison to the total charge) addition. Obtained metallic phase amounts are very similar to individually borax added experiments for the experimental set where borax and quartz were used together without 6% percent acidic flux added experiment. The hollow circle indicates the metallic lead phase recovery without the addition of acidic fluxes. It can be clearly understood that the acidity of slag phase is adequate before the addition of quartz and it can just provide accurate and reliable results after the high addition rates as 20%. Borax addition does not affect the recovery of lead phase. When borax and quartz were added together, it accelerates and reduces the flux addition rates to 13% to obtain acceptable metallic phase recovery rates.

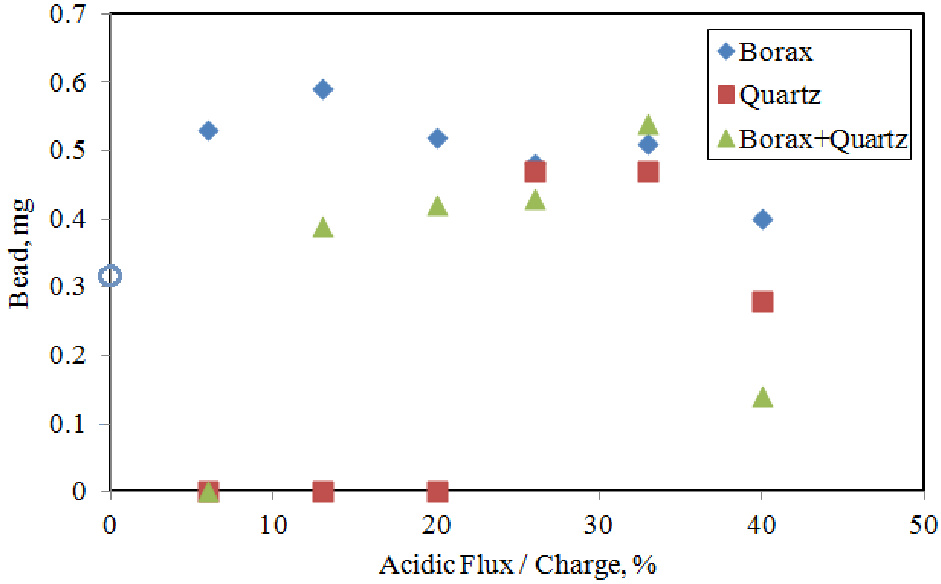

Fig. 4 The change of gold-silver containing bead weight with the increase in acidic flux addition

The weight of gold-silver containing beads changes similar to the change of metallic lead phase amounts with the acidic flux addition. Although silver content of the beads is another important parameter which affects the weight of the beads, the silver content of the samples were not investigated. The reason for that is the content in question is lower than the technological desired amount to focus on.

To obtain the results in a range is a usual phenomenon for the ppm level gold analysis of the gold ores because of the nugget effect. It is reported that if the gold content of ore is less than or equal to 4 g/t, the distribution of gold nuggets are not homogeneous in ore body which is called ‘Nugget Effect’ [9]. In this study, the results above 2 g/t were accepted as accurate. The results indicate that individually borax addition as an acidic flux gives very accurate results in all addition rates which vary from 6% to 40%, while the results are acceptable above 26% for individual quartz addition and above 20% for borax-quartz mixture addition. It is also observed that borax addition decreases the slag viscosity and it has a very important role on the gold recovery. When the gold recovery results are compared to the case where acidic flux was not added, it can be seen that slag formation is in a steady state without acidic flux addition. The increase in quartz addition decreases the gold recovery until 26% addition rate. Individually borax addition keeps the recovery same and the use of borax and quartz together reaches the steady state recovery rates after 13%.

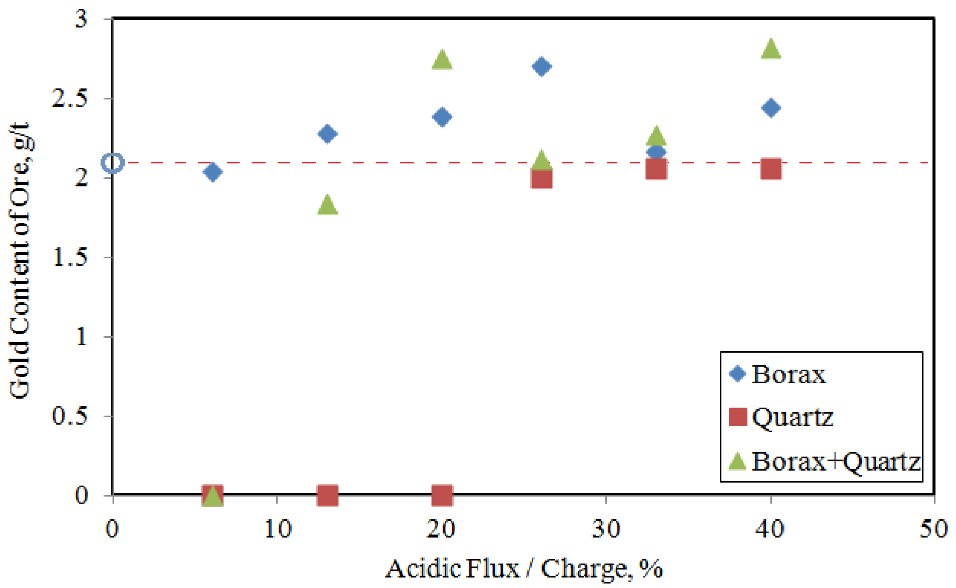

Fig. 5 The change of measured gold content with the increase in acidic flux addition

Table 5. The change of obtained metallic lead and bead amounts and measured gold values with acidic flux addition

Borax Addition / Charge, %	Quarts Addition / Charge, %	Lead Button, g	Au, Ag Containing Bead, mg	Gold Content of Ore, g/t
0*	0*	73.55	0.48	2.15
6	0	70.28	0.53	2.04
13	0	68.39	0.59	2.06
20	0	70.23	0.52	2.39
26	0	70.28	0.48	2.71
33	0	68.09	0.51	2.17
40	0	69.51	0.40	2.45
0*	0*	72.58	0.10	1.96
0	6	0	0	0
0	13	0	0	0
0	20	0	0	0
0	26	57.98	0.47	2.00
0	33	65.93	0.47	2.06
0	40	63.96	0.28	2.06
0*	0*	69.90	0.40	2.12
3	3	3.16	0	0
6.5	6.5	58.44	0.39	1.84
10	10	65.05	0.42	2.75
13	13	63.28	0.43	2.12
16.5	16.5	66.87	0.54	2.27
20	20	54.38	0.14	2.82
*Average values for the experiments where acidic flux was not added		72.01	0.32	2.07

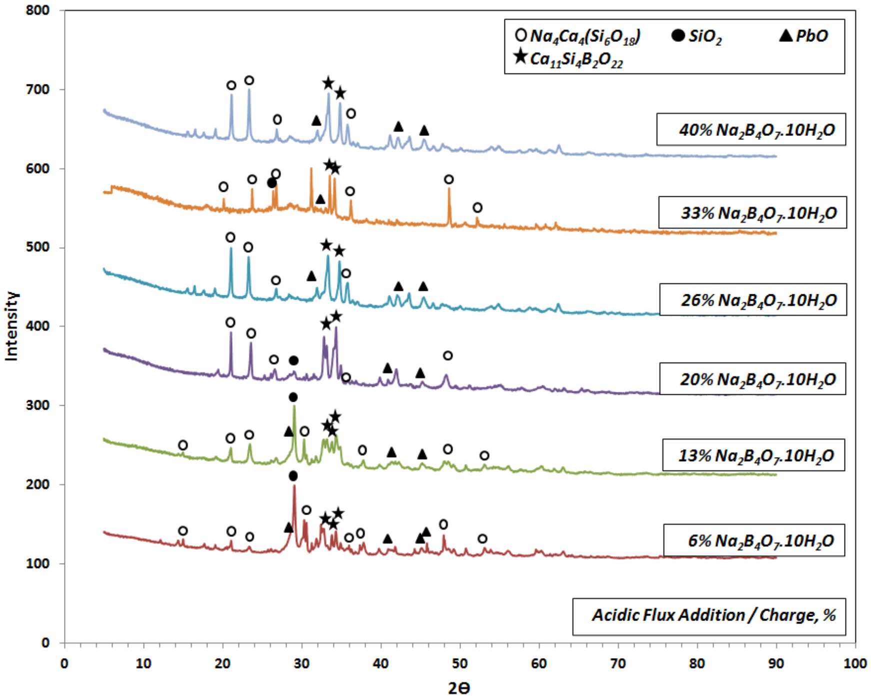

Fig. 6 XRD patterns of slag phases for the experiments conducted with borax addition

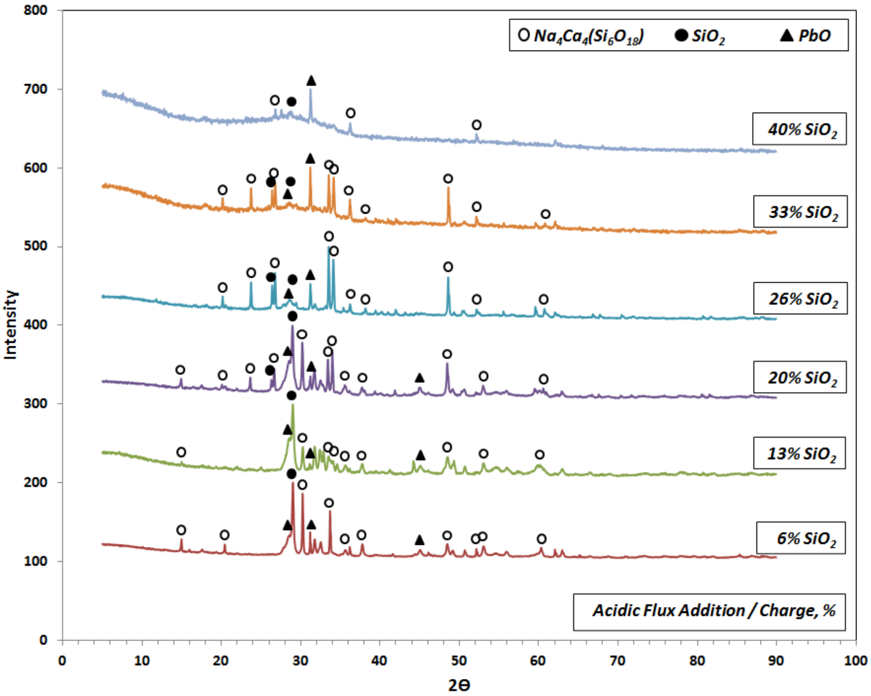

Fig. 7 XRD patterns of slag phases for the experiments conducted with quartz addition

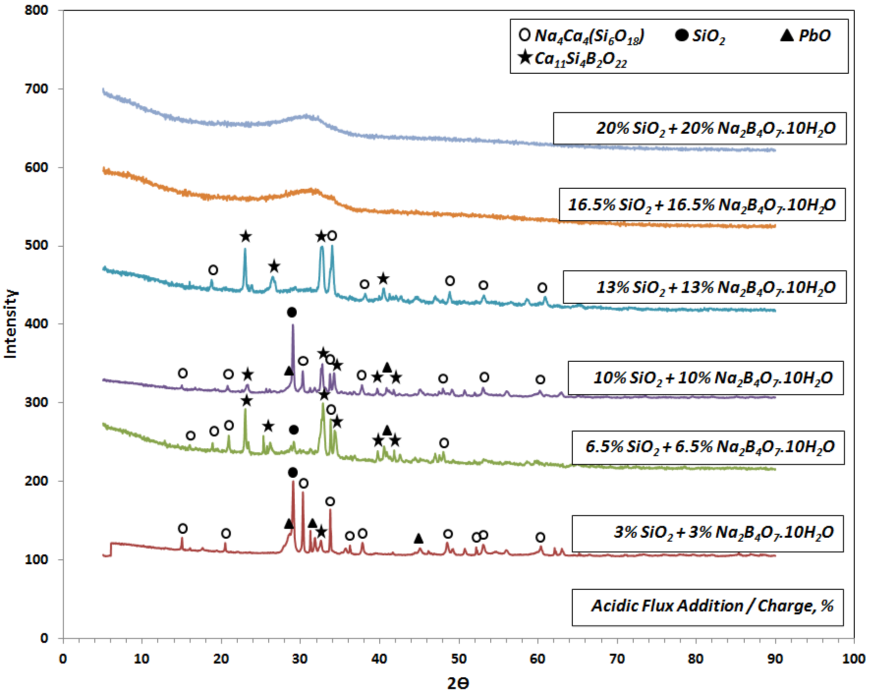

Fig. 8 XRD patterns of slag phases for the experiments conducted with borax and quartz together addition

XRD patterns show that $Na_4Ca_4(Si_6O_{18})$ and $Ca_{11}Si_4B_2O_{22}$ are dominant phases on the slag with the increase in acidic flux addition for the experiments conducted with individually sodium borax decahydrate addition. Slag phase also comprises PbO. For the experiment conducted with individually quartz addition, $Na_4Ca_4(Si_6O_{18})$ phase becomes dominant instead of SiO_2 with the increase in SiO_2 addition but formation of an amorphous glassy phase is clear. Although phases $Na_4Ca_4(Si_6O_{18})$ and $Ca_{11}Si_4B_2O_{22}$ are quite distinguished in low acidic flux addition rates for the experiments sodium borax decahydrate and quartz added together, an amorphous glassy phase occurs similar to the increase in the acidic flux addition rate.

4. Conclusion

In this study, the effects of acidic fluxes on the fire assay of oxide gold ores were determined. Sodium borax decahydrate and quartz were used as acidic fluxes, and these flux materials were added to the charge mixtures individually and together respectively. As a result of the smelting stage of the fire assay process, the relationship between the addition of acidic fluxes and the amounts of obtained metallic lead, gold-silver containing bead and measured gold values were carried out.

It was observed that borax has a positive effect on the recovery of metallic lead, bead and gold amounts and it also provides low viscosity for the slag phase. Because of the nugget effect encountered on this kind of analytical processes, the gold recovery values which are above 2 g/t was accepted as accurate. Acceptable results were obtained for the conditions which borax and quartz were not added. This case shows slag phase is in a steady state before the addition of acidic fluxes. Acceptable results were obtained for borax addition from 6% to 40% including all experimental set conducted with individually addition of borax. It was only possible to reach the accurate results above 26% for quartz addition and above 20% for borax-quartz mixture addition due to glassy slag phase formation. XRD patterns also indicate that formation of a glassy slag phase causes to obtain accurate results from the fire assay of oxide gold ores with SiO_2 presence in the slag. The experiments which the highest gold recoveries were obtained were duplicated by using calcinated ore and the similar – acceptable – results were obtained which demonstrates that determined flux mixtures provide accurate results and it can be successfully employed for the direct fire assay of ores instead of a fire assay technique consisting of the combination of calcination and fire assay.

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