




Fire Assay of Carbonate-Containing Oxide Gold Ores

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Abstract: To analyze gold and silver from ores and concentrates; fire assay still remains the only widely accepted technique. The method has three steps including smelting, cupellation and the characterization of precious metals-containing beads. Finding the ideal amounts of acidic flux materials (borax and SiO₂) to add to the smelting charge for the fire assay of carbonate gold ores was the aim of this study. Acidic fluxes, quartz (SiO₂), sodium borax decahydrate (borax, Na₂B₄O₇·10H₂O), and basic flux sodium carbonate (Na₂CO₃) were introduced separately and in combination to the charge mixtures containing samples of carbonate gold ore, lead oxide with flour providing as a carbon source, and lead oxide. The quantity of acidic flux additions was adjusted. Following the cupellation process, beads containing gold were produced. Using AAS and ICP, the beads were digested in nitric acid (HNO₃) and aqua regia, respectively, to determine the amount of gold present.

Keywords: Carbonate gold ore, cupellation, fire assay, flux material.

Karbonatlı Bileşikler İçeren Oksitli Altın Cevherlerinin Ateş Analizi

Özet: Cevherlerden ve konsantrelerden altın ve gümüş analizini yapmak için kullanılan ateş analizi hala en yaygın kabul gören tekniktir. Yöntem, ergitme, küpelasyon ve soy metal içeren dore metalin karakterizasyonu olmak üzere üç adımdan oluşur. Bu çalışmanın amacı, karbonatlı altın cevherlerinin ateş analizinde ergitme şarjına eklenmesi gereken optimum asidik curuflaştırıcı miktarını (boraks ve SiO₂) bulmaktır. Asidik curuflaştırıcılar, kuvars (SiO₂) ve sodyum boraks dekahidrat (boraks, Na₂B₄O₇·10H₂O), bazik curuflaştırıcı olarak sodyum karbonat (Na₂CO₃), karbon kaynağı olarak un, kurşun oksit ve karbonatlı altın cevherini içeren karışıma artan miktarlarda karıştırılmıştır. Deneysel çalışmaların neticesinde asidik curuflaştırıcıların katkı miktarları optimize edilmiştir. Ateş analizinin ergitme aşamasının sonunda, cevherdeki soy metalleri bünyesinde toplayan redüklenmiş kurşun külçeler elde edilmiş, bu metalik yapılar küpelasyona tabi tutulmuş ve küpelasyon neticesinde Au-Ag içeren dore metal boncuklar kazanılmıştır. Elde edilen dore metal fazları, sırasıyla nitrik asit (HNO₃) ve kral suyu içinde çözülerek AAS ve ICP yöntemleri yardımı ile mevcut altın miktarları belirlenmiştir.

Anahtar Kelimeler: Karbonatlı altın cevheri, küpelasyon, ateş analizi, curuflaştırıcı.

Article

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1. Introduction

Fire assay is a popular analysis method because it produces exceptionally reliable results when examining gold, silver, and platinum group metals (PGM) in ores and concentrates. Its fundamental ideas were presented in the 1556 book "De Re Metallica" by Agricola, and it was stated that the method has been used since the time of the ancient Greeks (Turan and Yucel, 2011; Renner, 1997).

First, a charge mixture is combined with grinded ore. Na_2CO_3 , $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, PbO , SiO_2 and a carbon source, like flour, make up the charge. After the charge is smelted in a ceramic crucible, precious metals are collected in the metallic lead phase. Carbon-based reductants reduce the Pb content of the PbO (Turan and Yucel, 2011; Turan, Morcalı and Yucel, 2009; Turan and Yucel, 2010; Turan and Yucel, 2009; Cerceau et. al., 2016; Yannopoulos, 1991).

After smelting, metallic lead and slag phases are separated from each other. The precious metal content of the lead phase is extracted through the "cupellation" technique. A unique crucible known as a "cupel" is used for the cupellation process, which absorbs oxidized lead at 950 °C (1223 K). When cupellation occurs, a precious metal bead stays at the bottom of the cupel. HNO_3 leaching is used to separate the silver from the bead. After the leaching process, precious metals that are still present in the bead are analyzed using a variety of techniques such as gravimetric analysis, inductively coupled plasma spectrometry (ICP), and atomic absorption spectrometry (AAS) (Turan and Yucel, 2011; Turan, Morcalı and Yucel, 2009; Turan and Yucel, 2010; Turan and Yucel, 2009; Cerceau et. al., 2016; Yannopoulos, 1991; Deal and Lorey, 1987).

Compared to other chemical analysis methods, the fire assay method yields more accurate results for precious metals analysis, which is what makes it significant. Gold nuggets are surrounded by contaminations during the leaching stage of chemical analysis because the dissolving of the gangue minerals is necessary for the chemical analysis of gold ores. Interferences with the chemical analysis that is carried out directly using AAS and ICP procedures arise in this way. In other words, fire assay entails the separation of valuable metals from gangue minerals followed by their examination. It can also be successfully used for the examination of refractory ores that contain sulphur and/or arsenic, according to earlier investigations. The phenomenon described below is what is meant to be understood by the term "refractory": these ores exhibit highly refractory behaviour and resistance to acid digestion. Because of its resilience, the fire assay method is the most reliable analytical option. The smelting step of the fire assay method is remarkably affected by the composition of the matte and slag phases. The composition of these phases affects the rates at which gold and silver may be collected in metallic lead, which is the explanation for this (Turan and Yucel, 2011; Turan, Morcalı and Yucel, 2009; Turan and Yucel, 2010; Turan and Yucel, 2009).

The purpose of this study is to determine the appropriate additional amounts of acidic flux materials (borax and/or SiO_2) to the smelting charge for the fire assay of carbonate gold ores. As a result, both independently and in combination, various concentrations of quartz and sodium borax decahydrate were added to the charge combinations. The amounts of metallic lead and the precious metals obtained were compared to the flux material addition rates.

2. Materials and Methods

In this study, low-grade and carbonate gold ores were utilized. Initially, a vibratory cup mill was used to grind the raw ore samples. After homogenizing the specimens, the average particle size was determined as 238 μm by means of the sieve analysis. The charge mixtures were made up of quartz (SiO_2), sodium carbonate (Na_2CO_3), sodium borax decahydrate (borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), flour as a carbon source, powdered raw ore, and lead oxide (PbO) as a collector. All materials utilized in the charge combinations were of a technical quality.

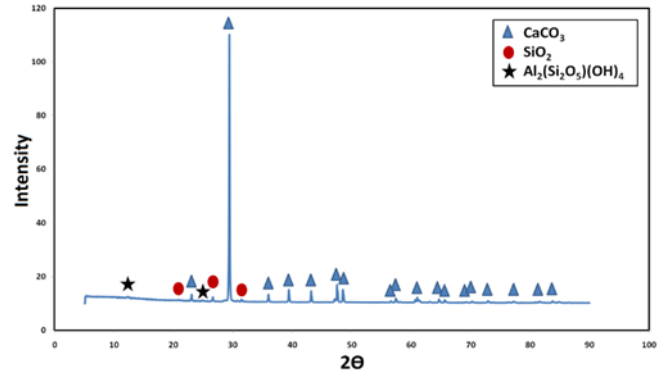


Figure 1. XRD Pattern of the Raw Ore.

Şekil 1. Ham Cevherin XRD Deseni.

The raw ore's XRD (X-ray diffraction spectrometer) pattern is shown in Figure 1. The quantitative analytical results for the raw ore, obtained using XRF (X-ray fluorescence spectrometer), AAS, and ICP, are shown in Table 1. The findings of the quantitative analysis show that the raw ore mostly consists of very high levels of SiO_2 and CaCO_3 , however, the gold concentration was below the AAS and ICP techniques' limit of detection.

Table 1. Quantitative analysis results of the raw ore.

Tablo 1. Ham cevherin kantitatif analiz sonuçları.

Comp.	Quantity, wt.%	Comp.	Quantity, wt.%
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

The experimental flowchart is presented in Figure 2. For the first experimental series, a mixture of lead oxide, flour, sodium carbonate, and varying amounts of borax were mixed with the ore sample. Since 1100 °C is the ideal temperature for the necessary reactions and to melt the slag phase, smelting was done at this temperature. Table 2 displays the charge mixture contents. The crucible made of fire clay has been selected to carry out the smelting procedure in a chamber furnace. There was enough time to finish the reactions during the 60-minute procedure period. Based on previously completed research, the amounts of the constituents in the charge combinations (apart from the acidic fluxes), as well as the process temperature and time, were determined (Turan and Yucel, 2011; Turan, Morcalı and Yucel, 2009; Turan and Yucel, 2010; Turan and Yucel, 2009). The resulting metal and slag fractions were mechanically separated from one another after the smelting process. The slag phases were grinded and characterized using XRF, XRD, and chemical analysis techniques. The cupellation process extracted valuable metals from the metallic phase in MgO -based cupels. Following the completion of the HNO_3 and aqua

regia (HNO_3/HCl : 1/3, mol) leaching processes, the amount of gold contained in the samples was determined by ICP and AAS analysis of the raw ore.

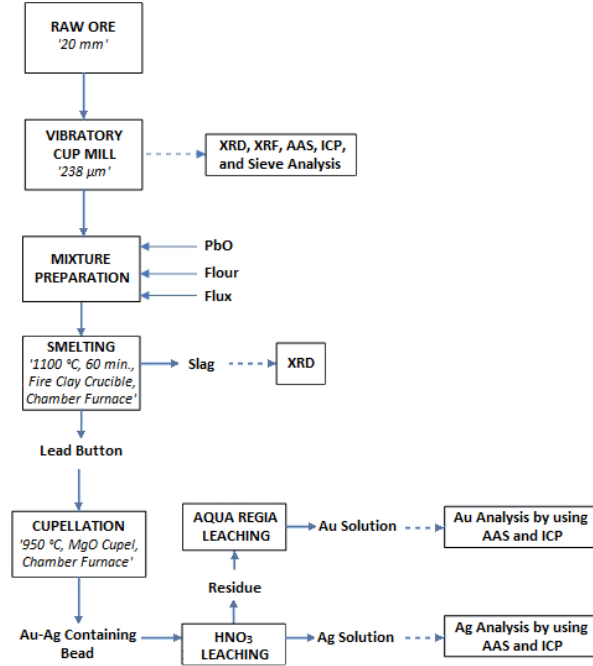


Figure 2. The flowchart of the experiments.
Şekil 2. Deneylerin akış şeması.

For the second experimental series, different amounts of quartz were combined with ore samples, flour, sodium carbonate, and lead oxide in place of sodium borax decahydrate. Similar to sodium borax decahydrate in its characteristics, quartz is similarly an acidic flux material. The prepared mixes' contents are listed in Table 2. The resulting phases were subjected to the same procedures and analysis techniques as the first experimental series following the smelting step.

The purpose of the last experimental series was to investigate the impact of combining quartz and borax in the charge mixes. The content of charge mixtures is displayed in Table 2. The borax/quartz ratio was set to 1 in every experiment. The resulting phases and precious metals underwent the same procedures and analysis methods. Figure 3 shows selected images of the experimental products including lead, slag, and precious metals in the form of beads.

Table 2. Contents of charge mixtures for the experiments conducted with borax addition (i), quartz addition (ii) and combined borax - quartz additions (iii).

Tablo 2. Boraks ilavesi (i), kuvars ilavesi (ii) ve kombine boraks - kuvars ilavesi (iii) ile yapılan deneyler için karışım içerikleri.

Component	Quantity, g		
	(I)	(II)	(III)
Ore	30	30	30
PbO	90	90	90
Na_2CO_3	30	30	30
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0-10-20-30-40-50-60	-	0-5-10-15-20-25-30*
SiO_2	-	0-10-20-30-40-50-60	0-5-10-15-20-25-30*
Flour	6.5	6.5	6.5
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ / SiO_2	-	-	*1/1 in all experiments

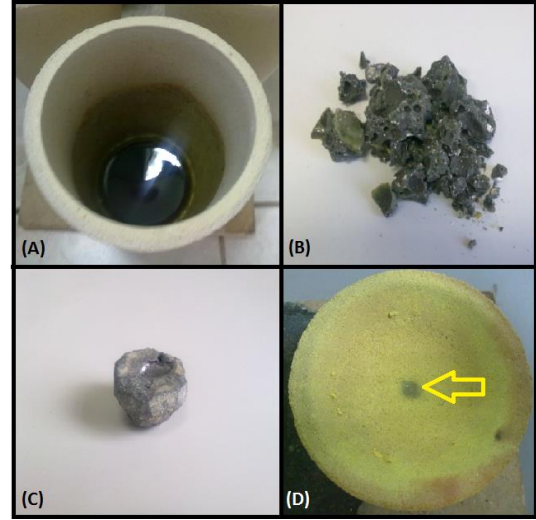


Figure 3. Selected photographs from the experiments; (a) crucible after smelting, (b) obtained slag, (c) obtained lead button and (d) gold-silver-containing bead after cupellation.
Şekil 3. Deneylerden seçilen fotoğraflar; (a) eritme sonrası pot, (b) elde edilen cüruf, (c) elde edilen kurşun düğmesi ve (d) küpelasyon sonrası altın-gümüş içeren külçe.

3. Results and Discussion

The reductive smelting stage produced metallic lead phases and slag. The weight of the produced metallic lead phases and the acidic flux additions to the charge mixtures were shared in Figure 4.

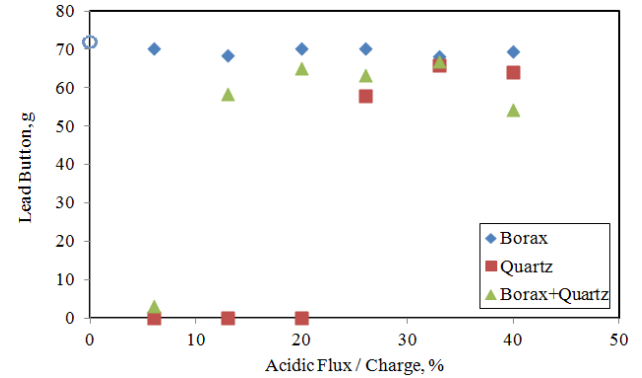


Figure 4. Weight change of metallic lead button with increasing acidic flux addition.
Şekil 4. Asidik akı ilavesinin artmasıyla metalik kurşun düğmesinin ağırlık değişimi.

The precious metals were extracted from the metallic lead phases using the cupellation process. The process was conducted in the chamber furnace that was previously utilized for the smelting operations. Beads comprising silver and gold were obtained by means of cupellation. Figure 5 shows the relationship between the weight of the beads and the acidic fluxes.

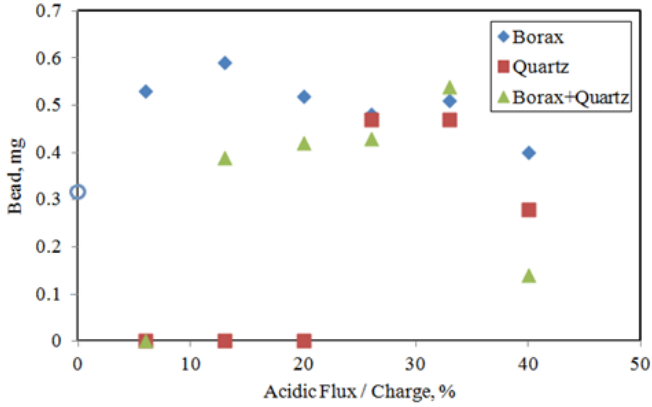


Figure 5. Weight change of gold-silver containing beads with increasing acidic flux addition.

Şekil 5. Asidik akı ilavesinin artmasıyla altın-gümüş içeren boncukların ağırlık değişimi.

The beads were leached using HNO_3 to extract the silver from them. Aqua regia was utilized for leaching the collected residues. ICP and AAS methods were employed to ascertain the aqua regia solutions' gold concentration. The amount of gold in the original ore samples was measured and calculated for each experiment. The variation in observed gold concentrations with varying acidic flux amounts was depicted in Figure 6.

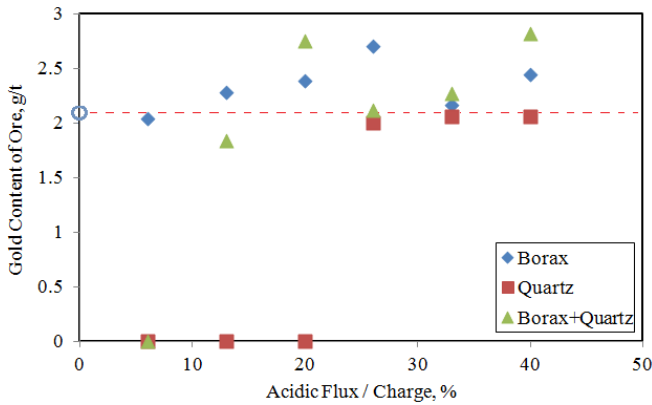


Figure 6. The weight change in measured gold content with increasing acidic flux addition.

Şekil 6. Asidik akı ilavesinin artmasıyla ölçülen altın içeriğindeki ağırlık değişimi.

Through the use of XRD patterns, Figures 7, 8, and 9 illustrate how the phase structure of the slag phases changed following the smelting stage. Table 3 shows how the addition of acidic fluxes changed the amounts of metallic lead phases, the beads that were formed, and the measured gold values.

Table 3. The change of measured gold values and obtained metallic lead and bead amounts with the addition of acidic flux materials.

Tablo 3. Asidik akı malzemelerinin ilavesi ile ölçülen altın değerleri ve elde edilen metalik kurşun ve boncuk miktarlarının değişimi.

Borax / Charge Ratio, wt. %	Quartz / Charge Ratio, wt. %	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	0.00	0.00	0.00
0	13	0.00	0.00	0.00
0	20	0.00	0.00	0.00
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	0.00	0.00
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 fluxes were not added.		72.01	0.32	2.07

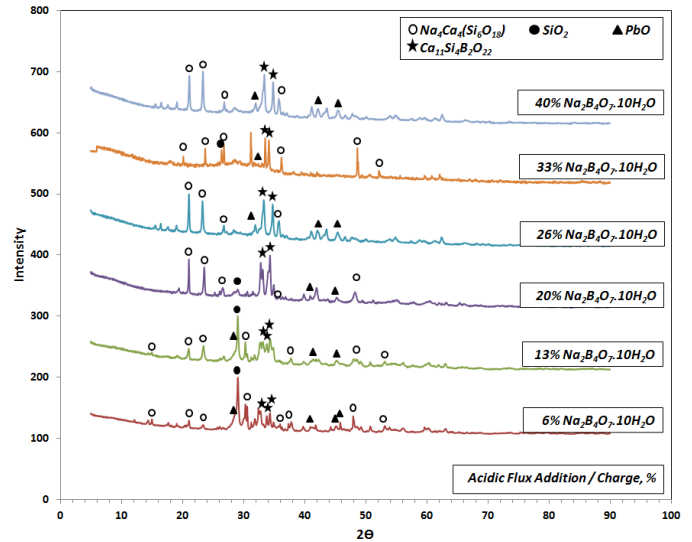


Figure 7. XRD patterns of slag phases for the borax addition experiments.

Şekil 7. Boraks ilavesi deneyleri için cüruf fazlarının XRD desenleri.

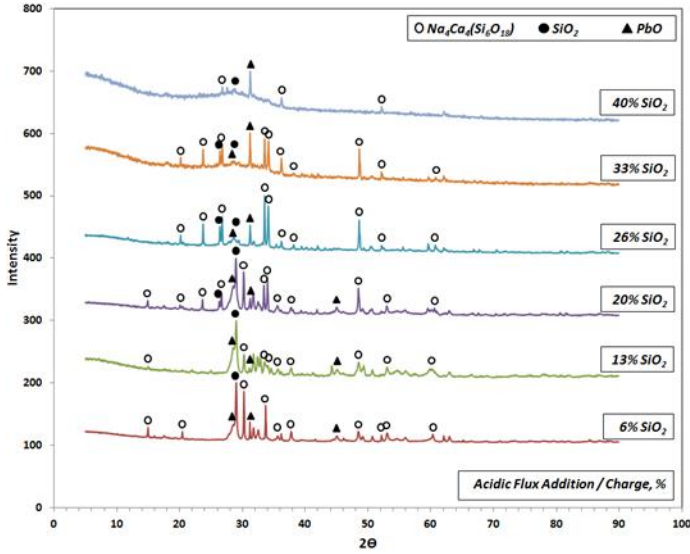


Figure 8. XRD patterns of slag phases for the quartz addition experiments.

Şekil 8. Kuvars ilavesi deneyleri için cüruf fazlarının XRD desenleri.

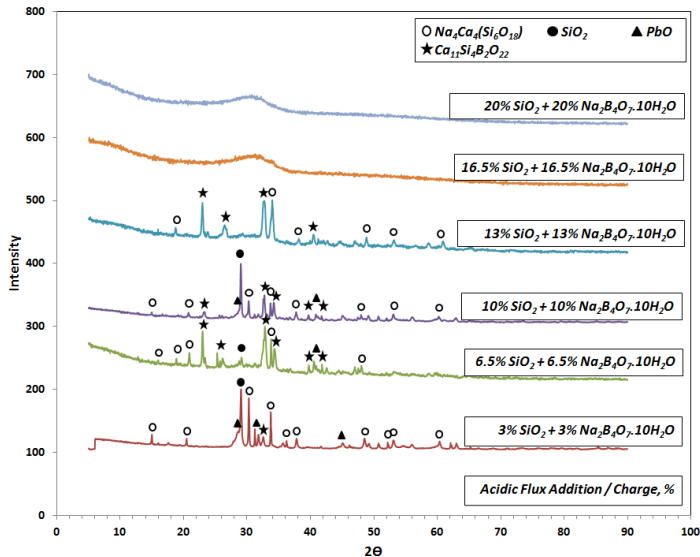


Figure 9. XRD patterns of slag phases for the experiments using quartz and borax together.

Şekil 9. Kuvars ve boraks birlikte kullanılan deneyler için cüruf fazlarının XRD desenleri.

The findings showed that, for all percentages of borax addition, the amount of lead phases obtained was almost consistent. After adding 26% weight percent quartz, it increased (in contrast to the overall charge). For the amounts of metallic lead phase that were obtained, the experimental series with borax added alone and borax-quartz added without a 6% addition ratio produced nearly identical findings. Figure 4 shows the metallic lead phase with a hollow circle and no acidic flux additions. As can also be seen from Figure 4, before the addition of quartz, the slag phase's acidity was sufficient that, following the high addition rates of 20 wt.%, produced precise and trustworthy outcomes. The addition of borax did not affect lead phase recovery. In order to attain acceptable metallic phase recovery rates, adding borax and quartz combined accelerated and decreased the flux addition rates to 13 wt.%.

When acidic flux was added, the weight variations of the gold-silver containing beads and the amounts of metallic lead phase were comparatively equal. The weight of the beads was impacted by the amount of silver they contained, but the samples' silver content was not examined because it was below the limit of detection.

Because of the nugget effect, it is common for ppm level gold analysis of gold ores to yield results in a range. The "Nugget Effect" is a geostatistical variability phenomenon resulting from the heterogeneous distribution of particularly valuable minerals (such as gold and diamonds) in mineral deposits. It can complicate the estimation of gold resources and reserves as it can lead to high variability in sample grades [Clark, 2010; Bachmann, 1993]. Results greater than 2 g/t were recognized as accurate in this investigation. When borax was added separately as an acidic flux, all addition rates between 6 and 40 weight percent yielded extremely accurate results. Over 26 weight percent, quartz addition resulted in satisfactory results. Finally, adding the borax-quartz mixture at a concentration higher than 20 percent showed results that were acceptable. Slag viscosity decreased with borax addition, which had a significant impact on gold recovery. Without the addition of acidic flux, slag production was stable. Gold recovery reduced to 26 wt.% as quartz adding increased. Individual borax addition maintained the same recovery rate, but the combination of quartz and borax achieved a steady state recovery rate at 13 wt.%.

In experiments with only sodium borax decahydrate addition, $\text{Na}_4\text{Ca}_4(\text{Si}_6\text{O}_{18})$ and $\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$ were the main phases in slag phases as the acidic flux addition increased. The slag phases also contained PbO. In the series of trials in which quartz was added separately, the $\text{Na}_4\text{Ca}_4(\text{Si}_6\text{O}_{18})$ phase emerged as dominant. The formation of an amorphous glassy phase was clearly seen as SiO_2 concentration increased. For the trials, sodium borax decahydrate and quartz were combined to produce $\text{Na}_4\text{Ca}_4(\text{Si}_6\text{O}_{18})$ and $\text{Ca}_{11}\text{Si}_4\text{B}_2\text{O}_{22}$ phases, with an amorphous glassy phase occurring at lower addition ratios.

4. Conclusion

The effects of quartz, sodium borax decahydrate, and acidic fluxes on the fire assay of carbonate gold ores were investigated in this study. It was obvious that borax provided a lower viscosity for the slag phase and improved the recovery of metallic lead, beads, and gold. Because of the nugget effect observed throughout these analytical methods, gold recovery levels greater than 2 g/t were recognized as accurate. The experimental series without borax and quartz resulted in virtually satisfactory results. Before the addition of acidic fluxes, the slag phase was in a stable condition.

For borax additions between 6 and 40 weight percent, the results were satisfactory. To achieve precise results, quartz addition must be greater than 26 wt.%, and the borax-quartz combination must be greater than 20 wt.% due to the production of glassy slag. The presence of SiO_2 in slag causes the production of the glassy slag phase, which allows for reliable findings from fire assays of carbonate gold ores, as seen by the XRD pattern. This case shows that this approach can be effectively preferred over a fire assay methodology that combines calcination and fire assay for the direct fire assay of carbonate gold ores.

5. Conflicts of Interest

The authors declare no conflict of interest.

6. References

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