Mile Dimitrijević, Daniela Urošević**, Snežana Milić*, Tamara Urošević***

COPPER EXTRACTION FROM COPPER SMELTER SLAG WITH PYRITE OR FLOTATION TAILINGS FOLLOWED BY WATER LEACHING ***

Abstract

This work presents the study of copper extraction from smelter slag, which is subjected to sulphating. Sulphating of slag was performed by pyrite concentrate or flotation tailings at temperatures from 500 to 650°C, and the resulting calcine was leached with water. The results showed that maximum copper leaching (70-73%) is obtained from calcine, obtained by two - and three hour sulphating at 550°C. The process is selective since only 3-5% of iron is leached. In addition to sulphating temperature, it was found that a great effect on copper leaching has the pyrite/flotation tailings: ratio. The best results were achieved by sulphating of 5.00 g slag with 2.00 g of pyrite or 3.00 g of tailings.

Keywords: *smelter slag, roasting, pyrite, leaching*

INTRODUCTION

Approximately 80% of the world copper production originates from pyrometallurgical processing of copper sulphide concentrates [1]. According to the International Copper Study Group, the copper production in 2013 reached a figure of 21 million tons, out of which the pyrometallurgical processing of sulphide concentrates produced about 16.8 million tons of copper. It is estimated that at every ton of produced copper there are about 2.2 to 3.0 tons of slag, which means that in the world, in 2013, about 40 million tons of slag was generated. Slag contains about 0.5 to 2.1% copper and was traditionally deposited as the waste material [2-5]. However, today's demand for copper is such that the slag of about 1% copper is

considered as the valuable secondary raw material [6].

This is explained by the fact that today the ore with low copper content $\leq 1.0\%$ (open pit mining the ore with $\leq 0.5\%$ Cu) are mined, which entails larger volume of mining operations, larger amount of solid waste and increasing environmental degradation. On the other hand, the slag processing avoids costly mining operations, except for crushing and grinding. In addition, the increasing restrictions on environmental protection and new knowledge that flushing the trace metals from slag can contaminate soil and groundwater have focused the research in the direction of slag use in the construction industry. Although large amounts of

* *University in Belgrade, Technical Faculty in Bor, VJ 12, 19210 Bor, Serbia*

** *Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor,*

contact person: daniela.urosevic@irmbor.co.rs

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copper and sometimes other metals (Co, Ni, Zn ...) lie in discarded slag, there are no simple ways of their separation. Copper slag consists mainly of fayalite and magnetite and sulphide solid solutions of Cu-Fe-S which are in the form of droplets embedded in the iron-silicate basis. Copper may be present as Cu_2S , Cu_2O , CuO , copper metal and in the form of residual sulfides (chalcopyrite, bornite) [2,7]. Generally, copper slag is a complex raw material which is confirmed by numerous studies carried out in order to find the most efficient way to extract copper and other valuable metals from slag. Studies are focused on the atmospheric leaching by various reagents (acids, bases, salts) or acid leaching under pressure in autoclaves. In addition, the combined procedures roasting-leaching were studied a lot, which proved to be the most effective, as well as different techniques of froth flotation [2-6,8]. Flotation of copper slag is applied at industrial scale for decades and it is similar to the flotation of sulphide ores. In RTB Bor, in the industrial site of Copper Smelter and Refineries, 16-18 million tons of slag is deposited with the average copper content of 0.65-0.80%. In June 2002, the industrial processing of flash furnace slag from the Copper Smelter in Bor has started using the existing production line for copper and pyrite flotation [9].

Although the flotation processing reached a figure of almost one million tons of slag per year, the copper recovery remained low ($\leq 50\%$) [10]. The reason for

this is the presence of 15-20 % of copper oxide in slag and concentrated sulphide copper in the size classes below $38\ \mu\text{m}$ [11]. Therefore, in the tailings from the flotation of slag, copper lags whose concentration is similar to the content of copper in the ore that is mined at the open pit in Veliki Krivelj. For these reasons, this work has studied the roasting-leaching of slag from flash furnace in order to determine the optimal parameters of copper extraction. Combined methods of roasting - leaching usually imply the suitable reagents (H_2SO_4 , $\text{Fe}_2(\text{SO}_4)_3$, H_2S , FeS_2 ...) perform firstly the sulphating of slag, and to leach by water the resulting sulphatic compounds and thus to convert the valuable metals solution [12,13]. This work has studied the sulphating potential of waste products, pyrite concentrates and flotation tailings, which contain the certain amount of copper.

EXPERIMENTAL PART

The experiments were performed with the flash furnace slag which was taken from the belt from the process of slag crushing in the Flotation Plant Bor. Slag was ground, classified and the class $-75\ \mu\text{m}$ was separated for testing. The purified pyrite concentrate from the Flotation Plant Veliki Krivelj and flotation tailings from the old flotation tailing dump in Bor were sieved and also separated in the same class $-75\ \mu\text{m}$. Chemical composition of tested samples is given in Table 1.

Table 1 Chemical analysis of slag, pyrite and tailings (% mass)

Metal content in samples (%)	Cu	Fe	Zn
Slag	0.97	39.09	0.79
Concentrate FeS_2	0.21	37.10	0.007
Flotation tailings	0.26	10.56	0.045

The experiments were carried out such as 5.00 g of slag was fine mixed and homogenized with the appropriate amount of

pyrite or tailings in ceramic pots, and then roasted at different temperatures ($500\text{--}650^\circ\text{C}$) in a classical laboratory annealing

oven. Roasting was 1, 2 or 3 hours, and the resulting calcine was cooled, comminuted and leached with distilled water at room temperature for the period of 30 minutes at stirring rate of 350 min^{-1} . Solutions for analyses were previously filtered, completed in the normal dishes and analyzed for copper, iron and zinc using the method of atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Slag sulphating with pyrite

Pyrite, FeS_2 , is the main tailings sulphide mineral that occurs in the production of sulphide copper concentrates, and it can be set aside as a selective concentrate containing gold if it contains the market value. Roasting of pyrite resulted into iron oxides and SO_2 is released, according to the following reactions:

The released CO_2 gas in the reaction with slag results into sulphating the present compounds of copper, iron and zinc, which are easily soluble in water. Although in the industrial conditions the pyrite roasting occurs at $700\text{-}900^\circ\text{C}$, TG and DTA analyzes show that pyrite decomposition begins at 440°C and that the main exothermic peak occurs at 540°C [14,15]. In this work, the temperature of slag roasting with pyrite at 550°C was selected based on previous studies where it was found that copper leaching begins to decrease rapidly above this temperature [12, 16]. The mass of pyrite as sulphating agents was 3, 5 and 7g. The results of copper, iron and zinc leaching are shown in Table 2. Copper leaching increases with time and it is the highest for 3 hours of roasting pyrite at the lowest weight of pyrite of 3g. Generally, copper leaching is low and it varies in the range of 10.49 to 25.73%. Regarding to the iron leaching, it is extremely low, while zinc leaching is higher but below 10%. Leaching of iron and zinc is followed by copper leaching so that the highest dissolution of Cu, Fe and Zn was achieved with a mixture of 5 g of slag and 3 g and pyrite in roasting time of 3 hours (Table 2).

Table 2 Metal leaching from calcine obtained by slag roasting with different amounts of pyrite at 550°C , at different roasting times

Mixture slag- pyrite	Roasting time (hour)	Metal leaching (%)		
		Cu	Fe	Zn
3.00 g FeS_2 and 5.00 g slag	1	14.06	0.56	4.53
	2	17.15	0.91	5.79
	3	25.73	1.39	8.31
5.00 g FeS_2 and 5.00 g slag	1	12.80	0.41	3.52
	2	16.00	0.57	5.28
	3	20.28	1.03	7.03
7.00 g FeS_2 and 5.00 g slag	1	10.49	0.25	3.25
	2	13.49	0.44	4.75
	3	15.84	0.46	5.50

Under similar experimental conditions (550°C, 2 hours of roasting) leaching was attained of 74% Cu, 22% Zn and 3% Fe from the flash furnace slag of the smelter Ergani in Turkey [16]. In doing so, the fraction of slag -63µm and ratio pyrite/slag 0.25 were used. On the other hand, Bulut et al. [17] determined by roasting of old slag from the region Küre in Turkey with pyrite and lea-

ching with water that the optimal parameters were: the roasting temperature of 450°C, the roasting time 1 hour, and the ratio of pyrite : slag 1: 2. This also resulted in leaching of 60% Cu and 13% Fe. For these reasons, a new series of experiments was carried out at 500, 550, 600 and 650°C in the ratio pyrite/slag 0.4. The obtained results are shown in Table 3.

Table 3 Metal leaching from calcine obtained by slag roasting at different temperatures 550°C and different roasting times (2.00g FeS₂ and 5.00g slag)

Roasting time (hour)	Temperature (°C)	Metal leaching (%)		
		Cu	Fe	Zn
1	500	48.04	2.68	11.36
2	500	64.06	2.88	15.66
3	500	65.84	2.88	15.91
1	550	48.04	2.32	15.15
2	550	67.62	4.00	22.72
3	550	72.95	4.76	22.72
1	600	56.94	1.78	19.70
2	600	51.60	0.92	19.70
3	600	48.04	0.48	18.18
1	650	49.82	0.48	18.94
2	650	48.04	0.04	18.18
3	650	40.93	0.02	18.18

The results show that maximum copper leaching of 72.95 % Cu (4.76 % Fe and 22.72 % Zn) was realized by three-hour roasting of slag with pyrite at temperature of 550°C.

Sulphating of slag with flotation tailings

Flotation tailing was used as sulphating agent since it contains pyrite but also copper. Since the content of pyrite in tailings is 3-4 times lower than in the pyrite concentrate, large amounts of tailings were used for sulphating of slag. Leaching of the obtained

calcine with water results into leachates of Cu, Fe and Zn and they are shown in Table 4.

Comparing the results in Table 4 with those given in Table 2, it can be said that there are no major differences. Copper leaching is slightly higher and it is in the range of 12.82 % to 26.37 %, but the overall leaching of Cu, Fe and Zn is quite low. Increasing the degree of leaching of Cu, Fe and Zn with roasting time, observed in slag roasting with, was also noticed in slag roasting with tailings, but only for mixture of 15.00 g tailings + 5.00 g of slag.

Table 4 Metal leaching from calcine obtained by slag roasting with different amounts of flotation tailings at 550°C, at different roasting times

Mixture slag- tailings	Roasting time (hour)	Metal leaching (%)		
		Cu	Fe	Zn
5.00 g tailings and 5.00 g slag	1	23.80	1.53	6.47
	2	24.61	1.49	6.47
	3	20.00	1.36	5.28
10.00 g tailings and 5.00 g slag	1	12.82	0.53	3.41
	2	21.79	1.42	5.45
	3	20.51	1.63	5.45
15.00 g tailings and 5.00 g slag	1	15.38	0.45	2.83
	2	21.98	1.14	5.45
	3	26.37	1.97	6.74

Following the same reasons, a new series of experiments was carried out here, at the same conditions as roasting with pyrite with, except that the ratio of flotation tailings/slag was 0.6. The obtained results are shown in Table 5. Analyzing the results, it is observed that the leachates of Cu, Fe and Zn are similar to roasting at 500 and 550°C. However, here is observed that maximum copper leaching was achieved by two-hour roasting of slag with tailings at 550°C. This also resulted in leaching of 70.23 % Cu, 2.97 % Fe and 17.11 % zinc. Sulphating of slag with flotation tailings yielded solid results, since the aim of this study was to transform into solution as more copper (and zinc) from slag, with minimum dissolution of iron. Comparing the sulphating potentials of tailings and pyrite (Tables 3 and 5, the shaded areas), it can be seen that they are similar and that the best effect is achieved by roasting at 550°C, two or three hours. Comparing these results with those obtained by sulphating of slag with sulfuric acid, also at 550°C [12], it can be said that the leaching of copper is higher, about 90%, and the leaching of iron about 40% when sulphating is done

done with sulfuric acid. So, from the point of copper leaching leaching, sulfuric acid is more efficient sulphating agent because using the pyrite or tailings, the leaching of copper is about 70 %. However, from the viewpoint of selectivity, it should be noted that by the use of pyrite or tailings (leaching of calcine) only 3 to 5 % Fe is transformed into solution. Low iron leaching, determined in this work, is desirable from the standpoint of the subsequent treatment of leaching solution, which was not the case with sulphating with sulfuric acid. Increasing temperature above 550°C leads to further decrease of iron leaching as at 600°C (and higher temperatures) iron is practically absent in alkaline solutions. However, the problem is that at 600°C it leads to decomposition of copper sulfate according to the reactions [16],

and with the possibility of ferrite formation:

In doing so, the newly compounds have limited solubility in water which leads to decrease of copper leaching. This can be seen in Tables 3 and 5, and in some ways

it can be considered as one of the limitations of the sulphating process of low-percentage copper raw materials.

Table 5 Metal leaching from calcine obtained by slag roasting at different temperatures and different roasting times (3.00 tailings and 5.00 g slag)

Roasting time (hour)	Temperature (°C)	Metal leaching (%)		
		Cu	Fe	Zn
1	500	61.87	2.41	13.49
2	500	61.87	2.31	13.45
3	500	63.55	2.55	15.89
1	550	61.87	3.13	14.67
2	550	70.23	2.97	17.11
3	550	63.55	4.09	17.11
1	600	51.84	0.39	13.89
2	600	46.82	0.19	12.71
3	600	31.77	0.18	11.98
1	650	45.15	0.10	12.96
2	650	33.44	0.05	12.71
3	650	28.43	0.02	11.00

CONCLUSION

Roasting of slag in a mixture with pyrite or flotation tailings and leaching of the obtained calcine with water yielded solid results. Roasting temperature of 550°C frying was determined as the optimum temperature because the leaching of calcine resulted into maximum leaching of copper of 70-73 %, zinc of 17-28 % and iron of 3-5 % with a two- or three-hour roasting. These results were achieved only by sulphating with lesser amounts of pyrite (2.00 g) or flotation tailings (3.00 g). With

larger amounts of pyrite or tailings, there was a drastic decline in copper leaching, although they were approximately stoichiometric needed amount for sulphating of 5.00 g of smelting slag. Comparing the results with scarce literature data, it can be said that the attained copper leaching from the smelter slag, roasted with pyrite, was maximum possible in one-stage roasting. Possible increase of copper leaching gives the possibility to reduce the ration pyrite (tailings)/slag to 0.2 (0.3).

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Mile Dimitrijević, Daniela Urošević**, Snežana Milić*, Tamara Urošević***

EKSTRAKCIJA BAKRA IZ TOPIONIČKE ŠLJAKE PRŽENJEM SA PIRITOM ILI FLOTACIJSKOM JALOVINOM I LUŽENJEM VODOM**

Izvod

U ovom radu ispitivana je ekstrakcija bakra iz topioničke šljake koja je podvrgnuta sulfatizaciji. Sulfatizacija šljake vršena je piritnim koncentratom ili flotacijskom jalovinom na temperaturama od 500 do 650°C, a dobijeni prženci su luženi vodom. Rezultati su pokazali da se maksimalno izluženje bakra (70 - 73%) dobija iz prženaca dobijenih dvo- i tročasovnom sulfatizacijom na 550°C. Sam proces je selektivan budući da se izlučuje samo 3-5% gvožđa. Pored temperature sulfatizacije utvrđeno je da na izluženje bakra veliki uticaj ima odnos pirit/flotacijska jalovina: šljaka. Najbolji rezultati su postignuti sulfatizacijom 5,00 g šljake sa 2,00 g pirita odnosno 3,00 g jalovine.

Ključne reči: topionička šljaka, prženje, pirit, luženje

UVOD

Oko 80% svetske proizvodnje bakra potiče iz pirometalurške prerade sulfidnih koncentrata bakra [1]. Prema podacima International Copper Study Group proizvodnja bakra u 2013. godini dostigla je cifru od 21 milion tona, od čega je pirometalurškom preradom sulfidnih koncentrata proizvedeno oko 16.8 miliona tona bakra. Procenjeno je da na svaku tonu proizvedenog bakra nastaje oko 2,2–3,0 tone šljake što znači da je u svetu, u 2013. godini, generisano oko 40 miliona tona šljake. Šljaka sadrži oko 0,5-2,1 % bakra i ona se tradicionalno odlagala kao otpadni materijal [2-5]. Međutim, danas je potražnja za bakrom takva da se i šljake sa oko 1% bakra

smatraju vrednom sekundarnom sirovinom [6]. Ovo se objašnjava činjenicom da se danas eksploatišu rude sa niskim sadržajem bakra $\leq 1,0$ % (površinskim kopovima eksploatišu se rude sa $\leq 0,5$ % Cu), što povlači za sobom veći obim rudarskih radova, veću količinu čvrstog otpada i veću degradaciju životne sredine. Sa druge strane, preradom šljake izbegavaju se skupe rudarske operacije, osim drobljenja i mlevenja. Pored toga, sve veća ograničenja vezana za zaštitu životne sredine i novija saznanja da ispiranje tragova metala iz šljake može da kontaminira zemljište i podzemne vode usmerilo je istraživanja i u pravcu upotrebe šljake u građevinskoj industriji.

* Univerzitet u Beogradu, Tehnički fakultet u Boru, VJ 12, 19210 Bor, Srbija,
e-mail: daniela.urosevic@irmbor.co.rs

** Institut za rudarstvo i metalurgiju, Zeleni bulevar 35, 19210 Bor

** Rad je proizašao iz projekata broj OI 172031 "Neki aspekti rastvaranja metala i prirodnih minerala" i TR 33023 „Razvoj tehnologija flotacijske prerade ruda bakra i plemenitih metala radi postizanja boljih tehnoloških rezultata“, koji je finansiran sredstvima Ministarstva za prosvetu, nauku i tehnološki razvoj Republike Srbije

Iako velike količine bakra a ponekad i drugih metala (Co, Ni, Zn...) leže u odbacenoj šljaci nema jednostavnih načina za njihovo izdvajanje. Bakarna šljaka se sastoji pretežno od fajalita i magnetita i čvrstih sulfidnih rastvora Cu-Fe-S koji su u obliku kapljica uklopljeni u gvožđe-silikatnoj osnovi. Sam bakar može biti prisutan kao Cu₂S, Cu₂O, CuO, metalni bakar i u obliku zaostalih sulfida (halkopirit, bornit) [2,7]. Generalno bakarna šljaka je kompleksna sirovina što potvrđuju brojna istraživanja vršena u cilju iznalaženja najefikasnijeg načina za ekstrakciju bakra i ostalih vrednih metala iz šljake. Istraživanja su fokusirana na atmosfersko luženje različitim reagensima (kiselina, baze, soli) ili na kiselinsko luženje pod pritiskom u autoklavima. Pored toga dosta su ispitivani i kombinovani postupci prženje-luženje, koji su se pokazali kao najefikasniji, kao i različite tehnike penske flotacije [2-6,8]. Flotacija bakarne šljake primenjuje se na industrijskom nivou već decenijama i slična je flotaciji sulfidnih ruda. U Rudarsko-topioničarskom basenu Bor, u industrijskom krugu Topionice i rafinacije bakra, deponovano je 16-18 miliona tona šljake sa prosečnim sadržajem bakra od 0,65-0,80 %. Juna meseca 2002. godine započela je industrijska prerada šljake plamene peći Topionice bakra u Boru korišćenjem već postojeće proizvodne linije za flotaciju bakra i pirita [9]. Iako je flotacijska prerada dostigla cifru od skoro milion tona šljake godišnje, iskorišćenje bakra ostalo je

nisko (≤ 50 %) [10]. Razlog za ovo je prisustvo 15-20 % oksidnog bakra u šljaci i skoncentrisanost sulfidnog bakra u klasama krupnoće ispod 38 μ m [11]. Zbog toga u jalovini od flotiranja šljake zaostaje bakar čija je koncentracija slična sadržaju bakra u rudi koja se eksploatiše površinskim kopom u Velikom Krivelju. Iz tih razloga u ovom radu ispitivano je prženje - luženje šljake plamene peći u cilju određivanja optimalnih parametara ekstrakcije bakra. Kombinovani postupci prženje - luženje najčešće podrazumevaju da se pogodnim reagensima (H₂SO₄, Fe₂(SO₄)₃, H₂S, FeS₂ ...) izvrši najpre sulfatizacija šljake, a da se nastala sulfatna jedinjenja izluže vodom i tako vredni metali prevedu u rastvor [12, 13]. U ovom radu ispitivan je sulfatizacioni potencijal otpadnih produkata, koncentrata pirita i flotacijske jalovine, koji u sebi sadrže i izvesnu količinu bakra.

EKSPERIMENTALNI DEO

Eksperimenti su izvedeni sa šljakom plamene peći koja je izuzeta sa trake iz procesa drobljenja šljake u pogonu Flotacije Bor. Šljaka je samlevena, klasirana i za ispitivanja izdvojena klasa -75 μ m. Prečišćeni koncentrat pirita iz Flotacije Veliki Krivelj i flotacijska jalovina sa starog flotacijskog jalovišta u Boru su prosejani i takođe izdvojeni u istoj klasi -75 μ m. Hemijski sastav ispitivanih uzoraka dat je u tabeli 1.

Tabela 1. Hemijska analiza šljake, pirita i jalovine (% mas.)

Sadržaj metala u uzorcima (%)	Cu	Fe	Zn
Šljaka	0,97	39,09	0,79
Koncentrat FeS ₂	0,21	37,10	0,007
Flotacijska jalovina	0,26	10,56	0,045

Eksperimenti su izvođeni tako što je 5,00g šljake fino mešano i homogenizovano sa odgovarajućom količinom pirita odnosno

jalovine, u keramičkim lončićima, a zatim prženo na različitim temperaturama (500-650°C) u klasičnoj laboratorijskoj peći za

žarenje. Prženje je trajalo 1, 2 ili 3 časa, a dobijeni prženac je hlađen, usitnjavan i lužen destilovanom vodom na sobnoj temperaturi u vremenu od 30 minuta, pri brzini mešanja od 350 min⁻¹. Rastvori za analize su prethodno filtrirani, kompletirani u normalne sudove i analizirani na bakar, gvožđe i cink, metodom atomske apsorpcione spektrofotometrije.

REZULTATI I DISKUSIJA

Sulfatizacija šljake piritom

Pirit, FeS₂ je glavni jalovinski sulfidni mineral koji se javlja pri proizvodnji sulfidnih koncentrata bakra, a može se izdvojiti i kao selektivni koncentrat koji ako sadrži zlato može imati i tržišnu vrednost. Prženjem pirita nastaju oksidi gvožđa i oslobađa se SO₂ prema sledećim reakcijama:

Oslobodeni SO₂ gas u reakciji sa šljakom dovodi do sulfatizacije prisutnih jedi-

njenja bakra, gvožđa i cinka koja su lako rastvorna u vodi. Iako se u industrijskim uslovima prženje pirita odvija na 700 - 900°C, TG i DTA analize pokazuju da razlaganje pirita počinje od 440°C i da se glavni egzotermni pik javlja na 540°C [14, 15]. U ovom radu temperatura prženja šljake sa piritom od 550°C odabrana je na osnovu prethodnih istraživanja u kojima je utvrđeno da izluženje bakra počinje naglo da opada iznad ove temperature [12, 16]. Masa pirita kao sulfatizacionog agensa bila je 3, 5 i 7 g. Rezultati izluženja bakra, gvožđa i cinka prikazani su u tabeli 2. Izluženje bakra raste sa vremenom prženja i najveće je za 3 časa prženja pri najmanjoj masi pirita od 3g. Generalno, izluženje bakra je nisko i kreće se u opsegu od 10,49 do 25,73 %. Što se tiče izluženja gvožđa ono je izuzetno nisko, dok je izluženje cinka veće ali je ispod 10 %. Izluženja gvožđa i cinka prate izluženje bakra tako da je najveće rastvaranje Cu, Fe i Zn postignuto sa mešavinom 5 g šljake i 3 g pirita i pri vremenu prženja od 3 časa (tabela 2).

Tabela 2. Izluženje metala iz prženaca dobijenih prženjem šljake sa različitim količinama pirita na 550°C, pri različitim vremenima prženja

Smesa šljaka- pirit	Vreme prženja	Izluženje metala (%)		
		Cu	Fe	Zn
3,00 g FeS ₂ i 5,00 g šljake	1 čas	14,06	0,56	4,53
	2 časa	17,15	0,91	5,79
	3 časa	25,73	1,39	8,31
5,00 g FeS ₂ i 5,00 g šljake	1 čas	12,80	0,41	3,52
	2 časa	16,00	0,57	5,28
	3 časa	20,28	1,03	7,03
7,00 g FeS ₂ i 5,00 g šljake	1 čas	10,49	0,25	3,25
	2 časa	13,49	0,44	4,75
	3 časa	15,84	0,46	5,50

Pri sličnim eksperimentalnim uslovima (550°C, 2 časa prženja) postignuto je izluženje od 74% Cu, 22% Zn i 3% Fe iz šljake plamene peći topionice Ergani u Turskoj [16]. Pri tome korišćena je frakcija šljake - 63 µm i odnos pirit/šljaka 0.25. S druge strane Bulut i saradnici [17] su, prženjem stare šljake iz regiona Küre u Turskoj sa

piritom i luženjem vodom, utvrdili da su optimalni parametri: temperatura prženja 450°C, vreme prženja 1 čas i odnos pirit : šljaka 1:2. Pri tome je postignuto izluženje od 60% Cu i 13% Fe. Iz tih razloga urađena je nova serija eksperimenata na 500, 550, 600 i 650°C pri odnosu pirit/šljaka 0,4. Dobijeni rezultati prikazani su u tabeli 3.

Tabela 3. Izluženje metala iz prženaca dobijenih prženjem šljake na različitim temperaturama i pri različitim vremenima prženja (2,00 g FeS₂ i 5,00 g šljake)

Vreme prženja (čas)	Temperatura (°C)	Izluženje metala (%)		
		Cu	Fe	Zn
1	500	48,04	2,68	11,36
2	500	64,06	2,88	15,66
3	500	65,84	2,88	15,91
1	550	48,04	2,32	15,15
2	550	67,62	4,00	22,72
3	550	72,95	4,76	22,72
1	600	56,94	1,78	19,70
2	600	51,60	0,92	19,70
3	600	48,04	0,48	18,18
1	650	49,82	0,48	18,94
2	650	48,04	0,04	18,18
3	650	40,93	0,02	18,18

Rezultati pokazuju da je maksimalno izluženje od 72,95% Cu (4,76% Fe i 22,72% Zn) postignuto tročasovnim prženjem šljake sa piritom na temperaturi od 550°C.

Sulfatizacija šljake flotacijskom jalovinom

Flotacijska jalovina iskorišćena je kao sulfatizacioni agens, jer u sebi sadrži pirit ali i bakar. Kako je sadržaj pirita u jalovini 3-4 puta manji nego u koncentratu pirita korišćene su veće količine jalovine za sulfati-

zaciju šljake. Luženjem dobijenih prženaca vodom dobijena su izluženja Cu, Fe i Zn prikazana u tabeli 4.

Poredeći rezultate u tabeli 4 sa onima datim u tabeli 2 može se reći da bitnijih razlika nema. Izluženje bakra je nešto veće i kreće se u opsegu od 12,82 % do 26,37 %, ali su generalno izluženja Cu, Fe i Zn dosta niska. Povećanje stepena izluženja Cu, Fe i Zn sa vremenom prženja, uočeno kod prženja šljake sa piritom, uočeno je i kod prženja šljake sa jalovinom ali samo za smesu 15,00 g jalovine + 5,00 g šljake.

Tabela 4. Izluženje metala iz prženaca dobijenih prženjem šljake sa različitim količinama flotacijske jalovine na 550°C, pri različitim vremenima prženja

Smesa šljaka- jalovina	Vreme prženja	Izluženje metala (%)		
		Cu	Fe	Zn
5,00 g jalovine i 5,00 g šljake	1 čas	23,80	1,53	6,47
	2 časa	24,61	1,49	6,47
	3 časa	20,00	1,36	5,28
10,00 g jalovine i 5,00 g šljake	1 čas	12,82	0,53	3,41
	2 časa	21,79	1,42	5,45
	3 časa	20,51	1,63	5,45
15,00 g jalovine i 5,00 g šljake	1 čas	15,38	0,45	2,83
	2 časa	21,98	1,14	5,45
	3 časa	26,37	1,97	6,74

Rukovodeći se istim razlozima i ovde je urađena nova serija eksperimenata, pri istim uslovima kao i kod prženja sa piritom s tim što je odnos flotacijska jalovina/šljaka bio 0,6. Dobijeni rezultati prikazani su u tabeli 5. Analizirajući rezultate uočava se da su izluženja Cu, Fe i Zn slična kod prženja na 500 i 550°C. Ipak i ovde se uočava da je maksimalno izluženje bakra postignuto dvočasovnim prženjem šljake sa jalovinom na 550°C. Pri tome je postignuto izluženje od 70,23% Cu, 2,97% Fe i 17,11% Zn. Sulfatizacija šljake flotacijskom jalovinom dala je solidne rezultate budući da je cilj ovog istraživanja bio da se prevede u rastvor što više bakra (i cinka) iz šljake, uz minimalno rastvaranje gvožđa. Poredeći sulfatizacije potencijale jalovine i pirita (tabele 3 i 5, osenčena polja) uočava se da su oni slični i da se najbolji efekat postiže prženjem na 550°C, dva odnosno tri časa. Poredeći ove rezultate sa onima dobijenim sulfatizacijom šljake sumpornom kiselinom, takođe na 550°C [12], može se reći da je izluženje bakra veće, oko 90%, a izluženje gvožđa oko 40% kada se sulfatizacija vrši

sumpornom kiselinom. Znači sa stanovišta izluženja bakra H₂SO₄ je efikasniji sulfatizacioni agens jer korišćenjem pirita ili jalovine izluženje bakra je oko 70%.

Međutim, sa stanovišta selektivnosti treba reći da se korišćenjem pirita odnosno jalovine (luženjem prženaca) samo 3 do 5% Fe prevodi u rastvor. Nisko izluženje gvožđa određeno u ovom radu je poželjno sa stanovišta kasnijeg tretmana lužnih rastvora, što nije bio slučaj kod sulfatizacije sumpornom kiselinom. Povećanje temperature iznad 550°C dovodi do daljeg opadanja izluženja gvožđa tako da na 600°C (i većim temperaturama) gvožđa praktično više i nema u lužnim rastvorima. Međutim, problem je što na 600°C dolazi do dekompozicije sulfata bakra prema reakcijama [16],

i uz mogućnost nastajanja ferita:

Pri tome novonastala jedinjenja imaju ograničenu rastvorljivost u vodi što dovodi do opadanja izluženja bakra. Ovo se može

videti u tabelama 3 i 5 i na neki način može se smatrati jednim od ograničenja procesa sulfatizacije niskoprocentnih sirovina bakra.

Tabela 5. Izluženje metala iz prženaca dobijenih prženjem šljake na različitim temperaturama i pri različitim vremenima prženja (3,00 g jalovine i 5,00 g šljake)

Vreme prženja (čas)	Temperatura (°C)	Izluženje metala (%)		
		Cu	Fe	Zn
1	500	61,87	2,41	13,49
2	500	61,87	2,31	13,45
3	500	63,55	2,55	15,89
1	550	61,87	3,13	14,67
2	550	70,23	2,97	17,11
3	550	63,55	4,09	17,11
1	600	51,84	0,39	13,89
2	600	46,82	0,19	12,71
3	600	31,77	0,18	11,98
1	650	45,15	0,10	12,96
2	650	33,44	0,05	12,71
3	650	28,43	0,02	11,00

ZAKLJUČAK

Prženje šljake u smesi sa piritom odnosno flotacijskom jalovinom i luženje dobijenih prženaca vodom dalo je solidne rezultate. Temperatura prženja od 550°C je određena kao optimalna temperatura jer je luženjem prženaca dobijeno maksimalno izluženje bakra od 70-73 %, cinka 17-28 % i gvožđa 3-5 % uz dvo- odnosno tročasovno prženje. Ovi rezultati su postignuti samo sulfatizacijom sa manjim količinama pirita (2,00 g) odnosno flotacijske jalovine (3,00 g). Pri većim količinama pirita odno-

sno jalovine dolazilo je do drastičnog opadanja izluženja bakra iako su to bile približno stehiometrijski potrebne količine za sulfatizaciju 5,00 g topioničke šljake. Poredeći dobijene rezultate sa oskudnim literaturnim podacima može se reći da je postignuto izluženje bakra iz topioničke šljake pržene sa piritom maksimalno moguće kod jedno-stadijalnog prženja. Malo prostora za eventualno povećanje izluženja bakra daje mogućnost smanjenja odnosa pirit (jalovina) / šljaka na 0,2 (0,3).

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