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UTICAJ MEHANO-HEMIJSKE AKTIVACIJE FLOTACIJSKE JALOVINE NA STEPEN IZDVAJANJA KORISNIH KOMPONENTI[****]

Izvod

Prikazani rezultati odnose se na ispitivanje uticaja mehano-hemijske aktivacije flotacijske jalovine na stepen izluženja bakra, gvožđa i sumpora u sumporno-hloridnom rastvoru uz dodatak H_2O_2 kao oksidansa. Uzorak borske flotacijske jalovine (BFJ) sa lokacije starog borskog flotacijskog jalovišta sadrži 23% pirita i 75,23% jalovine kao osnovne komponente, a aktiviran je suvim postupkom u vibro mlinu bez i sa dodatkom NaOH kao hemijskog reagensa, uzorci BFJ1 i BFJ2, respektivno. Suvom magnetnom separacijom u visokogradijentnom magnetnom separatoru "Sala", uzorci su razdvojeni na magnetičnu i nemagnetičnu frakciju, BFJ MF i BFJ NMF, respektivno.

Luženje različito tretiranih uzoraka pokazalo je da je najviši stepen izluženja bakra, 98,7 %, postignut kod uzorka BFJ2 MF dok je stepen izluženja Fe i S viši kod nemagnetičnih frakcija, i kreće se do 92,46 % kod uzorka BFJ1 NMF za Fe i 80,62 % za S iz uzorka BFJ2 NMF.

***Ključne reči:**, flotacijska jalovina, mehano-hemijska aktivacija, magnetna separacija, luženje, Cu, Fe, S*

UVOD

Mehanohemijska aktivacija u oblasti rudarsko-metalurške prerade sve više dobija na primatu na nivou industrijske proizvodnje mineralnih sirovina(1). Efekti mehaničke aktivacije se odnose na preuređenje kristalne strukture mineralne sirovine fizičkim procesima i dobijanju metala bez predhodnog oksidacionog prženja a samim tim i bez emisije štetnog gasa SO_2 u atmosferu. Takodje i hidrometalurški procesi sve više dobijaju na značaju zahvaljujući sve strožim ekološkim pravilima.

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Tehnološka ispitivanja prerade mehanohemijski aktiviranog pirita borske flotacijske jalovine imala su za cilj ispitivanje uticaja mehano-hemijske aktivacije na stepen izluženja bakra, gvožđa i sumpora korišćenjem kombinovanog sumporno-hloridnog rastvora uz dodatak H_2O_2 kao oksidansa.

Mehanohemijska aktivacija uzorka BFJ uradena je u laboratorijama ITNMS – Beograd. Efektivnost izluženja korisnih komponenti u velikoj meri zavisi od stepena otvaranja minerala i otvorenosti površina [2]. Brzina prelaza elemenata u rastvor u opštem slučaju zavisi od veličine površine čvrstih čestica, a za neke tipove ruda krupnoća pretstavlja osnovni faktor izlužljivosti [3].

EKSPERIMENTALNA ISTRAŽIVANJA

Fizičko-hemijska karakterizacija uzorka borske flotacijske jalovine (BFJ)

Hemijska karakterizacija uzorka borske flotacijske jalovine korišćene za proces luženja kombinovanim sumporno-hloridnim rastvorom uz dodatak H_2O_2 kao oksidansa, prikazana je u tabeli 1, a mineraloška analiza, u tabeli 2.

Tabela 1. *Hemijska analiza BFJ*

Elemenat ili jedinjenje	Sadržaj %
Fe	4,82
S	6,20
Cu–oksidni	0,006
Al_2O_3	15,63
SiO_2	61,60
MgO	0,014
Cu–ukupno	0,131
Fe_3O_4	0,359
SO_4^{2-}	/

Tabela 2. *Mineraloška analiza uzorka BFJ*

Minerali	Kvalitativno, %
Pirit	23
Halkopirit	0,124
Pirotin	< 1 ppm
Rutil	0,98
Limonit	0,234
Jalovina	75,23

Rezultati sitovne analize koja je urađena standardnom metodom prosejavanja, na seriji sita tipa TYLER, prikazani su u tabeli 3.

Tabela 3. *Sitovna analiza uzorka BFJ*

Klasa krupnoće mm	Maseno učešće %
-0,600+0,425	2,40
-0,425+0,300	5,60
-0,300+0,212	10,00
-0,212+0,106	24,80
-0,106+0,075	9,60
-0,075+0,038	11,60
-0,038+0,020	7,20
-0,020	28,80

Za određivanje nasipne mase uzorka BFJ, koja iznosi 2930 kg m^{-3}, korišćena je VMK (Validna metoda kuće – IRM Bor) - Određivanje zapreminske mase i nasipne mase uzoraka (E.b.11:2007).

Postupak mehano-hemijskog tretmana (MC-H) uzorka BFJ vršen je u laboratorijskom vibro mlinu Humbolt. Mlin ima radnu temperaturu oko 340 K kada radi u kontinuitetu. Mlin može da ostvari rad dispergovanja u visini 7,3 x10^3 $KJmol^{-1}$.

To je, prema literaturnim podacima (1), dovoljna energija da izazove cepanje pet nivoa d orbitala slobodnog jona feruma iz pirita u oktaedarskom ligandnom polju. Izvršena su dva opita MC-H tretiranja BFJ suvim postupkom. U prvom opitu izvršeno je optimalno aktiviranje BFJ bez dodataka reagenasa (BFJ1).
U drugom opitu je dodat NaOH u količini od 4%, (BFJ2).

Magnetna koncentracija vršena je na visokogradijentnom magnetnom separatoru (HGMS) Sala u vodenoj sredini.

Ispitivanja lužljivosti Cu, Fe i S iz dobijenih frakcija izvedena su na opremi laboratorijskog tipa korišćenjem 0.8 M H_2SO_4 uz dodatak 30 % H_2O_2 kao oksidansa i uz prisustvo hlornih jona koji su u rastvor dodavani u obliku NaCl pri čemu je inicijalna koncentracija NaCl odgovarala 1M rastvoru.

Proces luženja odvijao se pri radnoj temperaturi rastvora od je $90\pm5^{o}C$, uz mešanje od 600 min^{-1}, pri odnosu Č:T = 1:20, u trajanju od 8 h.

Za hemijsku karakterizaciju korišćene su sledeće hemijske metode: za određivanje sadržaja S - gasna volumetrija (spaljivanje) na opremi Marsova peć a za odrešivanje sadržaja Cu i Fe – atomska apsorpciona spektrofotometrija, na opremi Atomsko apsorpcioni Spektrofotometar PERKIN ELMER 403.

REZULTATI I DISKUSIJA

Magnetni koncentrator (HGMS) daje dva proizvoda od kojih je jedan magnetična frakcija (MF) a drugi nemagnetična frakcija (NMF). Indukcija magnetnog polja (MP) je izabrana da bude B = 0,6 T. Paramagnetični minerali kao što je pirit, pri srednjem iznosu intenziteta (MP), imaju izvestan mali maseni udeo (MF). Oba MC-H tretirana uzorka BFJ podvrgnuta su postupku magnetne koncentracije. Rezultat odvajanja pojedinih frakcija prikazan je u tabeli 4. Dejstvu istog magnetnog polja B=0,6 T bio je izložen i uzorak *BFJ* koji nije *MC-H* aktiviran, i on je imao 90 g MF i 210 g NMF.

Tabela 4. *Rezultati magnetne koncentracije MC-H tretirane BFJ*

Uzorak BFJ	MC-H tretman bez reagensa	MC-H tretman sa NaOH
Nemagnetična frakcija, g	206	50
Magnetična frakcija, g	94	250
Ukupno, g	300	300

Za kompleks:

$$Na\left[\begin{matrix} SO_4 \\ Fe^{\cdots}(OH)_3 \end{matrix} \quad Fe^{\cdot\cdot} \quad \begin{matrix} Fe^{\cdots}(OH)_3 \\ SO_4 \end{matrix}\right]^{-}$$

vrednost magnetnog momenta je:

$$\mu_S = \sqrt{1(1+2)} \cdot \mu_B = 2{,}8\ \mu_B\ (5),$$

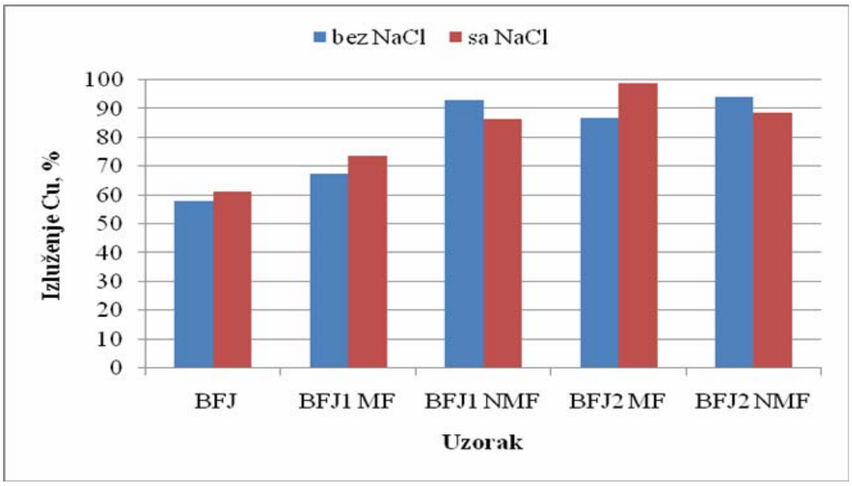
a upravo je i odnos magnetičnih frakcija iz opita magnetne koncentracije, tabela 4, približno 2,8 (94 x 2,8 = 263,2)

Tabela 5. *Hemijska karakterizacija frakcija dobijenih magnetnom separacijom*

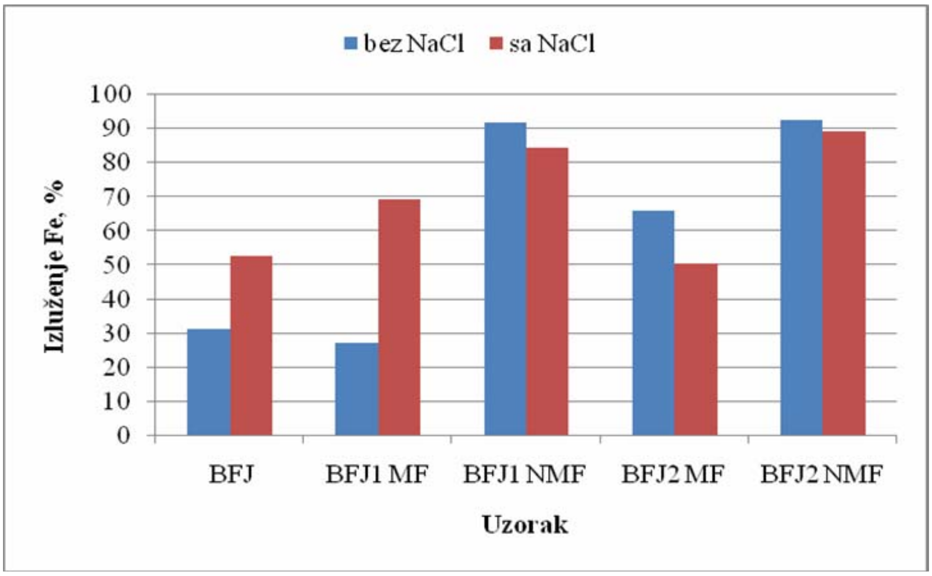
Opis	Oznaka uzorka			
	BFJ1 MF	BFJ1 NMF	BFJ2 MF	BFJ2 NMF
Fe, %	6,30	3,60	5,03	1,83
S, %	10,70	5,60	7,40	2,70
Cu–oxid, %	0,005	0,007	0,015	0,019
Al_2O_3, %	11,79	18,74	15,72	18,50
SiO_2, %	64,74	62,46	64,10	63,08
MgO, %	0,026	0,021	0,11	0,026
Cu–ukupno, %	0,152	0,153	0,135	0,134
Fe_3O_4, %	0,445	/	/	/
SO_4^{2-}, %	/	/		

Rezultati hemijske karakterizacije frakcija dobijenih magnetnom separacijom prikazani su u Tabeli 5.

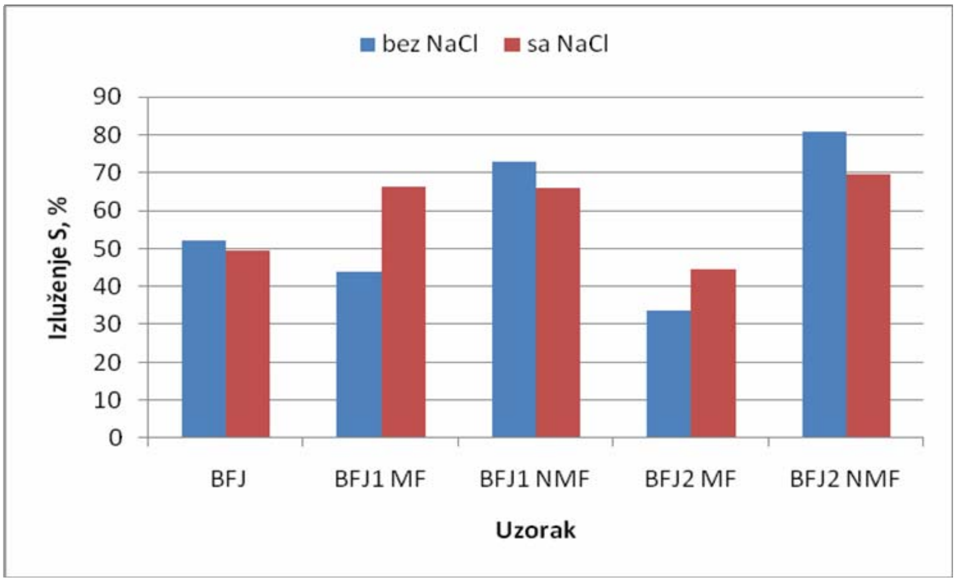
Rezultati postignutog izluženja Cu, Fe i S iz različitih uzoraka flotacijske jalovine, korišćenjem, u jednom slučaju sulfatnog rastvora bez dodatka NaCl a u drugom sa dodatkom NaCl, prikazani su na slikama 1, 2 i 3. Najviši stepen izluženja Cu postignut je kod uzorka BFJ2 MF u vrednosti od 98,75 %. Kod uzorka BFJ1 NMF karakteristično je da je postignut najviši stepen izluženja Fe a kod istog uzorka je postignut i najviši stepen izluženja S i to za proces luženja u sulfatnom rastvoru. Rezulatti izluženja pojedinih elemenata pokazuju da izluženje Cu, Fe i S ima isti trend kod svih uzoraka osim kod uzorka BFJ2 MF kod kog je izluženje gvožđa manje u kombinovanom sulfatno-hloridnom rastvoru.



Sl. 1. *Izluženje Cu iz različitih uzoraka BFJ primenom različitih lužnih rastvora*



Sl. 2. *Izluženje Fe iz različitih uzoraka BFJ primenom različitih lužnih rastvora*



Sl. 3. *Izluženje S iz različitih uzoraka BFJ primenom različitih lužnih rastvora*

ZAKLJUČAK

Na osnovu sprovedenih istraživanja vidi se da se uz pomoć *MC-H* tretmana i magnetne kocentracije može uticati na razvoj procesa koji bi omogućili odvajanje metaličnih od nemetaličnih minerala. Metalične mineralne sirovine imaju najmanje desetostruko veću vrednost u odnosu na nemetalične pa stoga treba u tom kontekstu shvatiti tehno-ekonomsku funkciju razvoja iznetog postupka tretiranja BFJ. Dalji tretman metalične i nemetaične komponente dovodi do izvlačenja korisnih komponenti i stvaranja uslova za korišćenje modifikovane nemetalične komponnte.

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EFFECT OF MECHANICAL-CHEMICAL ACTIVATION OF FLOTATION TAILINGS ON REMOVAL THE USEFUL COMPONENTS[****]

Abstract

The presented results refer to the investigation of effect the mechanical-chemical activation of flotation tailings on copper, iron and sulfur leaching degree in the sulfuric-chloride solution with the addition of H_2O_2 as oxidant. A sample of the Bor flotation tailings (BFT) from the old Bor flotation tailing dump consists of pyrite and tailings as the main components, and is activated in a dry process of the vibro mill with (BFT1) and without (BFT2) addition of NaOH as the chemical reagent. Using the dry magnetic separation in thed high-gradient magnetic separator Sala, the samples were separated into magnetic and non-magnetic fraction, BFT MF and BFT NMF, respectively.

Leaching of various treated samples showed that the highest level of copper leaching (98.7 wt %), was obtained for BFJ2 MF sample while the leaching degree of Fe and S was higher in non-magnetic fractions, up to 92.46 wt % in BFT1 NMF sample for Fe and 80.62 wt % for S in BFT2 NMF sample.

Key words: *flotation tailings, mechanical-chemical activation, magnetic separation, leaching, Cu, Fe, S*

INTRODUCTION

Mechanical-chemical activation becomes and more significant in the field of mining and metallurgy processing and industrial production of minerals [1]. The effects of mechanical activation refer to the rearrangement of mineral crystal structure by physical processes and obtaining-metal without previous oxidation roasting and therefore without emission of harmful SO_2 gas into the atmosphere.

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Also, the hydrometallurgical processes [2,3] increasingly gain in importance due to more strict environmental regulations.

Technological investigations of treatment the mechanical-chemical activated pyrite from the Bor flotation tailings was aimed to the investigation the effect of mechanical-chemical activation on the leaching degree of copper, iron and sulfur using combined sulfur-chloride solution with addition of H_2O_2 as the oxidizdant. Mechanical-chemical activation of BFT samples was done in the ITNMS-Belgrade laboratories. The efficiency of useful components leaching processes largely depends on mineral and surfaces opening [4]. Solubility rate of elements generally depends on the size of solid particle surface and, for some ore types, the grain size represents the main dissolution factor.

EXPERIMENTS

Physical-chemical characterization of the Bor flotation tailings sample (BFT)

The results of chemical characterization the Bor flotation tailings sample, used for leaching process by the mixed sulfate-chloride solution with addition of H_2O_2 as the oxidant are presented in Table 1, and mineralogical analyse in Table 2.

Table 1. *Chemical analyses of BFT*

Elements	**Content wt %**
Fe	4.82
S	6.20
Cu–oxide	0.006
Al_2O_3	15.63
SiO_2	61.60
MgO	0.014
Cu–total	0.131
Fe_3O_4	0.359

Table 2. *Mineralogical analyses of BFT*

Minerals	Content wt %
Pyrite	23
Chalcopyrite	0.124
Pyrrhotine	< 1 ppm
Rutile	0.98
Limonite	0.234
Tailings	75.23

The results of sieve analysis, carried out by the standard sieve analysis, on standard TYLER sieve, are shown in Table 3.

Table 3. *Sieve analysis*

Particle size mm	**Content wt %**
-0.600+0.425	2.40
-0.425+0.300	5.60
-0.300+0.212	10.00
-0.212+0.106	24.80
-0.106+0.075	9.60
-0.075+0.038	11.60
-0.038+0.020	7.20
-0.020	28.80

A valid method of MMI Bor - Determination of Volume Density and Apparent Density (E.b.11: 2007 was used for determination the sample apparent density.

The mechanical-chemical treatment (MC-H) was achieved using the Humboldt Wedag vibrating mill. Mill has the working temperature of about 340 K during the continual work and can achieve the dispersion work at height 7.3 x10^3 KJmol^{-1}. This is according to the literature data [1] the enough energy to cause the splitting of five levels of d orbital of free ferrum ion from pyrite in the octahedral ligand field.

Two experiments of M-CH treatment of BFT were carried out using dry procedure. In the first experiment, an optimal activation of BFT was carried out without addition of reagents (BFT1). In the second experiment, NaOH was added to the amount of 4 wt% (BFT2).

High gradient magnetic separator (HGMS) SALA was used for the magnetic concentration in aqueous medium.

Copper, iron and sulphur leaching investigations from the obtained fractions were tested in laboratory equipment using 0.8 M H_2SO_4 and with addition of 30 % H_2O_2 as the oxidant. The chlorine ions in a form of NaCl salt, with the initial concentration of 1M, were also added into the leaching solution. The leaching process was carried out at the temperature of 90±5°C with 600 min^{-1} stirring, with the proportion of solid: liquid = 1:20, for 8 hours.

The following chemical methods were used for determination the sulphur concentration: the gas volumetry (incineration) in the Mars furnace and copper and iron determination: the atomic absorption spectrophotometer PERKIN ELMER 403.

RESULTS AND DISCUSSION

Magnetic concentrator (HGMS) gives two products, one of which is magnetic fraction (MF) and the other nonmagnetic fraction (NMF). Induction of magnetic field (MP) was chosen to be B = 0.6 T. Paramagnetic minerals, such as pyrite, in the average amount of intensity (MP) have some small mass share of magnetic fraction (MF).

Both M-CH treated samples of BFT were subjected to the magnetic concentration process. The result of separation of some fractions is shown in Table 4. A sample of BFT was subjected to the effect of same magnetic field B = 0.6 T that was not MC-H activated, and had 90g MF and 210g NMF.

Table 4. *Results of magnetic concentration BFT treated by MC-H treatment*

BFT sample	MC-H treatment without chemical reagents	MC-H treatment with NaOH
NMF, g	206	50
MF, g	94	250
Total, g	300	300

For complex:

$$Na\left[\begin{matrix} SO_4 \\ Fe^{\cdot\cdot}(OH)_3 \end{matrix} \quad Fe^{\cdot\cdot} \quad \begin{matrix} Fe^{\cdot\cdot}(OH)_3 \\ SO_4 \end{matrix}\right]^-$$

Na the value of magnetic moment is

$$\mu_S = \sqrt{1(1+2)} \cdot \mu_B = 2.8\ \mu_B \quad (5),$$

and the relationship of magnetic fractions from the experiment of magnetic concentration, Table 4, is also approximately 2.8 (94 x 2.8 = 263.2).

Table 5. *Chemical characterization of fraction obtained by magnetic separation*

Element	Sample designation			
	BFJ1MF **wt %**	**BFJ1 NMF** **wt %**	**BFJ2 MF** **wt %**	**BFJ2 NMF** **wt %**
Fe	6.30	3.60	5.03	1.83
S	10.70	5.60	7.40	2.70
Cu–oxide	0.005	0.007	0.015	0.019
Al_2O_3	11.79	18.74	15.72	18.50
SiO_2	64.74	62.46	64.10	63.08
MgO	0.026	0.021	0.11	0.026
Cu–total	0.152	0.153	0.135	0.134
Fe_3O_4	0.445	/	/	/

Results of Cu, Fe and S leaching degree from different BFT samples using sulphuric acid solution without NaCl addition in one case, and sulphuric acid solution with NaCl addition in another case, are presented in Figures 1-3. The highest Cu leaching degree 98.75 wt % was obtained using BFT2 MF sample while the highest Fe and S leaching degree was obtained using BFJ1 NMF sample. The results of leaching the useful elements have shown that the possibility of Cu, Fe and S leaching have the same trend for all samples except for the BFJ2 MF sample where Fe leaching degree is lower in mixed sulphate-chloride solution.

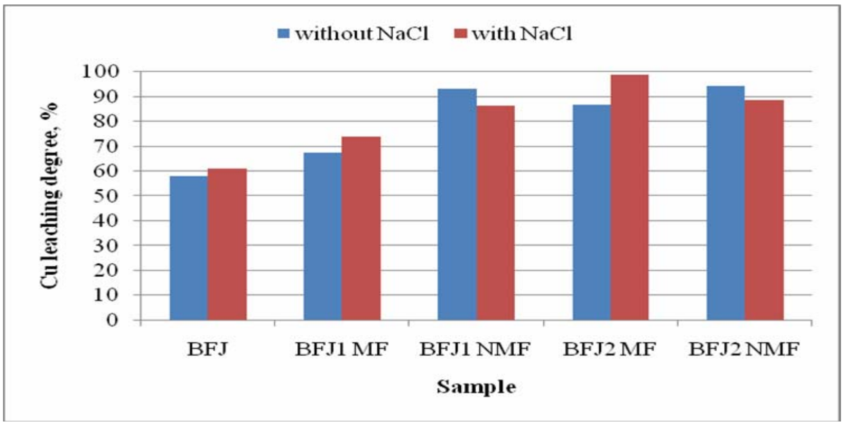

Figure 1. *Cu leaching degree from different BFT samples using various leaching solutions*

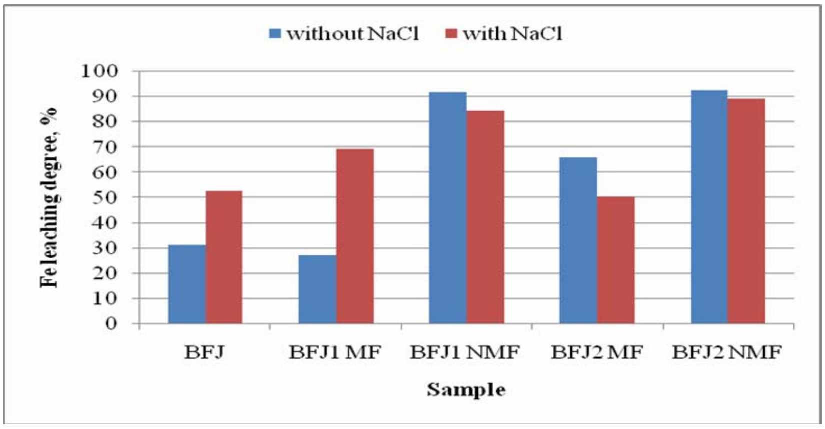

Figure 2. *Fe leaching degree from different BFT samples using various leaching solutions*

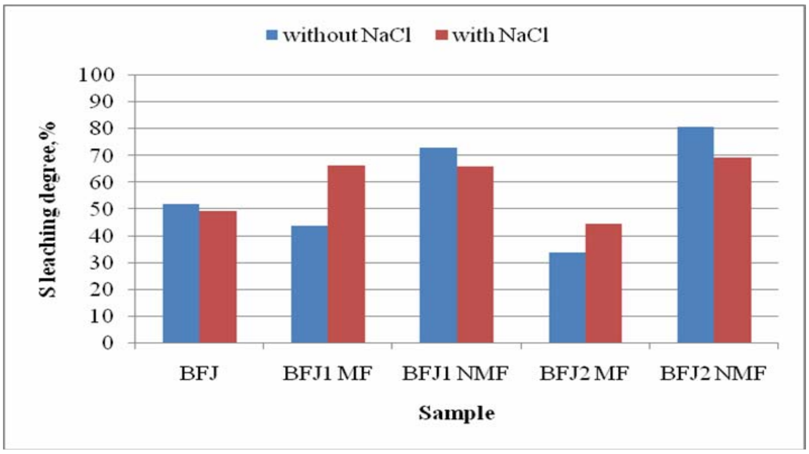

Figure 3. *S leaching degree from different BFT samples using various leaching solutions*

CONCLUSION

Based on realized investigations, it is seen that using MC-H treatment and magnetic concentration may affect a development process that would enable the separation of metallic from non-metallic phase from minerals. Metallic mineral resources have at least ten times higher value compared to non-metallic, and therefore it should be understood in this context the techno-economic development function of given treatment procedure of BFT. Further treatment of metallic and non-metallic fraction leads to obtaining the useful components and creating the conditions for use the modified non-metallic component.

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