

RODOLJUB D. STANOJLOVIĆ,\* JOVICA M. SOKOLOVIĆ\*

**A STUDY OF THE OPTIMAL MODEL OF THE FLOTATION KINETICS OF COPPER SLAG  
FROM COPPER MINE BOR****BADANIE OPTIMALNEGO MODELU KINETYKI PROCESU FLOTACJI ŻUŻŁA MIEDZIOWEGO  
Z KOPALNI MIEDZI BOR**

In this study the effect of mixtures of copper slag and flotation tailings from copper mine Bor, Serbia on the flotation results of copper recovery and flotation kinetics parameters in a batch flotation cell has been investigated.

By simultaneous adding old flotation tailings in the ball mill at the rate of 9%, it is possible to increase copper recovery for about 20%. These results are compared with obtained copper recovery of pure copper slag.

The results of batch flotation test were fitted by MatLab software for modeling the first-order flotation kinetics in order to determine kinetics parameters and define an optimal model of the flotation kinetics. Six kinetic models are tested on the batch flotation copper recovery against flotation time. All models showed good correlation, however the modified Kelsall model provided the best fit.

**Keywords:** copper slag, flotation tailings, flotation kinetics, first-order, model, MatLab

W pracy badano wpływ mieszanin żużła miedziowego i odpadów poflotacyjnych w kopalni miedzi Bor na efektywność odzysku miedzi na drodze flotacji oraz parametry kinetyki flotacji w urządzeniu do flotacji pracującego w trybie cyklicznym.

Poprzez równoczesne wprowadzenie starych odpadów poflotacyjnych rozdrobnionych w młynie kulowym w ilości 9%, możliwe jest podniesienie poziomu odzysku miedzi o około 20%. Wyniki te porównać można z poziomem odzysku miedzi z czystego żużła.

Wyniki badań flotacji porcji wsadu zostały dopasowane przy użyciu oprogramowania MatLab do modelowania kinetyki flotacji (model pierwszego rzędu) w celu określenia parametrów kinetycznych i dla zdefiniowania optymalnego modelu kinetyki procesu flotacji. Przebadano sześć modeli kinetyki, analizując wielkość odzysku miedzi ze wsadu w stosunku do czasu flotacji. Wszystkie modele wykazywały dużą korelację, a najlepsze dopasowanie wykazywał zmodyfikowany model Kelsalla.

**Słowa kluczowe:** żużel miedziowy, odpady poflotacyjne, kinetyka flotacji, model pierwszego rzędu, MatLab

\* UNIVERSITY OF BELGRADE, TECHNICAL FACULTY IN BOR, VOJSKE JUGOSLAVIJE 12, 19210, BOR, SERBIA.

## 1. Introduction

Over 100 years the Copper and Smelting Complex Bor (RTB Bor), as an integrated mining and metallurgical company, produced large quantities of mine waste such as: mining waste, flotation tailing and smelting slag (Sokolovic et al., 2007). As a result of mining and metallurgy production of copper, more than  $1,2 \times 10^9$  tonnes of mining waste,  $0,9 \times 10^9$  flotation tailings, and  $18 \times 10^6$  tonnes of smelting slag are stored on the territory of Bor municipality. This waste generally has different physical and chemical properties, resulting in different potential environmental impacts. On the other hand, the contents of useful components in these wastes, first of all copper and precious metals, are a few times higher than in the primary copper ores. Therefore, mine wastes present a very important resource, which could be processed in the future (Stanojlovic et al., 2013).

Recycling today's copper slag is similarly possible. In the past decades, many methods have been proposed, on a laboratory scale, for valorization of copper from slag, including various processes such as flotation (Osborn et al., 1986; Barrios, 1991; Bota et al., 1995; Bruckard et al., 2004; Arslan & Arslan, 2002; Stanojlovic et al., 2002; Sarrafi et al., 2003; Stanojlovic et al., 2008; Stanojlovic & Sokolovic, 2011; Das et al., 2010; Stirbanovic & Markovic, 2011), leaching (Tumen & Bailey, 1990; Altundogan & Tumen, 1997; Herreros et al., 1998; Jia et al., 1999; Ahmed et al., 2000; Ziyadanogullari, 2000; Banza et al., 2002; Gul et al., 2003; Kongolo et al., 2003; Bulut, 2006) and combination of these methods for metal recovery (Stanojlovic et al., 2008). Some of these methods were briefly reviewed by Gorai et al. (2003).

The difficulty in processing the slag is directly linked to the association of the copper values with other metals and compounds present in the slag (Das et al., 2010). Therefore, the flotation has been identified as the most economical option to recover copper from slag (Bota et al., 1995; Bruckard et al., 2004).

There are a few industrial flotation facilities for treatment of copper slag, where the feed grades are much higher than would be economic on a mined ore, such as: Magma Copper San Manuel facility, USA (USEPA, 1993), Altonorte Flotation Plant, Chile (Demetrio et al., 2000), Outokumpu facility, Finland, (Stirbanovic et al., 2008), Mount Isa Mines, Australia (Barnes et al., 1993) Aurubus, Bulgaria (Nishkov & Grigorova, 2009), Black Sea Copper Works, Samsun, Turkey (Arslan & Arslan, 2002), Copper Mine Bor, Serbia (Stanojlovic et al., 2002).

Based on the available data, it is estimated that about 18 million tonnes of copper slag have been historically dumped and disposed of without any prior solid waste treatment in areas around the industrial facility in Bor, Serbia. Therefore, the Copper Mine Bor started production in 2001, treating about 90 tonnes per hour of complex slag by flotation process, after being crushed and ground, to recover additional copper values.

The plant feeds are of about 0,7% Cu respectively and containing mainly sulphide copper minerals, with a significant amounts of oxide minerals. Precious metals are also presents in the copper slag.

In the copper slag flotation plant is achieved unexpectedly poor metal recovery of copper (31,66%), gold (22,99%) and silver (22,10%), with the average value of copper, gold and silver in the produced copper concentrate about 11,22%, 2,71 g/t and 20,18 g/t, respectively). Unfortunately the flotation of copper slag is relatively inefficient, recoveries rarely being above 30%, so that the flotation tailings contain between 0,3 and 0,4% copper, of which 0,1-0,2% is a oxide minerals.

During the last years attempts have been made by Stanojlovic and Sokolovic (2011) with aim to optimize flotation process of copper slag to achieve maximum flotation recovery of copper in Copper Mine Bor.

The latest investigation show that the common problem of copper slag flotation is the association of the copper with other metals, higher specific gravity of copper slag as well as lower viscosity and stability of flotation pulp. Obviously the pulp formed from copper smelter slag in the mill/flotation process, due to high resistance to comminuting, increased density as well as the lack of fine aluminate and alumina-silicate has lower viscosity and stability. This characteristic of pulp has negative effect on the grinding and classification as well as on the efficiency of flotation process.

Improving the stability and viscosity of the pulp, adding flotation tailings in the process of grinding slag has been investigated by Stanojlovic et al. (2012). Results of settling rate tests are shown that lower settling rate of the mixture comes from the fact that lighter and much finer flotation tailing were settling slower than pure slag and this way affecting the height of the settled material.

Kinetic models can be used to analyze batch flotation results. Batch flotation test data in the literature support the first-order rate equation under reasonable operating conditions (Tomlinson & Fleming, 1963; Imaizumi & Inoue, 1965; Harris & Chakravarti, 1970; Jameson et al., 1977; Dowling et al., 1985; Xu, 1998; Agar et al., 1998; Oliveira et al., 2001; Cilek, 2004; Sokolovic et al., 2012). Many models of flotation kinetics were developed, from the deterministic and adsorption models to statistical and stochastic ones, out of which each dealt with another aspect (Brozek et al., 2003; Brozek & Mlynarczykowska, 2006; 2007; 2010; Kalinowski & Kaula, 1995; 2013).

This study presents a continued research on the effect of mixtures of copper slag and flotation tailings on the results of copper flotation in order to determine an optimal flotation kinetics model of copper slag. The results of batch flotation test were fitted by MatLab software because some of the first-order flotation kinetic models are implemented in this tool (Brezani & Zelenak, 2010)

In this paper, six different kinetic flotation models: **Classical model** (Dowling et al., 1985; Agar et al., 1998; Oliveira et al., 2001; Cilek, 2004), **Klimpel model** (Klimpel, 1980), **Kelsall model** (Kelsall, 1961), **Modified Kelsall model** (Jowett, 1974), **Gamma model** (Loveday, 1966; Imaizumi & Inoue, 1968) and **Fully mixed model** (Imaizumi & Inoue, 1965) were used to analyze batch flotation results and to optimize the flotation parameters using kinetics models. The following models are summarized in table 1 and tested and analyzed in this paper.

TABLE 1

Models applied and implemented in MatLab tool

Kinetics models	Relation
1	2
Classical model	$R = R_{\infty}(1 - e^{-k\tau})$
Klimpel model	$R = R_{\infty} \left( 1 - \frac{1}{k\tau} (1 - e^{-k\tau}) \right)$
Kelsall model	$R = (1 - \varphi)(1 - e^{-k_f\tau}) + \varphi(1 - e^{-k_s\tau})$
Modified Kelsall model	$R = R_{\infty} [(1 - \varphi)(1 - e^{-k_f\tau}) + \varphi(1 - e^{-k_s\tau})]$

1	2
Gamma model	$R = R_{\infty} \left[ 1 - \left( \frac{\lambda}{\lambda + \tau} \right)^P \right]$
Fully mixed model	$R = R_{\infty} \left[ 1 - \left( \frac{1}{1 + \frac{\tau}{k}} \right) \right]$

where:

- $R$  — flotation recovery after time  $t$ , (%)
- $R_{\infty}$  — maximum theoretical flotation recovery, (%)
- $k$  — flotation rate constant, (1/min)
- $k_f$  — fast flotation rate constant, (1/min)
- $k_s$  — slow flotation rate constant, (1/min)
- $\varphi$  — fraction of flotation components with the slow rate constant, (%)
- $\lambda$  — kinetic constant, (min)
- $P$  — exponent
- $\tau$  — flotation time, (min).

Two kinetic parameters such as flotation rate constant ( $k$ ) and the maximum recovery ( $R_{\infty}$ ) are obtained from the model fit to an experimental recovery-time curve. They can be effectively used to evaluate variables affecting flotation process.

## 2. Experimental

### 2.1. Material

In this study, the samples of copper slag and old flotation tailings were obtained from Copper Mine Bor, Serbia. The first representative samples were collected from flotation plant of discarded copper slag, as grinding product in the rod mill with the upper size limit of about 4,15 mm and the second from the „old“ flotation tailngs pond from the Field I. The Field I was sampled at several points, at a distance of 2 meters in the zone where flotation tailings is pumped to the pond. The upper size limit of the flotation tailings is about 0,833 mm.

The collected samples of about 200 kg was subsampled by coning and quartering to obtain a representative sample. The prepared samples was used for mineralogical, grain size and chemical analysis and saved for laboratory flotation testing. Microscopic and mineralogical studies were carried out on microscope Carl Zeiss-Jena “JENAPOL-U”. Chemical analysis of the samples was carried out using different analytical methods.

#### 2.1.1. Characterization of copper slag

Mineralogical and chemical composition of copper slag sample is shown in Table 2.

TABLE 2

Mineralogical and chemical composition of copper slag

Mineralogical composition		Chemical composition		
Minerals	Composition (%)	Elements	Content (%) <sup>a</sup> (g/t)	Analytical method
Fayalite	60,00	Fe	37,05	VT
Magnetite	30,00	SiO <sub>2</sub>	32,77	G
Bornite	6,50	Fe <sub>3</sub> O <sub>4</sub>	9,68	A-Fe 304
Chalcopyrite	1,50	Al <sub>2</sub> O <sub>3</sub>	4,86	ICP-AES
Copper mattes	0,30	S	0,40	G
Chalcocite	0,15	Ca	3,21	AAS
Covellite (Covelline)	0,05	Mg	0,62	AAS
Pyrite	1,00	Cu	0,56	SF
		Cu <sub>sul</sub>	0,535	R
		Cu <sub>ox</sub>	0,025	PO
		Ag	3,3 <sup>*</sup>	FA
		Au	0,5 <sup>*</sup>	FA

As a result of mineralogical studies of the copper slag samples, the fayalite, magnetite, bornite, chalcopyrite, native copper, pyrite, chalcocite and covellite were estimated. Also, mineralogical study showed that Bor copper slag has a fayalite structure. Bornite is the most present copper mineral but secondary copper sulfides such as chalcopyrite and covellite were also present.

The copper slag composition was found to be 60% fayalite (Fe<sub>2</sub>SiO<sub>4</sub>), 30% magnetite (Fe<sub>3</sub>O<sub>4</sub>), 6,50% bornite (Cu<sub>5</sub>FeS<sub>4</sub>), 1,50% chalcopyrite (CuFeS<sub>2</sub>) and 3% other minerals and metals such as chalcocite (Cu<sub>2</sub>S), covellite (CuS), copper mattes and pyrite (FeS<sub>2</sub>).

It contained around 0,56% Cu, 37,05% Fe, 32,77% SiO<sub>2</sub> and 0,4% S. Precious metals were also presents in the copper slag (0,50 g/t Au and 3,3 g/t Ag).

The contents of copper and precious metals in the discarded copper slag shows that it contained 2-3 times higher concentration of these useful components comparing to their contents in the primary copper ores (0,25 - 0,35% Cu), which are now exploited in the Copper Mine Bor.

The grain size analysis of the copper slag sample is given in table 3.

TABLE 3

Grain size distribution and assay by characteristics size class of copper slag

Grain size <i>d</i> (mm)	Partial Mass <i>W</i> (%)	Cumulative Passing Values, <i>D</i> (%)	Content (%)			
			Cu	S	Cu <sub>ox</sub>	Cu <sub>sul</sub>
-4,156+3,327	0,91	100,00	0,51	0,39	0,026	0,484
-3,327+2,362	3,28	99,09				
-2,362+1,651	8,08	95,81				
-1,651+1,168	15,44	87,73				
-1,168+0,833	20,25	72,39				
-0,833+0,589	13,63	52,04				
-0,589+0,417	12,78	38,78				
-0,417+0,295	6,94	25,63				
-0,295-0,149	8,80	18,69				
-0,149+0,074	0,16	9,89				
-0,074+0	9,63	9,63				

The physical properties of copper slag are given in Table 4.

TABLE 4

Physical properties of copper slag

Physical characteristics of slag sample	
Moisture	0,11%
Density	3487 kg/m <sup>3</sup>
Natural pH value	8,09
Bond work index	
– rod mill, $W_{irm}$	19,13 kWh/t
– ball mill, $W_{ibl}$	31,97 kWh/t
Magnetability	
– magnetit fraction	9,87%
– nonmagnetic fraction	90,13%

The physical properties such as specific gravity and the Bond work index of the copper slag sample were found to be similar to those of other discarded copper slags found elsewhere (Shen & Forssberg, 2003).

The Bond work index of the slag sample was determined by using the standard grindability test. The feed material for the test was prepared by passing the sample through a 3,35 mm sieve. The Bond's work index in the ball mill for smelter slag is  $W_i = 31$  kWh/t, which is about two times higher comparing to copper ore. This fact points to the expected high energy consumption in grinding process.

The specific gravity of copper slag is approximately 3500 kg/m<sup>3</sup>. This value is about 500-700 kg/m<sup>3</sup> higher than specific gravity of copper ore, which leads to a conclusion that settling rate of slag particles in the pulp is higher compared to the settling rate of the copper ore particles of the same size.

### 2.1.2. Characterization of flotation tailings

In this study "old" flotation tailings sample produced in the flotation process of copper ore from the first half of the last century has been used. Mineralogical compositions of the flotation tailings sample from different depths of the old flotation ponds from Field I are shown in Table 5. The chemical analysis of these sample is shown in Table 6. The grain size analysis of old flotation tailings sample is given in table 7.

Based on qualitative mineralogical analyses of flotation tailings sample (table 5), the following minerals such as: pyrite, chalcopyrite, covellite, enargite, chalcocite, quartz and gangue minerals are identified.

As can be seen in Table 6, the flotation tailings contained significant levels of SiO<sub>2</sub> (58,03%) and Al<sub>2</sub>O<sub>3</sub> (12,04%), whereas the contents of total copper was about 0,22%. Precious metals were also presents in the flotation tailings (0,30 g/t Au and 2,14 g/t Ag).

TABLE 5

## Mineralogical composition of old flotation tailing samples

Minerals	Content (%)	
	Sample 1 (0-16 m)	Sample 2 (16-40 m)
Chalcopyrite	0,16	0,12
Covellite	0,03	0,11
Energite	0,01	0,02
Chalcocite	0,01	0,01
Bornite	in traces	0,01
Azurite	in traces	0,03
Cuprite	0,01	0,04
Pyrite	14,27	22,20
Gangue minerals	80,63	71,96
Other minerals	4,88	5,50
<b>Σ</b>	<b>100,00</b>	<b>100,00</b>

TABLE 6

## Chemical composition of old flotation tailing samples

	Content (%) (g/t)*	Analytical method
Cu	0,220	SF
Cu <sub>ox</sub>	0,016	PO
Cu <sub>sul</sub>	0,204	R
S	8,810	G
Fe	8,860	VT
SiO <sub>2</sub>	58,030	G
Al <sub>2</sub> O <sub>3</sub>	12,040	ICP-AES
Au	0,300*	FA
Ag	2,140*	FA

TABLE 7

## Grain size distribution and assay by characteristics size class of flotation tailings

Grain size <i>d</i> (mm)	Partial Mass <i>W</i> (%)	Cumulative Passing Values, <i>D</i> (%)	Content (%)			
			Cu	S	Cu <sub>ox</sub>	Cu <sub>su</sub>
+0,589	0,244	100,00	0,20	7,42	0,005	0,195
-0,589+0,417	1,41	99,75				
-0,417+0,295	6,54	98,34				
-0,295+0,149	21,29	91,80				
-0,149+0,074	14,33	77,46				
-0,074+0	56,16	56,16	0,30	8,06	0,098	0,202

Flotation tailings is much finer and softer and higher content of  $-74 \mu\text{m}$  in the grinding product of the mixture, compared to pure slag, comes from flotation tailing. Its specific gravity was  $2800 \text{ kg/m}^3$ . Natural pH was typically very low (2,21).

## 2.2. Methods

The grinding of the material (pure copper slag and mixture of copper slag and old flotation tailings) was carried out using a laboratory ball mill (400×125 mm), at 15% ball charge and at 16 minutes and 25 seconds grinding time.

Standard batch flotation tests were carried out in laboratory flotation machine DENVER DR-12 with cell volume of 2,6 l. During this laboratory flotation batch test, the impeller speed and solids content were kept constant at 1,600 rpm and 30% (by weight), respectively and the pH was adjusted to about pH 12. In the flotation experiments, freshly prepared sodium isopropyl xanthate (NaIPX) was used as the collector. Consumption of NaIPX was 60 g/t. Dowfroth D-250 has been used as the frother. 15 g/t of D-250 is added in pulp conditioning and 20 g/t into flotation cell. Lime was used as pH regulator.

In each flotation kinetics tests, the pulp was first agitated in the flotation cell for 9 min, after which the required dosage of flotation reagents was added and the slurry was conditioned for an additional minute. Air (460 l/min) was then introduced and the concentrates and tailings of the flotation process were collected separately, dried, weighed, and analysed for copper to assess product quality and recovery.

The kinetic studies were carried out by collecting the concentrate at cumulative time intervals of 1, 3, 6, 12 and 20 minutes of flotation.

## 3. Results and discussion

An important parameter investigated in this research was the effect of the mixture of copper slag and old flotation tailings on its flotation behavior. Obtained results are given in figure 1 to 2. These results are compared with obtained copper recovery of pure copper slag.

Figure 1 shows the flotation results of copper slag flotation with different mixture ratio of copper slag and flotation tailings (1 to 9%) prior to flotation using 60 g/t NaIPX. The effect of mixture ration of copper slag and flotation tailings on copper grade is shown on figure 2.

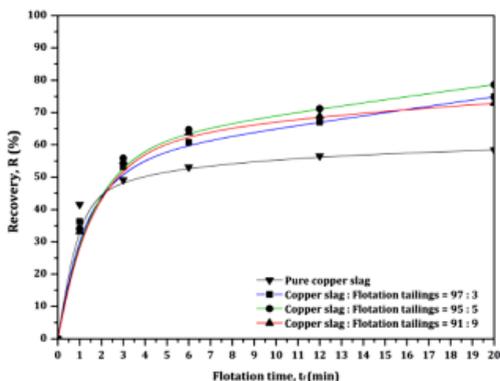


Fig. 1. Comparison of the flotation recovery obtained in the batch flotation tests of the pure copper slag and mixture of copper slag and flotation tailings samples

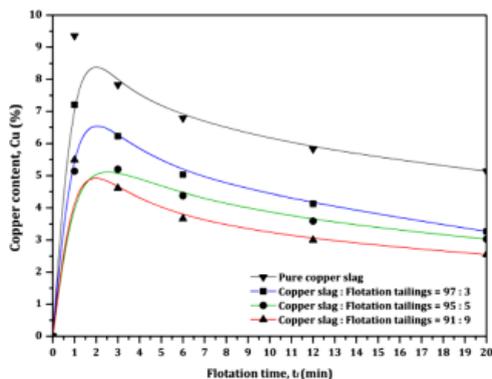


Fig. 2. Comparison of the copper content obtained in the batch flotation tests of the pure copper slag and the mixture of copper slag and flotation tailings samples

The results of copper flotation shows that the mixture of copper slag and flotation tailings has a positive effect on copper valorization from slag. Higher copper recovery and lower copper content are the results of using mixture of copper slag and flotation tailings samples. The copper recovery increased with increasing mixture ratio of copper slag and flotation tailings for all samples tested.

As can be seen from figure 1, the mixture of copper slag and flotation tailings increase from 1 to 9%, copper recovery increase from 58.40% to 78.68%, in the presence of 60 g/t NaIPX. The copper content was in the range from 5.14 and 2.55%. It was observed that the concentrate copper grade was higher in the flotation of pure copper slag.

The highest copper recovery of 78.68% with 3.03% of copper grade was achieved at a mixture ratio of copper slag and flotation tailings 95 : 5. As shown in Figure 1, a significant improvement in flotation occupied after 3 minutes of flotation time. It was stated that the copper content in concentrate has the best growth after 3 minutes of flotation time and was 5.14%.

However, with further increasing of flotation time, copper content in the concentrate decreased slightly and after 20 minutes of flotation, copper content in the concentrate was 3.02%.

Based on this it can be concluded that the flotation of copper from the composite sample after 3 min due to the continued successful participation fine grain of flotation tailings and increased pulp stability compared to the flotation of copper from pure slag.

The flotation data was used to study the kinetics by means of a different first-order flotation kinetics models (see table 1).

Figures 3-6 shows cumulative recovery of various copper slag and flotation tailings samples against flotation time based on the batch flotation test results using different models. For each experimental data, flotation kinetics parameters are summarized in Tables 8-11.

The fitted flotation kinetics curves and generated kinetics parameters confirm the results achieved in the flotation tests of the pure copper slag and the mixture of copper slag and flotation tailings.

The results clearly show that the flotation followed first-order kinetics.

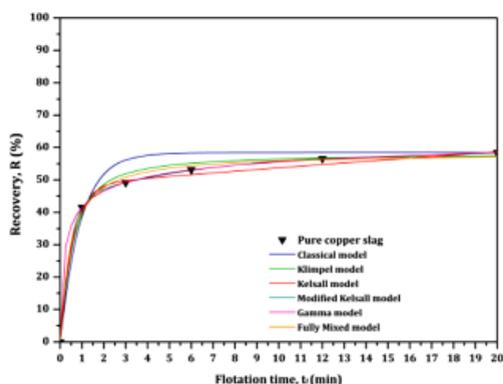


Fig. 3. Comparison of the fitted flotation kinetics curve of the pure copper slag sample using different first-order flotation kinetic models

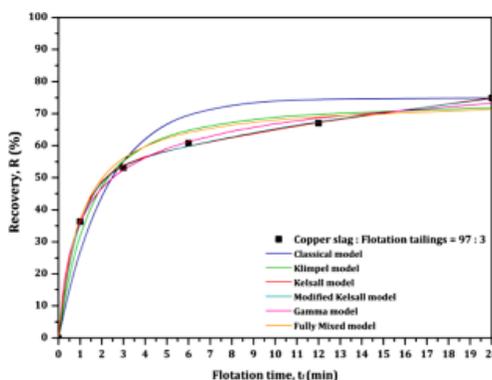


Fig. 4. Comparison of the fitted flotation kinetics curve of the mixture of copper slag and flotation tailings in the ratio 97 : 3 using different first-order flotation kinetic models

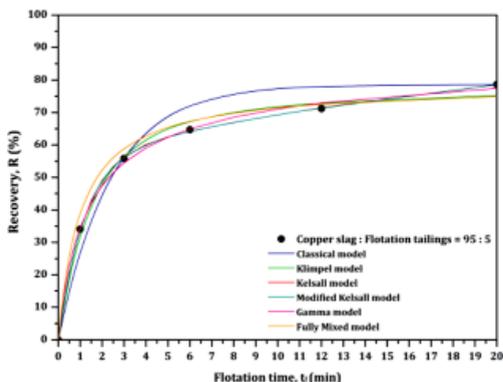


Fig. 5. Comparison of the fitted flotation kinetics curve of the mixture of copper slag and flotation tailings in the ratio 95 : 5 using different first-order flotation kinetic models

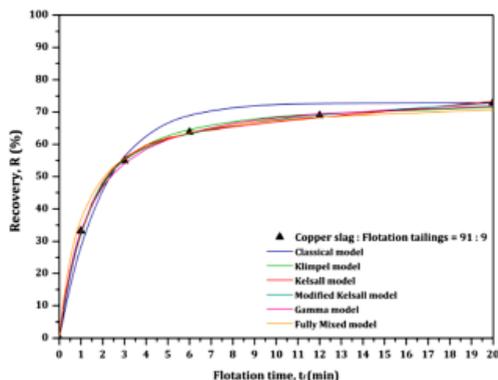


Fig. 6. Comparison of the fitted flotation kinetics curve of the mixture of copper slag and flotation tailings in the ratio 91 : 9 using different first-order flotation kinetic models

TABLE 8

Flotation kinetics parameters generated by the different model in batch flotation test of pure copper slag (R: regression coefficient)

Flotation kinetic parameters	Classical model	Klimpel model	Kelsall model	Modified Kelsall model	Gamma model	Fully Mixed model
$R_{\infty}$	58,40	58,40		58,956	73,791	58,40
$k$	1,1092	3,0249				0,4435
$\varphi$			0,51809	0,26818		
$k_f$			1,8125	2,4018		
$k_s$			0,011283	0,16169		
$\lambda$					0,038449	
$P$					0,25148	
$R$	0,98917	0,96478	0,991	0,99999	0,99999	0,99843

TABLE 9

Flotation kinetics parameters generated by the different model in batch flotation test of mixture of copper slag slag and flotation tailings 97 : 3 (R: regression coefficient)

Flotation kinetic parameters	Classical model	Klimpel model	Kelsall model	Modified Kelsall model	Gamma model	Fully Mixed model
$R_{\infty}$	74,92	74,92		89,256	100	74,92
$k$	0,44859	1,2521				1
$\varphi$			0,49074	0,44398		
$k_f$			1,1298	1,1707		
$k_s$			0,033729	0,050324		
$\lambda$					0,31891	
$P$					0,31785	
$R$	0,98086	0,9752	0,99978	0,99981	0,9992	0,9955

TABLE 10

Flotation kinetics parameters generated by the different model in batch flotation test of mixture of copper slag and flotation tailings 95 : 5 (R: regression coefficient)

Flotation kinetic parameters	Classical model	Klimpel model	Kelsall model	Modified Kelsall model	Gamma model	Fully Mixed model
$R_{\infty}$	78,68	78,68		99,477	92,111	78,68
$k$	0,41981	1,1554				1
$\varphi$			0,4405	0,43812		
$k_f$			0,86233	0,86335		
$k_s$			0,036158	0,036846		
$\lambda$					0,73865	
$P$					0,55207	
$R$	0,98879	0,98933	0,99994	0,99994	0,99421	0,99445

TABLE 11

Flotation kinetics parameters generated by the different model in batch flotation test of mixture of copper slag and flotation tailings 91 : 9 (R: regression coefficient)

Flotation kinetic parameters	Classical model	Klimpel model	Kelsall model	Modified Kelsall model	Gamma model	Fully Mixed model
$R_{\infty}$	72,91	74,37		75,488	75,371	74,26
$k$	0,49653	1,2796				1
$\varphi$			0,40865	0,29679		
$k_f$			0,77099	0,86669		
$k_s$			0,021297	0,10627		
$\lambda$					1,5587	
$P$					1,1767	
$R$	0,99468	0,99802	0,99978	0,99995	0,9998	0,9977

In tables 8 to 11, it shows that there are also significant effects of mixtures of copper slag and flotation tailings on the first-order flotation rate constant and maximum theoretical flotation recovery.

It was found that the first-order flotation rate constant, for the Classical model, was in the range from 0.41981 to 1.1092 min<sup>-1</sup> and decreased as results of copper flotation from composite samples of copper slag and flotation tailings. But, the first-order rate constant is higher to the typical rate constant associated with flotation of copper sulfide ores (Kracht et al., 2005). Obviously, this trend is the reason for the increasing of  $R_{\infty}$  (maximum theoretical flotation recovery) from 58.40% to 78.68%.

For all tested model, the maximum theoretical flotation recovery are obtained in the flotation kinetics test of composite samples with mixture ratio of copper slag and flotation tailings was 95 : 5.

It was observed that major differences occurred amongst the tested kinetics models after 3 minutes of flotation time. By using Modified Kelsall model for fitting a flotation data of all tested samples, it was found that maximum theoretical flotation recovery were higher when the mixture ratio of copper slag and flotation tailings was 95 : 5. The maximum theoretical flotation recovery was 99.477%.

Also, it was found that  $k_f$  (fast flotation rate constant) is greater than  $k_s$  (slow flotation rate constant). Obtained fast flotation rate constant ( $k_f$ ) was in the range from  $1.1707 \text{ min}^{-1}$  to  $0.86335 \text{ min}^{-1}$  for the different mixture ratio of copper slag and flotation tailings.

However, Modified Kelsall model was considered to be the best fit and most suitable model for understanding the copper flotation from pure copper slag and the mixture of copper slag and flotation tailings.

## 4. Conclusion

Process of flotation concentration of copper and precious metals from mixture of copper smelting slag and flotation tailings presents unique and original solution for processing these two waste materials.

Due the lower content of fine particles in grinding product of copper slag, as well as higher density and lack of alum-silicates, flotation pulp has lower viscosity and stability. This characteristic of pulp has negative effect on both processes of grinding and classification and efficiency of flotation concentration.

The lower pulp stability and viscosity causes higher energy consumption during the grinding process, decreasing plant capacity and lower recovery of copper and precious metals in process of flotation concentration of copper slag.

Enhanced flotation was observed on the all composite copper slag samples by simultaneous adding old flotation tailings in the ball mill at the rate of 1 to 9%. The results has shown that the mixture of copper slag and flotation tailings provided positive flotation effects and greatly improved flotation kinetics compared to the flotation of pure copper slag. The improvement in copper recovery was about 15 to 20%, respectively as well as a slight reduction of copper grade, clearly demonstrated better flotation recovery and thus flotation kinetics.

Based on batch flotation test data of copper slag, the non-linear fitting was conducted using MatLab tool for modeling the first order flotation kinetics. The results clearly show that the flotation followed first-order kinetics. It was found that all tested models can be used for simulation of the copper slag flotation kinetics and showed good correlation, but the best fitted model was the modified Kelsall model.

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## References

- Agar G.E., Chia J., Requis C.L., 1998. *Flotation rate measurements to optimize an operating circuit*. Min. Eng., 11 (4), p. 347-360.
- Ahmed I.B., Gbor P.K., Ji C.Q., 2000. *Aqueous sulfur dioxide leaching of Cu, Ni, Co, Zn, and Fe from smelter slag in the absence of oxygen*. Can. J. Chem. Eng., 78 (4), p. 694-703.

- Altundogan H.S, Tumen F., 1997. *Metal recovery from copper converter slag by roasting with ferric sulfate*. Hydrometallurgy, 44 (1-2), p. 261-267.
- Arslan C., Arslan F., 2002. *Recovery of copper, cobalt, and zinc from copper smelter and converter slags*. Hydrometallurgy, 67, p. 1-7.
- Banza A.N., Gock E., Kongolo K., 2002. *Base metals recovery from copper smelter slag by oxidizing leaching and solvent extraction*. Hydrometallurgy, 67, p. 63-69.
- Barnes C.D., Lumsdaine J., O'Hare S.M., 1993. *Copper converter slag treatment at Mount Isa Mines Limited, Mount Isa, Qld*. In: AusIMM Proceedings, 298 (1), p. 31.
- Barrios M., 1991. *Study of flotation of slags*. Oficina Minera Osvaldo Martinez, Taltal, Chile.
- Bota G., Gican I., Poputa G., 1995. *The beneficiation of the non-ferrous metals from secondary resources at regia autonoma a Cuprului Deva-Romaina*. [In:] Krstev, B. & Golomeov, B. (Eds.): Proceedings of 6th Balkan Mineral Processing Symposium, Ohrid, Macedonia, p. 426-431.
- Brezani I., Zelenak F., 2010. *MatLab tool for modeling first order flotation*. [http://www.mathworks.com/matlabcentral/fix\\_files/28703/2/content/html/Flotation\\_modeling.html](http://www.mathworks.com/matlabcentral/fix_files/28703/2/content/html/Flotation_modeling.html).
- Brożek M., Młynarczykowska A., Turno A., 2003. *The relationships between deterministic and stochastic models of flotation*. Arch. Min. Sci., Vol. 48, No 3, p. 299-314.
- Brożek M., Młynarczykowska A., 2006. *Application of the stochastic model for analysis of flotation kinetics with coal as an example*. Physicochem. Probl. Miner. Process., Vol. 40, p. 31-44.
- Brożek M., Młynarczykowska A., 2007. *Analysis of kinetics models of batch flotation*. Physicochem. Probl. Miner. Process., Vol. 41, p. 51-65.
- Brożek M., Młynarczykowska A., 2010. *Probability of detachment of particle determined according to the stochastic model of flotation kinetics*. Physicochem. Probl. Miner. Process., Vol. 44, p. 23-34.
- Bruckard W.J., Somerville M., Hao F., 2004. *The recovery of copper, by flotation, from calcium-ferrite-based slags made in continuous pilot plant smelting trials*. Miner. Eng., 17, p. 495-504.
- Bulut G., 2006. *Recovery of copper and cobalt from ancient slag*. Waste Manage. Res., 24, p. 118-124.
- Cilek E.C., 2004. *Estimation of flotation kinetic parameters by considering interactions of the operating variables*. Miner. Eng., 17 (1), p. 81-85.
- Das B., Mishra B.K., Angadi S., Pradhan S.K., Prakash S., Mohanty J., 2010. *Characterization and recovery of copper values from discarded slag*. Waste Manage. Res., 28 (6), p. 561-567.
- Demetrio S., Ahumada J., Duran A., Mast E., Rojas U., Sanhueza J., Reyes P., Morales E., 2000. *Slag cleaning: The Chilean copper smelter experience*. JOM, 52 (8), p. 20-25.
- Dowling E.C., Klimpel R.R., Aplan F. F., 1985. *Model discrimination in the flotation of a porphyry copper ore*. Miner. Metall., 2 (2), p. 87-101.
- Gorai B., Jana R., Premchand K., 2003. *Characteristics and utilisation of copper slag – a review*. Resour. Conserv. Recy., 39, p. 299-313.
- Gul A., Bulut G., Kangal O., Önal G., 2003. *Beneficiation of ancient copper slags*. In: Proceedings of X Balkan Mineral Processing Congress, Varna, Bulgaria, Sofia, p. 831-836.
- Harris C.C., Chakravarti A., 1970. *Semi-batch flotation kinetics: species distribution analysis*. Trans. AIME, 247, p. 162-172.
- Herreros O., Quiroz R., Manzano E., Bou C., Vinals J., 1998. *Copper extraction from reverberatory and flash furnace slags by chlorine leaching*. Hydrometallurgy, 49, p. 87-101.
- Imaizumi T., Inoue T., 1965. *Kinetic consideration of froth flotation*. In: Proceedings of 6th International Mineral Processing Congress, Cannes, p. 563-579.
- Imaizumi T., Inoue T., 1968. *Some aspects of flotation kinetics*. In: Proceedings of 8th International Mineral Processing Congress, Leningrad, p. S-15.
- Jameson C.J., Nam S., Young M.M., 1977. *Physical factors affecting recovery rates in flotation*. Miner. Sci. Eng., 9 (3), p. 103-118.
- Jia C.Q., Xiao J.Z., Orr R.G., 1999. *Behavior of metals in discard nickel smelting slag upon reacting with sulfuric acid*. J. Environ. Sci. Heal. A. 34 (5), p. 1013-1034.
- Jowett A., 1974. *Resolution of flotation recovery curves by a differential plot method*. Trans. Inst. Min. Metall., 85, p. C263-C266.
- Kalinowski K., Kaula R., 1995. *Transport delay in a mathematical models of batch coal flotation kinetics*. Arch. Min. Sci., Vol. 40, p. 339-349.

- Kalinowski K., Kaula R., 2013. *Verification of flotation kinetics model for triangular distribution of density function of flotability of coal particles*. Arch. Min. Sci., Vol. 58, 4, p. 1279-1287.
- Kelsall D.F., 1961. *Application of probability assessment of flotation systems*. T. Am. I. Min. Met. Eng., 70, p. 191-204.
- Klimpel R.R., 1980. *Selection of chemical reagents for flotation*. In: Mular A., Bhappu R. Eds., Mineral Processing Plant Design, 2nd edn. AIME, New York, p. 907-934.
- Kongolo K., Mwema M.D., Banza A N., Gock E., 2003. *Cobalt and zinc recovery from copper sulphate solution by solvent extraction*. Miner. Eng. 16, p.1371-1374.
- Kracht W., Vallebuona G., Casali A., 2005. *Rate constant modeling for batch flotation, as a function of gas dispersion properties*. Miner. Eng., 18 (11), p. 1067-1076.
- Loveday B.K., 1966. *Analysis of froth flotation kinetics*. Trans. IMM, 75: p. C219-C225.
- Nishkov I., Grigorova I., 2009. *Practical experience and education of waste recycling and sustainable development in Bulgaria*. In: Proceedings of 4<sup>th</sup> Symposium Recycling technologies and sustainable development, Kladovo, Serbia, p. 54-63.
- Oliveira J. F., Saraiva S.M., Pimenta J. S., Oliveira A.P.A., 2001. *Kinetics of pyrochlore flotation from Arax mineral deposits*. Miner. Eng. 14 (1), p. 99-105.
- Osborn G.A., Garner F.A., Veasey T.J., 1986. *Recovery of metal values from secondary copper slags*. In: Proceedings of the 1<sup>st</sup> International Mineral Processing Symposium, Izmir, Turkey, p. 46-64.
- Sarrafi A., Rahmati B., Hassani H.R., Shirazi H.H.A., 2003. *Recovery of copper from reverberatory furnace slag by flotation (technical note)*. Miner. Eng. 17: p. 457-459.
- Shen H., Forssberg E., 2003. *An overview of recovery of metals from slags*. Waste Manage., 23, p. 933-949.
- Sokolovic J., Stanojlovic R., Barbulovic B., Markovic Z.S., Stirbanovic Z., 2007. *Analysis of state pollution on environmental in RTB Bor*. In: Proceedings of XV Ecological Truth 2007, Sokobanja, Serbia, p.174-180.
- Sokolovic J., Stanojlovic R., Markovic Z., 2012. *The effects of pretreatment on the flotation kinetics of waste coal*. Int. J. Coal Prep. Util., 32 (3), p. 130-142.
- Stanojlovic R., Stankovic Z., Markovic Z.S., Antic D., Sokolovic J., Trujic D., Milovanovic S., Stefanovic T., Sukletovic P., Nikolic M., 2002. *The study of techno-Economic Justification for Processing Smelter Slag in Existing Technological Process*. The Study, University of Belgrade, Technical faculty in Bor, Serbian Edition.
- Stanojlovic R., Stirbanovic Z., Sokolovic J., 2008. *Wastefree technology for processing smelter slag from Bor Copper Mine*. J. Min. Metall. Sect. A, 44 (1), p.44-50.
- Stanojlovic R., Sokolovic J., 2011. *Smelting slag - Production and processing of copper slag from Smelter in Bor*. The Monographs, University of Belgrade, Technical Faculty in Bor, Bor, Serbia.
- Stanojlovic R., Stirbanovic Z., Sokolovic J., 2012. *New technological procedure for sustainable processing of mining technological wastes*. Min. Eng., 1 (2012), p. 75-88.
- Stanojlovic R., Sokolovic J., Milosevic N., 2013. *Integrated environmental pollution by wastes from Copper Mine Bor, Serbia*. Environ. Eng. Manag J., (forthcoming in press).
- Stirbanovic Z., Markovic Z.S., Stanojlovic R., Sokolovic J., 2008. *World experience in the processing of smelter slag as examples of economic and environmental feasibility*. In: Proceedings of XVI Ecological Truth 2008, Sokobanja, Serbia, p.197-201.
- Stirbanovic Z., Markovic Z., 2011. *The Effect of Copper Bearing Particles Liberation on Copper Recovery from Smelter Slag by Flotation*. Sep. Sci. Technol., 46 (16), p. 2496-2500.
- Tomlinson H.S., Fleming M.G., 1963. *Flotation rate studies*. In: Proceedings of VI IMPC, Cannes, Pergamon Press, Oxford – New York, p. 563-579.
- Tumen F., Bailey N.T., 1990. *Recovery of metal values from copper smelter slags by roasting with pyrite*. Hydrometallurgy, 25, p. 317-328.
- USEPA, 1993. *Slag Reprocessing, Magma Copper Company's San Manuel Facility*. Report to U.S. Environmental Protection Agency.
- Xu M., 1998. *Modified flotation rate constant and selectivity index*. Miner. Eng., 11 (3), p. 271-278.
- Ziyadanogullari B., 2000. *Recovery of copper and cobalt from concentrate and converter slag*. Sep. Sci. Technol., 35, p. 1963-1971.