

# APPLICATION OF MODIFIED NANOFIBRILLATED CELLULOSE AS A COLLECTOR IN SULPHIDE FLOTATION

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## ABSTRACT

The aim of this study was to evaluate the efficiency of a nanofibrillated cellulose collector (BAC) in chalcopyrite flotation. This reagent was synthesized at University of Oulu (Finland) using a sulphide ore sample from Panasqueira mine.

The BAC collector efficiency was tested using two sulphide ore samples, one from Panasqueira mine and, the other one, from Neves-Corvo mine. For the Panasqueira sulphide ore sample, a factorial plan of experiments ( $3^3$ ) was conducted in order to study the BAC collector selectivity for chalcopyrite using the mineral sample for which the collector was designed.

On the other hand, a new factorial plan of experiments ( $2^3$ ) was conducted for the Neves-Corvo sulphide ore. The purpose of these trials was to analyze the BAC collector selectivity for chalcopyrite using a mineral sample different to the one for which the collector was synthesized.

The results of these two sets of trials showed that the BAC collector is a chalcopyrite collector, which is selective for chalcopyrite when it is added in low concentrations (0.1 g BAC/kg of mineral), although this selectivity can be conditioned by the pulp pH and the added  $ZnSO_4$  concentration (sphalerite depressant). Chalcopyrite was concentrated in the floated product, with reasonable values of recovery. However, the presence of smelter penalizing minerals in the floated product, which were not well depressed, decreased the quality of the copper concentrate.

**Key words:** chalcopyrite; collector; flotation; nanocellulose; selectivity

## 1. INTRODUCTION

Chalcopyrite, the major commercial source of copper, is commonly concentrated by froth flotation from complex sulphide ores. This process is carried out with the aid of some thiol collectors, which increase the flotation performance (Fuerstenau, *et al.*, 2007). The most employed thiol collector is xanthate, although there are other types also very used, like dithiophosphate or thionocarbamate, with higher selectivity against Fe-sulphides and sphalerite (Güler, *et al.*, 2006).

However, the application of thiol collectors can have pernicious effects on the environment, being xanthates the best example of this. Xanthates are toxic not only for humans' health, but also for the aquatic ecosystems, due to their decomposition in toxic compounds like carbon disulphide ( $CS_2$ ) (Shen, *et al.*, 2016).

In order to reduce the environmental impact of flotation, a nanofibrillated cellulose collector (butylamine cellulose, BAC) was synthesized at University of Oulu (Finland) using a Panasqueira mine sulphide ore sample. This new reagent constitutes an environment-friendly alternative that could

replace the present synthetic chemicals. Nanofibrillated celluloses (NFCs) are produced from cellulosic materials, the most abundant natural polymeric source, using mechanical treatment, typically following chemical or enzymatic treatments (Laitinen, *et al.*, 2014).

The aim of this study was to evaluate the BAC collector efficiency in chalcopyrite flotation. This was tested using two sulphide ore samples, one from Panasqueira mine and, the other one, from Neves-Corvo mine. For the Panasqueira sulphide ore sample, a factorial plan of experiments was conducted in order to study the BAC collector selectivity for chalcopyrite using the mineral sample for which the collector was designed.

On the other hand, a new factorial plan of experiments and a kinetic analysis were conducted for the Neves-Corvo sulphide ore. The purpose of these trials was to analyze the BAC collector selectivity for chalcopyrite using a mineral sample different to the one for which the collector was synthesized.

## 2. EXPERIMENTAL

### 2.1. Sulphide ore samples and reagents

Two sulphide ore samples were used in this study. The first one was collected in the copper circuit of the Panasqueira mine's plant and transported to the GeoLab in Instituto Superior Técnico (IST), where it was ground in dry conditions until to achieve 80% passing size of 75 µm, the liberation size of the chalcopyrite ore. The second sulphide ore sample used was a "fresh" sample, collected in the copper circuit of the Neves-Corvo mine's plant with 80% passing size of 50 µm. The mineral composition of these samples, obtained by MLA, is shown in Table 1. In Table 2, the feed grade in copper, zinc and arsenic for the Panasqueira sulphide ore and, the feed grade in copper, zinc and iron for the Neves-Corvo sulphide ore, are represented. While copper (chalcopyrite) is the element to concentrate, zinc (sphalerite), arsenic (arsenopyrite) and iron (pyrite) are the main elements which its flotation should be depressed in order to avoid smelter penalties.

Table 1. Panasqueira and Neves-Corvo sulphide ore samples mineral composition (EPDM, 2016).

Mineral	Pyrite	Chalcopyrite	Arsenopyrite	Sphalerite	Enargite	Tetrahedrite	Tennantite	Stannite	Others
<b>Panasqueira Grade (%)</b>	31.03	2.09	49.06	3.93	-	-	-	-	13.89
<b>Neves-Corvo Grade (%)</b>	63.6	5.1	1.32	1.05	0.36	0.12	0.12	0.12	28.21

Table 2. Copper, zinc and arsenic grade for the Panasqueira sulphide ore and copper, zinc and iron grade for the Neves-Corvo sulphide ore.

<b>Panasqueira</b>	<b>Element</b>	Cu	Zn	As
	<b>Grade (%)</b>	0.72	2.52	22.57
<b>Neves-Corvo</b>	<b>Element</b>	Cu	Zn	Fe
	<b>Grade (%)</b>	2.09	0.58	36.14

The reagents used in the flotation tests in addition to the BAC collector were HCl and NaOH (to adjust the pH of the pulp), ZnSO<sub>4</sub> (sphalerite depressant), AEROFROTH® 65 (frother in the Panasqueira tests) and MIBC (frother in the Neves-Corvo tests).

## 2.2. Flotation tests

The flotation tests were carried out with a Denver D12 laboratorial flotation cell with a 2.5 L tank. In the trials with the Panasqueira sulphide ore, this cell worked in self-aspiration mode while, in the trials with the Neves-Corvo sulphide ore, the cell worked with compressed air. In the tests with the Panasqueira sulphide ore, it was also used a laboratorial rod mill Brown Boveri with a diameter of 13 cm and length of 26.5 cm. The fill factor of the rod mill was approximately 40% (13 rods with a diameter of 3.4 cm and length of 24.5 cm) and the grinding time was 51 minutes.

The flotation tests with the Panasqueira sulphide ore were performed with 20% of solids by weight, a pulp volume of 2.2 L and an impeller speed of 700 r.p.m. The conditioning time and the flotation time were 5 minutes and the products (sunk and floated) were dried in a laboratorial oven and sampled with a riffle sampler (Jones type) in order to do a chemical analysis (XRF). On the other hand, the trials with Neves-Corvo sulphide ore were performed following the conditions established by this mine's laboratory: 40% of solids by weight, a pulp volume of 2.2 L, an impeller speed of 1300 r.p.m and an air flow of 5 L/min. The conditioning time was 5 minutes and the froth was collected at 0.5, 1.5, 3.5 and 7.5 minutes of the flotation time in order to do a kinetic analysis. The sunk and the floated products were filtered, dried in an oven and sampled for the chemical analysis (XRF).

## 2.3. Panasqueira sulphide ore experiments

The BAC collector efficiency was evaluated with a factorial design of experiments (DOE). Three factors (BAC concentration, pH and ZnSO<sub>4</sub> concentration) were modified in three levels (Table 3). The responses studied were the copper, zinc and arsenic grade and recovery in the floated product. The BAC collector selectivity was analyzed comparing the values of recovery of the three chemical elements. The software package Design Expert 10.0.3.1<sup>®</sup>, Stat-Ease, Inc., Minneapolis, USA, was used to build a model which studied the relationship between the copper grade and recovery and the three factors modified. The analysis of variance (ANOVA) was used to estimate the statistical parameters. F-test was used to estimate the significance of all terms in the polynomial equation within 95% confidence interval. A kinetic analysis was not carried out due to the large number of products to analyze.

Table 3. Levels of variation for the variables BAC concentration, pH and ZnSO<sub>4</sub> concentration used in the Panasqueira sulphide ore tests.

Factor	-1	0	1
BAC Concentration (g BAC/kg of mineral)	0.1	0.3	0.5
pH	7	8	9
ZnSO <sub>4</sub> Concentration (mol of ZnSO <sub>4</sub> /L of water)	1x10 <sup>-4</sup>	3x10 <sup>-4</sup>	5x10 <sup>-4</sup>

## 2.4. Neves-Corvo sulphide ore experiments

The BAC collector selectivity for chalcopyrite was evaluated with a kinetic analysis. The kinetic parameters were calculated using the values of chalcopyrite, sphalerite and pyrite recovery with respect to the flotation time obtained carrying out a factorial design of experiments with three factors (BAC concentration, pH and ZnSO<sub>4</sub> concentration) and two levels (Table 4). Furthermore, using the

software package Design Expert 10.0.3.1<sup>®</sup>, Stat-Ease, Inc., Minneapolis, USA, was built a model which studied the relationship between the copper grade and recovery and the three factors modified. The analysis of variance (ANOVA) was used to estimate the statistical parameters. F-test was used to estimate the significance of all terms in the polynomial equation within 95% confidence interval.

Table 4. Levels of variation for the variables BAC concentration, pH and ZnSO<sub>4</sub> concentration used in the Neves-Corvo sulphide ore tests.

Factor	-1	1
BAC Concentration (g BAC/kg of mineral)	0.1	0.5
pH	7	9
ZnSO <sub>4</sub> Concentration (mol of ZnSO <sub>4</sub> /L of water)	1x10 <sup>-4</sup>	5x10 <sup>-4</sup>

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Panasqueira sulphide ore experiments

The values of copper, zinc and arsenic grade and recovery (which can be read as chalcopyrite, sphalerite and arsenopyrite recovery) in the floated product of the factorial design of experiments carried out with BAC collector are shown in Table 5. The copper grade values were slightly above the feed grade (0.7%). The best results were those obtained adding the lowest concentration of BAC collector (0.1 g/kg of mineral) and the lowest level of pH (7), with copper recovery values between 40-55%. For the other trials, the copper recovery is lower than 30%. Sphalerite and arsenopyrite were not well depressed and they achieved values of recovery of 35% for zinc and 17% for arsenic.

The BAC collector selectivity for chalcopyrite (the ability for collecting chalcopyrite instead of other minerals) was evaluated comparing the values of copper, zinc and arsenic recovery for the 32 trials carried out. The separation was deemed selective when the difference between the copper recovery and the zinc and arsenic recovery was equal or greater than 30%. Following this criterion, the collector was selective for chalcopyrite in trials 1, 4, 7 and 8, which were carried out with 0.1 g BAC/kg of mineral and pH 7 (trials 1, 4 and 7) and with 0.1 g BAC/kg of mineral, pH 8 and 5x10<sup>-4</sup> mol of ZnSO<sub>4</sub>/L of water (trial 8).

Finally, in order to obtain a model to describe the variables copper grade and recovery, it was used the software Design Expert 10.0.3.1<sup>®</sup>, Stat-Ease, Inc. The fitness of these models was tested using an analysis of variance (ANOVA). The ANOVA for copper recovery and the ANOVA for copper grade are shown in Table 6 and Table 7. These are simplified ANOVA that only include the variables with statistical significance (p<0.05), which are the BAC collector concentration (A), the pH (B) and the interaction between themselves and between them and the ZnSO<sub>4</sub> concentration (C) for copper recovery and, the BAC collector concentration, the pH and the interaction between themselves for copper grade. The values in Table 6 and Table 7 indicate the well-fitting of the experimental results to the quadratic model equations for both responses and hence, these models accuracy.

Table 5. Copper, zinc and arsenic grade and recovery in the floated product of the DOE carried out with BAC collector for the Panasqueira sulphide ore.

Trial	Modified Variables			Results					
	BAC (g/kg mineral)	ZnSO <sub>4</sub> (x10 <sup>-4</sup> mol/L water)	pH	Copper		Zinc		Arsenic	
				Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
1	0.1	1	7	3.55	50.93	1.17	8.03	23.51	9.73
2	0.1	1	8	2.13	13.69	2.35	7.28	27.54	4.94
3	0.1	1	9	1.82	25.75	1.84	12.46	20.19	9.29
4	0.1	3	7	3.98	41.13	1.36	6.83	20.58	6.68
5	0.1	3	8	2.18	12.03	2.82	7.56	24.06	4.06
6	0.1	3	9	1.84	18.74	2.19	11.03	23.52	7.13
7	0.1	5	7	3.29	53.92	1.07	8.34	20.92	10.83
8	0.1	5	8	2.16	36.41	0.88	7.14	16.65	9.05
9	0.1	5	9	1.81	24.67	1.97	13.07	20.11	8.58
10	0.3	1	7	2.05	9.60	3.28	7.25	22.81	3.16
11	0.3	1	8	1.81	17.25	3.17	15.00	22.63	6.66
12	0.3	1	9	1.74	23.33	3.19	20.74	23.01	9.56
13	0.3	3	7	2.24	12.28	3.28	8.51	22.91	3.92
14	0.3	3	8	1.84	16.67	3.19	13.77	23.28	6.16
15	0.3	3	9	1.79	23.01	3.28	20.65	23.61	9.43
16	0.3	5	7	2.07	9.65	3.35	7.60	23.03	3.23
17	0.3	5	8	1.82	15.02	3.14	12.67	23.36	5.82
18	0.3	5	9	1.79	19.68	3.27	17.83	23.76	8.20
19	0.3	3	8	1.81	14.72	3.26	13.09	23.09	6.01
20	0.3	3	8	1.85	13.13	3.18	11.05	23.29	5.45
21	0.3	3	8	1.71	16.96	3.14	15.35	23.41	7.29
22	0.3	3	8	1.76	14.31	3.18	12.70	23.38	6.26
23	0.3	3	8	1.87	13.33	3.20	11.36	23.03	5.26
24	0.5	1	7	1.71	13.49	3.35	12.92	22.99	5.42
25	0.5	1	8	1.61	20.53	3.16	19.59	23.93	9.11
26	0.5	1	9	1.54	35.14	3.07	34.36	24.78	16.74
27	0.5	3	7	1.65	9.49	3.41	9.59	23.42	4.50
28	0.5	3	8	1.63	23.80	3.06	22.42	23.71	10.23
29	0.5	3	9	1.56	27.39	3.13	26.69	24.19	12.59
30	0.5	5	7	1.66	11.90	3.42	11.96	23.55	5.00
31	0.5	5	8	1.63	20.13	3.26	19.53	23.70	9.16
32	0.5	5	9	1.61	24.29	3.15	23.22	23.96	11.30

Equations 1 and 2 are the quadratic model equations for the responses copper recovery and copper grade in terms of coded levels (the high levels of the factors were coded as +1 and the low levels as -1). The relative impact of each factor can be identified by comparing the coefficients.

$$\begin{aligned}
 Cu \text{ Recovery} = & 14.34 + 3.58A + 5.75B + 10.73AB - 5.78AC + 4.74A^2 + 3.04C^2 \\
 & - 7.82A^2B + 5.58A^2C - 8.18AB^2 - 4.79AC^2 + 6.97A^2B^2 + 3.99AB^2C \\
 & - 6.90A^2B^2C
 \end{aligned} \tag{1}$$

$$Cu \text{ Grade} = 1.78 - 0.27A - 0.17B + 0.42AB + 0.16A^2 + 0.21B^2 - 0.30A^2B - 0.28AB^2 \tag{2}$$

The equation coefficients show that the copper recovery was mainly affected by the interaction between the BAC collector concentration and the pH, followed by the interaction between these variables and the ZnSO<sub>4</sub> concentration. This means that the BAC collector is a chalcopyrite collector and that its efficiency is greatly dependent on the flotation conditions. For a better understanding of the equation, the predicted model for copper recovery is presented in Figure 1. It can be observed that the maximum copper recovery values correspond to the addition of 0.1 g BAC/kg of mineral and pH 7.

The equation for the copper grade obtained was less complex than the copper recovery one. Its coefficients show that this variable was mainly affected by the interaction between the BAC collector concentration and the pH, followed by the BAC concentration by its own. In Figure 2, the model

response surface for a  $\text{ZnSO}_4$  concentration of  $3 \times 10^{-4}$  mol/L of water is presented. It can be observed that the maximum values of copper grade correspond to the combination of 0.1 g BAC/kg of mineral and pH 7. The BAC concentration increase or the pH rise lead to lower values for the copper grade due to the increase in the gangue mineral recovery.

Table 6. ANOVA for copper recovery (tests with the Panasqueira sulphide ore)

Source	Sum of Squares	Degrees of Freedom	Mean Square	F	p Value Prob>F
Model	3817.06	13	293.62	36.5	< 0.0001
A - BAC Collector	46.14	1	46.14	5.73	0.0277
B - pH	198.26	1	198.26	24.64	0.0001
AB	1381.59	1	1381.59	171.72	< 0.0001
AC	133.63	1	133.63	16.61	0.0007
A <sup>2</sup>	91.26	1	91.26	11.34	0.0034
C <sup>2</sup>	68.73	1	68.73	8.54	0.0091
A <sup>2</sup> B	244.71	1	244.71	30.42	< 0.0001
A <sup>2</sup> C	124.55	1	124.55	15.48	0.001
AB <sup>2</sup>	267.32	1	267.32	33.23	< 0.0001
AC <sup>2</sup>	91.68	1	91.68	11.4	0.0034
A <sup>2</sup> B <sup>2</sup>	194.42	1	194.42	24.16	0.0001
AB <sup>2</sup> C	42.37	1	42.37	5.27	0.034
A <sup>2</sup> B <sup>2</sup> C	126.82	1	126.82	15.76	0.0009
Residual	144.82	18	8.05	-	-
Lack of fit	131.48	13	10.11	3.79	0.0751
Pure Error	13.34	5	2.67	-	-
Cor Total	3961.88	31	-	-	-

Table 7. ANOVA for copper grade (tests with the Panasqueira sulphide ore)

Source	Sum of Squares	Degrees of Freedom	Mean Square	F	p Value Prob>F
Model	9.66	7	1.38	100.93	< 0.0001
A- BAC Collector	0.43	1	0.43	31.21	< 0.0001
B - pH	0.18	1	0.18	13.19	0.0013
AB	2.12	1	2.12	154.85	< 0.0001
A <sup>2</sup>	0.18	1	0.18	13.37	0.0012
B <sup>2</sup>	0.34	1	0.34	24.78	< 0.0001
A <sup>2</sup> B	0.36	1	0.36	26.04	< 0.0001
AB <sup>2</sup>	0.31	1	0.31	22.94	< 0.0001
Residual	0.33	24	0.014	-	-
Lack of fit	0.31	19	0.016	4.4	0.0541
Pure Error	0.019	5	3.707x10-3	-	-
Cor Total	9.99	31	-	-	-

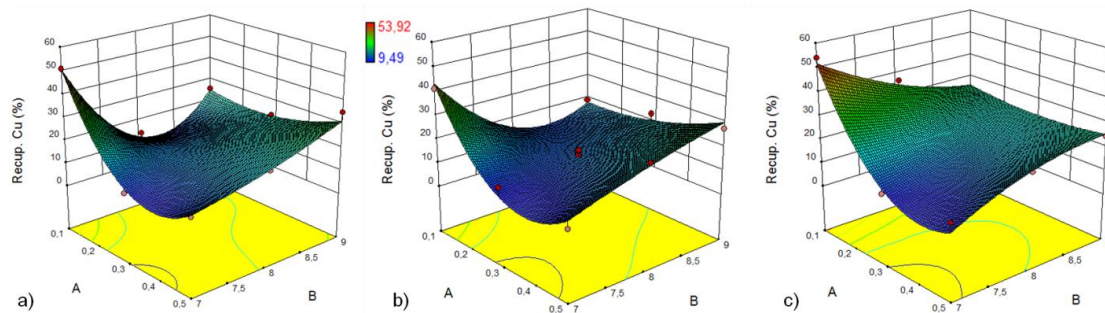


Figure 1. Response surface of copper recovery as function of BAC collector and pH for a  $\text{ZnSO}_4$  concentration of (a)  $1 \times 10^{-4}$  mol/L water, (b)  $3 \times 10^{-4}$  mol/L water and (c)  $5 \times 10^{-4}$  mol/L water for the trials carried out with the Panasqueira ore.

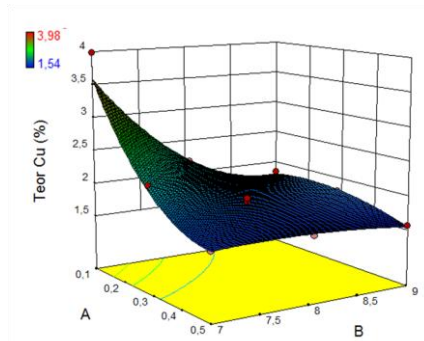


Figure 2. Response surface of copper grade as function of BAC collector and pH for a ZnSO<sub>4</sub> concentration of 5x10<sup>-4</sup> mol/L water for the trials carried out with the Panasqueira ore.

### 3.1. Neves-Corvo sulphide ore experiments

The values of copper, zinc and iron grade and recovery in the floated product of the factorial design of experiments carried out with BAC collector are shown in Table 8. Copper recovery cannot be read as chalcopyrite recovery because this is not the only copper mineral in the flotation feed. However, for the calculation of the kinetic parameters, it was considered that all the copper in the floated product corresponds to chalcopyrite because this is the prevailing copper mineral. The same criterion was applied to iron and pyrite.

The copper grade was slightly above the feed grade (2.1%). The maximum values of grade and recovery were reached with the addition of 0.1 g BAC/kg of mineral, while the lowest correspond to the addition of 0.5 g BAC/kg of mineral. Zinc and iron were not well depressed and they achieved values of recovery of 19% for zinc and 17% for iron, equal to the copper ones in some tests.

Table 8. Copper, zinc and iron grade and recovery in the floated product of the DOE carried out with BAC collector for the Neves-Corvo sulphide ore.

Trial	Modified Variables			Results					
	BAC (g/kg mineral)	ZnSO <sub>4</sub> (x10 <sup>-4</sup> mol/L water)	pH	Copper		Zinc		Iron	
				Grade (%)	Recovery (%)	Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
1	0.1	1	7	7.88	56.28	1.26	19.66	34.62	17.17
2	0.1	1	9	6.73	56.04	1.22	22.57	34.32	19.96
3	0.1	5	7	4.76	46.51	0.95	23.26	34.59	21.67
4	0.1	5	9	6.4	50.44	1.19	20.67	34.09	19.06
5	0.5	1	7	2.58	14.88	0.99	14.45	34.12	12.59
6	0.5	1	9	2.56	20.23	1.23	21.67	32.93	18.44
7	0.5	5	7	2.61	22.12	1.08	21.53	33.7	19.29
8	0.5	5	9	2.45	13.92	1.12	14.98	33.09	12.72
9	0.1	1	7	6.95	42.29	1.05	15.09	34.36	13.53
10	0.1	1	7	9.91	47.31	1.22	12.87	34.78	11.32

The kinetic parameters of the adjusted first order equation for chalcopyrite, sphalerite and pyrite for all the tests are shown in Table 9. It can be seen a clear difference between the kinetic parameters obtained with 0.1 g BAC/kg of mineral and the ones obtained with 0.5 g BAC/kg of mineral, as Figure 3 confirms. In this figure are shown the adjusted plots of chalcopyrite and gangue minerals (sphalerite and pyrite) recovery function for trials 1 (0.1 g BAC/kg of mineral) and 5 (0.5 g BAC/kg of mineral). In trial 1, the recovery functions show a different kinetic behaviour between the chalcopyrite and the other minerals, which means that the separation was selective for chalcopyrite. However, in trial 5, the

kinetic behaviour was very similar between chalcopyrite, sphalerite and pyrite. It means that there was not selectivity during the flotation process.

Table 9. Kinetic parameters of the adjusted first order equation (floated product) for the trials carried out with the Neves-Corvo sulphide ore

Trial	BAC (g/kg mineral)	ZnSO <sub>4</sub> (x10 <sup>-4</sup> mol/L water)	pH	Chalcopyrite R <sub>lim</sub> (%)	Chalcopyrite k (min <sup>-1</sup> )	Sphalerite R <sub>lim</sub> (%)	Sphalerite k (min <sup>-1</sup> )	Pyrite R <sub>lim</sub> (%)	Pyrite k (min <sup>-1</sup> )
1	0.1	1	7	71.74	0.21	19.98	0.42	17.20	0.47
2	0.1	1	9	80.27	0.16	25.50	0.28	23.50	0.25
3	0.1	5	7	93.21	0.09	25.95	0.28	24.21	0.28
4	0.1	5	9	57.50	0.28	23.00	0.39	21.50	0.40
5	0.5	1	7	13.00	0.28	15.00	0.43	13.50	0.36
6	0.5	1	9	22.00	0.38	23.00	0.38	20.00	0.45
7	0.5	5	7	25.00	0.35	23.00	0.40	22.00	0.36
8	0.5	5	9	15.30	0.45	17.00	0.35	14.50	0.35
9	0.1	1	7	100.00	0.07	21.00	0.18	19.00	0.18
10	0.1	1	7	76.41	0.13	16.30	0.23	15.00	0.21

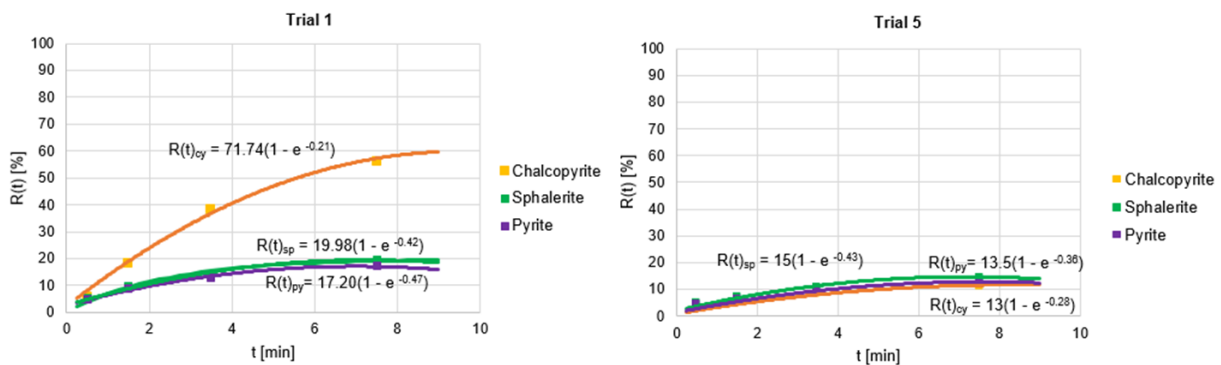


Figure 3. Adjusted plots of the chalcopyrite, sphalerite and pyrite recovery functions for trials 1 and 5 of the Neves-Corvo DOE

Finally, in order to obtain a model to describe the variables copper grade and recovery, it was used the software Design Expert 10.0.3.1<sup>®</sup>, Stat-Ease, Inc. The fitness of these models was tested using an analysis of variance (ANOVA). The ANOVA for copper recovery and the ANOVA for copper grade are shown in Table 10 and Table 11. These are simplified ANOVA that only include the variables with statistical significance ( $p < 0.05$ ). It can be seen that the only significant factor for the two responses is the BAC collector concentration (A). The values in Table 10 and Table 11 indicate the well-fitting of the experimental results to the linear model equations for both responses and hence, these models accuracy.

The linear model equations obtained for copper recovery and grade (equations 3 and 4) show that these variables were only affected by the BAC concentration, which implies that this is a copper collector. The increase in the BAC concentration leads to a reduction in the selectivity of the separation, decreasing the copper recovery and grade.

$$Cu \text{ Recovery} = 33.80 - 16.01A \quad (3)$$

$$Cu \text{ Grade} = 4.83 - 2.28A \quad (4)$$



Table 10. ANOVA for copper recovery (tests with the Neves-Corvo sulphide ore)

Source	Sum of Squares	Degrees of Freedom	Mean Square	F	p Value Prob>F
Model	2461.31	1	2461.31	97.04	< 0.0001
A - BAC Collector	2461.31	1	2461.31	97.04	< 0.0001
Residual	202.91	8	25.36	-	-
<i>Lack of fit</i>	102.45	6	17.07	0.34	0.8713
<i>Pure Error</i>	100.46	2	50.23	-	-
Cor Total	2664.22	9	-	-	-

Table 11. ANOVA for copper grade (tests with the Neves-Corvo sulphide ore)

Source	Sum of Squares	Degrees of Freedom	Mean Square	F	p Value Prob>F
Model	49.8	1	49.8	27.2	0.0008
A - BAC Collector	49.8	1	49.8	27.2	0.0008
Residual	14.64	8	1.83	-	-
<i>Lack of fit</i>	10.06	6	1.68	0.73	0.6757
<i>Pure Error</i>	4.58	2	2.29	-	-
Cor Total	64.44	9	-	-	-

#### 4. CONCLUSIONS

The efficiency of a nanofibrillated cellulose collector (BAC) was tested using two sulphide ore samples, one from Panasqueira mine and, the other one, from Neves-Corvo mine. For the Panasqueira sulphide ore sample, a factorial plan of experiments ( $3^3$ ) was conducted in order to study the BAC collector selectivity for chalcopyrite using the mineral sample for which the collector was created. The results obtained in terms of copper, zinc and arsenic grade and recovery were analyzed and it was concluded that the BAC collector is a chalcopyrite collector. The BAC was selective for chalcopyrite for the trials carried out with 0.1 g BAC/kg of mineral and pH 7 (for all the  $\text{ZnSO}_4$  concentrations) and with 0.1 g BAC/kg of mineral, pH 8 and  $5 \times 10^{-4}$  mol  $\text{ZnSO}_4/\text{L}$  of water. The collector efficiency in terms of copper recovery was mainly affected by the interaction between the BAC collector and the pH followed by the interaction between these variables and the  $\text{ZnSO}_4$ . The variable copper grade was mainly affected by the interaction between the BAC collector concentration and the pH, followed by the BAC concentration by its own. The BAC collector concentration increase or the pH rise lead to lower values for the copper grade due to the increase in the sphalerite and arsenopyrite recovery.

For the Neves-Corvo sulphide ore, a new factorial plan of experiments ( $2^3$ ) and a kinetic analysis were conducted. The purpose of these trials was to analyze the BAC collector selectivity for chalcopyrite using a mineral sample different to the one for which the collector was synthesized. The results obtained confirmed that BAC is a chalcopyrite collector. The kinetic parameters obtained from the values of chalcopyrite, sphalerite and pyrite recovery with respect to the flotation time showed that the BAC collector was selective for chalcopyrite when the flotation tests were carried out with 0.1 g BAC/kg of mineral. The variables copper recovery and grade were only affected by the BAC concentration. The BAC concentration increase leads to a reduction in the selectivity of the separation, decreasing the copper recovery and grade.

It can be concluded that the BAC collector is a chalcopyrite collector, which is selective for chalcopyrite when it is added in low concentrations (0.1 g BAC/kg of mineral), although this selectivity can be conditioned by the pulp pH and the added ZnSO<sub>4</sub> concentration (sphalerite depressant). Chalcopyrite was concentrated in the floated product, with reasonable values of recovery. However, the presence of smelter penalizing minerals in the floated product, which were not well depressed, decreased the quality of the copper concentrate.

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