Study of Butyl-Amine Nanocrystal Cellulose in the Flotation of Complex Sulphide Ores

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Abstract

Froth flotation is a widely used process for the beneficiation of complex sulphide ores. Thiol collectors (mostly xanthates) are usually effective collectors for sulphide minerals but may have a low selectivity between different sulphide minerals when associated in complex sulphide ores. Additionally, a concern is their suggested harmfulness on human health and impact on the environment. In this study, a green sustainable reagent, butyl-amine cellulose (BAC), was synthesized from hardwood kraft pulp, a renewable abundant resource, for the selective separation of chalcopyrite and sphalerite. The performance evaluation was made using samples of two ores containing chalcopyrite and sphalerite, one was from Panasqueira mine (Portugal) and the other with a different mineral association (from the massive sulphide deposits of the Iberian Pyrite Belt). The study demonstrated that when chalcopyrite is associated with sphalerite, BAC is selective for chalcopyrite, i.e., it is a collector for this mineral and not for sphalerite. The recovery of chalcopyrite in the floated product was a function of interaction between BAC concentration and pulp pH. The study showed that the novel cellulose-based collector had a better performance than the reagents used in the industrial flotation of Panasqueira ore.

1. Introduction

Froth flotation is the most used method for the beneficiation of sulphide minerals (Wills and Napier-Munn, 2006). In this process, minerals are separated in a vessel fed with pulp composed of finely ground ore and water, through which air bubbles rise, transporting hydrophobic particles attached to the bubbles to the top of the vessel. Because minerals are predominantly hydrophilic, the mineral's surface wetting properties must be previously modified using different types of chemicals to enable particle-bubble attachments. This is done by collectors that render the mineral's surface to the desired hydrophobicity, and depressants that prevent the adsorption of collectors on the other mineral particles. Additional chemicals may also be used; activators, which prepare the surface of the minerals to react with the collectors; pH regulators, because pulp pH affects the electrochemical state of mineral surfaces and the pulp potential; and frothers, used to stabilize the air bubbles that carry the hydrophobic particles to the surface and form the meta-stable particle-laden froth on top of the vessel (Kelly, 1982).

Complex sulphide ores represent a substantial raw material source for non-ferrous base metals and they often consist of platinum group metals and gold, which increases their economical attractiveness for beneficiation. The most common base metal in these ores is typically zinc, followed by lead and copper (Barbery, 1986). However, the selectivity between different sulphide minerals, such as chalcopyrite and sphalerite, may be a challenge in froth flotation due to their high degree of similarity. Galvanic interaction, being well-recognized phenomenon and linked to

the oxidation of mineral surfaces, can interfere significantly the selectivity. In grinding, the sulphide minerals - depending on their rest potentials - can act as a cathode or an anode against each other or against grinding medium. Consequent electrochemical reactions lead to changes in the chemistry of pulp and particle surfaces (Rabieh, et al, 2016). Besides galvanic interactions, also hydroxyl radicals are recently proposed to cause surface oxidation. Defects on the sulfide minerals surfaces can serve as a catalyst and break down water molecules to hydroxyl radicals (Carabineiro, et al, 2016). The effect is prevailing in wet grinding but it was shown to happen even in dry grinding after ground powder was suspended into water (Nooshabadi, et al, 2014). Therefore, different states of activation prevail for sulphide ores dependent on their processing. Thus, generated hydroxyl radicals responsible for the oxidation of mineral surfaces, may affect the flotation selectivity between sulphide minerals in beneficiation of complex sulphide ores.

Generally, thiol collectors are applied as sulphide mineral collectors. The most commonly used thiol collectors are xanthates, although other types are also used, such as dithiophosphates or thionocarbamates. The latter are less efficient than xanthates but have higher selectivity against iron sulphides and sphalerite, minerals that appear frequently associated with chalcopyrite (Fairthorne, et al., 1996; Woods, et al., 1999; Güler, et al., 2006; Guang-yi, et al., 2006; Liu, et al., 2008). Although thiols have shown to be efficient in the separation of sulphide minerals from gangue, their performance may not be effective when a highly selective separation between sulphide minerals from complex sulphide ores is targeted (Sirkeci, 2000). They also have disadvantages due to their significant impact on the environment and on human health. This is the case of xanthate, which may hydrolyze in the flotation of pulp, thus generating highly toxic species such as carbon disulphide, CS₂ (Shen, et al., 2016). Taking this into account, releasing xanthate into the aquatic environment, even at low concentrations (lower than 1 mg/L), can be toxic for the ecosystem, even though it degrades quite rapidly (Xu, et al., 1988).

The negative environmental impact associated with xanthate led to the development of a novel chemical reagent obtained from cellulose, the most abundant natural polymeric source, as a green alternative to replace synthetic chemicals. Recently, the method to produce tailored cellulose nanocrystals by combining regioselective oxidation and reductive amination followed by mechanical disintegration was introduced by Sirviö, et al. (2016). The performance of these modified nanocrystals in the flotation of oxide minerals was studied by Laitinen, et al., (2016) and their interactions with mineral surfaces by Hartmann, et al. (2016, 2017). One of those cellulose nanocrystal reagents, butyl-amine cellulose (here referred to as BAC) was chosen for this study to investigate its applicability for complex sulphide ores in the selective separation of chalcopyrite and sphalerite. These two minerals are frequently associated and they must be separated to correspond to the quality of final product. For the present study, BAC was considered to be the most efficient choice in terms of selectivity and hydrophobicity. Therefore, aminated cellulose nanocrystals with shorter hydrocarbon chains do not possess a sufficient degree of hydrophobicity to render a mineral's surface wetting properties adequately, while nanocrystals with longer hydrocarbon chains do not possess a sufficient degree of protonation at pH values higher than 7 to selectively adsorb on a target mineral (Hartmann, et al. 2016).

An experimental study was performed to analyze the performance of this new reagent as follows. First, a sample of the complex sulphide ore from Panasqueira mine was studied in order to evaluate the selectivity of BAC in the presence of chalcopyrite and sphalerite. The effect of three variables, BAC and ZnSO₄ (sphalerite depressant) concentration and pH value, on the recovery and grade of copper and zinc in the floated product were analyzed. The responses of copper recovery and grade to flotation conditions were also modelled. Also, experimental tests were conducted with the reagents used in the Panasqueira mine industrial plant (here referred to as

commercial reagents) and the results were compared with those obtained with BAC. Finally, the new cellulose-based reagent was also tested on another type of complex sulphide ore containing chalcopyrite and sphalerite but with different mineralogical association (from the massive sulphide deposits of the Iberian Pyrite Belt). This will be referred to as IPB sulphide ore.

2. Materials and Methods

2.1. Mineral Samples

The Panasqueira sample was collected from the flow that feeds the chalcopyrite concentration circuit before it enters the grinding stage and the addition of any reagents. The sample was ground under dry conditions to 80% passing 75 μm so that it resembled the size distribution of the feed of the Panasqueira industrial flotation circuit. The Cu and Zn contents (%) of the sample were 0.72 and 2.52, respectively. The IPB sulphide ore sample was collected from the stream that feeds the copper flotation circuit after grinding (80% passing 50 μm) and before adding reagents (with the exception of lime, which was added before grinding). The Cu and Zn contents (%) were 2.09 and 0.58, respectively.

Table 1 shows the mineral composition of the Panasqueira and IPB sulphide ore samples, obtained using MLA (Mineral Liberation Analyser). It should be noted that the IPB sulphide sample contains other copper minerals in addition to chalcopyrite, such as enargite, tetrahedrite, tennantite and stannite, chalcopyrite being the predominant copper mineral.

Table 1. Mineral composition of the Panasqueira and IPB sulphide samples (EPDM, 2016).

	Py (%)	Cy (%)	Ay (%)	Sph (%)	En (%)	Tet (%)	Tenn (%)	Stan (%)	Others (%)
Panasqueira	31.03	2.10	49.06	3.93	-	-	-	-	13.89
IPB sulphide	63.60	5.10	1.32	1.05	0.36	0.12	0.12	0.12	28.21

Legend: Py – Pyrite Cy–Chalcopyrite; Ay -Arsenopyrite; Sph- Sphalerite; En-Enargite; Tet-Tetrahedrite; Tenn-Tennantite; Stan-Stannite

2.2 Butyl-Amine Cellulose – Synthesis and Characterization

Macromolecular butyl-amine cellulose nanocrystals (BAC) represent a new type of reagent used in flotation and therefore, its synthesis and main physicochemical properties are shortly described. BAC was prepared from dried bleached kraft birch pulp (*Betula pendula*) as described by Sirviö, et al. (2016). In brief, the procedure was as follow: oxidized dialdehyde cellulose (DAC) was synthesized by oxidizing 15 g of cellulose (dry weight) using 12.3 g of sodium periodate as an oxidant and 27 g of lithium chloride as a cellulose activator. The three-hours-reaction was carried out at 75°C. After washing, the reductive amination of DAC was performed by using tenfold excess of amine in relation to the aldehyde groups of DAC (3.86 mmol/g) mixed in deionized water. Solution pH was adjusted to 4.5 with a dilute HCl. Non-dried DAC and a twofold excess of 2-picoline borane in relation to the aldehyde groups of DAC were added. The reaction was continued at room temperature for 72 h under stirring in a closed container followed by filtration

127 and washing of fibre cake first with ethanol and then with de-mineralized water. The BAC was
 128 diluted to a 0.3% consistency and disintegrated using a two-chamber high-pressure homogenizer
 129 (APV-2000, Denmark). Then, the suspension was passed through the homogenizer five times at
 130 pressures of 200, 400, 600, 800, and 1000 bar to obtain a colloidal BAC suspension.

131 The simplified synthesis route for BAC is illustrated in Figure 1.

132

133

134 Figure 1. Synthesis route from cellulose to butyl-amine cellulose (BAC).

135

136 The nanocrystals were visualized using transmission electron microscopy (Tecnai G2 Spirit
 137 transmission electron microscope, FEI Europe, Netherlands) shown in Figure 2.

138

139

140 Figure 2: TEM image of BAC nanocrystals. Photo by Juho Sirviö.

141 The electrophoretic mobility of BAC in a 10^{-3} M potassium chloride background solution at
 142 different pH values was determined using a Beckman Coulter Delsa Nano C. For each sample, one
 143 measurement was conducted and three individual values for the zeta potential obtained, its
 144 distribution is shown in Figure 3.

146

147 Figure 3: The zeta-potential distribution of butyl-amine cellulose over different pH values in a 10^{-3}
 148 M KCl background salt solution, error bars represent the standard deviation.

149

150 The isoelectrical point of the examined BAC is approximately at pH 10 indicating the presence of
 151 amine groups (positive zeta-potential in acidic pH range) as well as hydroxide and aldehyde
 152 groups (negative zeta-potential in basic pH range) within the cellulose structure. The presence of
 153 amine groups in similarly fabricated BAC was also shown by Sirviö et al (2016) using DRIFT
 154 (diffuse reflectance infrared Fourier transform) analysis.

155 With respect to the experiments performed for this study, the maximal pH value set was 9 and thus
 156 BAC is expected to possess a positive net surface charge during the experiments originating from
 157 protonated amine groups which leads theoretically to the physisorption of BAC on mineral
 158 surfaces bearing a negative surface charge under equivalent conditions. In regard to the wetting
 159 properties of BAC, previous studies have shown that BAC increases the water contact angle after
 160 adsorption on quartz, and simultaneously leads to high flotation recovery (Laitinen 2016,
 161 Hartmann 2016), which is going to be further examined in this study using chalcopyrite as mineral
 162 phase.

2.3 Commercial Flotation Reagents

The flotation performance of BAC was studied with three auxiliary reagents: a pH regulator, sphalerite depressant and frother. Sodium hydroxide (NaOH) was used for pH control in the tests performed on the Panasqueira sulphide ore. Hydrochloric acid (HCl) was used in the IPB sulphide ore tests because the sample had a higher pH (acquired in the grinding circuit) than the desired one. The frother used with both samples was AEROFROTH® 65. When chalcopyrite is associated with sphalerite, the latter is easily activated by dissolved Cu^{2+} ions in the pulp leading to an inefficient separation. To prevent this from happening, an additional salt such as ZnSO_4 must be used to depress sphalerite (Cao & Qi, 2006). The reagents used in the experimental tests are presented in Figure 4, including also the commercial reagents applied in the Panasqueira mine, which were used in the reference flotation.

REAGENTS			
Function	Panasqueira sample	Panasqueira sample (industrial conditions)	IPB sulphide sample
➤ Chalcopyrite collector ➤ Sphalerite depressant ➤ pH regulator ➤ Frother ➤ Pyrrothite, sphalerite and arsenopyrite depressant (CYTEC, 2002) ➤ Sphalerite and pyrite depressant (Dávila-Pulido, et al., 2011)	➤ BAC ➤ ZnSO_4 ➤ NaOH ➤ AEROFROTH® 65 ➤ --- ➤ ---	➤ AEROFLOAT® 208 ➤ Lime (pH 12.5) ➤ AEROFROTH® 65 ➤ AERO® 7261A ➤ Sodium metabisulphite	➤ BAC ➤ ZnSO_4 ➤ HCl ➤ AEROFROTH® 65 ➤ --- ➤ ---
	Part I	Part II	Part III

Figure 4. Reagents used in the flotation tests.

2.4. Experimental Procedure

The flotation tests were carried out in Denver D12 laboratory flotation cell equipped with a 2.5 l tank with 40% of solids by weight. The experimental procedure was carried out under the practices and conditions commonly used in each plant's laboratory tests. In the tests performed with the Panasqueira sample the conditioning time and the flotation time were both set at 5 min, whereas in the IPB sulphide sample tests the conditioning time was set at 5 min and the flotation time at 7.5 min. The sunk and floated products were filtered, dried in an oven and analysed using X-Ray Fluorescence (XRF).

2.5. Experimental Methodology

Design of Experiments (DOE) methodology is an efficient approach for setting up experiments where factors (variables) are manipulated independently and the results are verified using recognized statistical methods. It provides a basis to draw inferences about the process and reveals

190 the presence of interactions between factors (Anderson & Whitcomb, 2007). DOE also minimizes
191 the number of experiments needed (in comparison with the “one factor at a time” approach) and
192 minimizes the variance of the estimated coefficients obtained through regression (Jordão et al,
193 2016).

194 As mentioned above, the factors considered were: BAC collector concentration, pH value and
195 ZnSO₄ (sphalerite depressant) concentration. The experimental plan was divided into three parts,
196 which are presented in Figure 5. Two designs of experiments were executed: a three-level factorial
197 design for the Panasqueira sample (Part 1) and a two-level factorial design for the IPB sulphide
198 sample (Part 3). The study with Panasqueira sample was detailed (3 level factorial design with 32
199 trials) since the objective was to identify the factors and interactions that affect the flotation
200 responses (Cu recovery and grade). In case of the IPB sample, the efficiency of BAC for the
201 flotation of a different sulphide ore was tested, using a simpler experimental design (2 level
202 factorial design with 10 trials). The BAC concentrations were chosen based on previous
203 experiments (Laitinen, et al. 2016). Three additional tests were conducted on the Panasqueira
204 sample using the same reagents and flotation conditions used in the Panasqueira plant (Part 2).

205 The efficiency of BAC as a collector for chalcopyrite was analysed by modelling the copper and
206 zinc grade and recovery responses. The statistical analysis of the results was performed using the
207 software package Design Expert 10.0.3.1®, Stat-Ease, Inc., Minneapolis, USA.

208

Figure 5. Experimental plan for the Panasqueira and IPB sulphide samples. BAC values are in g_{BAC}/kg_{mineral} and ZnSO₄ values are in g_{ZnSO₄}/kg_{mineral}.

To calculate the pure error, replicate tests were performed on the Panasqueira sample using the intermediate values of each factor (0.3 g_{BAC}/kg_{mineral}, 0.12 g_{ZnSO₄}/kg_{mineral} and pH 8), and on the IPB sulphide sample using the minimum values of each factor (0.1 g_{BAC}/kg_{mineral}, 0.04 g_{ZnSO₄}/kg_{mineral} and pH 7). The grades were determined by XRF. The recovery of each element was calculated using the well-known Eq. (1) (see, for instance, Wills and Napier-Munn, 2006)

$$Recovery (\%) = \frac{c(f-t)}{f(c-t)} \times 100 \quad (\text{Eq.1})$$

221 Where f , c and t are the grades of the feed, concentrate and tailings, respectively.

222 Although copper is present in more than one mineral, chalcopyrite is the predominant one in the
223 IPB sulphide ore, so it was considered that the recovery of copper corresponds to the recovery of
224 chalcopyrite.

225 3. Results and Discussion

226 3.1. Panasqueira Sample Experiments

227 3.1.1. Flotation with BAC

228 The copper and zinc grade and recovery in the floated product obtained in the tests conducted with
229 the BAC collector on the samples from the Panasqueira sulphide mine are listed in Table 2 and
230 illustrated in Figure 6.

231 It appeared that recovery and grade for Cu remained at low level in most of the flotation tests.
232 Nevertheless, the copper grade in the floated product, with a mean value of 2.0%, were always
233 higher than the feed grade (0.7%). On proper conditions, however, stepwise improvements could
234 be seen with recovery over 50% and grades above 3.2%. Simultaneously, Zn recovery and grade
235 remained at low level – around 8.2% and 1.1 %, respectively. Thus, BAC had tendency to adsorb
236 rather onto chalcopyrite than sphalerite surfaces. This is beneficial because Cu and Zn are aimed
237 to be separated into different products. Cu recovery and grade may not seem to be impressive but
238 Panasqueira ore is know to be difficult for beneficiation by flotation even with commercial
239 chemicals.

240 The best results (higher recovery values and grade of copper in the floated product), were obtained
241 with the lowest BAC concentration (0.1 g_{BAC}/kg_{mineral}) and the lowest pH level (7). At higher
242 values of pH and BAC concentration, the sphalerite recovery increases, indicating an enhanced
243 adsorption of BAC on sphalerite at higher BAC concentrations.

244 Table 2. Copper and zinc grade and recovery in the floated product obtained in the DOE carried
245 out with BAC - Panasqueira ore sample.

246

BAC (g/kg _{mineral})	ZnSO ₄ (g/kg _{mineral})	pH	Cu		Zn	
			Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
0.1	0.04	7	3.55	50.93	1.17	8.03
0.1	0.04	8	2.13	13.69	2.35	7.28
0.1	0.04	9	1.82	25.75	1.84	12.46
0.1	0.12	7	3.98	31.13	1.36	6.83
0.1	0.12	8	2.18	12.03	2.82	7.56
0.1	0.12	9	1.84	18.74	2.19	11.03
0.1	0.20	7	3.29	53.92	1.07	8.34
0.1	0.20	8	2.16	36.41	0.88	7.14
0.1	0.20	9	1.81	24.67	1.97	13.07
0.3	0.04	7	2.05	9.6	3.28	7.25
0.3	0.04	8	1.81	17.25	3.17	15.00
0.3	0.04	9	1.74	23.33	3.19	20.74

0.3	0.12	7	2.24	12.28	3.28	8.51
0.3	0.12	8	1.84	13.67	3.19	13.77
0.3	0.12	9	1.79	23.01	3.28	20.65
0.3	0.20	7	2.07	9.65	3.35	7.60
0.3	0.20	8	1.82	15.02	3.14	12.67
0.3	0.20	9	1.79	19.68	3.27	17.83
0.3	0.12	8	1.81	14.72	3.26	13.09
0.3	0.12	8	1.85	13.13	3.18	11.05
0.3	0.12	8	1.71	16.96	3.14	15.35
0.3	0.12	8	1.76	14.31	3.18	12.70
0.3	0.12	8	1.87	13.33	3.20	11.36
0.5	0.04	7	1.71	13.49	3.35	12.92
0.5	0.04	8	1.61	20.53	3.16	19.59
0.5	0.04	9	1.54	35.14	3.07	34.36
0.5	0.12	7	1.65	9.49	3.41	9.59
0.5	0.12	8	1.63	23.80	3.06	22.42
0.5	0.12	9	1.56	27.39	3.13	26.69
0.5	0.20	7	1.66	11.90	3.42	11.96
0.5	0.20	8	1.63	20.13	3.26	19.53
0.5	0.20	9	1.61	24.29	3.15	23.22

3.1.2 Modelling the copper grade and recovery responses

The efficiency of BAC as a collector for chalcopyrite was analysed by modelling the copper grade and recovery responses. The fitness of the models obtained was tested using Analysis of Variance (ANOVA). A p-value ≤ 0.05 was used as a significance criterion, and the corrected Akaike Information Criterion (AICc) was used to select the terms kept in the models. The R-squared, adjusted R-squared and predicted R-squared values were also calculated to evaluate the model fit.

Copper Recovery Model

The test of the fitness of the model via ANOVA given in Table 3 shows that copper recovery is mainly affected by the BAC concentration and the pH value, whereas zinc sulphate showed to have insignificant effect (thus eliminated from individual analysis). The interaction between BAC concentration and the pH value was significant thus the individual effect of one of the two factors (BAC concentration or pH value) depends on the level at which the other factor was set. The quadratic behaviour of the model was determined by BAC concentration term (A^2).

The fitness of the copper recovery model was considered significant ($p \leq 0.05$). Because replicates were performed, the residual sum of squares was divided into “lack of fit” and pure error. Thus, it was possible to determine the part of the residual sums of squares that explains to which extent the model failed to accurately describe the functional relationship between the factors and the response. The other part, which corresponds to the pure error, represents the error that cannot be predicted, since it results from the variability obtained when testing under the same conditions (random noise).

Table 3: ANOVA for copper recovery (inverse square root transformation ($\lambda = -0.5$)).

Source	Sum of Squares	Degrees of Freedom	Mean Square	F	P –value
Model	0.053	4	0.013	12.00	<0.0001
A-BAC	5.4×10^{-3}	1	5.41×10^{-3}	4.93	0.0350
B-pH	9.62×10^{-3}	1	9.62×10^{-3}	8.76	0.0063
AB	0.023	1	0.023	20.62	0.0001
A^2	0.015	1	0.015	13.69	0.0010
Residual	0.030	27	1.10×10^{-3}		
Lack of fit	0.029	22	1.30×10^{-3}	6.59	0.0227
Pure error	9.89×10^{-4}	5	1.98×10^{-4}		
Total	0.082	31			

The Box-Cox power transformation was used to determine if the data could be transformed and the model could be improved. Using the inverse squared root transformation ($\lambda = -0.5$), the significance of the lack of fit was minimized; nevertheless, it remained below 0.05 (significant). The goodness-of-fit coefficients are presented in Table 4. The accuracy for predicting responses for new observations (predicted R-squared) and the accuracy for estimating the actual responses (R-squared) are reasonably similar (0.49 and 0.64, respectively). Furthermore, the adjusted R-squared, with a value of 0.59, shows no evidence of overfitting. Based on the low values of these coefficients and on the significant “lack of fit”, the copper recovery model does not accurately fit the data and thus

283 should not be used for predictions. To overcome the presence of lack of fit and thus improve the
 284 values of goodness-of-fit coefficients, other variables that may affect the flotation products should
 285 be studied, experiments repeated or additional values for the examined parameters studied. The lack
 286 of fit can occur if important/critical terms from the model are not included.

287 To better understand the results, the copper recovery model was presented as three-dimensional
 288 response surface plot (Fig.7). The red dots above and below the response surface represent the
 289 actual values of the responses (the results measured in the trials). If the model predicts the
 290 response with perfect accuracy, the red dots belong to the response surface. The results suggest that
 291 higher values of copper recovery may be reached outside the experimental space, such as for
 292 lower values of BAC concentration and pH or higher values of BAC concentration and pH value.
 293 Although BAC was presumed to function best in alkaline or neutral surrounding (on reason of a
 294 appropriate share of protonated and de-protonated amine groups), it is possible that the optimum
 295 exists in slightly acidic conditions due to the more complex conditions of the flotation pulp, such
 296 as the presence of several mono- and multivalent ions. Finally, also the effect of ZnSO_4 as
 297 depressant was almost negligible for the examined concentrations at otherwise constant
 298 conditions. A possible explanation for this behaviour may not be the insufficient depression of
 299 sphalerite by Zn^{2+} -ions, but the reduction of the electric surface potential of BAC by SO_4^{2-} - ions
 300 leading to a reduction of selective interactions between BAC and chalcopyrite. Therefore, ZnSO_4
 301 may possess an antagonistic effect on the BAC adsorption on chalcopyrite, rather than acting as
 302 depressant and studies should be performed on the selectivity of BAC without the presence of
 303 ZnSO_4 .

304

305 Table 4: R-squared coefficients and corrected Akaike information criterion (copper recovery
 306 model).

R-squared	0.64
Adjusted R-squared	0.59
Predicted R-squared	0.49
AICc	-120.38

Design-Expert® Software

Factor Coding: Actual

Original Scale

RCu (%)

● Design points above predicted value

○ Design points below predicted value

53.92

9.49

X1 = A: BAC

X2 = B: pH

Actual Factor

C: ZnSO4 = 1

307

308 Fig.7: Response surface plot for the copper recovery with respect to the BAC concentration and
309 pH value for a ZnSO₄ concentration of 0.04 g/kg_{mineral} (Panasqueira sulphide ore).

310

311 Equation 2, presented below, was the selected response surface model for copper recovery. This
312 equation is presented in terms of coded levels (the high levels of the factors were coded as +1, the
313 intermediate levels as 0 and the low levels as -1). Thus, the relative impact of each factor can be
314 identified by comparing the coefficients. The model was validated and the residuals were
315 considered independent and normally distributed with null average and constant variance by
316 means of graphical analysis.

317

$$\frac{1}{\sqrt{Cu_{Recovery}}} = -0.201 + 2.479A + 0.0420B - 0.217AB - 1.092A^2 \quad (\text{Eq.2})$$

318

319 **Copper Grade Model**

320 The copper grade model (Eq.3) was less complex than the copper recovery model (Eq.2). Despite
321 the fact that a quadratic model could be adjusted to the data, a linear model with two factor
322 interaction proved to be more suitable. A Box-Cox power transformation was applied with a
323 lambda equal to -2.73. This transformation improved the behaviour of residuals. The ANOVA of
324 the transformed data showed a significant model and a non-significant “lack of fit” shown in Table

325 5. The relationship between the factors and the response was described by the interaction term
 326 between BAC concentration and the pH value. In Figure 8, it can be seen that when the BAC
 327 concentration was set to the maximum level, the values of copper grade obtained were almost the
 328 same whether pH was set to maximum or minimum level. But when BAC concentration was set to
 329 minimum level, higher values of copper grade were reached when pH was set to 7 and lower
 330 values were reached when pH was equal to 9.

331

332 Table 5: ANOVA for copper grade (transformation $\lambda = -2.73$).

Source	Sum of Squares	Degrees of Freedom	Mean Square	F	P-value
Model	0.160	3	0.052	185.48	<0.0001
A-BAC	0.100	1	0.100	371.00	<0.0001
B-pH	0.042	1	0.042	149.43	<0.0001
AB	0.010	1	0.010	36.02	<0.0001
Residual	7.87×10^{-3}	28	2.81×10^{-4}		
Lack of fit	6.05×10^{-3}	23	2.63×10^{-4}	0.72	0.73
Pure error	1.82×10^{-3}	5	3.64×10^{-4}		
Total	0.16	31			

333

334

335

336 Figure 8. BAC concentration and pH value interaction plot for copper grade (Panasqueira sulphide
 337 ore).

338

339 The R-squared, adjusted R-squared and predicted R-squared coefficients presented high values
 340 indicating that the model describes the observed data with a high degree of accuracy and that it is
 341 capable of providing valid predictions for new observations (see Table 6).

342

343 Table 6: R-squared coefficients and corrected Akaike information criterion (copper grade model).

R-squared	0.95
Adjusted R-squared	0.95
Predicted R-squared	0.94
AICc	-165.66

344

345 Figure 9 presents the surface of the copper grade response with respect to the BAC concentration
 346 and pH value. It can be seen that the maximum copper grade values correspond to the optimal Cu
 347 recovery setting obtained in the trials: 0.1 g_{BAC}/kg_{mineral} and pH 7. Increasing the BAC
 348 concentration or the pH value leads to a reduction of the copper grade.

349

350

351 Figure 9. Response surface plot for the copper grade with respect to the BAC concentration and
 352 pH value for a ZnSO₄ concentration of 0.04 g/kg_{mineral} (Panasqueira sulphide ore).

353

354 Eq. (3) was the selected response surface model for copper grade. The model was validated and
 355 the residuals were considered independent and normally distributed with null average and constant
 356 variance by means of graphical analysis.

357

$$(Cu\ Grade)^{-2.73} = 0.190 + 0.076A + 0.048B - 0.029AB \quad (Eq.3)$$

358

359 3.1.3 Comparison of BAC and Commercial Collector

360 In the second part of the study, the results obtained, using BAC as collector in tests conducted
 361 under optimized conditions (the lowest variable values), were compared to the ones obtained with
 362 the reagents used in Panasqueira mine (industrial conditions). The results are given in Figure 10
 363 showing the recovery and grade of copper, zinc and additionally arsenic (since arsenic is an
 364 important penalty element). The Cu recovery values achieved with the commercial reagents were
 365 very similar to the values obtained with the BAC collector. Interestingly, the recovery of Zn was
 366 significantly reduced using BAC relative to commercial reagents indicating a considerable
 367 selectivity. Simultaneously, the recovery of the penalty element (arsenic) was lower when BAC
 368 was used. These results highlight the potential of BAC to be used as a selective collector for
 369 copper-bearing minerals.

370

371

372 Figure 10. Comparison between the recovery/grade curves for copper, zinc and arsenic in the trials
 373 carried out with the commercial reagents and with BAC. The ffed grades of Cu, Zn and As were
 374 0.72%, 2.52% and 22.57%, respectively.

375

376 The interactions between BAC and minerals are complex complicating the evaluation of the
 377 obtained results. The adsorption of BAC on the chalcopyrite surface strongly depends on
 378 electrostatic interactions given that BAC possesses positive free surface charges under the
 379 examined conditions while chalcopyrite is negatively charged. Further, the action of ZnSO_4 has to

be taken into consideration due to the reduction of the electric surface potentials of the mineral and BAC through dissociated Zn^{2+} - and SO_4^{2-} - ions. Consequently, the results indicate that with increasing pH value the electrostatic attraction between BAC and chalcopyrite is reduced leading to insufficient adsorption of BAC on the mineral surface and change of the surface wetting properties, respectively. This is based on the strong reduction of protonated amines in the BAC structure and the associated increasing effect of dissociated ions on BAC-mineral interactions. The explanation of the tendency of decreasing floatability of chalcopyrite with increasing BAC concentration is not trivial and demands further studies. One explanation could be the formation of polylayers of BAC on the mineral surface, where protonated amine groups of BAC nanocrystals are oriented towards the aqueous phase forming a higher electric potential as physically adsorbed BAC nanocrystals (where protonated amine groups are oriented to the mineral surface) leading to a stable liquid film on the mineral surface (Hartmann, et al., 2018). Further, weak attractions between BAC nanocrystals and the mineral surface (only attractive van der Waals interactions) increases the probability of particle-bubble detachment due to hydrodynamic turbulences in the flotation cell.

3.2. IPB Sulphide Sample Experiments

The results with BAC and IPB ore are listed in Table 7 and illustrated in Figure 11. The copper grade of the floated products was higher than the feed grade (2.1%) in all the trials, and the highest copper grade reached was 9.9%, obtained by adding 0.1 g_{BAC}/kg_{mineral}, pH 7 and 0.04 g_{ZnSO₄}/kg_{mineral}. The zinc grade of the floated product was slightly higher than the feed grade (0.6%) in all tests.

With respect to the copper recovery in the floated product, the highest percentage reached was 56.3%, obtained when 0.1 g_{BAC}/kg_{mineral}, 0.04 g_{ZnSO₄}/kg_{mineral} and pH 7 was used (the same settings that resulted in the highest Cu grade), while the lowest value, 13.9%, was obtained with 0.5 g_{BAC}/kg_{mineral}, 0.20 g_{ZnSO₄}/kg_{mineral} and pH 9. For zinc, the average recovery value was 18.7%, but the grade was higher than that of the feed.

In general, BAC performed with IPB sulphide ore similarly than with Panasqueira ore with respect to the recovery of copper. With low concentration (0.1 g_{BAC}/kg_{mineral}) chalcopyrite floated preferably compared to sphalerite. However, while the selectivity for the Panasqueira ore was remarkable, leading to higher grade in copper and lower grade in zinc and arsenic, the zinc grade remained at a similar level in the case of the IPB sulphide ore and only the copper grade increased. For both ores, the higher concentration of BAC caused a loss in selectivity between chalcopyrite and sphalerite. Notably, IPB sulphide ore was less sensitive for pH than Panasqueira ore. The reason behind different behaviour of the ores lays probably on mineralogical and morphological differences of them, but further studies are needed to clarify the issue. Also the presence of lime in the IPB ore, added to the ore at the grinding stage, introduced an unknown concentration of Ca^{2+} -ions to the pulp, which may have an effect on interactions between BAC and the minerals.

It is worth of emphasise that the used BAC was not optimized but the reductive amination with butyl amine was the first assumption of chemical modification of cellulose that could work with complex sulphide ores. There is a lot of room for the optimization of tailored green reagents, such as the degree of substitution of amine groups, which could be increased or decreased by changing

421 reaction conditions. The amine chain length could also be adjusted in order to affect
 422 hydrophobicity as described by Sirviö et al (2016) or different organic end groups apart from
 423 linear hydrocarbon chains linked to the amine group. It is also possible that another functional
 424 group instead of amines in cellulose backbone would interact better with sulphide minerals. The
 425 reagent development is still in its early phase, but these results indicate that chemically modified
 426 cellulose nanocrystals potentially be a promising candidate as green alternative in the selective
 427 flotation of sulphide minerals.

428

429 Table 7. Copper and zinc grade and recovery in the floated product obtained in the DOE carried
 430 out with the BAC collector - IPB sulphide ore sample.

BAC (g/kg _{mineral})	ZnSO ₄ (g/kg _{mineral})	pH	Cu		Zn	
			Grade (%)	Recovery (%)	Grade (%)	Recovery (%)
0.1	0.04	7	7.88	56.28	1.26	19.66
0.1	0.04	9	6.73	56.04	1.22	22.57
0.1	0.20	7	4.76	46.51	0.95	23.26
0.1	0.20	9	6.40	50.44	1.19	20.67
0.5	0.04	7	2.58	14.88	0.99	14.45
0.5	0.04	9	2.56	20.23	1.23	21.67
0.5	0.20	7	2.61	22.12	1.08	21.53
0.5	0.20	9	2.45	13.92	1.12	14.98
0.1	0.04	7	6.95	42.29	1.05	15.09
0.1	0.04	7	9.91	47.31	1.22	12.87

431

432

433 Figure 11. Copper, zinc and iron recovery and grade for the trials carried out with BAC and the
434 IPB sulphide ore. The feed grades of Cu and Zn were 0.58% and 2.09%, respectively.

435

436 **4. Conclusions**

437 A green reagent, butyl-amine cellulose nanocrystals (BAC), was synthesized to be studied as a
438 selective collector for complex sulphide ores. Flotation tests were conducted with two ores
439 containing chalcopyrite and sphalerite: the Panasqueira ore and the IPB sulphide ore possessing
440 different mineral associations. The manipulated variables were BAC concentration, pH value, and
441 ZnSO_4 concentration (sphalerite depressant).

442 It was shown for the first time that macromolecular BAC can serve as an efficient and selective
443 collector for sulphide minerals. BAC interacted selectively with different minerals in complex
444 sulphide ores, including chalcopyrite and sphalerite, but also arsenopyrite. Results indicate that
445 BAC has a much greater affinity onto the surfaces of chalcopyrite than sphalerite, and a very low
446 affinity onto arsenopyrite. The efficiency was affected by the physicochemical state of BAC and
447 the pulp pH value but only slightly by ZnSO_4 within the examined concentration. Under the
448 flotation conditions investigated, neutral pH and low BAC dosing seemed to work best. BAC
449 overdosing was found to be detrimental for both tested ores whereas the role of pH seems to
450 depend on the mineralogy of the ore to be examined.

451 Despite the fact that the functionality of aminated cellulose nanocrystals was not optimized in
452 terms of the degree of substitution of amine groups and spatial dimensions (length and diameter of

453 the nanocrystals), the present flotation results are very promising. The performance of BAC
454 exceeded the one of commercial thiol collector that is used for the Panasqueira ore. BAC collector
455 floated chalcopyrite quite selectively in the presence of arsenopyrite and sphalerite. The recovery
456 of these two penalizing minerals in the floated product was remarkably reduced to less than 10%.
457 This was achieved without the addition of an arsenopyrite depressant and a very small
458 concentration of sphalerite depressant.

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466

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