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Evaluation of the Effect of pH and Concentration of Calcium and Sulfate Ions on Coal Flotation

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Abstract: The presence of calcium sulfate in the process water during the coal flotation greatly influences the recovery and selectivity of the separation. The concentrations of calcium and sulfate ions modify mineral hydrophobicity by altering surface properties resulting in depression or activation of the mineral species. An investigation to evaluate the statistical significance of the effect of the pH and concentration of calcium and sulfate ions on coal flotation was carried out; for this purpose, a 2^3 factorial design was implemented. A p-value < 0.05 was determined for the effect of calcium and sulfate ion concentrations, indicating that it is statistically significant. The interactions between factors (pH × calcium, pH × sulfate, calcium × sulfate and pH × calcium × sulfate) are also statistically significant, but the interaction between the concentration of calcium and sulfate ions has a notable influence according to the F statistic value. Employing 800 and 1920 mg/L of calcium and sulfate ions as experimental conditions yields a recovery of 90.4% with a concentrate containing 13% ash.

Keywords: coal flotation; sulfate ions; calcium ions; process water; hydrophobicity; analysis of variance; factorial design

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1. Introduction

Flotation, a widely used mineral processing technique, selectively concentrates valuable minerals from the accompanying gangue through complex interactions between solid particles, conditioning reagents and dissolved ions [1]. The presence of dissolved ions is unavoidable due to the dissolution of target minerals and gangue, the release of fluid inclusions during crushing or grinding of the mineral, the depletion of grinding media and the reuse of water during mineral flotation [2]. These ions can significantly alter the chemistry of the process water, which can affect flotation performance [3,4]. The dissolved ions in the mineral pulp can interact with the flotation reagents, increasing their consumption and influencing the adsorption behavior of the reagents on the mineral surface; these ions have an activating or deactivating effect on the target minerals [5]. While clean water is ideal for flotation, the increasing necessity of using recycled water in the mineral processing industry, driven by environmental regulations and resource scarcity, introduces challenges due to the presence of dissolved ions [4,6–8].

The flotation of sulfide minerals is generally influenced by several factors, including the mineralogy and chemical species present in the pulp and the grinding method, among others [4,8,9]. Calcium and sulfate ions are two very common components in the process water of these mineral flotation processes. Calcium ions originate from the dissolution of minerals such as dolomite and calcite when they are present in the pulp, as well as from the addition of lime used to maintain an alkaline pH. Sulfate, on the other hand, originates from the ore and other flotation reagents, such as $NaHSO_3$, which is used to control surface properties [4]. Alternatively, the flotation of non-metallic minerals (i.e., barite and fluorite) is generally associated with calcite and dolomite minerals (a source of calcium ions) and other embedded dense-sized particles [10].

Coal contains varying amounts of ash, sulfur, moisture, volatile matter, phosphorus and alkaline impurities. Low-rank coals are hydrophilic, like most minerals. Therefore, there is a need to make them hydrophobic with the help of collectors. High-rank coals, on the other hand, are highly hydrophobic. Their particles can attach to air bubbles more easily if no collectors are added [11].

Calcium and sulfate ions are particularly common in coal flotation due to the composition of the coal deposits and the associated mineral oxidation [12,13]. Typically, process water contains a calcium concentration of around 700 mg/L, while sulfate concentrations can reach saturation (approximately 1700 mg/L) or even exceed it under metastable conditions [14,15].

Fluctuations in the concentration of calcium and sulfate ions in the process water can lead to significant variations in flotation performance. An increase in calcium concentration, for example, may result in the precipitation of undesirable compounds on the mineral surface, while a high sulfate concentration could destabilize froth, thereby compromising coal recovery [16]. Additionally, these ions influence the reactivity of mineral surfaces, which directly affects the selective adsorption of the collector. This adsorption is one of the most critical factors for ensuring the effective separation of coal particles during flotation [17].

In the literature, various investigations showed that dissolved ions in a pulp influence the flotation response. This is because the presence of certain ions often reduces the hydrophobicity of the coal surface and increases the electrostatic charge [18]. Güngören et al. [19] investigated the effects of K^+, Na^+, Ca^{2+} and Mg^{2+} ions on the hydrophobicity and bubble–particle interaction of high-rank coal. The contact angle results showed that the use of Mg^{2+} at a concentration of 0.1 mol/L slightly increased the contact angle of coal from 62° to 67°. It was also observed that the contact angle increased with increasing concentration of Ca^{2+} (0.001 to 1 mol/L) [19].

While previous research has explored the effects of dissolved ions on mineral floatability, a comprehensive understanding of the individual and combined impacts of calcium and sulfate ions on coal recovery remains elusive. This study aims to address this knowledge gap by systematically investigating the individual and interaction effects of calcium and sulfate ion concentrations on coal flotation efficiency. The influence of ions on key performance indicators, such as coal recovery and grade (concentrate quality), was determined by means of a 2^3 factorial experimental design. The findings of this research will contribute to optimizing flotation processes in the context of recycled water usage, promoting sustainable practices in the mineral processing industry.

2. Materials and Methods

2.1. Coal Characterization

A coal sample obtained from a mining company located in the northeast of the state of Coahuila, Mexico, was used for the investigation. The coal was ground using a disc mill (Retsch model DM 200) and subjected to particle size distribution analysis with the Tyler sieve series and a Ro-tap (model RX-29). ASTM standards were followed to perform proximate analyses for determining ash content [20], moisture [21], volatile matter [22], and calorific value [23]. The results of the proximate analysis, conducted in accordance with ASTM standards, are summarized in Table 1, classifying the coal as sub-bituminous. For ash characterization, a Philips X-Pert (PANalytical, UK) was used for X-ray diffraction.

Table 1. Proximate analysis of the coal sample.

Analysis	Value	ASTM Standard
Ash (%)	13.8	D 3174-02 [20]
Moisture (%)	2.0	D 3173-00 [21]
Volatile matter (%)	37.6	D 3175-07 [22]
Calorific value (cal/g)	6292.3	D 5865-19 [23]

2.2. Reagents

Analytical-reagent-grade sodium sulfate (Na_2SO_4) and calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) were added as ion sources. The levels of the experimental design were determined based on the concentrations typically present in recirculated water, ensuring they did not exceed their saturation limits [6]. Diesel and MIBC were used as a collector and frother, respectively. The pH was adjusted using 1 M solutions of sodium hydroxide (NaOH) and hydrochloric acid (HCl). The concentrations of the collector and frother, as well as the solid percentage, were determined based on the literature review detailed in Table 2.

Table 2. Optimal experimental conditions for coal flotation according to the literature.

Collector (g/t)	Frother (g/t)	Solids (%)	Reference
160–680	227–454	35	Seitz [24]
700–9000	--	--	Polat et al. [1]
--	2	24	Aydin et al. [25]
128–384	145	7	Wei et al. [26]
500	30–150	25	Lee et al. [27]
320–1600	10–50	25	Piñeres et al. [28]
400–450	400–450	9–10	Kumar-Sahoo et al. [29]

2.3. Flotation Test

A Denver flotation cell (Nelson Machinery model D-1, Canada) with a capacity of 1 L and a consistent air flow rate of 5 L/min was employed. The solids-to-liquid ratio was maintained at 15% (i.e., 176 g/L), with a particle size range of −150 to +106 µm. To initiate the experiment, reagents (calcium and sulfate ions) were added according to the experimental conditions for each treatment, as described by the factorial experimental design. The pH of the solution was adjusted to specific values by adding 1 M NaOH or HCl, and the pulp was conditioned for 5 min. After the conditioning stage, the collector and frother were added and conditioned for 4 and 3 min, respectively. Flotation was carried out for 5 min based on findings from preliminary tests. The ash content in each concentrate was determined following ASTM standard D 3174-02 [20]. Finally, the results of the response variable (i.e., coal recovery) were analyzed using Minitab 18 statistical software, in accordance with the factorial experimental design.

2.4. Factorial Experimental Design

The factors under investigation were (1) pH, (2) calcium ion concentration and (3) sulfate ion concentration. The % coal recovery was designated as the response variable. Table 3 outlines the factorial design, specifying the level of each factor and its codification. Meanwhile, Table 4 details the combinations of factors for each experimental treatment. It is worth mentioning that each experimental treatment was carried out with one replicate.

Table 3. Coding of factors and levels used in the experimental design.

Factor	Level	Codification
pH	7	−1
	9	+1
Ca^{2+} (mg/L)	400	−1
	800	+1
SO_4^{2-} (mg/L)	960	−1
	1920	+1

Table 4. Factorial experimental design employed in coal flotation.

pH	Ca^{2+} (mg/L)	SO_4^{2-} (mg/L)
−1	−1	−1
		+1
	+1	−1
		+1
+1	−1	−1
		+1
	+1	−1
		+1

3. Results and Discussion

3.1. Preliminary Test

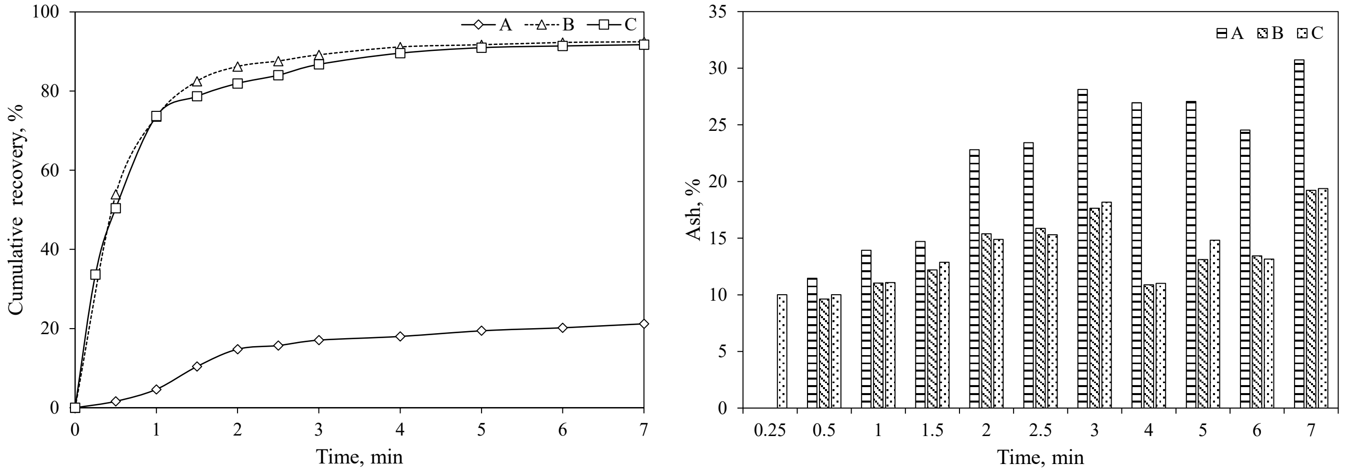
Preliminary tests were conducted to propose the experimental conditions of each experimental treatment (pH, calcium and sulfate concentrations). The tests were instrumental in defining the flotation time, which means the time-lapse at which the response variable was measured. In Table 5, the experimental conditions employed for the preliminary tests can be observed.

Table 5. Experimental conditions of the preliminary test.

Test	Collector (g/t)	Frother (g/t)
A	--	--
B	500	200
C	250	100

In Figure 1A the flotation kinetics of the preliminary tests can be observed for a time of seven minutes. According to the behavior of kinetics “A”, the recovery was 20%; this low recovery is the result of not employing any flotation reagent to enhance the floatability. In kinetic curves “B” and “C” of the figure, the % coal recovery when employing two different reagent doses can be observed. The two kinetic behaviors are similar; it appears that collector and frother concentrations do not have an effect on the response variable. Thus, coal recovery would not be positively affected by adding greater concentrations of the floatation reagents.

The ash content (wt.-%) of samples of the floated material withdrawn at different times for the preliminary tests A, B and C can be observed in Figure 1B. The floated material for test A shows a higher ash content, approximately 30% at 7 min of flotation. The addition of reagents leads to a reduced percentage of ash in the produced concentrate. However, it is noteworthy that the ash content remains constant at approximately 15% regardless of the collector and frother concentration used. Consequently, the optimal conditions correspond to 250 g/t of the collector and 100 g/t of the frother, thereby mitigating repercussions in terms of reagent consumption and environmental concerns.



(**A**) (**B**)

Figure 1. Preliminary test on coal flotation −150/+106 µm, 15% solids and pH 7. (**A**) Recovery as a function of time and (**B**) % ash as a function of time.

3.2. Analysis of Variance

Table 6 shows the results obtained for the experimental treatments of the statistical design; replicates are indicated as "2". The average recovery is indicated in the last column.

Table 6. Response variable (recovery) of the statistical treatments of the experimental design.

Test	pH	Ca^{2+}	SO_4^{2-}	Recovery (%)		
				1	2	Average
1	−1	−1	−1	78.30	75.69	76.99
2	−1	−1	+1	90.11	87.15	88.63
3	−1	+1	−1	82.25	83.97	83.11
4	−1	+1	+1	60.41	59.39	59.90
5	+1	−1	−1	34.31	40.87	37.59
6	+1	−1	+1	91.14	89.60	90.37
7	+1	+1	−1	86.74	86.01	86.38
8	+1	+1	+1	86.90	88.46	87.68

The analysis of variance is detailed in Table 7. It is evident that all factors and their interactions significantly influence the coal flotation process as indicated by *p*-values below 0.05. pH was the only factor that exhibited a *p*-value greater than 0.05 (i.e., 0.147).

Table 7. ANOVA for coal recovery, experimental factors: pH and calcium and sulfate ion concentrations.

Source	D.F.	S.C.	C.M.	F	*p*-Value
pH	1	10.93	10.93	2.57	0.147
Calcium	1	137.83	137.83	32.43	0.00
Sulfate	1	451.81	451.81	106.30	0.00
pH × Calcium	1	1180.22	1180.22	277.68	0.00
pH × Sulfate	1	1077.78	1077.78	253.57	0.00
Calcium × Sulfate	1	1862.92	1862.92	438.30	0.00
pH × Calcium × Sulfate	1	69.16	69.16	16.24	0.004
Error	8	34.00	4.25	--	--
Total	15	4824.65	--	--	--

The F-statistic value is interpreted inversely to the *p*-value; thus, a higher value means a greater effect of the factor on the response variable. Accordingly, it is observed that the interaction between calcium and sulfate ions exerts a substantial influence (F = 438.3) on the response variable.

To complement the analysis of variance, individual and interaction effect graphs were constructed. Individual effects denote the differences between groups solely attributable to a particular factor (e.g., pH), while interaction effects consider multiple factors influencing the response variable.

The individual effects of pH and calcium and sulfate ion concentrations are presented in Figure 2. Regarding pH, as the level increased from −1 to 1 (i.e., from 7 to 9), coal recovery decreased by 2%, from 77 to 75%. This variation can be attributed to the influence of the pH on the hydrophobicity of coal particles by altering surface charge and their interaction with floatation reagents, primarily the collector. However, pH is not deemed a significant factor according to its *p*-value of 0.147.

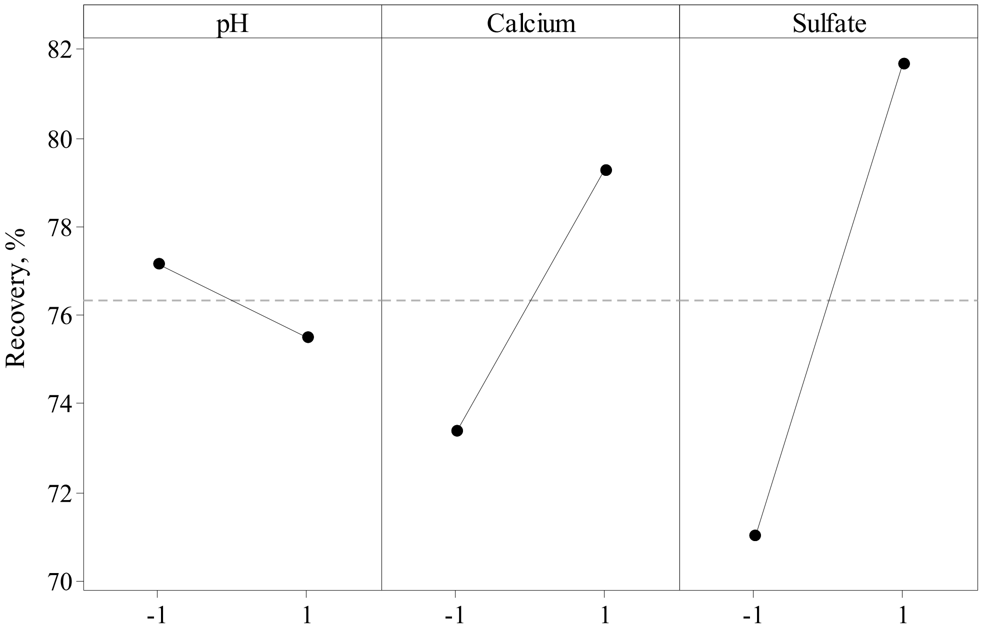


Figure 2. Individual effects of pH, calcium and sulfate on the recovery (response variable) of coal flotation.

When calcium and sulfate ion concentration was increased the coal recovery also increased. Evaluating calcium concentration effects at levels −1 and 1 (i.e., 400 and 800 mg/L) resulted in recoveries of 73% and 79%, respectively. Meanwhile, when sulfate concentration effects were varied, it resulted in recoveries of 71% and 82% at levels of −1 and 1 (960 and 1920 mg/L), respectively.

Apparently, the results contradict the findings reported in the literature, as Wan et al. [30] suggest that a substantial presence of calcium ions in process water may lead to a low flotation coal index. However, it is imperative to note that Wan et al. solely examined the individual effect of calcium ions. Therefore, with sulfate ions present, they may act as activators, promoting collector adsorption on the coal surface [31]. Consequently, sulfate ions enhance particle hydrophobicity, contributing to a higher recovery.

Figure 3 shows the interaction matrix among the factors pH, calcium and sulfate at the designated levels of interest. In Figure 3A, the interaction between calcium and sulfate factors can be observed. When assessing the −1 level of calcium and sulfate (i.e., 400 and 960 mg/L, respectively), a coal recovery of approximately 60% was achieved. However, maintaining this calcium level and increasing sulfate concentration to level 1 (1920 mg/L) significantly enhances recovery, reaching up to 90%. This effect can be attributed to an augmentation in the surface charge of coal particles due to the adsorption of calcium species. This facilitates the subsequent adsorption of SO_4^{2-} ions (reducing the surface charge), resulting in increased collector adsorption.

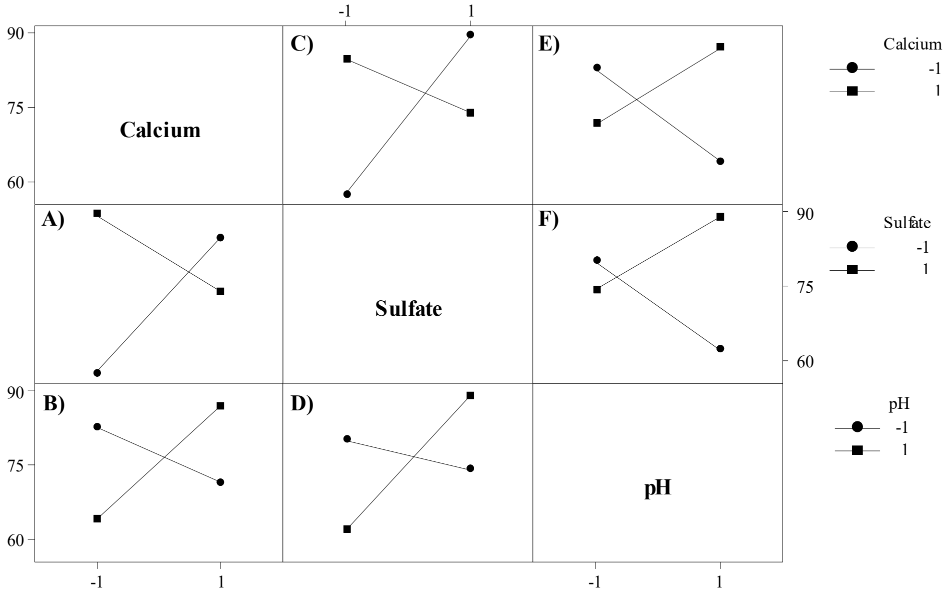


Figure 3. Interaction matrix between: (**A**) calcium and sulfate, (**B**) calcium and pH, (**C**) sulfate and calcium, (**D**) sulfate and pH, (**E**) pH and calcium and (**F**) pH and sulfate on the recovery (response variable).

Figure 3 shows the interaction between calcium concentration and pH at the two designated levels. Recovery is higher when employing level 1 of both factors (i.e., 800 mg/L of Ca^{2+} and pH 9) and decreases when employing pH level −1 (i.e., 7). This behavior mirrors the one observed between sulfate and pH interactions (see Figure 3D). This behavior may be associated with an increased adsorption of $CaOH^+$ on the coal surface, as this species exhibits higher activity at this pH, whereas at pH 7, the predominant species will be Ca^{2+} [30].

According to Raichur et al. [32], pH and zeta potential are closely related. These authors reported that sub-bituminous coal at neutral pH (i.e., 7) exhibits a surface charge ranging from −10 to −30 mV, while at alkaline pH (i.e., 9), the potential varies between −35 and −45 mV. This decrease is attributed to the adsorption of OH^- ions on the particle surface. Figure 3C,E,F correspond to the reverse interaction of Figure 3A,B,D, without affecting the response variable.

Figure 4 presents a Pareto diagram of standardized effects in which the studied factors are illustrated in order of importance. The diagram shows a reference line at 2.31 to indicate which factors are statistically significant. The longest bar represents the factor with the greatest influence on the process, which corresponds to the calcium × sulfate interaction. As can be seen, pH, as an individual factor, is the last bar, and it is below the Pareto line, indicating that it does not have statistical significance on its own within the range that was studied.

The simultaneous effect of Ca^{2+}, SO_4^{2-} and alkaline pH in the flotation process enables carbon yields between 37.5% and 90.3%. To maximize coal recovery, it is important to control the process conditions such as calcium, sulfate and pH, to improve the efficiency of the flotation process. The use of excessive resources, such as flotation reagents, can result in an increase in operational cost and the formation of undesirable species which can negatively impact the coal recovery. Statistical analysis and graphical representations of the effect of factors also contribute to the state of the art and allow for a better understanding of the interfacial chemistry of coal in the flotation media.

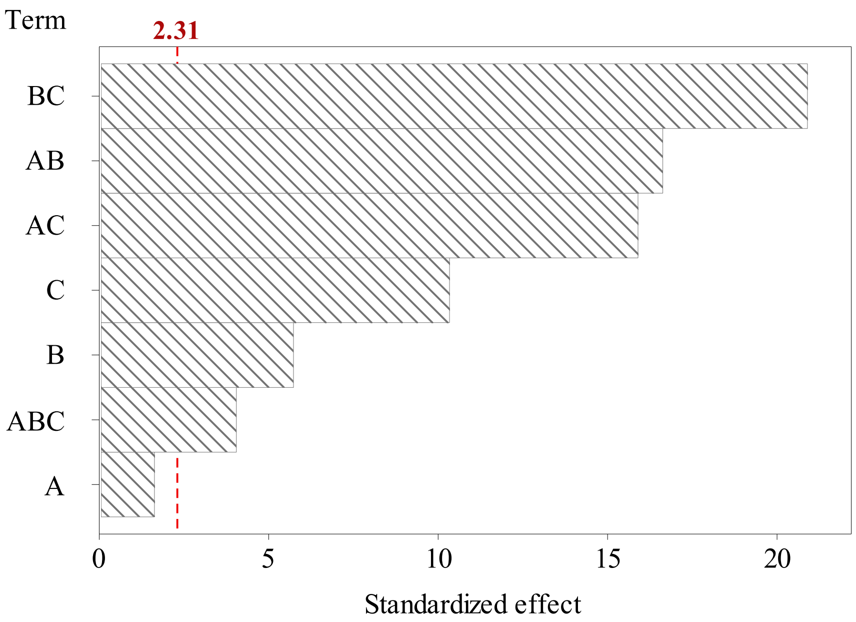


Figure 4. Pareto chart of the standardized effects of the independent variables and their interactions on the response variable. (A) pH. (B) Calcium. (C) Sulfate.

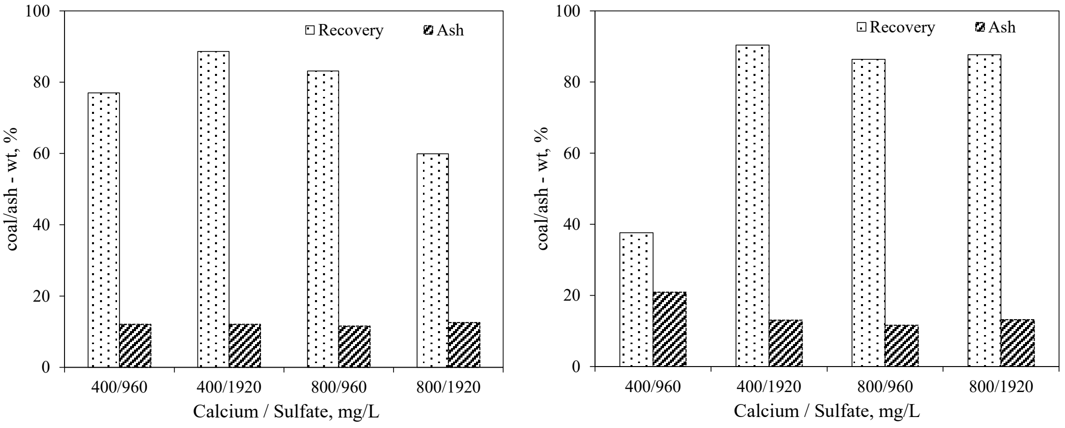
Equation (1) presents the regression equation, which describes the behavior of the variable of interest as a function of the individual factors and their interaction.

$$\begin{gathered} Recovery, \% = 76.332 + 0.827a - 0.827A - 2.935b + 2.935B - 5.314c + 5.314C + 8.589ab - 8.589aB - \\ 8.589Ab + 8.589AB + 8.207ac - 8.207aC - 8207Ac + 8.207AC - 10.790bc + 10.790\ bC + 10.790Bc - \\ 10.790BC + 2.079abc - 2.079abC - 2.079aBc + 2.079aBC - 2.079Abc + 2.079AbC + 2.079ABc - \\ 2.079ABC \end{gathered} \quad (1)$$

In Equation (1), the coded values −1 and +1 represent the lower and upper levels of each factor, as indicated in Table 3 of the experimental design. The variable 'a' corresponds to pH levels in the range of [−1, 0), while '*A*' is used for the range of [0, +1]. For intermediate pH values, such as 0.5, interpolated or extrapolated values could be applied within these ranges. This approach is similarly applied to other factors, such as calcium ions (*b* and *B*) and sulfate ions (*c* and *C*). Therefore, this equation provides an effective means to estimate coal recovery within the studied factor range.

3.3. Relationship Between Coal Recovery and Ash Content

Figure 5 shows the wt.-% of floated material and its ash content as a function of calcium and sulfate concentration. The results at pH 7 are depicted in Figure 5A. The highest recovery, approximately 88.6%, was obtained when utilizing 400 mg/L of Ca^{2+} and 1920 mg/L of $SO_4{}^{2-}$, yielding an ash content of 12.1%. Conversely, maintaining the $SO_4{}^{2-}$ concentration while increasing the Ca^{2+} concentration (i.e., 800 mg/L) adversely affected recovery, resulting in 59.9% with a slightly elevated ash content of 12.6%. The results at pH 9 are depicted in Figure 5B. Analogous to the previous scenario, the highest recovery was achieved with a $Ca^{2+}/SO_4{}^{2-}$ ratio of 400/1920 mg/L, attaining recoveries of 90.4% and an associated ash content of 13%. Conversely, the lowest recovery, 37.6%, was observed at the lowest concentrations of Ca^{2+} and $SO_4{}^{2-}$ (i.e., 400/960 mg/L). Additionally, under these conditions, the highest ash content was observed, reaching 20.9%. For the remaining tests, the ash content remained below 13%.



(**A**) (**B**)

Figure 5. Recovery and ash content from coal flotation −150/+106 µm, 250 g/t collector and 100 g/t frother, 15% solids for 5 min: (**A**) pH 7 and (**B**) pH 9.

The correlation between recovery and ash content fluctuated based on coal characteristics and process conditions, as constituents of ash (i.e., inorganic compounds) tend to float alongside coal, thereby diminishing the quality of the final product. Figure 6 presents the X-ray diffraction of the ash of a coal concentrate obtained under the conditions of test 6, described in Table 6, namely pH 9, 400 mg/L of Ca^{2+} and 1920 mg/L of SO_4^{2-}. The diffraction pattern reveals constituents such as anhydrite ($CaSO_4$), quarts (SiO_2) and hematite (Fe_2O_3). It is important to determine the ash composition in order to evaluate its suitability for diverse industrial applications, environmental impact and implications for public and occupational health.

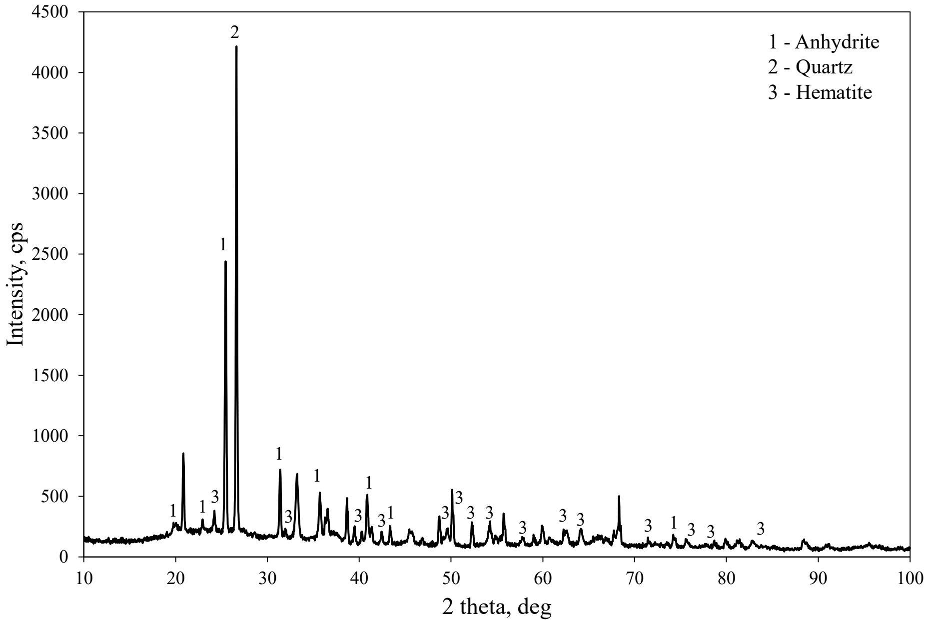


Figure 6. X-ray diffraction pattern of the ash of a coal concentrate obtained at the experimental conditions of pH 9, 400 mg/L Ca^{2+} and 1920 mg/L of SO_4^{2-}.

4. Conclusions

The factorial design implemented in this study allowed the precise evaluation of the individual and combined effects of calcium and sulfate ions on coal recovery. The interaction between calcium and sulfate ions was found to have a significant influence on coal flotation; when 400 mg/L of Ca^{2+} and 1920 mg/L of $SO_4{}^{2-}$ were used, the recovery reached 90.37% with an ash content of 13%.

pH conditions also influenced flotation efficiency, although to a lesser degree than ion concentrations. A pH of 9, combined with optimal concentrations of calcium and sulfate, improved coal flotation, demonstrating that proper pH control in alkaline environments can maximize coal recovery and reduce the formation of undesirable species on particle surfaces.

This study highlights the importance of controlling ion concentrations in recycled process water. Unlike previous research that only evaluated the effect of ions in isolation, this work demonstrates that the combined use of Ca^{2+} and $SO_4{}^{2-}$ under controlled conditions can significantly enhance flotation performance, with important implications for optimizing industrial processes aimed at maximizing recovery and minimizing environmental impact.

Author Contributions: Conceptualization, methodology, writing, formal analysis, experimentation, supervision and project administration, A.A.G.-I. and G.I.D.-P.; methodology, writing, data curation and review, B.R.G.-B. and D.A.C.; review, editing, support in experimentation and experimental design, J.C.R.-H. and A.S.-R. All authors have read and agreed to the published version of the manuscript.

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