

Utilization of polymeric binders to agglomerate oxidized copper ore

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Abstract: Permeability reduction is a major challenge in heap leaching, primarily caused by the accumulation of fines that move with the leaching agent, leading to the formation of dead zones and channeling within the heap. In the Aria copper beneficiation plant, the 0–2 mm fraction with a copper grade of 1.4% undergoes pre-separation prior to heap loading without further processing. This study investigated the potential of using the agglomeration method to improve permeability in the case of using the 0–2 mm fraction of ore. Mineral compounds, such as sodium silicate and calcium sulfate, and non-ionic, cationic, and anionic polymer compounds, were used in the agglomeration process. The strength of interparticle bonding was evaluated by measuring the fine migration percentage (FMP) in the soak test. The results revealed that agglomerates produced using non-ionic compounds had the highest bonding strength, with an FMP of 3.89%, the lowest of all the compounds tested. This enhanced bonding strength was attributed to the combined influence of hydrogen bonding forces and van der Waals forces.

Keywords: heap leaching, permeability, agglomeration, polymeric compounds, copper ore

1. Introduction

Hydrometallurgy has become increasingly important in the mining industry as ore grades decline, mineralogy becomes more complex, and the need to extract minerals from secondary sources grows (Golpayegani and Abdollahzadeh 2017; Bennett et al. 2006). Heap leaching is a cost-effective method for processing low-grade copper ores. However, it can be challenging to achieve optimal recovery and kinetics due to issues such as impermeability, channelization, and clogging. These problems are often caused by the transfer and compression of fine particles in the heap, which can lead to the formation of dead zones (Bennett et al. 2006; Kappes 2006; Schlitt 1992; Dhawan et al. 2013). The particle size distribution of the feed material is also a significant factor, as it can affect the transfer and accumulation of fines. Inappropriate particle size distribution can lead to the formation of dead zones in specific areas of the heap, particularly in the lower sections. This can reduce permeability over time and further decrease leaching recovery and kinetics (Chamberlin 1986; Peacey et al. 2004).

To improve permeability, prevent channeling, and increase recovery and leaching kinetics, agglomeration prior to heap loading has been proposed. This method involves feeding the heap with agglomerates that have almost uniform dimensions. Fine and coarse particles with different size distributions are agglomerated by bonds created by certain additives (Ghorbani et al 2016; Lewandowski and Kawatra 2008; Lewandowski and Kawatra 2009; Lewandowski and Kawatra 2009). Fig. 1 illustrates a schematic of how agglomeration can help improve permeability and prevent channeling (Dhawan et al. 2013).

Agglomerates used in copper heap leaching must be able to withstand the acidic conditions in the heap without breaking apart. This requires the use of additives that can create strong interparticle bonds (Lewandowski and Kawatra 2009; Bouffard 2008). However, the traditional method of creating interparticle bonds by combining raffinate solution with sulfuric acid is not very effective in acidic conditions, as the bonds created by surface tension and capillary action are not strong enough to withstand the acidic environment (Kawatra et al. 2006; Pietsch 2002). Literature indicates that the

strength of interparticle bonds in agglomerates is dependent on the type of additive, the surface properties of the particles, and the pH of the solution. In acidic conditions, the additive molecules can be deprotonated, which weakens the bonds (Dhawan et al. 2013; Kodali et al. 2011).

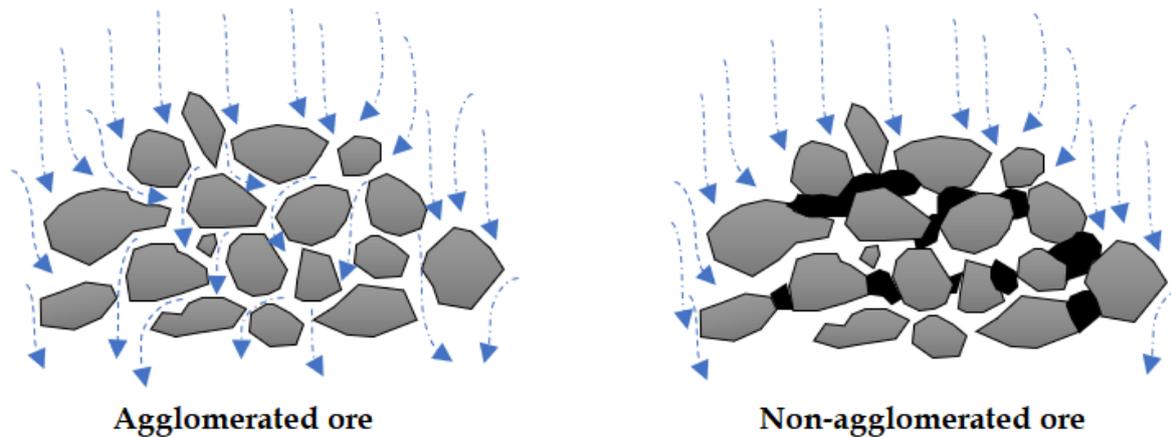


Fig. 1. Comparison of heap permeability in agglomerated vs. non-agglomerated ore (adapted from Chamberlin, 1980)

There are three main types of additives that can be used to enhance the stability of agglomerates in acidic conditions: organic, inorganic, and polymer additives (Lewandowski and Kawatra 2009; Dhawan et al. 2013). Organic and inorganic additives are not suitable for copper leaching because they are not resistant to acidic environments (Dhawan et al. 2013; Wang L et al. 2023). Polymer compounds, on the other hand, are more resistant to acidic conditions (Pietsch 2002; Dhawan et al. 2013). Research has shown that polymer additives can improve the strength and permeability of agglomerates. Pautler et al. 1990 conducted fundamental studies using combinations of polyacrylamides, carboxylates, and sulfonates for agglomerating a copper sulfide ore, demonstrating that an increase in polyacrylamide concentration enhances both agglomerate strength and solution permeability. Green et al. 2001 found that the strength of interparticle bonds in agglomerates increases with the molecular weight of polyacrylamides. Lewandowski & Kawatra 2009 showed that polyacrylamide compounds can produce acid-resistant agglomerates of copper sulfide ore. They examined the role of van der Waals forces and hydrogen bonding in determining the strength of interparticle bridges. However, research has not investigated the agglomeration of oxidized copper ores and related economic factors.

In recent years, a new method of agglomeration, known as geopolymerization, has been gaining interest. However, there are still some challenges that need to be addressed before geopolymerization can be widely adopted for the agglomeration of copper ore. These challenges include the cost of raw materials, the need for specialized equipment, and the lack of long-term field data (Chen et al. 2020; Chen et al. 2021; Chen et al. 2022).

At the Aria beneficiation plant, crushed ore between 2 and 20 mm is sent to the heap for processing. The fine fraction (<2 mm), which makes up 20% of the feed mass and has a high copper grade of 1.34%, is separated and stored (see Fig. 2). This study investigated the potential of agglomeration to produce acid-resistant agglomerates by incorporating the fine fraction into the heap leaching process at the Aria plant, with the aim of increasing the plant's capacity. The most effective additive to yield agglomerates with superior resistance to acidic conditions was identified using the fines migration percentage (FMP) parameter obtained from the soak test.

2. Materials and methods

2.1. Sample characterization

The sample examined in this study was sourced from the oxide copper ore obtained from the Aria mine, located in Iran. X-ray fluorescence (XRF) analysis was employed to determine the chemical composition, while microscopic analysis and X-ray diffraction (XRD) were utilized to identify the mineralogical

composition of the sample under investigation. The findings from the microscopic analysis, XRD, and XRF are presented in Fig. 3a, Fig. 3b, and Table 1, respectively.

XRF analysis was performed separately for the 0-2 mm fraction, which is separated before heap loading, and the 2-20 mm fraction, which is used as the feed for the heap loading. The results of the XRF analysis reveal that the studied sample contains 1.34% copper (1.68% in oxide form) in the 0-2 mm fraction and 0.86% copper (1.08% in oxide form) in the 2-20 mm fraction. The considerably higher copper grade observed in the 0-2 mm fraction highlights its critical role in the copper production process.

The outcomes of the microscopic analysis and XRD confirm the presence of malachite as the primary mineral, with major gangue components consisting of albite ($\text{NaAlSi}_3\text{O}_8$) and quartz (SiO_2).

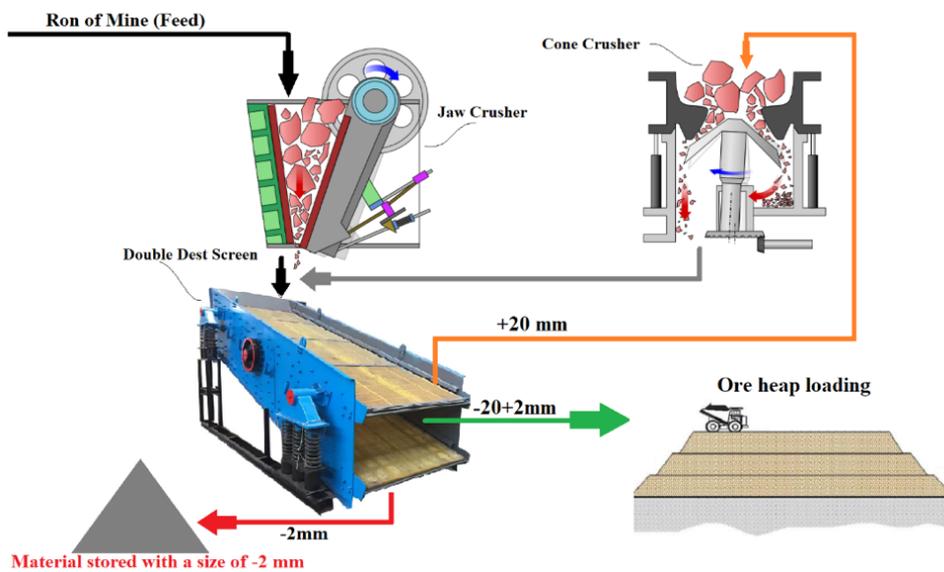


Fig. 2. Flowsheet of the Aria beneficiation plant

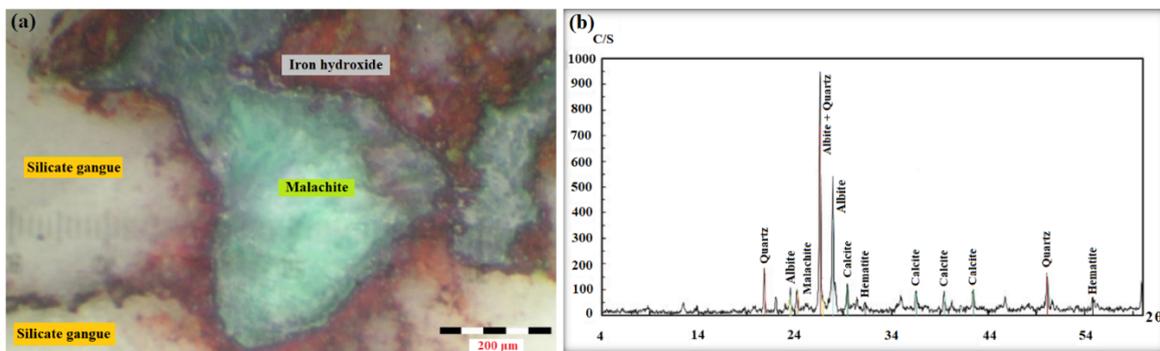


Fig. 3. Mineralogy studies results of the sample used. (a) Microscopic analysis result. (b) XRD analysis result

Table 1. XRF analysis results of the sample used

| Oxide compound | Mass percentage (%) (in the fraction of 0-2 mm) | Mass percentage (%) (in the fraction of 2-20 mm) |
|-------------------------|--|---|
| SiO_2 | 65.91 | 59.86 |
| Al_2O_3 | 15.11 | 16.74 |
| Fe_2O_3 | 2.92 | 3.77 |
| CaO | 2.32 | 3.42 |
| Na_2O | 3.26 | 2.21 |
| K_2O | 2.59 | 2.99 |
| MgO | 0.98 | 1.21 |
| CuO | 1.08 | 1.68 |
| L.O. I | 5.84 | 8.12 |

A representative sample was obtained after sampling from the crusher product of the Aria mine beneficiation plant and combining the 0–2 mm and 2–20 mm fractions in a weight ratio of 20–80 percent (similar to the actual conditions in the beneficiation plant). Then the prepared representative sample underwent particle size analysis and its results are presented in Table 2.

According to the literature, particle sizes ranging from 2–10 millimeters are preferable for heap leaching due to enhanced process kinetics and improved copper recovery compared to 2–20 millimeters (Dhawan et al. 2013). Consequently, the prepared representative sample within the 0–20 mm size range was further crushed to smaller than 10 millimeters using a roller crusher under controlled conditions with the use of a 10-millimeter control screen. To assess the level of fines generation resulting from the re-crushing process, which could potentially lead to heap blockage if excessive, the 0–10 mm product underwent particle size analysis, and the results are presented in Table 2.

As shown in Table 2, the proportion of particles finer than 100 microns in the 0–20 mm sample accounted for 2.7% of the total sample. Moreover, the results presented demonstrate that after controlled crushing, the fraction smaller than 100 microns constituted 3% of the total sample. This represents a marginal increase of 0.3% compared to the initial percentage of finer materials in the 0–20 mm sample, which is not considered statistically significant. Given the limited generation of fines, it can be inferred that the disintegration of agglomerates under acidic conditions is unlikely to pose any significant issues.

Table 2. Particle size distribution of sample used

| Before controlled crushing (particle size of 0-20 mm). | | |
|---|---|--|
| Size range (mm) | Cumulative percentage remained (%) | Cumulative percentage passing (%) |
| -20+10 | 25.5 | 74.5 |
| -10+2 | 67.9 | 32.1 |
| -2+0.1 | 97.3 | 2.7 |
| -0.1 | 100 | - |
| After controlled crushing (particle size of 0-10 mm). | | |
| Size range (mm) | Cumulative percentage remained (%) | Cumulative percentage passing (%) |
| -10+6.35 | 28.4 | 71.6 |
| -6.35+4.75 | 42.5 | 57.5 |
| -4.75+3.35 | 54.7 | 45.3 |
| -3.35+2.38 | 62.7 | 37.3 |
| -2.38+2 | 64.8 | 35.2 |
| -2+1 | 77 | 23 |
| -1+0.6 | 82.7 | 17.3 |
| -0.6+0.425 | 87 | 13 |
| -0.425+0.3 | 80.7 | 9.3 |
| -0.3+0.15 | 95.9 | 4.1 |
| -0.15+0.1 | 97 | 3 |
| -0.1+0.075 | 97.7 | 2.3 |
| -0.75 | 100 | - |

2.2. Material and equipment used

To prepare the binder solution, water, acid, and polymer were thoroughly mixed using a mechanical stirrer. The agglomeration experiments were conducted in a rotary drum agglomerator equipped with a vibrating feeding system. The prepared binder solution was sprayed on the ore particles through an air-pressure spray system. Fig. 4 shows the agglomeration device used in the experiments.

The strength of interparticle bonding within the agglomerates was assessed using the soak test, employing an 8-mesh sieve. The pH level was continuously monitored using a digital pH meter. Sulfuric acid at various concentrations was utilized to adjust pH. Sodium silicate and calcium sulfate were employed as mineral compounds, serving as bonding agents between the particles. Additionally, polymer compounds from three different groups, namely anionic, cationic, and non-ionic, were utilized

for the ore agglomeration process. Table 3 provides detailed information regarding the polymer compounds, including their properties.



Fig. 4. Illustration of the agglomeration equipment (feeding unit and rotary drum agglomerator)

Table 3. Specifications of the used polymer compounds

| polymeric compounds' name | Type | Molecular weight | Manufacture | Price (U.S. dollar / kg) |
|---------------------------|-----------|------------------|-----------------------------|--------------------------|
| Co polymer C-2 | Cationic | Ultra-high | Isfahan copolymer (in Iran) | 0.91 |
| Actafloc C85 | Cationic | Moderate | Akhtar Shimi Yazd (in Iran) | 4.14 |
| Superfloc C581 | Cationic | High | Cytec | 2.61 |
| Aktafloc A-26 | Anionic | Ultra-high | Akhtar Shimi Yazd (in Iran) | 3.21 |
| copolymer A-28 | Anionic | Moderate | Isfahan copolymer (in Iran) | 2.99 |
| Superfloc A1820 | Anionic | High | Cytec | 6.53 |
| Superfloc N300 | Non-ionic | Ultra-high | Cytec | 11.50 |
| Superfloc N100 | Non-ionic | High | Cytec | 5.94 |
| Superfloc N300LMW | Non-ionic | Moderate | Cytec | 11.99 |
| Actafloc N12 | Non-ionic | High | Akhtar Shimi Yazd (in Iran) | 3.34 |

2.3. Agglomeration test procedure

Before starting the agglomeration experiment, a binder solution containing water, acid, and polymer is prepared with predetermined ratios for each test. First, a specific amount of water is mixed with sulfuric acid in a 1000-mL volumetric flask to prepare a 10% w/w sulfuric acid solution. Next, the prepared acid solution is poured into a 1000-mL beaker. Then to prepare the binder solution, a specific amount of polymeric or mineral powder is added while the solution is stirred with a mechanical stirrer for 30 minutes.

After the binder solution was prepared, 1-kilogram samples were weighed accurately and introduced into the vibrating feeder hopper. The samples were then fed into the rotary drum agglomerator at a controlled rate of 50 grams per minute. The rotational speed of the rotary drum agglomerator was adjusted based on the observed particle movement behavior to ensure appropriate rolling and contact between particles. The rotational speed was approximately 20 revolutions per minute.

Once the rotation of the material in the rotary drum agglomerator was deemed stable, the binder solution was sprayed onto the rotating samples using a pressure spray mechanism. After the specified retention time for each experiment (25 minutes), the agglomerated samples were extracted from the agglomeration device and dried at ambient temperature. After a curing time of 48 hours, which is necessary for the formation of bonds between particles (Lewandowski and Kawatra 2009), samples were obtained from the agglomerates. These samples were then subjected to a soak test to evaluate the quality and resistance of the agglomerates under acidic conditions.

It shall be noted that for experiments utilizing calcium sulfate as the binder, the calcium sulfate was blended with the ore prior to agglomeration. In these cases, only the acid solution of 10% w/w was sprayed during agglomeration. Table 4 reports the conducted tests along with the test operating parameters.

Table 4. Conducted agglomeration tests along with the operating parameters

| Test No. | Binder Type | Additives Additive | Acid | agglomerator | Retention | Agglomerates | | |
|----------|----------------------|------------------------------|----------------------------|-------------------|-----------|--------------|----|----|
| 1 | Raffinate + Acid | (*Not 1) | 0 | 10 | 20 | 25 | 7 | |
| 2 | | | 0 | 10 | 20 | 25 | 9 | |
| 3 | | | 0 | 10 | 20 | 25 | 13 | |
| 4 | mineral compounds | sodium silicate | 4.9 (5% w/w solution) | 10 | 20 | 25 | 9 | |
| 5 | | | 9.9 (10% w/w solution) | 10 | 20 | 25 | 9 | |
| 6 | | | 14.8 (15% w/w solution) | 10 | 20 | 25 | 9 | |
| 7 | | | 19.8 (15% w/w solution) | 10 | 20 | 25 | 9 | |
| 8 | | calcium sulfate (*Note 2) | 25 | 10 | 20 | 25 | 9 | |
| 9 | | | 50 | 10 | 20 | 25 | 9 | |
| 10 | | | 100 | 10 | 20 | 25 | 9 | |
| 11 | polymer compounds | Anionic Actafloc A-26 | 0.5 | 10 | 20 | 25 | 9 | |
| 12 | | | 1 | 10 | 20 | 25 | 9 | |
| 13 | | | 2.5 | 10 | 20 | 25 | 9 | |
| 14 | | Copolymer A-28 | 0.5 | 10 | 20 | 25 | 9 | |
| 15 | | | 1 | 10 | 20 | 25 | 9 | |
| 16 | | | 2.5 | 10 | 20 | 25 | 9 | |
| 17 | | Superfloc A1820 | 0.5 | 10 | 20 | 25 | 9 | |
| 18 | | | 1 | 10 | 20 | 25 | 9 | |
| 19 | | | 2.5 | 10 | 20 | 25 | 9 | |
| 20 | | Cationic | Copolymer C2 | 0.5 | 10 | 20 | 25 | 9 |
| 21 | | | | 1 | 10 | 20 | 25 | 9 |
| 22 | | | | 2.5 | 10 | 20 | 25 | 9 |
| 23 | | | Actafloc C85 | 0.5 | 10 | 20 | 25 | 9 |
| 24 | | | | 1 | 10 | 20 | 25 | 9 |
| 25 | | | | 2.5 | 10 | 20 | 25 | 9 |
| 26 | | | Superfloc C581 | 0.5 | 10 | 20 | 25 | 9 |
| 27 | | | | 1 | 10 | 20 | 25 | 9 |
| 28 | | | | 2.5 | 10 | 20 | 25 | 9 |
| 29 | | | Non-ionic | Superfloc N300 | 0.5 | 10 | 20 | 25 |
| 30 | 1 | 10 | | | 20 | 25 | 9 | |
| 31 | 2.5 | 10 | | | 20 | 25 | 9 | |
| 32 | Superfloc N100 | 0.5 | | 10 | 20 | 25 | 9 | |
| 33 | | 1 | | 10 | 20 | 25 | 9 | |
| 34 | | 2.5 | | 10 | 20 | 25 | 9 | |
| 35 | Superfloc N300LMW | 0.5 | | 10 | 20 | 25 | 9 | |
| 36 | | 1 | | 10 | 20 | 25 | 9 | |
| 37 | | 2.5 | 10 | 20 | 25 | 9 | | |
| 38 | Actafloc N12 | 0.5 | 10 | 20 | 25 | 9 | | |
| 39 | | 1 | 10 | 20 | 25 | 9 | | |
| 40 | | | 2.5 | 10 | 20 | 25 | 9 | |

Note 1: Without the addition of mineral or polymeric compounds.

Note 2: Calcium sulfate was blended with ore.

2.4. Soak test procedure

The inter-particle bonding behavior and resistance level of agglomerates produced under heap leaching conditions (pH of 1.5) were evaluated using the soak test (Lewandowski and Kawatra 2009; Kawatra et

al. 2006). The agglomerates were first dried for 48 hours at ambient temperature. Then, they were placed on an 8-mesh sieve and submerged in acid at pH 1.5 for 30 minutes. After that, the agglomerates were removed from the container, dried, and weighed. The percentage of fine migration percentage (FMP) was calculated as follows (Peacey et al. 2004; Lewandowski and Kawatra 2009):

$$FMP = \frac{M_f}{M_t} \times 100 \quad (1)$$

where M_f is the mass of fine material passing through the 8-mesh sieve and M_t is the mass of fine material that is smaller than the 8 mesh in the feed for the agglomeration test.

The FMP serves as an indicator of the agglomerates' resistance under acidic conditions, similar to those encountered in heap leaching (Lewandowski and Kawatra 2009). A lower value of the FMP through the 8-mesh sieve indicates a higher level of resistance and quality of the agglomerates under acidic conditions. Fig. 5 provides an overview of the agglomeration and soak test procedure.

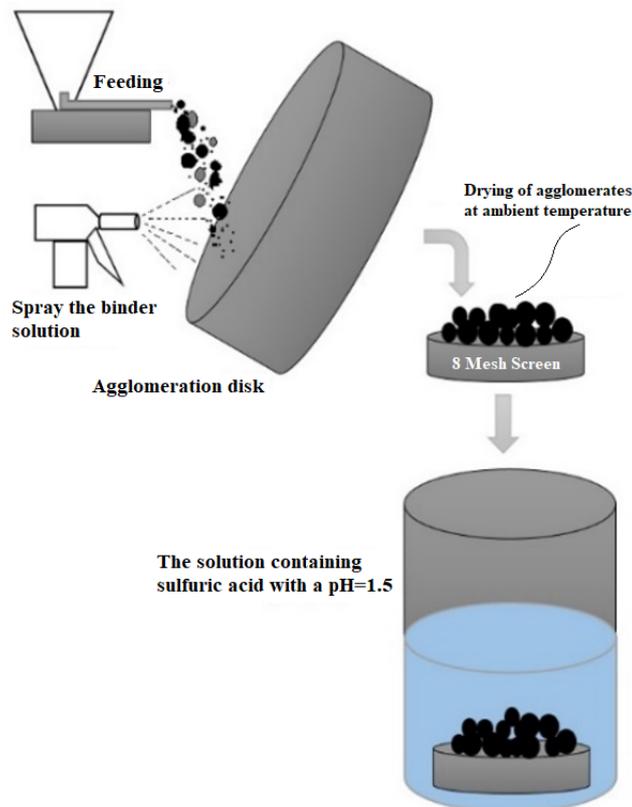


Fig. 5. A schematic of the agglomeration test and the soak test

3. Results and discussion

3.1. Agglomeration by using the raffinate solution as the binder

To investigate the feasibility of using a combination of raffinate solution and sulfuric acid as a binder in the agglomeration process, three experiments were conducted at different binder solution dosage rates to produce agglomerates with moisture levels of 7%, 9%, and 13%. The specifications of the raffinate solution are provided in Table 5, and the results of the soak test following agglomeration are presented in Fig. 6a. The findings of all three experiments indicated an unacceptably high FMP, meaning that a significant amount of fine material was washed away from the agglomerates during the soak test.

The graph in Fig. 6a shows that increasing the moisture content of the agglomeration feed led to an increase in the FMP. This means that the agglomerates were less resistant to disintegration under acidic conditions. Raffinate solutions and sulfuric acid can bond particles together through interparticle surface tension forces and capillary action. These forces are especially important for bonding fine particles smaller than 75 μm (Pietsch 2002). However, the agglomeration feed in this study had a low

percentage of fine particles (see Table 2), so the influence of surface tension and capillary action was minimized. In this case, moisture content played a more significant role in the bonding of particles. An increase in moisture content reduces the effect of capillary action, which can lead to a decrease in the bond strength between particles. This is because the water molecules can form a film around the particles, which prevents the surface tension forces from acting (Pietsch 2002; Kawatra et al. 2006). Figs. 6b and 6c illustrate the agglomerates produced with a moisture content of 7% before and after the soak test. It is evident that the agglomerates disintegrated after the soak test and the fines have separated from the surface of the larger particles.

Table 5. Specifications of raffinate solution of the Aria Copper Plant

| Cu concentration (g/lit) | Fe concentration (g/lit) | Fe concentration (g/lit) | pH |
|--------------------------|--------------------------|--------------------------|------|
| 0.08 | 0.52 | 2.45 | 3.17 |

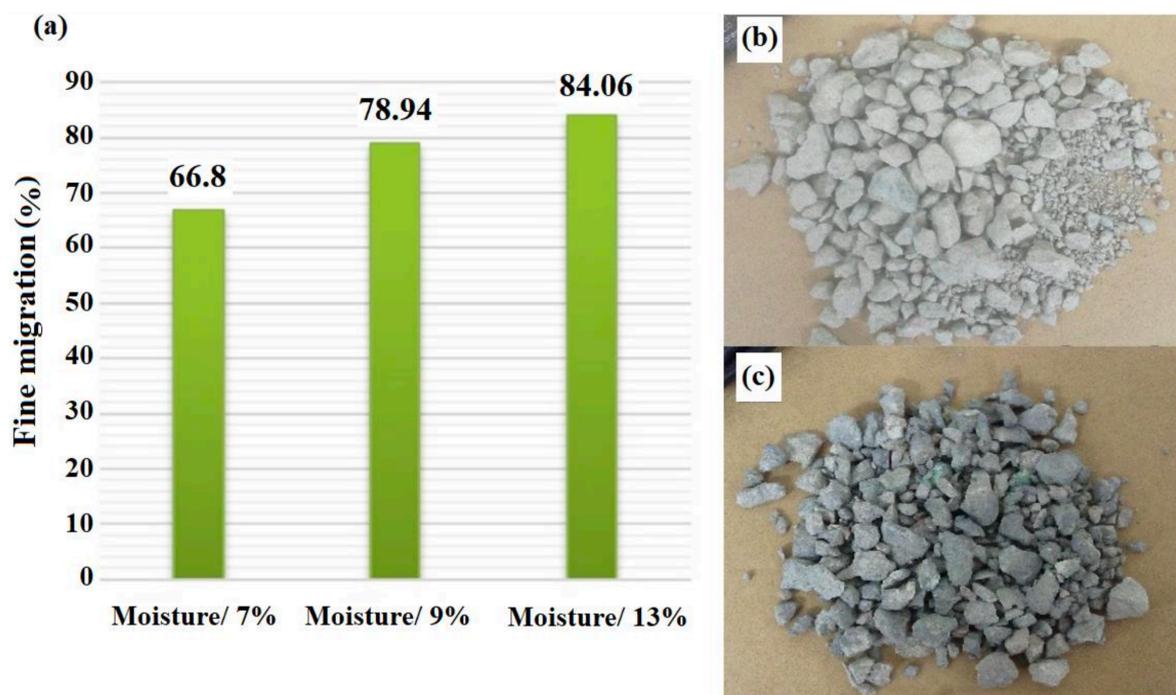


Fig. 6. The soak test result for produced agglomerates using the combination of raffinate and acid. (a) fines migration percentage. (b) Produced agglomerates before the soak test. (c) Produced agglomerates after the soak test

3.2. Agglomeration by using mineral compounds as the binder

To examine the impact of mineral compounds, sodium silicate, and calcium sulfate were employed as binders. The performance of sodium silicate was studied through four agglomeration experiments using solutions containing 5%, 10%, 15%, and 20% w/w sodium silicate. The binder solution was prepared by dissolving sodium silicate in a sulfuric acid solution with a concentration of 10% w/w. The binder solution dosage rate was the same for all experiments, which aimed to produce agglomerates with a moisture content of 9%. The outcomes of the experiments are illustrated in Fig. 7a. The results showed that the FMP was undesirable in all experiments. The reduced strength of the agglomerates can be attributed to the conversion of sodium silicate to silicic acid in the presence of sulfuric acid (Kawatra et al. 2006). Additionally, it was observed that the FMP decreased as the sodium silicate concentration increased. This can be explained by the fact that, with a fixed concentration of sulfuric acid in the binder solution prior to the addition of sodium silicate, a certain amount of silicic acid was able to be produced. Therefore, the addition of more sodium silicate led to an increase in the amount of unreacted sodium silicate in the environment, which resulted in an increase in the strength of the bond between the particles (Kawatra et al. 2006).

To study the performance of calcium sulfate, three experiments were performed using different dosages of this compound: 25 kg/t, 50 kg/t, and 100 kg/t. In these experiments, calcium sulfate was blended with the agglomeration feed, and a sulfuric acid solution with a concentration of 10% w/w was sprayed during the agglomeration process. The sulfuric acid solution dosage rate was the same for all experiments, which aimed to produce agglomerates with a moisture content of 9%. The results are depicted in Fig. 7b. It is evident that the FMP in these experiments was also unsatisfactory. Although calcium sulfate remains stable in an acidic environment, its ability to form strong interparticle bonds against acid is limited (Kawatra et al. 2006). Figs. 7c to 7f show the agglomerates produced with mineral compounds before and after the soak test. As can be seen, the agglomerates created using these compounds disintegrated after the soak test.

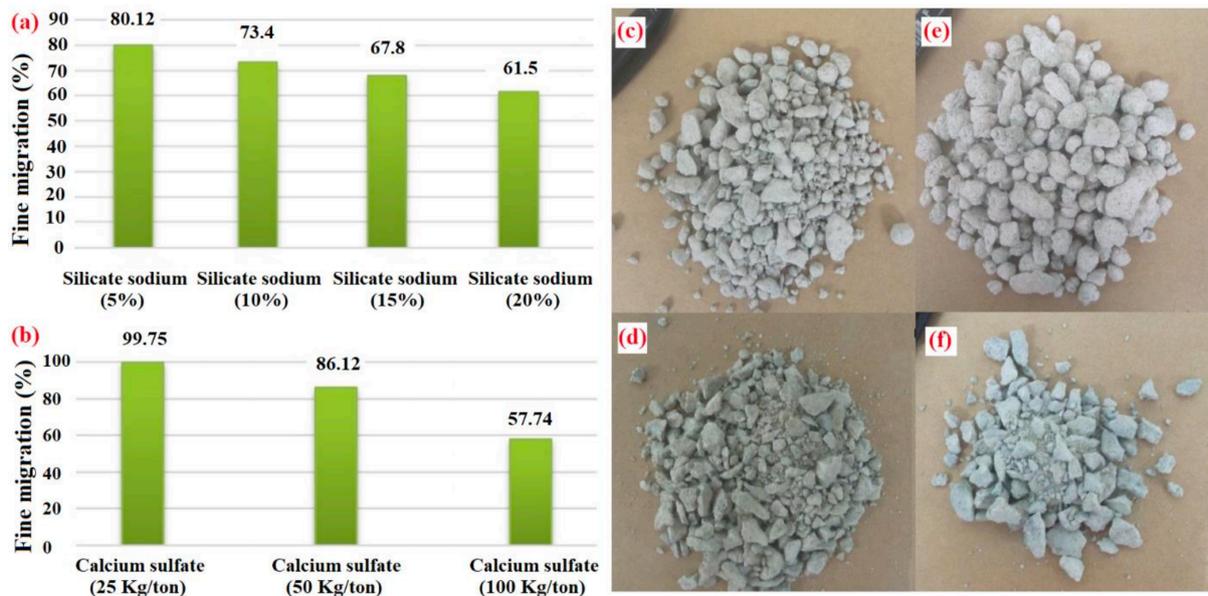


Fig. 7. The soak test result for produced agglomerates using sodium silicate and calcium sulfate as the binder (a) The FMPs obtained by utilizing sodium silicate. (b) Obtained FMPs by utilizing calcium sulfate. (c) Produced agglomerates using sodium silicate before the sock test. (d) Produced agglomerates using sodium silicate after the sock test. (e) Produced agglomerates using calcium sulfate before the sock test. (f) Produced agglomerates using calcium sulfate after the sock test

3.3. Agglomeration by using polymer compounds as the binder

To enhance the quality of agglomerates, polymer compounds were used as binders in three different types: cationic, anionic, and non-ionic (see Table 3). To this end, several agglomeration tests were designed and conducted. In these tests, a binder solution composed of a diluted sulfuric acid solution (10% w/w) and varying amounts of the polymer compound (0.5, 1, and 2.5 kg per ton of ore) was used. The experiments were conducted with the aim of producing agglomerates with a moisture content of 9%. The results of the agglomeration tests for different polymer compounds and concentrations are shown in Fig. 8. As can be seen, the use of polymer compounds led to a significant reduction in the FMP, regardless of their type (cationic, anionic, or non-ionic). This resulted in improved agglomerate strength. Additionally, it was found that increasing the polymer concentration enhanced the strength of the agglomerates. The high molecular weight of these compounds plays a vital role in reinforcing the bonding forces between particles, thereby contributing to the strength of agglomerates under acidic conditions (Nasser and James 2006).

In general, the binding forces between particles in agglomeration using polymer compounds are predominantly governed by the interaction of van der Waals forces, electrostatic attraction, and hydrogen bonding (Nasser and James 2006; Lewandowski and Kawatra 2009). Van der Waals bonds are physical forces that are present in all three types of compounds: cationic, anionic, and non-ionic (Nasser and James 2006; Lewandowski and Kawatra 2009). These bonds are significantly influenced by molecular weight, with higher molecular weight compounds typically having stronger van der Waals

bonds. Electrostatic bonds result from the physical attraction between charged particles (due to the formation of an electrical double layer in the leaching environment) and ionic polymer compounds (Zhuravlev 2000; Lewandowski and Kawatra 2009). In acidic leaching conditions, anionic polymer compounds lose their electric charge, while cationic compounds remain stable and can form bonds with ore particles when their surface zeta potential is negative (Nasser and James 2006). Hydrogen bonding arises from the attraction between an electronegative atom (hydrogen bond acceptor) and a hydrogen atom (hydrogen bond donor) that is bonded to another electronegative atom (such as fluoride, oxygen, or nitrogen) (Jeffrey 1997). Among these interactions, hydrogen bonding exhibits the greatest strength compared to van der Waals and electrostatic bonds (Jeffrey 1997).

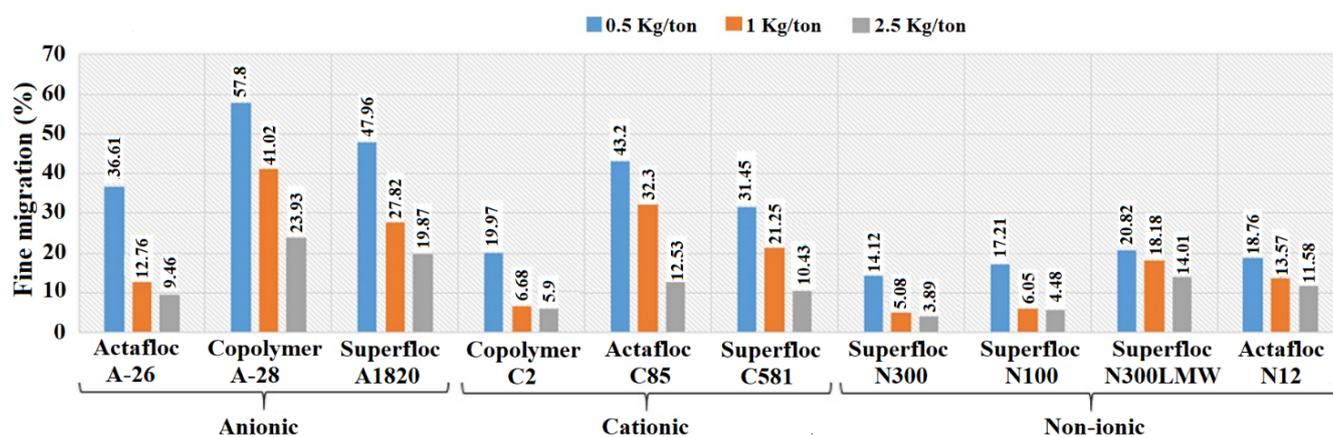


Fig. 8. Results of the agglomeration experiments using polymer compounds

The optimal results from the agglomeration test were chosen from the graph in Fig. 8 and summarized in Fig. 9 for the cationic, anionic, and non-ionic groups. In all three groups, favorable outcomes were observed with compounds that had high molecular weight. Based on the results, the interparticle bonds were found to be the strongest when using Superfloc N300 (with an FMP of 3.89%), followed by Superfloc N100 (with an FMP of 5.48%), and Copolymer C2 (with an FMP of 5.9%), all at a consumption rate of 2.5 kg/ton of these polymer compounds. Hence, the agglomerates produced using non-ionic and cationic compounds exhibited superior results compared to those using anionic compounds. This phenomenon can be attributed, in part, to the electric charge and zeta potential of the particles under acidic conditions (pH of 1.5). Based on XRD and XRF analyses, a substantial portion of the studied ore comprises silicate minerals such as quartz and albite. In an aqueous environment, silica particles acquire a negative charge due to their high affinity for hydration and subsequent surface hydrolysis, resulting in the formation of SiO^- groups through the loss of H^+ ions (Van 1963; Zhuravlev 2000). Furthermore, the presence of isomorphous substitution in aluminosilicate minerals (e.g., albite in the studied ore) contributes to a significant negative surface charge arising from the valence differences between Na^{2+} , Al^{3+} , and Si^{4+} ions in the aluminosilicate crystal structure (Van 1963; Zhuravlev 2000). As a consequence of the electrostatic attraction between the negatively charged particle surfaces and cationic compounds, such as Copolymer C2, they outperformed the anionic compounds. The lack of attraction between anionic compounds and the particle surfaces appears to be the main reason for the weaker performance of anionic compounds. Under acidic conditions, the electric charge of anionic compounds diminishes, resulting in the absence of electrostatic repulsion between the ore particles and the anionic compounds (Nasser and James 2006). Otherwise, electrostatic repulsion could lead to further weakening of the performance of anionic compounds.

Although van der Waals and electrostatic forces play a role in establishing strong bond connections between the ore particles, the most significant impact on interparticle bond strength is attributed to hydrogen bonding formed between the particles and the polymer compounds. Hydrogen bonding forces are involved in the bond paths created by all three groups: cationic, anionic, and non-ionic. The structure of repeating units in these compounds is depicted in Fig. 10. As evident, hydrogen atoms bonded to electronegative nitrogen atoms serve as hydrogen bond donors in establishing the interparticle bonds.

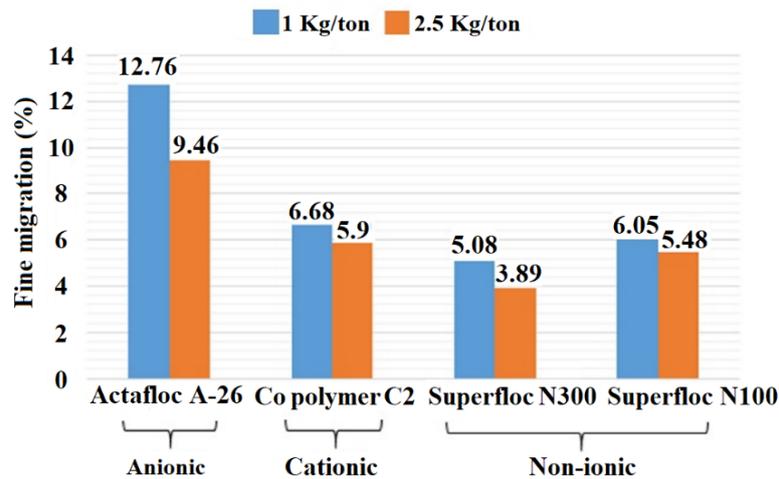


Fig. 9. Best results of the agglomeration experiments using polymer compounds

As mentioned, the studied ore particles contain a significant amount of silicate minerals. When these particles come into contact with an aqueous environment, hydration, and hydrolysis processes lead to the formation of silanol groups (Si-OH) on their surfaces (Van 1963; Zhuravlev 2000). The electronegative oxygen atoms in the silanol groups can act as hydrogen bond acceptors. Fig. 11 graphically describes the process of establishing hydrogen bonding on the surface of silica particles. Fig. 10 illustrates that non-ionic compounds predominantly consist of units involved in hydrogen bonding without additional units. In contrast, cationic and anionic compounds possess both ionic units and hydrogen bond-forming units. Consequently, the soak test results were highly favorable when non-ionic compounds were used.

Fig. 12 shows the agglomerates produced using the cationic compound Copolymer C2 and the non-ionic compound Superfloc N300, both before and after the soak test. As can be seen, the agglomerates produced with both compounds maintain their quality and shape after undergoing the soak test, indicating their resistance to disintegration under acidic conditions.

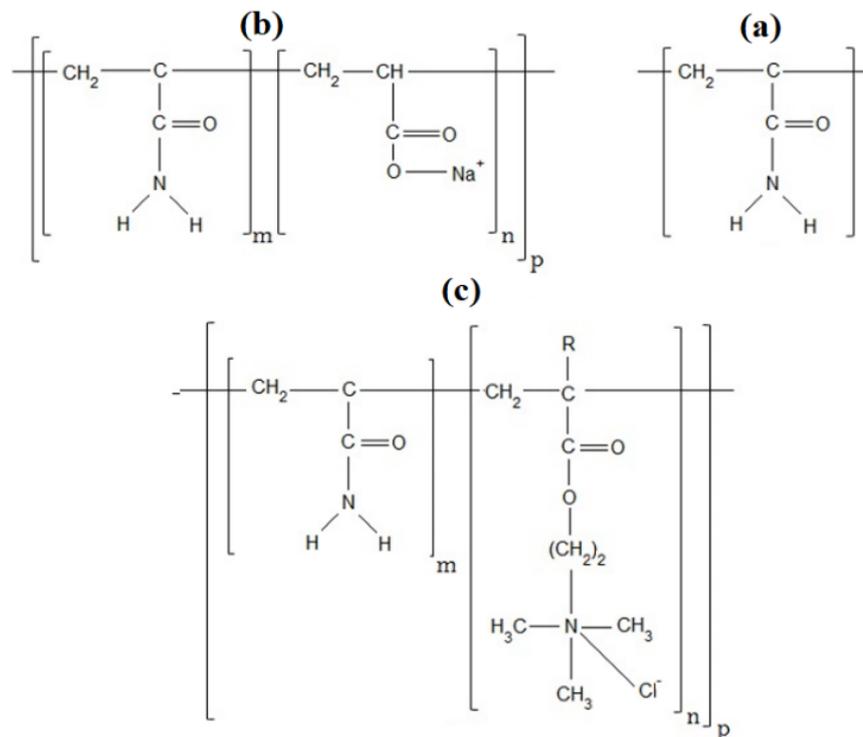


Fig. 10. Repeating units of polymer compounds. (a) non-ionic compound. (b) anionic compound. (c) cationic compound (Zhuravlev 2000; Nasser and James 2006)

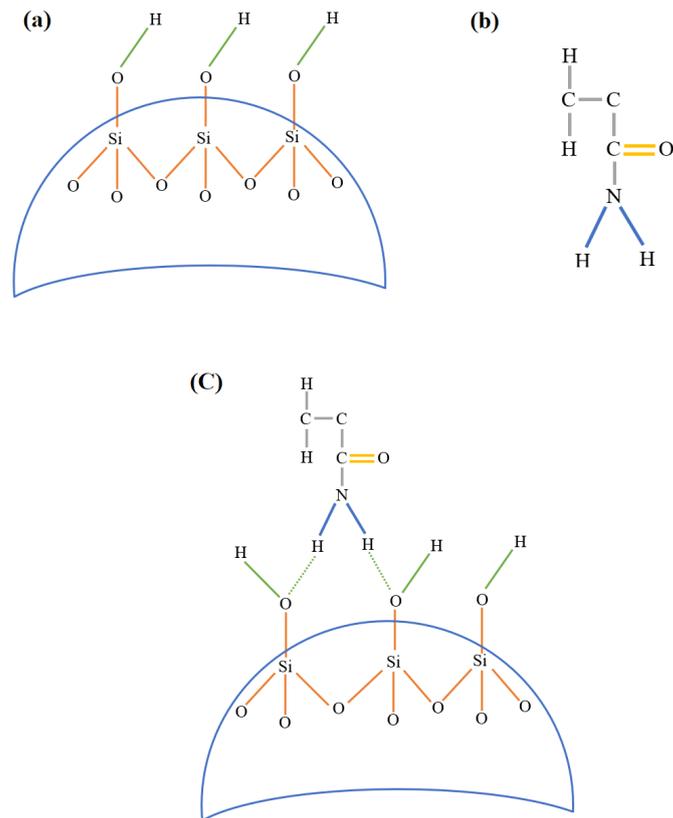


Fig. 11. Schematics of establishing hydrogen bonding on the silica particles' surface. (a) silanol groups on the surface of silicates, featuring a hydrogen bond acceptor region. (b) units with a hydrogen bond donor region in the polymer compound. (c) hydrogen bonding formed on the silica surface (Zhuravlev 2000; Nasser and James 2006)



Fig. 12. Produced agglomerates with desirable quality. (a) Using Superfloc N300 before the soak test. (b) Using Superfloc N300 after the soak test. (c) Using Copolymer C2 before the soak test. (d) Using Copolymer C2 after the soak test

To select an optimal additive material as a binder for heap leaching, three key factors should be considered in addition to the stability of agglomerates: availability, low cost, and the ability to enhance recovery rates without increasing acid consumption (Pietsch 2002; Kawatra et al. 2006). Based on Table 3, the cationic compound Copolymer C2 was recommended for agglomerating the studied ore due to its availability (domestically produced) and lower purchasing cost compared to Superfloc N300.

The implementation of the agglomeration method in the Aria copper mine beneficiation plant can result in a new feed with a copper grade of 0.956%. This can be achieved by adding materials with a particle size of 0-2 mm (20% by weight of the crusher circuit product) containing a copper grade of 1.34% to the heap feed with a copper grade of 0.86%. This means that approximately 153 tons of feed material are required to produce one ton of cathode. In comparison, without the agglomeration method, approximately 170 tons of feed material with a copper grade of 0.86% would be needed. Therefore, by increasing the grade and reducing the volume of required feed material through agglomeration, costs associated with crushing, heap loading, acid consumption, maintenance, personnel, electricity, water, diesel fuel, and other factors are significantly reduced per ton of cathode production. This research therefore recommends that the Aria copper mine beneficiation plant utilize the agglomeration method using the cationic compound Copolymer C2. However, further studies are required to understand its impact on the leaching kinetics and recovery. Further investigations are also required to check the stability of agglomerates against destruction under load, simulating conditions in the lower part of the heap under the pressure of the ore material.

4. Environmental considerations

The polymer compounds employed in this study are classified as polyacrylamides (PAM), synthetic polymers widely utilized across diverse industrial sectors, and play a crucial role in applications ranging from water treatment, and paper production, to oil drilling, and mineral processing. In the mineral processing industry, it predominantly serves in the dewatering sector as a flocculant and filter aid. Despite its significant benefits in these industries, the use of PAM requires careful consideration of its environmental implications (Wong et al. 2006; Rulyov et al. 2011; Cheng et al. 2016; Xiong et al. 2018; Qian et al. 2018; Peng et al. 2020; Mohamed Hizam et al. 2020; Wang et al. 2022).

A primary environmental concern associated with PAM application revolves around the potential release of acrylamide, a monomer integral to PAM synthesis. Recognized as a neurotoxin and carcinogen, acrylamide poses substantial threats to both human health and ecosystems (McCollister et al. 1965; Tanii and Hashimoto 1981; Xiong et al. 2018). It is imperative, however, to differentiate between the toxicity of acrylamide monomers and the stability of PAM polymers. While acrylamide monomers in their original state can indeed present hazards to plant life and contribute to the formation of cancerous glands in animals and humans (Shipp et al., 2006; Xiong et al. 2018), the polymerization of these monomers into PAM results in their secure encapsulation within the polymer chains, substantially minimizing their mobility and potential for environmental contamination (Shipp et al., 2006; Xiong et al. 2018). Notably, the discharged degraded PAM must be monitored, given that literature suggests acrylamide concentrations exceeding 0.06 mg/l in water pose dangers (Tanii and Hashimoto 1981). Hence, the level of consumption as well as the concentration of acrylamide monomers in the wastewater shall be traced using instruments and analytical methods to prevent environmental impact (Lande 1979).

Studies affirm the inherent stability of PAM polymer compounds in aqueous solutions, impeding their reversion into monomeric units. Simultaneously, the literature supports the hypothesis that naturally occurring microbes in soils, sediments, and water systems can break down acrylamide into non-toxic byproducts like ammonia and acrylic acid over periods ranging from days to months (Shanker et al. 1990, Smith et al. 1997; Shukor et al. 2009; Labahn et al. 2010). For instance, under aerobic conditions, Shanker et al. (1990) observed the complete disappearance of 500 mg/l of acrylamide in the water within 5 days. Even in aquatic systems, complete degradation of acrylamide can persist for over 2 months (Brown et al. 1980; Zhao et al. 2016). Despite the readily biodegradable nature of acrylamide in the environment, diligent monitoring remains imperative to prevent hazardous releases from various applications (Xiong et al. 2018).

While PAM polymer exhibits high stability in degrading into a non-toxic form, and acrylamide has the potential to degrade into non-toxic products, careful monitoring of PAM levels and wastewater treatment in plant operations is crucial to mitigate any environmental impact. Prior to loading the heap, meticulous preparation of the heap pad, including the use of impermeable liners, is imperative to prevent the penetration of leach solutions to the ground level. This foundational element in environmental risk management ensures the effective containment of leach solutions that may contain PAM. During heap leaching, where the pregnant leach solution (PLS) is processed to recover metals, the recirculation of the raffinate can accumulate impurities. To address this, a portion of the raffinate is released as bleed and replaced with fresh water, typically discharged into a holding pond or evaporation basin before environmental release (Habashi 1999).

In summary, to mitigate risks, using impermeable liners in heap leach pad construction, employing an appropriate amount of PAM, monitoring potential PAM contamination in bleeding and leached ore, and treating the bleed solution for acrylamide removal or degradation, such as through biological treatment, could be essential considerations. Further comprehensive studies are warranted in this domain.

5. Conclusions

In this study, the agglomeration method was employed to utilize the 0-2 mm fraction of the crusher circuit product in the heap loading at the Aria copper mine beneficiation plant. XRF analysis revealed that the examined sample contained 1.34% copper in the 0-2 mm fraction and 0.86% copper in the 2-20 mm fraction. The fractions also contained 59.86% and 65.91% silica, respectively. Microscopic and XRD analyses identified malachite as the primary copper mineral. The gangue minerals predominantly consisted of albite and quartz, which significantly influenced the surface charge of the particles in an aqueous environment.

The strength of interparticle bonds in the produced agglomerates was assessed using the FMP parameter in the soak test. The results indicated that the FMP for the agglomerates produced using a combination of raffinate solution and sulfuric acid was 66.8%, which was undesirable due to the weak interparticle bonding forces. Similarly, the FMPs obtained for the agglomerates produced using sodium silicate and calcium sulfate under the optimal conditions were 61.5% and 57.74%, respectively, indicating the low resistance of the produced agglomerates under these conditions.

Based on the results, agglomerates produced using high molecular weight polymer compounds in the non-ionic, cationic, and anionic groups exhibited adequate strength. The best results were observed for agglomerates produced using Superfloc N300 (with an FMP of 3.89%), Superfloc N100 (with an FMP of 5.48%), and Copolymer C2 (with an FMP of 5.9%), all at a consumption rate of 2.5 kg/ton of these polymer compounds. Notably, agglomerates produced using cationic and non-ionic polymer compounds outperformed those produced using the anionic compound. This was attributed to the electrostatic attractive forces between the negatively charged silica particles and the binder in the case of cationic compounds, and the more effective hydrogen bonding with the silanol groups on the surface of silicates in the case of non-ionic compounds.

Overall, the findings demonstrated that agglomeration using high molecular weight non-ionic compounds, which exhibit strong hydrogen bonding forces alongside van der Waals forces, resulted in the most resistant agglomerates under acidic conditions for the studied ore with a significant percentage of silica. However, the cationic compound Copolymer C2 was recommended for the agglomeration process at the Aria copper mine beneficiation plant due to its availability (domestically produced) and lower cost compared to Superfloc N300.

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