



# **Gangues and Clays Minerals as Rate-Limiting Factors in Copper Heap Leaching: A Review**

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**Abstract:** Heap leaching is a firm extractive metallurgical technology facilitating the economical processing of different kinds of low-grade ores that are otherwise not exploited. Nevertheless, regardless of much development since it was first used, the process advantages are restricted by low recoveries and long extraction times. It is becoming progressively clear that the selection of heap leaching as an appropriate technology to process a specific mineral resource that is both environmentally sound and economically feasible very much relies on having an ample understanding of the essential underlying mechanisms of the processes and how they interrelate with the specific mineralogy of the ore body under concern. This paper provides a critical overview of the role of gangues and clays minerals as rate-limiting factors in copper heap leaching operations. We aim to assess and deliver detailed descriptions and discussions on the relations between different gangues and clays minerals and their impacts on the operational parameters and chemical dynamics in the copper heap leaching processes.

Keywords: hydrometallurgy; leaching; gangues; clays minerals; heap leaching; agglomeration

## 1. Introduction

According to Toro et al. [1], copper mining is an industry that is in constant growth, and approximately 25 million tons are produced annually worldwide [2]. Among the copper minerals on the planet, the vast majority correspond to sulfide ores [3]. Within these copper minerals, chalcopyrite stands out as the most abundant, representing 70% of all minerals that contain copper in the Earth's crust [4–7]. Copper is recovered from these minerals mainly through flotation, followed by pyrometallurgical processing, representing 80–85% of world's copper production [8,9]. However, pyrometallurgical treatment is difficult and expensive for low-grade copper ores producing high emissions of sulfur dioxide (SO<sub>2</sub>), NOx, and CO<sub>2</sub>, which cause problems, such as acid rain and increased local pollution [10–12].

In addition, flotation techniques generate a large amount of waste, which results in tailings dams with a high possibility of generating acid mine drainage (AMD) due to the oxidation of minerals with a high presence of pyrite [13]. The latter is essential to consider since the drainage of mining waste rocks is one of the most important environmental challenges facing the global mining industry due to its dynamics and persistence [14–17]. AMD creates a severe environmental problem allied with mining and mineral processing due to its very low pH (<3.0) and high concentrations of possibly toxic dissolved metals, metalloids, and sulfate. Without appropriate management, AMD can result in considerable



Citation: Toro, N.; Ghorbani, Y.; Turan, M.D.; Robles, P.; Gálvez, E. Gangues and Clays Minerals as Rate-Limiting Factors in Copper Heap Leaching: A Review. *Metals* 2021, *11*, 1539. https://doi.org/ 10.3390/met11101539

Academic Editor: Alexandre Chagnes

Received: 16 August 2021 Accepted: 24 September 2021 Published: 27 September 2021

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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). environmental degradation, water, and soil contamination, severe health deterioration among neighboring communities, and damaged biodiversity in aquatic ecosystems [18–21].

All of the above has led to the need to investigate the development of a profitable hydrometallurgical process to treat these minerals since hydrometallurgy is a good alternative to process both oxidized minerals and sulfide minerals environmentally friendly [22–24]. Heap leaching is a hydrometallurgical approach and continuously developing mineral processing and extraction technology that is gaining attractiveness and recognition in the mineral industry. Heap leaching has solid benefits over traditional metallurgical methods where economically viable options have become limited [25].

In this paper, a critical review and overview are provided covering scientific publications of the last 20 years on the role of gangues and clays minerals as rate-limiting parameters in copper heap leaching operations and the dissolution and recovery of copper. We offer a detailed description and discussion on the links and relationships between different types of gangues and clays minerals and their impact on the operational parameters (e.g., heap leach permeability and dissolution kinetics) and chemical dynamics (e.g., pH and redox potential (Eh)) in the copper heap leaching processes.

## 2. Heap Leaching as an Alternative Route in Hydrometallurgy

For Watling et al. [26], certain issues motivate the use of hydrometallurgical methods, even for sulfide ores, for example, the high copper demand; the continuous decay of the ore grades; and the extensive exploitation of oxide and secondary sulfide minerals. The low-grade may eventually leave large amounts of low-grade chalcopyrite ores as an important, but so far, uneconomical source of copper. This has prompted the use of processes such as heap leaching. Heap leaching began to be used in the middle of the 20th century.

Nevada's gold and silver heap leaching as the "birthplace" of modern gold heap leaching [25,27,28]. The first modern copper heap leach operation may have been the Bluebird copper oxide mine in 1968, followed in the early 1970s by other small operations in the United States. Uranium producers have already utilized the heap leaching of uranium through either acid or alkaline solutions since the late 1950s. Large-scale heap leaching can be said to have started in 1980 when three major copper projects were commissioned in Chile, and, at approximately the same time, a large number of gold projects were commissioned in the United States [25].

Heap leaching has been developed for many different types of minerals, climates, and operations of any size [25]. Further than copper oxide, uranium, and gold, today there are an extensive variety of applications, including copper sulfide ores, gold-bearing pyritic ores, and non-metallic minerals (such as saltpeter [29]) as well as soil remediation [25,30,31]. Heap leaching is typically applied for low-grade deposits; however, it might also be applied to small higher-grade deposits in remote or politically high-risk locations to reduce capital cost. Heap leaching from low-grade ores has contributed to the total global production of copper, gold, silver, and uranium [25,32,33]. Heap leaching has also been considered for zinc [25,34,35] and nickel [36] and more lately for platinum group metal (PGM)-bearing ores and electronic scrap [37,38].

In heap leaching, the crushed ore is stacked on an impermeable pad, and leaching reagents (a strong acid, commonly sulfuric acid for copper or nickel ores or a dilute cyanide solution for gold and silver-bearing ores) are added by irrigation from the top. The wanted mineral is extracted, and the solution is gradually loaded as it penetrates through the pile. Leaching may be aided by microorganisms resident within the ore bed, particularly in the existence of sulfide minerals. A drainage system collects the pregnant leach solution (PLS) at the base of the heap. The PLS is then pumped to the processing units to extract the value metal.

The barren leach solution (BLS) is sent to the barren solution pond, from where, after solution makeup, it is reapplied to the heap's surface [25]. A typical heap leaching circuit is shown in Figure 1. This process is conducted in leaching piles, where their typical height is between 4 and 10 m, although in some cases, they can reach 18 m [28]. In addition, the

largest sizes generally range between 10 and 40 mm in heap leaching, and sizes less than 6 mm are unacceptable. This is because small-sized particles affect the heap's permeability, mainly clay minerals result in increased clogging of heaps over time due to swelling and gradual decrepitation [39].



Figure 1. Typical heap leach flow diagram for copper (modified from [25]).

For the leaching process to be efficient, the fine particles tend to agglomerate around the larger particles with water and concentrated sulfuric acid, a process known as "curing." This process improves the strength of the material while having good mineral permeability in heap leaching. In addition, it helps to achieve adequate heap heights, improve copper recovery rates, and control processing times [40,41]. It is worth mentioning that another emerging method is bio-hydrometallurgy, which plays an important role in the recovery of copper with economic, environmental, and social benefits. To date, it has been reported that many investigations on the acid bioleaching of secondary [42–46] and primary sulfides have presented good results.

# 3. Effect of Ore Mineralogy on Copper Heap Leaching Performance

Copper heap leach projects are sometimes evaluated without adequate mineralogy, despite the lack of a clear and comprehensive mineralogical sturdy, which could significantly affect the heap efficiency and expected recovery and operating costs [47–49]. Heap leaching processes operate over approximately three months for sulfide minerals in chlorinated media and lower ore grades in typical operations. This is why several studies have emphasized the essential need to characterize the mineral's physical, chemical, and mineralogical properties to be leached [49,50].

Problems with copper heap leaching may arise from the ore mineralogy, more specifically, the presence of reagent consuming gangues and clays minerals. Ghomi et al. [51] analyzed the effect of polar organic reagents on chalcopyrite leaching, Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) analysis was performed (Figure 2), where the presence of aluminosilicate or clay-type gangues was detected in area 4, with a high percentage of aluminum, silicon, and oxygen, which can be corroborated by Figure 3.







Figure 3. EDS microanalysis of areas indicated in the SEM (Modified from [51]).

For their part, Helle and Kelm [52] studied leaching with sulfuric acid, focusing on the retention of copper by the reactive gangue. Gangue minerals can considerably affect acid consumption and copper recovery and change the acid requirements in different unit operations [53,54]. Critical factors for acid consumption in oxidized copper ores include the presence of carbonate; the presence of other short-term and long-term acid consumers; and the degree of acid adsorption by different non-carbonate minerals (e.g., clays, oxides of hydrated iron, highly porous copper minerals, and/or mineral-forming silts) [48].

#### 4. Effect of Reactive Gangue on Copper Leaching

The reactivity of the gangue mainly results in acid consumption, loss of permeability, exchange, and absorption of copper, and finally, retention of copper in a pile [52], where the acid consumption is considered as the main economic factor for oxidized minerals [55].

For instance, carbonates (such as calcite) in copper oxide mineral deposits can cause a high increase in acid consumption. The low acid concentration is not desired since it leads to the precipitation of hydrated ferric oxides that negatively influence the extraction of copper and filtration of the solution [25].

## 4.1. Effect of Iron-Bearing Minerals on Copper Heap Leaching

The microorganisms are responsible for providing sulfuric acid for proton attack and keeping the iron in an oxidized ferric state for the oxidative attack, knowing that ferric ions are an oxidizing agent and the soluble iron species determinate the redox potential. Iron can occur in the form of secondary phases, such as jarosite, which, according to Harmer et al., [56] and Ahonen and Tuovinen, [57], can limit the extraction of metals in bioleaching since jarosite obstructs mineral–microbe contact by forming a mass transfer barrier to nutrients, oxygen, and carbon dioxide, which impairs the extraction of minerals of interest, such as copper [25]. A clear example of iron in leaching is that of limonite and hematite minerals, which, mentioned by Jansen and Taylor, [48] react with acid to form ferric ions in solution.

The effect that iron may have on the extraction of copper is also related to the pH at which the leaching is conducted. According to a study conducted by Nikoloski and O'Malley [10], exceeding a pH of approximately 1.03, the extraction tends to decrease, understanding that there is a range within which copper extraction becomes optimal. In a study conducted by Phuong Thao et al. [58], the relationship between copper extraction and potential was evaluated considering different Fe<sup>3+</sup> ratios. As shown in Figure 4, at the lower initial concentration of Fe<sup>3+</sup>, the copper extraction tends to increase, presenting a higher extraction at 0.45 E/V.



**Figure 4.** Effects of ferric ion concentration on the potential redox dependence of chalcopyrite leaching: copper extraction rate as a function of redox potential, temperature 343 K, HCl concentration 0.1 kmol m<sup>-3</sup>, initial Cu<sup>2+</sup> concentration of 0.01 kmol m<sup>-3</sup>, solid to liquid ratio of 0.3 g CuFeS<sub>2</sub>/15 mL and stirring speed of 400 rpm) (Modified from [58]).

#### 4.2. Effect of Clay Minerals on Copper Heap Leaching

Among the reactive gangues that most affect the recovery of copper are clays, which are mostly the end products of the weathering of silicates formed at high temperatures and pressures [59]. Silicates are the most common minerals in Earth's crust and mantle, making up 95% of the crust and 97% of the mantle by most estimates. Thus, it is necessary

to understand their reactivity under the sulfuric acid regimes used in heap leaching to predict the behavior of the mineral and its impact on operations [60].

Since the reactivity of silicates and their effects on the general consumption of acid in leaching can become more complex than the carbonates themselves, as indicated [61], it is worth mentioning that some silicate and aluminosilicate minerals, such as mica and clay minerals, can consume acid generated by the oxidation phenomenon [62–64]. Minerals, such as montmorillonite, kaolinite, and smectite, can quickly adsorb acid [65,66]. However, together with mordenite, the latter is the clay species that most retains copper and acid. In a study by Helle and Kelm [52], the effect of gangues and clay minerals in the leaching of copper oxides was evaluated. Three groups of smectites (SAZ, NAU, and BENT Rock) were identified, with the mordenite having the highest copper retention percentage (Figure 5).



**Figure 5.** Copper retention (Wt%) in gangues of the malachite, atacamite, and chrysocolla series (Modified from [52]).

A study that supports this was conducted by Pérez et al. [67], in which two samples of pure and impure black copper were compared. They demonstrated that the impure sample with the presence of montmorillonite and kaolinite clays and the bargains (e.g., chlorite) presented a higher acid consumption concerning the pure sample.

Silicate minerals and limonite, like gangue, also consume acid. As mentioned by Jansen and Taylor [48], reaction by-products can partially regenerate sulfuric acid in subsequent reactions with each other and/or fresh minerals, where minerals from silicate consume acid by decomposition in a wide range of soluble solution products, such as feldspar and plagioclase, and the case of limonite minerals, such as goethite.

## 4.3. Effect of Clay Minerals on Copper Heap Leaching

In addition to iron-bearing minerals and silicates, other minerals, such as carbonate, can affect the recovery of the mineral of interest in copper heap leaching. Within these cases, calcite minerals are known for their high reactivity in acid, dissolving even in very dilute sulfuric acid conditions [68]. On the other hand, minerals like biotite, which, according to a study by Free [69], can consume acid more quickly at lower pH than chlorite (see Figure 6). Even chlorite itself has a particular effect on the process since, according to comprehensive studies by Jansen and Taylor [48] and Sequeira and Leite [65], it shows a significant long-term consumption of acid. Furthermore, as pointed out by SERNAGEOMIN (National



**Figure 6.** pH and acid consumption data for constant acid addition rate experiments (0.04 mL/min in 20 mL) with pure minerals (1 g mineral/20 mL water) Data for sodalite, chlorite, biotite, and montmorillonite represent the mean values and associated standard deviation ranges from two to four test runs for each mineral (Modified from [69]).

## 5. Methods to Reduce Acid Consumption in Heap Leaching

Agglomeration is a process before heap leaching that has made it possible to solve the percolation problems associated with the high content of fines and clays [50]. This is because clay minerals can generate complications in the leaching processes, as expressed by Li et al. [66], since the action of the acid on a silicate can result in the formation of silica gel due to the easy polymerization silica in solution. Gel formation can cause blinding and prevent seepage; therefore, it is detrimental in heap leaching operations [66,70]. It is necessary to have a minimum humidity level when agglomerating the mineral to allow the acid to distribute well but avoid forming a gel by the silicate minerals [40].

In a study by Bouffard [71], water and sulfuric acid concentrations were added for 14 copper heap leaching operations. The highest proportional relationship between water and acid additions was associated with a more finely crushed mineral with a higher acid demand, and the lowest additions considered the particles' roughness. The initial moisture was higher than the typical values, and the presence of gangue minerals led to a suitable range of 15–25 kg of sulfuric acid/t of mineral and 60–100 kg of water/t of mineral (see Figure 7).

Acid curing is performed before heap leaching to accelerate the reaction with copper ores through concentrated  $H_2SO_4$ . However, a critical consequence for gangue ores is that the strong acid dehydrates the polymeric silica in the gangue, inhibiting further gangue reaction and, thus, silica dissolution, under heap leaching conditions [66,70]. The moisture content is considered a factor that affects the reactivity of the acid gangue during curing. Acid consumption appears to increase significantly in water, therefore, increasing the amount of clay minerals and fines.



**Figure 7.** Study of sulfuric acid and water additions from 14 copper heap leaching operations (Modified from [50]).

Soft surfaces require monitoring, which could affect the wettability and moisture retention in the agglomerates [71]. Lu et al. [40] indicated that acid curing can avoid the silica dissolution and control problems that often occur in heap leaching. Under the conditions of acid curing and agglomeration, the copper extraction rate is improved by the sulphation of the copper mineral; there is an improved permeability of the mineral and a reduction of the competition for acid by passivating the consuming gangue.

# **6. Parameters That Are Affected by the Presence of Clays and Reactive Gangues** *6.1. Dissolution Rate*

The rate at which a mineral dissolves can vary according to its environment. For example, pure pyrite shows a higher rate than sphalerite, galena, or chalcopyrite, but when this is in contact with one of these minerals, the situation is reversed [72–75]. This response is due to the galvanic interaction between the minerals, a factor that, according to Watling [76], could be studied to improve the leaching rates of the base metal sulfides of interest. In an X-ray photoelectron spectroscopy (XPS) study of chalcopyrite conducted by Parker et al. [77] and Klauber et al. [78], it was found that the reaction products causing its slow dissolution contained sulfur and iron. They detected four species, among which are sulfur and ferric sulfate, that show similarity to jarosite, which accumulates to the point of preventing further oxidation of chalcopyrite.

## 6.2. Particle Size

The size distribution is among the important factors for determining the leaching rate and the intrinsic kinetics of mineral dissolution, as stated by Bartlett [79]. This is because both the amount of fines and soft clay minerals require monitoring, thereby, affecting the wettability and moisture retention in the agglomerates [71]. In addition, as mentioned by Bouffard [50], both organic and inorganic silts and the mixture of sands, silts, and clays have very low permeability, which can negatively influence heap leaching. In a study by Yin et al. [80], the effect of particle size on the permeability of the pile was evaluated, among other things (see Table 1 and Figure 8a,b). It was found that the hydraulic conductivity increased proportionally by the particle size.

	Column							
Parameters			C1		C2	C3	C4	C5
Concentration of sulfuric acid $(g/L)$			25		30	35	40	45
Irrigation rate $(L/m^2 \cdot h^{-1})$			40		60 1 E	20	60 . E	20 1 E
raticle size distribution (mm)			+3		1~3	-1	+3	1~3
Hydraulic conductivity (cm/s)		C1 C4 C2 C5 C3	Copper extraction rate (%)	80 <b>^</b> 70 60 50 40 30 20 10			(1 ( (2 ( (3	24 25 →
	3 6 9 12	15 18 21			2 4 6	8 10 12 14	4 16 18 20	22
Leaching time (days) (a) Hydraulic conductivity				Leaching time (days) (b) Copper extraction rate				

0.1

Table 1. The operational conditions for column leaching tests (Modified from [80]).

**Figure 8.** Critical permeability and leaching parameters with leaching time in different groups (Modified from [80]), (**a**) Hydraulic conductivity, (**b**) Copper extraction rate.

On the contrary, the particle size decreased because the particles blocked the pores and compressed the mineral heap [81]. It is known that clays tend to have a very fine granulometry, which, according to many researchers [64,82–84], can be decisive for an agglomeration, considering a proportion of fines smaller than a 50–75 mm size fraction. While grinding the ore to a smaller particle size often increases copper recovery at any given time [85], the benefit conferred by the treatment leads to higher acid consumption and energy, as well as the presence of more fine particles in the pile that can decrease its permeability. High iron precipitation can also contribute to the formation of fines in a pile, as Watling [76] indicated in a study at high pH and high concentrations of ferric ions.

## 6.3. pH

In the bioleaching study of a chalcopyrite mineral sample through mixed culture conducted by Dorado et al. [86], the pH of the leaching was shown to have a significant effect on the extraction of copper. This is in agreement with a study performed by Viramontes-Gamboa et al. [87]. They demonstrated that the maximum critical current (which indicated the greatest extraction of copper) increased with the decrease in pH and temperature. In a similar study by Vilcáez et al. [88], they proposed that acid was necessary for generating ferric ions, which were necessary to oxidize chalcopyrite.

Córdoba et al. [89], in their study, demonstrated a direct relationship between pH and the passivating layer in chalcopyrite. The precipitation of iron generates jarosite at a pH higher than 2, which indirectly affects the rate of dissolution of chalcopyrite. On the other hand, Watling [76] indicated that the maintenance of the pH in a range of 1 to 2 for the microbial oxidation of iron and sulfur is important for the regeneration of ferric and acid ions by the microbial population.

A study conducted by Holden et al. [90], working in a higher pH range, showed greater precipitation of ferric compounds, thus, reducing the concentration of ferric ions available to oxidize the sulfide mineral. Rawlings et al. [91] also observed that bacterial species responsible for iron oxidation are favored at a high ratio of Fe<sup>3+</sup>/Fe<sup>2+</sup> (high redox

potential), low pH, and high temperature. Nikoloski and O'Malley [10] indicated that the iron extraction curves show improved leaching below pH 1.03 (see Figure 9); on the contrary, extraction decreases at higher pH values due to iron precipitation.



**Figure 9.** Copper and iron extraction in 25 g/L [Fe<sup>3+</sup> /Fe<sup>2+</sup>], 10 g/L [Al<sup>3+</sup>], 1 g/L [Mg<sup>2+</sup>], 0.2 g/L [Cu<sup>2+</sup>], 125 g/L [SO<sub>4</sub><sup>2–</sup>], pH of 1.2, Eh of 700 mV, and temperature of 50 °C at different pH (Modified from [10]).

# 6.4. Redox Potential

Another factor affected by the ore mineralogy in heap leaching is the oxidation potential that must move within a certain range to obtain a good copper extraction. This can be supported by studies such as those of [92–94], who, working at low solution potentials, presented better bioleaching of chalcopyrite. On the contrary, [10] indicated, through a study of chalcopyrite leaching, that, when working at potentials higher than 718 mV, iron tends to precipitate as jarosite (see Figure 10). This is detrimental in the long term for copper extraction. It is known that, at a high  $Fe^{3+}/Fe^{2+}$  ratio, the potential is higher (>750 mV SHE, and, on the contrary, at low  $Fe^{3+}/Fe^{2+}$  ratios, the potential is lower (<600 mV SHE). On the other hand, Hansford and Vargas indicated that the behavior of the bacteria significantly depends on the  $Fe^{3+}/Fe^{2+}$  ratio in the extracellular polymeric substances (EPS) layer in the leaching, which is highly dependent on the redox potential in solution and the concentration of soluble iron.



**Figure 10.** Copper and iron extraction in 25 g/L [Fe<sup>3+</sup>/Fe<sup>2+</sup>], 10 g/L [Al<sup>3+</sup>], 1 g/L [Mg<sup>2+</sup>], 0.2 g/L [Cu<sup>2+</sup>], 125 g/L [SO<sub>4</sub><sup>2-</sup>], pH of 1.2, and temperature of 50 °C at different Eh (Modified from [10]).

#### 6.5. Temperature

Temperature is an important factor to evaluate within copper extraction since it is often observed that indigenous bacteria, by acclimating to high levels of selected metals in their environment, are more effective as bioleaching catalysts [76]. Considering what was mentioned by Harmer et al. [56] and Ahonen and Tuovinen, [57] of the obstruction to mineral–microbe contact due to the formation of jarosite, which damages the long run leaching process. It is understood that the temperature must move in a certain range in order to avoid this precipitation of iron. Thus, according to a study conducted by Nikoloski and O'Malley, [10] it was discovered that, even though copper extraction increased by 9–32% when the temperature increased from 26–70 °C, after the 40 °C, iron dissolution tends to decrease, but not exceeding what was initially obtained at 26 °C. This is due to its precipitation as jarosite (see Figure 11).



**Figure 11.** Extraction of copper and iron in  $25 \text{ g/L Fe}^{3+}/\text{Fe}^{2+}$ ,  $10 \text{ g/L Al}^{3+}$ ,  $1 \text{ g/L Mg}^{2+}$ ,  $0.2 \text{ g/L Cu}^{2+}$ ,  $125 \text{ g/L SO}_4^{2-}$ , pH of 1.2, E h of 700 mV, and pH 1.2 at varied temperature (Modified from [10]).

# 7. Conclusions

Heap leaching is desirable for mineral treatment due to the techno-economic and environmentally sound capabilities in processing low-grade and complex minerals. However, certain mineralogical aspects, such as acid-consuming gangues and clays minerals, may act as rate-limiting factors in copper heap leaching. Among these factors, the iron (released from iron-bearing minerals), if not managed within specific parameters of pH (1–2), temperature (less than 40 °C), and potential (less than 728 mV), precipitates as jarosite. This phenomenon can harm mineral–microbe interactions, reagent penetration, the permeability of the pile, and the dissolution rate of the mineral. The presence of carbonates results in the high consumption of acid in the leaching processes. Among carbonate minerals, calcite is known for its high reactivity in acid, dissolving even in very dilute sulfuric acid conditions. Carbonates, such as chlorite and epidote, can dramatically increase acid consumption when working in long leaching periods.

Additionally, the silicates' impact on general acid consumption may be more significant than that of carbonates. Montmorillonite, kaolinite, smectite, and mordenite are the clay minerals that generate the highest acid consumption and decrease copper recoveries. In addition, due to its low granulometry (<50–75 mm) there is a risk of silica gel formation due to the reaction between acid and silicate (due to the easy polymerization of silica in solution) being the most damaging aspect of the heap leaching operations. This can be controlled and avoided by a good agglomerate process, maintaining a minimum humidity, allowing a better distribution of the acid, and avoiding silica gel formation. **Author Contributions:** N.T. and M.D.T. contributed in research and wrote paper, P.R., E.G. and Y.G. contributed with research, review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: Pedro Robles thanks the Pontificia Universidad Católica de Valparaíso for the support provided.

Conflicts of Interest: The authors declare no conflict of interest.

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