

**ATMOSPHERIC LEACHING OF ENARGITE  
IN IRON SULFATE SOLUTIONS  
CATALYZED BY ACTIVATED CARBON**

**by**

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## Abstract

Traditionally, smelting has been the primary method of treatment for copper sulfide concentrates. In modern smelters the environmental problem of sulfur dioxide emission has been addressed effectively, but pyrometallurgical treatment of concentrates containing elevated levels of arsenic is still difficult and costly. Therefore, arsenic is considered a penalty element for smelters. However, the depletion of “clean” (non-arsenical) copper deposits and the increasing demand for copper will make the treatment of copper-arsenic sulfides such as enargite and tennantite unavoidable. Thereby a viable processing method is required. Hydrometallurgical treatment of enargite using atmospheric leaching promises a comparatively simple method for managing arsenic by co-precipitating it with iron in the form of scorodite. The major challenge involved with this option is the slow rate of enargite leaching.

A novel treatment for enargite-rich copper concentrates through atmospheric ferric leaching catalyzed by activated carbon is presented in this study. Enargite concentrates from three different sources in Chile and Peru and one enargite mineral sample from the United States were used in the leaching experiments. Batch leaching tests were conducted in sealed, jacketed, glass stirred-tank reactors. The results showed that enargite leaching was up to 6 times faster in the presence of activated carbon, making it possible to achieve virtually complete copper extraction within 24 hours. SEM studies revealed changes in the morphology of the passive layer on enargite particles which is

formed as a product of leaching. The laboratory-scale tests indicated that desirable leaching kinetics could be maintained after recycling activated carbon particles multiple times to new leaching tests and also at a carbon:enargite concentrate mass ratio as low as 0.25. Activated carbon loss was reduced from 26 % to 5 % of the initial carbon mass by decreasing the impeller speed from 1200 rpm to 800 rpm, while the leaching performance remained similar. The effects of concentrate grind size, solution redox potential and initial total iron concentration on copper extraction have also been studied. The presented method promises a commercially attractive route to treat enargite concentrates.

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# 1. Introduction

The world's demand for copper is steadily increasing, requiring the exploitation of a greater number of copper resources. Moreover, the depletion of high grade copper deposits has led to an increase in impurity levels in available deposits.

The majority of copper deposits comprise of copper sulfides which are generally treated in the form of flotation concentrates in smelters. The presence of deleterious impurities in copper concentrates makes their treatment in smelters difficult and costly since it requires the addition of several steps for removal and safe disposal of them. One of the most problematic elements of this kind is arsenic. Most smelters either refuse to accept copper concentrates with high levels of arsenic, or accept them and impose heavy financial penalties. Thus, developing a viable alternative route for treating these deposits is needed.

Hydrometallurgical methods can be considered as potentially suitable alternatives to their pyrometallurgical counterparts for treating these types of concentrates since arsenic management is simpler. This is due to the presence of extracted arsenic only in the solution phase. Among different developed methods, atmospheric leaching with iron sulfate salts offers several merits which result in relative ease in operation and lower costs. However, a major problem with this route is the refractory behavior of copper sulfides in sulfate media which

leads to a slow and incomplete copper extraction. Catalysts, including silver (Banerjee et al., 1990), pyrite ( $\text{FeS}_2$ ) (Abraitis et al., 2004a) and carbon have been proposed by researchers to enhance the leaching of copper sulfides. Previous studies have investigated the use of carbon catalysts in bioleaching (Liang et al., 2010; Nakazawa et al., 1998), sulfuric acid leaching (Okamoto et al., 2004) and ferric sulfate leaching (Wan et al., 1984) of chalcopyrite ( $\text{CuFeS}_2$ ).

The objective of this research was to develop a simple, economically viable and environmentally friendly catalytic leaching process in ferric sulfate media under atmospheric conditions for arsenical copper concentrates and to investigate some of its aspects from technical and operational points of view.

## **2. Literature review**

### ***2.1. Arsenical copper deposits***

#### **2.1.1. Occurrence**

Arsenic can be detected in traces everywhere in nature, but it is often found in higher concentrations (60 ppm or more) in sulfide-bearing minerals deposits (Grund et al., 2000). Copper is often associated with arsenic in sulfosalts, i.e., thioarsenate, thioarsenite, and thioarsenide minerals. The most common of these minerals are enargite ( $\text{Cu}_3\text{AsS}_4$ ) and tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ). In deep epithermal copper-gold deposits, enargite is usually present with pyrite, tennantite, covellite ( $\text{CuS}$ ) and chalcocite ( $\text{Cu}_2\text{S}$ ). Enargite is generally not associated with chalcopyrite, but they may co-exist in adjacent hydrothermal alteration zones, as happens in the Chilean mines of Chuquicamata and Escondida. Furthermore, arsenopyrite ( $\text{FeAsS}$ ), as the most abundant arsenic mineral, may be the source of arsenic in sulfidic copper deposits. The United States, Argentina, Chile, Peru, Mexico, Spain and the Philippines are some of the countries that have enargite-bearing copper-zinc-lead deposits with the average arsenic concentration of 0.1 wt. %. Some of the arsenical pyritic copper deposits (containing arsenopyrite and tennantite) with the average arsenic concentration of 4 wt. % can be found in the United States, Sweden, Germany, Japan and France (Filippou et al., 2007; Mandal and Suzuki, 2002).

### **2.1.2. Treatment**

Along with antimony and bismuth, arsenic is a highly problematic impurity in copper production. Treating arsenic-containing copper concentrates poses a major challenge to smelters due to the need for arsenic emission control and safe disposal, as arsenic is an extremely toxic element with carcinogenic, cardiovascular, and neurological effects (Mandal and Suzuki, 2002). Nonetheless, the growing world's demand for copper and the depletion of relatively "clean" (non-arsenical) copper deposits will render treating arsenic-bearing copper minerals inevitable in the future. As a result, mining companies are paying more attention to such deposits. Moreover, the presence of enargite in the flotation concentrates of a number of current large projects (for example, the Tampakan Project in the Philippines and the El Galeno Project in Peru) is a reminder of the need for a feasible route for treating high-arsenic copper concentrates.

Smelters are conventionally used for treating copper sulfide flotation concentrates. Smelting is a well-established technology which has been generally successful in adapting to meet today's strict environmental regulations. A notable example is the high sulfur dioxide emission problem that is effectively addressed in modern smelters. However, the complication of arsenic management has caused arsenical copper concentrates to remain one of the most difficult types of concentrates to treat by smelting.

Arsenic in smelter feeds is a major concern since it interferes with copper extraction, lowers product purity and mechanical properties, poses disposal and environmental problems, and increases production costs due to arsenic presence in a variety of streams (Grund et al., 2000). In the copper production process, it is difficult to remove arsenic completely by pyrometallurgical treatment. As a result, arsenic is present in copper anodes and is submitted to a subsequent electrolytic refining process, which is carried out in an aqueous sulfuric acid solution (Wang, 2004). Accordingly, a variety of arsenic compounds in various physical phases are released through different streams: vapors (as volatilized  $\text{As}_4\text{O}_6$ ), dusts from electrostatic precipitators (in the form of  $\text{As}_2\text{O}_3$ ), electrorefining electrolytes, electrorefining anode slimes, copper cathodes, final slag, sulfuric acid, and gases from the sulfuric acid plant. The treatment of these streams requires the application of a diverse range of arsenic capture, removal and disposal technologies (Castro, 2008; Piret, 1999). Therefore, high financial penalties are imposed by smelters to treat copper concentrates with usually more than 0.2 % arsenic (Smith and Bruckard, 2007). In many cases the penalties are so high that the ore is not economical to process. The few copper-arsenic deposits that have been exploited so far have high precious metals contents, which justify their treatment. In comparison, all of the extracted arsenic in a hydrometallurgical circuit will remain in leaching solution which makes it a potentially better choice for treating arsenical copper concentrates.

A number of hydrometallurgical processes have been proposed and developed for treating copper concentrates, which can also be considered for high-arsenic copper concentrates. In principle, these processes can be generally divided into two categories, sulfate and chloride. Within the sulfate group, leaching processes can be categorized further as either atmospheric or pressure and chemical or biological (Dreisinger, 2006).

### **2.1.3. Sulfate-based hydrometallurgical processes**

A number of sulfate-based hydrometallurgical processes have been developed to treat copper concentrates or ore. Most of these processes are designed for chalcopyrite leaching, but can be modified for arsenical copper concentrates. In these processes, copper is dissolved along with arsenic and other metals. Arsenic is then co-precipitated with iron in a stable form for disposal. Compounds containing Fe(III) and As(V) are considered to be the most stable forms for arsenic disposal, either in the form of poorly crystalline arsenical ferrihydrite, which is obtained at relatively low temperatures, or as crystalline ferric arsenates (such as scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) that are usually obtained at higher temperatures (Riveros et al., 2001).

Dreisinger (2005) has briefly reviewed some of the hydrometallurgical process options for arsenical copper concentrates or ores treatment. Brief

descriptions of the leaching technologies of some of these processes (presented in Table 1) are given below:

### **The Albion process**

The Albion process (Hourn et al., 1999) utilizes fine grinding of sulfide minerals, followed by atmospheric leaching with acidic ferric sulfate solutions while sparging with an oxygen-containing gas in an open tank reactor at a temperature of near the boiling point of the solution. Fine grinding (P80 of 20 microns or less) increases the activity of the ground product, as measured by its response to subsequent oxidation.

### **The BIOCOP™ process**

The BIOCOP™ process (Dreisinger, 2005; Tunley, 1999) was developed by the BHP Billiton biotechnologies group based in Johannesburg, South Africa. The process employs thermophilic bacteria to oxidize sulfide minerals to metal sulfates and sulfuric acid at a temperature range of 65 – 80 °C. Oxygen is used for bioleaching and pH is controlled during leaching to prevent too low levels of pH in leaching. Excess acid may be used in heap leaching if appropriate. The BIOCOP™ plant that was commercialized in Chuquicamata, Chile was specifically designed to treat arsenical concentrates from the Mansa Mina deposit.



**Table 1.** Some features of sulfate-based hydrometallurgical processes for copper concentrate or ore treatment.

Process name	Temperature (°C)	High pressure	Special feature(s) utilized	Reference
Activox®	90 – 110	YES	Fine grinding and high oxygen overpressure	Corrans et al., 1993
Albion	90	NO	Fine grinding	Hourn et al., 1999
Anglo American Corporation – University of British Columbia	150	YES	Modest grinding and surfactants for chalcopyrite leaching	Dempsey et al., 2003
Mintek – BacTech bacterial oxidation	37 – 40	NO	Fine grinding and low temperature bioleach	Neale et al., 2000
BIOCOP™	65 – 80	NO	Thermophilic bacteria	Tunley, 1999
Dynatec	150	YES	Low grade coal as an additive	Collins et al., 1998
Galvanox™	80	NO	Pyrite as a catalyst	Dixon et al., 2008
Mount Gordon	90	YES	Low temperature pressure oxidation	Richmond et al., 2002
Sepon Copper	80	NO	Autoclave treatment of pyrite concentrate to make acid and ferric sulfate	Baxter et al., 2003
Total pressure oxidation	200 – 230	YES	Extreme conditions of temperature and pressure	Marsden et al., 2003

## **The Galvanox™ process**

The Galvanox™ process (Dixon et al., 2008) which was developed at the University of British Columbia uses pyrite as a catalyst for atmospheric leaching of chalcopyrite in acidic ferric/ferrous sulfate solutions. The typical leaching process conditions include temperature of approximately 80 °C, a feed P80 of 53 to 75 microns and solution redox potential of 470 mV<sub>Ag/AgCl</sub> or higher. The pyrite:chalcopyrite ratio is roughly 2:1 to 4:1. Recently, Rivera-Vasquez and Dixon (2009) evaluated the leaching behavior of enargite under Galvanox™ process conditions.

## **The total pressure oxidation process**

The total pressure oxidation process (Dreisinger, 2005; Marsden et al., 2003) utilizes high temperature and pressure (200 – 230 °C and 30 – 40 atm) to oxidize all sulfide minerals to sulfate and sulfuric acid. The concentrates are leached in a single autoclave and the produced acid from pressure leaching may be used beneficially. One of the advantages of the process is convenient precipitation of iron as hematite. Phelps Dodge is employing this technology at the Bagdad plant in Arizona, USA.

Among these processes, atmospheric ferric sulfate leaching has several advantages, including utilizing comparatively low-cost equipment and flowsheet simplicity.

## ***2.2. Atmospheric ferric sulfate leaching***

### **2.2.1. Characteristics**

Atmospheric leaching of copper concentrates in acidic ferric/ferrous sulfate media offers a number of potential advantages over other developed hydrometallurgical processes. It operates under atmospheric pressure and temperatures below 100 °C, so it utilizes low-cost leaching tanks as opposed to expensive, high-pressure autoclaves. The process requires no bacteria, surfactants, or special solution additives such as chloride or ammonia. Therefore, the conditions are not particularly corrosive, and since ferric sulfate leaching is compatible with the conventional SX-EW operations, a simpler flowsheet in comparison to other methods such as chloride leaching can be achieved. In addition, sulfuric acid used in the leaching solution is less expensive than other strong acids such as hydrochloric acid. The process generates primarily elemental sulfur which reduces both oxygen consumption for mineral leaching and the amount of excess sulfuric acid to be neutralized. These features provide lower capital and operational costs (Dixon et al., 2008).

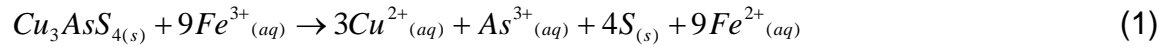
Despite these merits, ferric sulfate leaching of primary copper sulfides suffers from a major drawback in that copper extraction is slow and incomplete. It is generally accepted that the formation of a passivating layer on the surface of copper sulfides during leaching is the cause of this refractory behavior. The literature that has emerged in the case of ferric sulfate leaching of chalcopyrite offers contradictory findings about the mechanism of formation and the nature of this passivating layer (Córdoba et al., 2008). As one of the hypotheses, Hackl et al. (1995) postulated that a thin (less than one micron) copper-rich polysulfide layer, which forms due to preferential leaching of iron over copper in acidic sulfate media, is responsible for chalcopyrite passivation since its eventual decomposition to cupric ions and elemental sulfur is very slow.

### **2.2.2. Principles**

It is agreed by most researchers that the dissolution of semiconducting sulfides (such as chalcopyrite or enargite) in oxidizing solutions is of an electrochemical nature. Sulfide leaching mechanisms are generally considered to be complex. Some reasons include formation of different intermediate or final sulfide products depending on the conditions, galvanic interactions caused by host minerals and possible contribution of different redox couples, such as Fe(III)/Fe(II), Cu(II)/Cu(I),  $O_2 / H_2O$ ,  $O_2 / H_2O_2$ , and  $H_2O_2 / H_2O$ , to the oxidation process (Senanayake, 2009).

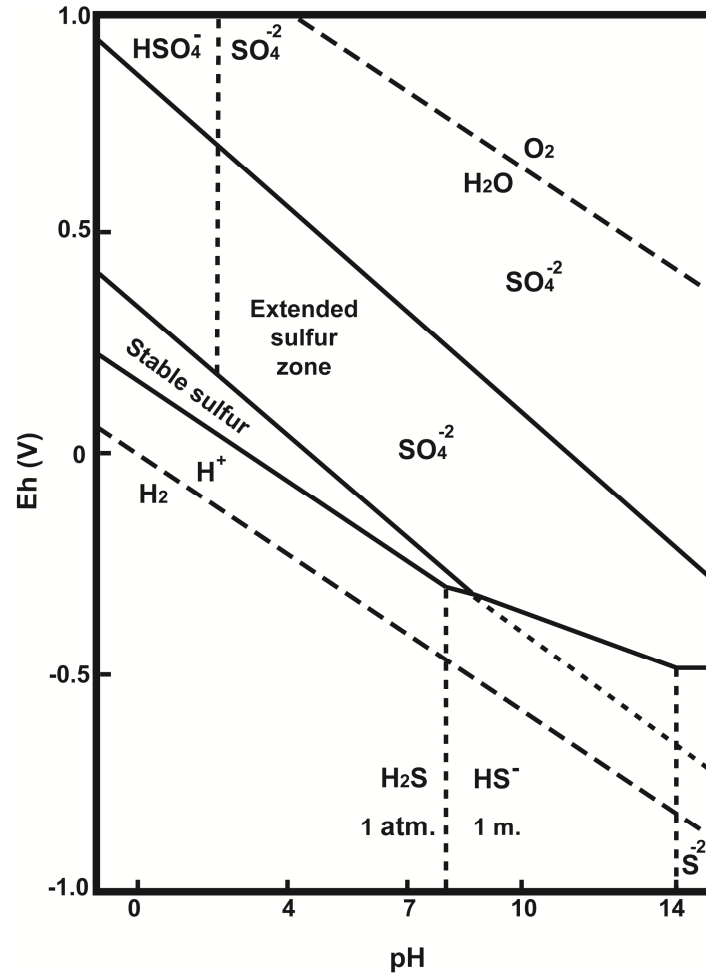
## Thermodynamic considerations

The predominant oxidation reaction of enargite in acidic ferric sulfate media occurs as per reaction (1):



where some portion of the produced elemental sulfur can be oxidized to sulfate, depending on the selected ranges of oxidizing potential and pH. Generally, thermodynamics is employed to predict the ranges of stability of different chemical species. Thermodynamic and electrochemical equilibria in aqueous systems can be graphically presented by potential-pH (Pourbaix) diagrams. Despite their convenience, there are a number of limitations to these diagrams which arise from the fact that several relevant characteristics, including reaction kinetics, catalyzing and galvanic effects, and formation of intermediate product layers (such as sulfur or hydroxides) are not considered in their construction. These limitations may lead to some discrepancies between the diagram predictions and experimentally-observed phases. One of these discrepancies is found in the case of acidic ferric sulfate leaching of copper sulfides in that the formation of sulfate ions is predicted in some regions of the associated Pourbaix diagram, where in actuality, elemental sulfur is the predominant product. This is due to the slow kinetics of sulfur oxidation by ferric ions.

The metastability region of elemental sulfur (extended sulfur zone) in the potential-pH diagram for the sulfur-water system is shown in Figure 1, which considers only those oxy-sulfur species that are stable in the acidic pH range ( $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$ ). The alkaline pH-stable species have been excluded for simplicity. As a result, this diagram expresses the hydrometallurgical observations in extremely acidic conditions (around pH 0) quite well, but fails to adequately describe the species observed at higher pH.

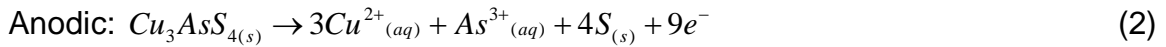


**Figure 1.** The range of metastability of elemental sulfur in the potential-pH diagram for the S-H<sub>2</sub>O system (Peters, 1986).

As a general comment, Pourbaix diagrams express the correct thermodynamic properties of a system for geologic time spans, while pseudo-thermodynamic considerations should be taken into account for hydrometallurgical situations, in which the time span is in the order of minutes to days (Peters, 1986; Woods et al., 1987).

### Galvanic coupling

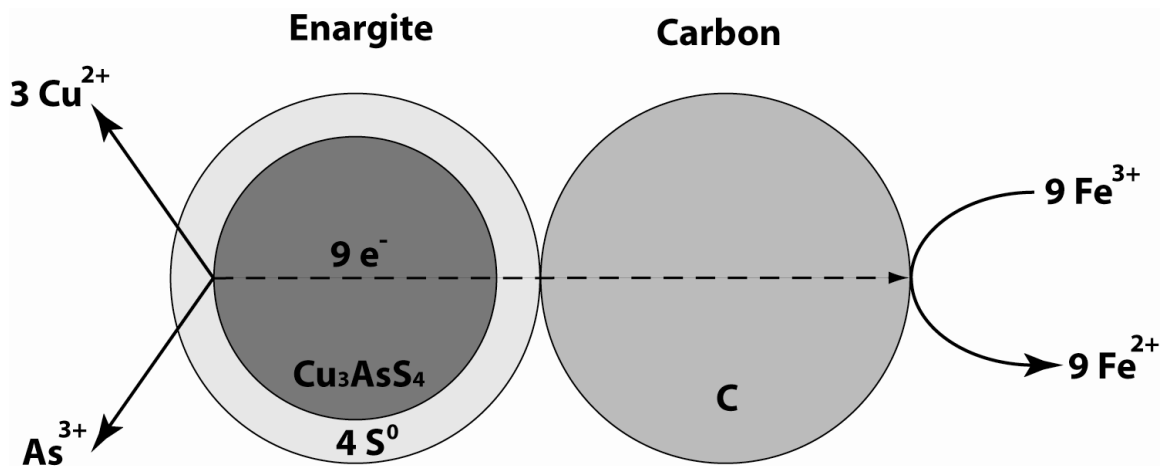
In order to demonstrate the electron transfer, reaction (1) can be considered as two anodic and cathodic half-cell reactions:



The dissolution of enargite as a semiconducting sulfide is a galvanic corrosion process, during which both anodic and cathodic areas on the mineral surface are formed. Some surface regions (such as impurity sites and grain boundaries) become anodic, while the rest of the surface becomes cathodic. The dissolution of enargite, as per reaction (2), occurs in anodic regions and ferric ions (as oxidant) are reduced on the surface of the mineral in cathodic areas, according to reaction (3). Electrons are transferred between these two areas

through the enargite bulk. Formation of product layers during leaching can limit the cathodic areas and hinder the dissolution rate.

When, under oxidative leaching conditions, an electrical contact between enargite and a conductive material with a higher rest potential (such as pyrite or activated carbon) is established, these two may act as a single galvanic couple. In this situation enargite is the electron-donating anode and dissolves, while the conductive material is the electron-accepting cathode and provides an extra surface area for the reduction of ferric ions. As a result, the dissolution rate of enargite increases (Rivera-Vasquez, 2010). Figure 2 shows a schematic representation of the described mechanism for leaching of enargite in the presence of an activated carbon catalyst. Moreover, the ferrous ion oxidation (for ferric regeneration) can be enhanced in the presence of such a catalyst.



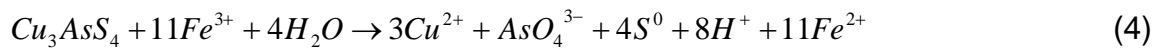
**Figure 2.** A schematic illustration of galvanic interactions between enargite and activated carbon particles.



### **2.3. Studies on leaching of enargite in sulfate media**

The literature regarding oxidative leaching of enargite in sulfate-based systems is relatively scarce. However, the few available studies have revealed that enargite leaching rates in acidic solutions are extremely slow and a strong oxidant is required to obtain appreciable levels of extraction.

The first systematic study of enargite leaching in acidic ferric sulfate media was conducted by Dutrizac and MacDonald (1972). They observed the formation of elemental sulfur as a result of both synthetic and natural enargite leaching over the temperature range of 60 °C – 95 °C and suggested the following leaching reaction:



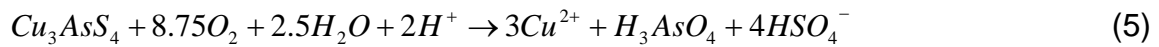
where a portion (5 % – 50 %) of the produced elemental sulfur was subsequently oxidized to sulfate. The average Cu/As molar ratio measured in the leaching solution was close to the stoichiometric value of 3 predicted by reaction (4). The reaction proved extremely slow, as one experiment only achieved 50 % copper extraction from fine enargite (< 149 µm) after 7 days of leaching at 80 °C – 85 °C in 0.1 M  $Fe^{3+}$  and 0.1 M  $H_2SO_4$ .

Elsener et al. (2007) reported the formation of a copper-deficient sulfide layer after 24 h of exposing enargite to acidic solutions with 0.025 M  $Fe^{3+}$ . They

proposed that once this copper-deficient layer is formed, it remains unchanged (steady state) on top of the dissolving surface and the leaching of enargite continues stoichiometrically. Lattanzi et al. (2008) presented a review of enargite oxidation stating that in acidic media, copper mobility from enargite seems to be at least equal to, if not greater than, that of arsenic; while in alkaline conditions, the preferential release of arsenic over copper is observed.

Researchers have employed different methods to increase the rate of enargite leaching and maximize the copper recovery. Hourn et al. (1999), in a study of the Albion process, achieved more than 92 % copper extraction in 10 h from a copper flotation concentrate (containing 20.9 % enargite and 11.9 % chalcocite). The concentrate was milled to a P80 of 3.5 microns and leached at 90 °C in an open reactor utilizing a ferric ion, sulfuric acid lixiviant solution (30 g/L  $\text{Fe}^{3+}$  and 50 g/L  $\text{H}_2\text{SO}_4$ ) with oxygen sparging. The key to the successful leaching of the enargite-chalcocite concentrate in this study was ultrafine grinding of the feed material. As another method to enhance the leaching of enargite, different catalysts have been employed. Flynn et al. (1989) effectively catalyzed enargite leaching at atmospheric pressure in a hot lixiviant containing 0.8 M ferric sulfate and 1 M sulfuric acid using silver sulfate or mercuric sulfate. Employing a specific type of pyrite as a catalyst for leaching of an enargite sample under Galvanox™ process conditions, Rivera-Vasquez and Dixon (2009) obtained almost complete extraction of copper within 24 h in an acidic ferric/ferrous solution at 80 °C, using a stirring speed of 1200 rpm, a solution redox potential of 435 mV vs. SCE and a

pyrite:enargite ratio of 4:1. Pressure leaching of enargite has also been studied. Dreisinger and Saito (1999) investigated the total pressure oxidation of gold-bearing enargite ore and concentrate (from the El Indio mine, Chile) in sulfate solutions. They reported more than 95 % copper extraction at 220 °C and 689 kPa O<sub>2</sub> after 180 minutes. Padilla et al. (2008) observed that in the pressure leaching of enargite in a sulfuric acid-oxygen system, temperature had a significant effect on the dissolution rate whereas sulfuric acid concentration was not important. The enargite leaching occurred as predicted by thermodynamics according to the following reaction:



Studies on the bioleaching of enargite (Canales et al., 2002; Curreli et al., 1997; Escobar et al., 1997, 2000; Muñoz et al., 2006) suggested that *Acidithiobacillus ferrooxidans* bacteria were capable of enhancing the kinetics of enargite leaching and could survive relatively high levels of arsenic in the environment. Watling (2006) reviewed the bioleaching of sulfide minerals and categorized enargite among the most refractory copper minerals to treat with bioleaching.

## ***2.4. Activated carbon as catalyst***

The term activated carbon encompasses a group of substances, none of which is characterized by a specific structural formula nor separately identified by chemical analysis. The only basis for differentiation is by adsorptive and catalytic properties (Hassler, 1963).

In heterogeneous catalysis, the use of activated carbon as a catalyst support is well-established. Activated carbon satisfies most of the desirable requirements for a suitable support: chemical inertness, stability, mechanical resistance, high surface area and optimum porosity (Calvino-Casilda et al., 2010; Radovic and Rodriguez-Reinoso, 1997).

Carbon materials have also been shown to display catalytic properties. The catalytic effect of carbon materials (including activated carbon) has been observed in different reactions including hydrogenation, oxidation-reduction, polymerization and chlorination. The catalytic properties of carbon may depend on its crystal structure, microscopic physical structure, electronic behavior, surface chemistry and the presence of impurities within the carbon (Coughlin, 1969; Radovic and Rodriguez-Reinoso, 1997).

There are a limited number of studies pertaining to the use of activated carbon as a catalyst in hydrometallurgy. Most of these studies focus on chalcopyrite:

Nakazawa et al. (1998) investigated the use of activated carbon in the bioleaching of a chalcopyrite concentrate. They observed an enhanced rate of chalcopyrite dissolution in the presence of activated carbon and speculated that the enhancement could be attributed to a galvanic coupling between activated carbon and chalcopyrite. The authors used *Thiobacillus ferrooxidans* bacteria for bioleaching and suggested that the presence of the bacteria could favor the galvanic interactions. Zhang and Gu (2007) reported that activated carbon accelerated the rate and efficiency of copper dissolution in the bioleaching of low-grade primary copper sulfide ores using a mixture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*. Activated carbon increased the copper extraction from 11 % to 79 % after 25 days of bioleaching. Liang et al. (2010) conducted another study on the effect of activated carbon on chalcopyrite bioleaching by extreme thermophile *Acidianus manzaensis* at 65 °C. They reported a significant increase in copper extraction from 64 % to 95 % from a chalcopyrite concentrate in 10 days. Like Nakazawa et al. (1998), Zhang and Gu (2007) and Liang et al. (2010) attributed the observed catalytic effect to a galvanic interaction between activated carbon and chalcopyrite.

The catalytic effect of activated carbon on chalcopyrite leaching was observed in a study by Okamoto et al. (2004), in which chalcopyrite was leached in sulfuric acid solutions. Wan et al. (1984) examined ferric sulfate leaching of chalcopyrite in the presence of different types of carbon catalysts and found that the dissolution rate of chalcopyrite was increased by a factor of as much as 4. They claimed that the conductivity and particle size of the carbon material were determining its catalytic effect and proposed that the change in the conductivity of the sulfur product layer and its less protective character when formed in the presence of conductive carbon particles were the reasons for the increase in the chalcopyrite leaching rate.

### **3. Objectives of the present study**

The objective of this study was to develop a simple, economically viable and environmentally friendly catalytic leaching process for atmospheric leaching of arsenical copper concentrates (i.e. mainly enargite) in ferric/ferrous sulfate media using activated carbon as a catalyst. The present research was done utilizing bench-scale leaching reactors in order to elucidate some fundamental aspects of the process. Answers were sought for the following questions:

1. To what extent are the leaching rates of various arsenical copper concentrates enhanced in the presence of activated carbon?
2. How well do different types of activated carbon catalysts perform?
3. How sensitive is the leaching process to the copper concentrate source and activated carbon type?
4. Do activated carbon, pyrite and silver have any synergistic catalytic effects when present in the leach?
5. How does the leaching rate of enargite vary relative to the amount of activated carbon catalyst present?
6. What amount of activated carbon is lost after each test due to attrition caused by impellers?
7. Can the activated carbon catalyst be recycled in this leaching system and how do the carbon loss values compare after each recycle?
8. What is the effect of stirring speed on the leaching rate of enargite and how do the carbon loss values change at different stirring speeds?

9. Do the arsenical copper concentrates need to be finely ground in order to obtain satisfactory leaching rates in the presence of an activated carbon catalyst?
10. How do variations in the initial total iron concentration and solution redox potential affect the leaching behavior of enargite with an activated carbon catalyst?
11. What are the optimum leaching conditions?

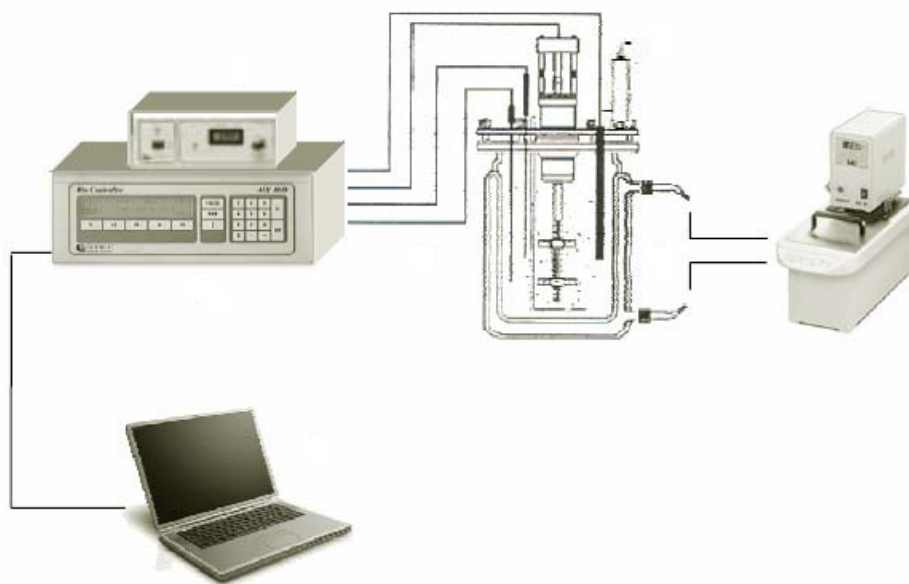


## 4. Experimental

Enargite samples used in this study were obtained from four different sources in three countries: an enargite sample from the Leonard Mine in Butte, Montana, USA (referred to as S1), two flotation concentrates from Peru (S2 and S4) and another flotation concentrate from Chile (S3). Four different types of activated carbon were: generic activated carbon granules (abbreviated to GC), NORIT<sup>®</sup> GCA 612 (NC), NORIT DARCO<sup>®</sup> H<sub>2</sub>S (NC2) and CALGON CPG<sup>®</sup> LF 12x40 (CC). The generic activated carbon and NORIT<sup>®</sup> GCA 612 were coconut shell-based activated carbon granules. For the sake of brevity, “carbon” always refers to activated carbon in this work.

Batch leaching tests were conducted in sealed, jacketed glass stirred tank reactors made by Applikon Biotechnology, Inc. Each reactor had a total volume of 3 L (internal diameter of 12.7 cm and height of 24.0 cm) and was equipped with a pair of axial impellers (pitched blade turbines) and three baffles, all made of 316 stainless steel. Solids suspension and gas-liquid mixing were achieved by the use of Applikon stirrer controller P140 (ADI 1032). Furthermore, on top of each reactor three probes were mounted to monitor temperature, pH and redox potential: a thermocouple made by Omega, an AppliSens glass pH sensor provided by Applikon and an ORP electrode (KCl-saturated Ag/AgCl reference electrode) made by Analytical Sensors & Instruments. These three probes were connected to an Applikon bio-controller (ADI 1030) which employed proportional integral derivative (PID) control logic. A redox potential setpoint was defined in

the bio-controller for each leaching test. The calculated difference between the recorded redox and the setpoint values was used by the controller to determine the rate of oxygen flow from a compressed gas cylinder (containing oxygen with 99.5 % purity) into the reactor through an Aalborg GFC17 mass flow controller and a sparger. Excess oxygen exited the reactor through a condenser to minimize water evaporation. Temperature was controlled within  $\pm 0.5$  °C of the desired value (80 °C) employing a Haake DC10-P14 open bath circulator. All the monitored parameters were continuously recorded by a computer throughout the tests. Figure 3 shows a schematic of the experimental setup.



**Figure 3.** A schematic representation of the experimental setup.

The leaching solution consisted of deionized water, sulfuric acid (97 % purity) and reagent grades of ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and

ferric sulfate pentahydrate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ) with 99.9 % and 97 % purity respectively. The experimental conditions are presented in Table 2. When the temperature and the redox potential of the solution reached the desired values, the catalytic experiments were initiated by adding enargite samples and activated carbon simultaneously. Solution samples (about 2 mL each) were taken at various intervals and analyzed for copper using a Varian AA240 atomic absorption spectrometer. At the end of each test, the remaining carbon particles were separated from the leach residue and washed using a USA standard test sieve (No. 25 – 710 microns). They were subsequently dried in an oven at 110 °C for 2 h and weighed. The remaining contents of the reactor were filtered through 1- $\mu\text{m}$  filter paper, using a vacuum pump. The obtained solid residue of each test was dried, weighed and a representative sample of it was sent to a local laboratory for a 30-element suite by complete digestion in aqua regia followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis. The obtained leaching curves (copper extraction vs. time) through atomic absorption analysis were normalized using the copper assays from ICP-MS results. Morphological and mineralogical studies were conducted on the enargite samples and some selected leach residues using SEM/EDX analysis on a Hitachi S-3000N variable pressure SEM and quantitative X-ray powder diffraction (XRD) on a Bruker D8 Focus Bragg-Brentano diffractometer. Malvern Mastersizer 2000 was utilized to determine the particle size distribution of the mineral samples.

**Table 2.** Experimental conditions of the leaching tests.

Test ID	Enargite sample type <sup>α</sup>	Enargite sample mass (g)	Carbon type <sup>β</sup>	Carbon mass (g)	Initial acid amount (g)	Deionized water mass (g)	Initial total iron content (g)	Fe <sup>3+</sup> /Fe <sup>2+</sup> ratio	Redox potential setpoint (mV vs. Ag/AgCl)	Temperature (°C)	Stirrer speed (rpm)
R1	S1 / B	15	-	-	80	1500	24.5	0.19	485	80	1200
R2	S2 / A	40	-	-	80	1500	25.9	0.17	490	80	1200
R3	S3 / A	50	-	-	80	1500	23.8	0.97	515	80	1200
R4	S4 / A	60	-	-	80	1500	2.4	0.97	515	80	1000
R5	S1 / B	15	GC / 0	15	80	1500	24.5	0.19	485	80	1200
R6	S2 / A	40	GC / 0	40	80	1500	25.9	0.17	490	80	1200
R7	S3 / A	50	GC / 0	50	80	1500	23.8	0.97	515	80	1200
R8	S4 / A	60	NC / 0	60	80	1500	2.4	0.97	515	80	1000
R9	S1 / B	15	-	-	80	1500	24.5	0.19	485	80	1200
R10	S1 / B	15	GC / 0	15	80	1500	24.5	0.19	485	80	1200
R11 <sup>η</sup>	S1 / B	15	GC / 0	15	80	1500	24.5	0.19	485	80	1200
R12 <sup>η</sup>	S1 / B	15	GC / 0	3	80	1500	24.5	0.19	485	80	1200
R13 <sup>η</sup>	S1 / B	15	GC / 0	15	80	1500	24.5	0.19	490	80	1200
R14 <sup>η</sup>	S1 / B	15	-	-	80	1500	24.5	0.19	485	80	1200
R15 <sup>η</sup>	S1 / B	15	-	-	80	1500	24.5	0.19	485	80	1200
R16 <sup>η</sup>	S1 / B	15	-	-	80	1500	24.5	0.19	485	80	1200
R17 <sup>η</sup>	S1 / B	15	GC / 0	15	80	1500	24.5	0.19	485	80	1200
R18 <sup>η</sup>	S1 / B	15	GC / 0	15	80	1500	24.5	0.19	485	80	1200
R19	S1 / B	15	NC / 0	15	80	1500	24.5	0.19	485	80	1200
R20	S1 / B	15	NC2/0	15	80	1500	24.5	0.19	485	80	1200
R21	S1 / B	15	CC / 0	15	80	1500	24.5	0.19	485	80	1200
R22	S2 / B	40	GC / 0	40	80	1500	23.8	0.97	515	80	1200
R23	S2 / B	40	GC / 0	20	80	1500	23.8	0.97	515	80	1200
R24	S2 / B	40	GC / 0	10	80	1500	23.8	0.97	515	80	1200
R25	S2 / B	40	GC / 0	40	80	1500	25.9	0.17	490	80	1200
R26	S2 / B	20	GC / 1	20	80	1500	25.9	0.17	490	80	1200
R27	S4 / A	54	NC / 1	54	80	1500	2.4	0.97	515	80	1000
R28	S4 / A	46.5	NC / 2	46.5	80	1500	2.4	0.97	515	80	1000
R29	S4 / A	41	NC / 3	41	80	1500	2.4	0.97	515	80	1000
R30	S2 / B	40	GC / 0	40	80	1500	23.8	0.97	515	80	1000
R31	S2 / B	40	GC / 0	40	80	1500	23.8	0.97	515	80	750
R32	S2 / B	40	GC / 0	40	80	1500	23.8	0.97	515	80	450
R33	S4 / A	60	NC / 0	60	80	1500	2.4	0.97	515	80	1200
R34	S4 / A	60	NC / 0	60	80	1500	2.4	0.97	515	80	800
R35	S2 / B	40	-	-	80	1500	25.9	0.17	490	80	1200
R36 <sup>η</sup>	S2 / B	40	GC / 0	40	80	1500	25.9	0.17	490	80	1200
R37	S2 / B	40	GC / 0	40	80	1500	26.2	0.10	450	80	1200
R38	S2 / B	40	GC / 0	40	80	1500	23.8	0.97	530	80	1200
R39	S1 / B	15	NC / 0	15	80	1500	0.0	-	515	80	1200
R40	S1 / B	15	NC / 0	15	80	1500	2.4	0.97	515	80	1200
R41	S1 / B	15	NC / 0	15	80	1500	7.9	0.97	515	80	1200
R42	S1 / B	15	NC / 0	15	80	1500	23.8	0.97	515	80	1200

<sup>α</sup> **A** means the enargite sample was used as received and **B** means it was (re)ground.

<sup>β</sup> The corresponding numbers show how many times the carbon particles have been recycled.

<sup>η</sup> There are specific details regarding the experimental procedures of these tests in the corresponding results and discussions sections.

## **5. Results and discussion**

The Effects of different parameters on the activated carbon-catalyzed, atmospheric leaching of copper from enargite samples, in iron sulfate solutions were studied. Efforts were made to develop a basic understanding of the operational parameters which govern this catalytic leaching process via a series of bench-scale, batch leaching tests. The catalytic performance of different types of activated carbon catalysts for leaching of four different enargite samples and the synergism among activated carbon, pyrite and silver were investigated. In order to explore the possibility of reducing process costs, the effects of catalyst amount, catalyst recycle and stirring speed on leaching performance were studied. Moreover, the effects of enargite concentrate grind size, solution redox potential and initial total iron concentration were investigated.

### 5.1. Mineralogical and elemental composition of enargite samples

The mineralogical composition of the four enargite samples used in this study (Table 3) was investigated using quantitative X-ray powder diffraction (XRD). Table 4 provides the results of ICP-MS analysis of the samples.

**Table 3.** Quantitative phase analysis of the four enargite samples used in this study.

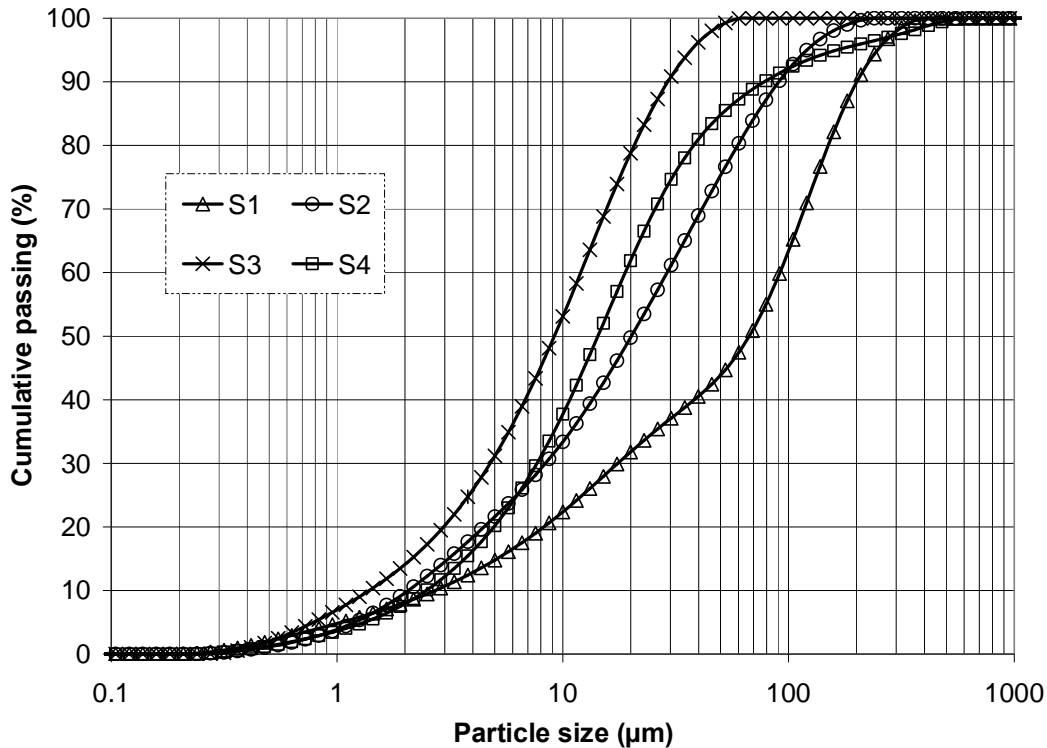
Mineral	Formula	S1 (wt. %)	S2 (wt. %)	S3 (wt. %)	S4 (wt. %)
Enargite	$\text{Cu}_3\text{AsS}_4$	61.7	20.4	23.2	44.1
Tennantite	$(\text{Cu}, \text{Ag}, \text{Fe}, \text{Zn})_{12}\text{As}_4\text{S}_{13}$	7.0	-	-	4.6
Luzonite (antimonian)	$\text{Cu}_3(\text{As}, \text{Sb})\text{S}_4$	-	2.9	-	2.3
Arsenopyrite	$\text{FeAsS}$	0.6	-	-	-
Pyrite	$\text{FeS}_2$	15.7	61.5	53.8	34.6
Chalcopyrite	$\text{CuFeS}_2$	-	3.9	-	6.5
Covellite	$\text{CuS}$	1.9	-	-	-
Chalcocite	$\text{Cu}_2\text{S}$	1.5	-	-	-
Bornite	$\text{Cu}_5\text{FeS}_4$	2.0	-	-	-
Sphalerite	$(\text{Zn}, \text{Fe})\text{S}$	1.9	-	-	4.2
Galena	$\text{PbS}$	-	-	-	1.2
Sulfur (elemental)	$\text{S}$	-	-	9.0	-
Alunite	$\text{K}_2\text{Al}_6(\text{SO}_4)_4(\text{OH})_{12}$	-	3.9	8.0	-
Quartz	$\text{SiO}_2$	7.7	7.4	6.0	2.5

**Table 4.** Elemental analysis of the four enargite samples used in this study.

Element	S1 (wt. %)	S2 (wt. %)	S3 (wt. %)	S4 (wt. %)
Cu	38.35	15.56	11.94	28.30
Fe	7.35	27.28	26.00	15.03
As	12.01	4.75	4.33	9.44
Sb	0.47	0.26	0.06	0.40
Bi	0.00	0.00	0.00	0.26
Ag	0.02	0.01	0.05	0.04
Zn	0.99	0.19	0.06	2.55
Ni	0.00	0.00	0.02	0.00
Al	0.08	0.62	2.00	0.00
Ca	0.00	0.14	0.00	0.05
Pb	0.03	0.11	0.14	1.25

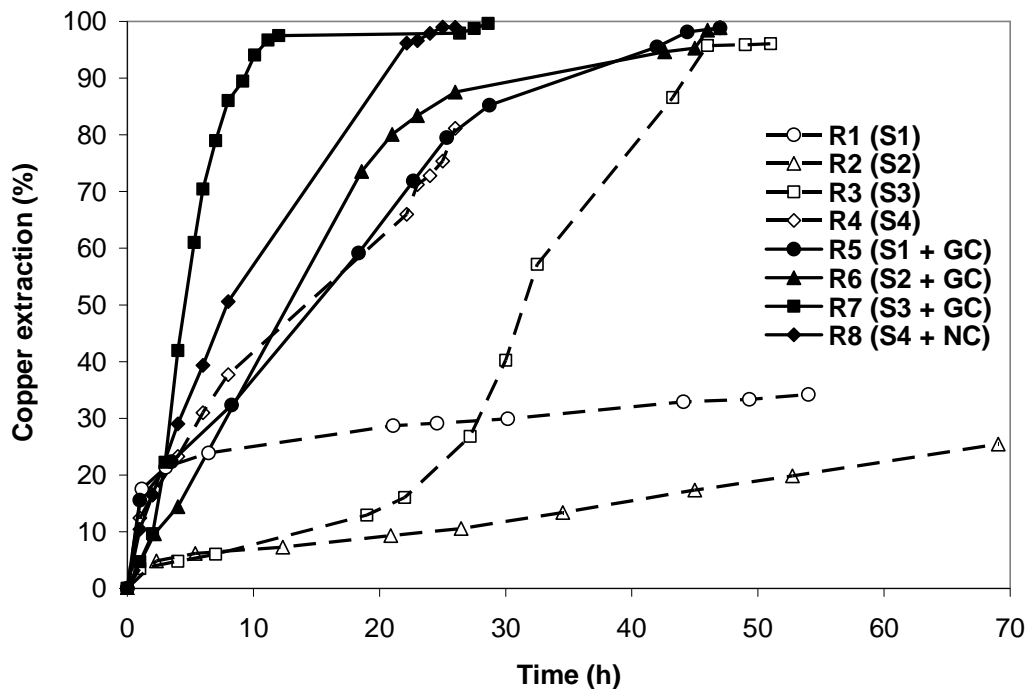
## 5.2. Effect of catalyst addition

Experiments R1 to R8 were conducted to examine the effect of adding granular activated carbon as a catalyst on leaching of four different enargite samples. The leaching conditions are presented in Table 2. Tests R1 to R4 were carried out on the enargite samples alone, while tests R5 to R8 were performed in the presence of activated carbon. Enargite sample S1 which originally was a massive enargite specimen from Montana, USA, was ground before leaching. The other three enargite samples (S2, S3 and S4) were flotation concentrates and were leached as-received. Figure 4 presents the particle size distributions for these four enargite samples.



**Figure 4.** Particle size distributions for enargite samples used in the leaching tests.

The P80 values of S1 to S4 were 150  $\mu\text{m}$ , 59  $\mu\text{m}$ , 21  $\mu\text{m}$  and 38  $\mu\text{m}$  respectively. A carbon to enargite sample mass ratio of one was maintained in the carbon-containing experiments (tests R5 to R8); NORIT<sup>®</sup> GCA 612 activated carbon (NC) was used in test R8 while generic activated carbon (GC) granules were utilized in the other three tests. The results are shown in Figure 5.



**Figure 5.** Effect of granular activated carbon catalyst addition on copper extraction from four different enargite samples.

As can be seen from Figure 5, carbon had a significant effect on the copper extraction from the enargite samples. In a potential range of 485 mV to 490 mV (vs. Ag/AgCl), leaching enargite samples S1 and S2 without using activated carbon yielded less than 35 % and 25 % copper extraction respectively within 70 h (tests R1 and R2). However, by employing a carbon catalyst (tests R5



and R6), virtually complete leaching of copper was achieved in approximately 45 h. A shorter leaching time (less than 24 h) was obtained at a higher potential (515 mV vs. Ag/AgCl) for catalytic leaching of enargite samples S3 and S4 (tests R7 and R8). During that period of time, less than 20 % and 73 % copper extraction was achieved in tests R3 and R4 respectively.

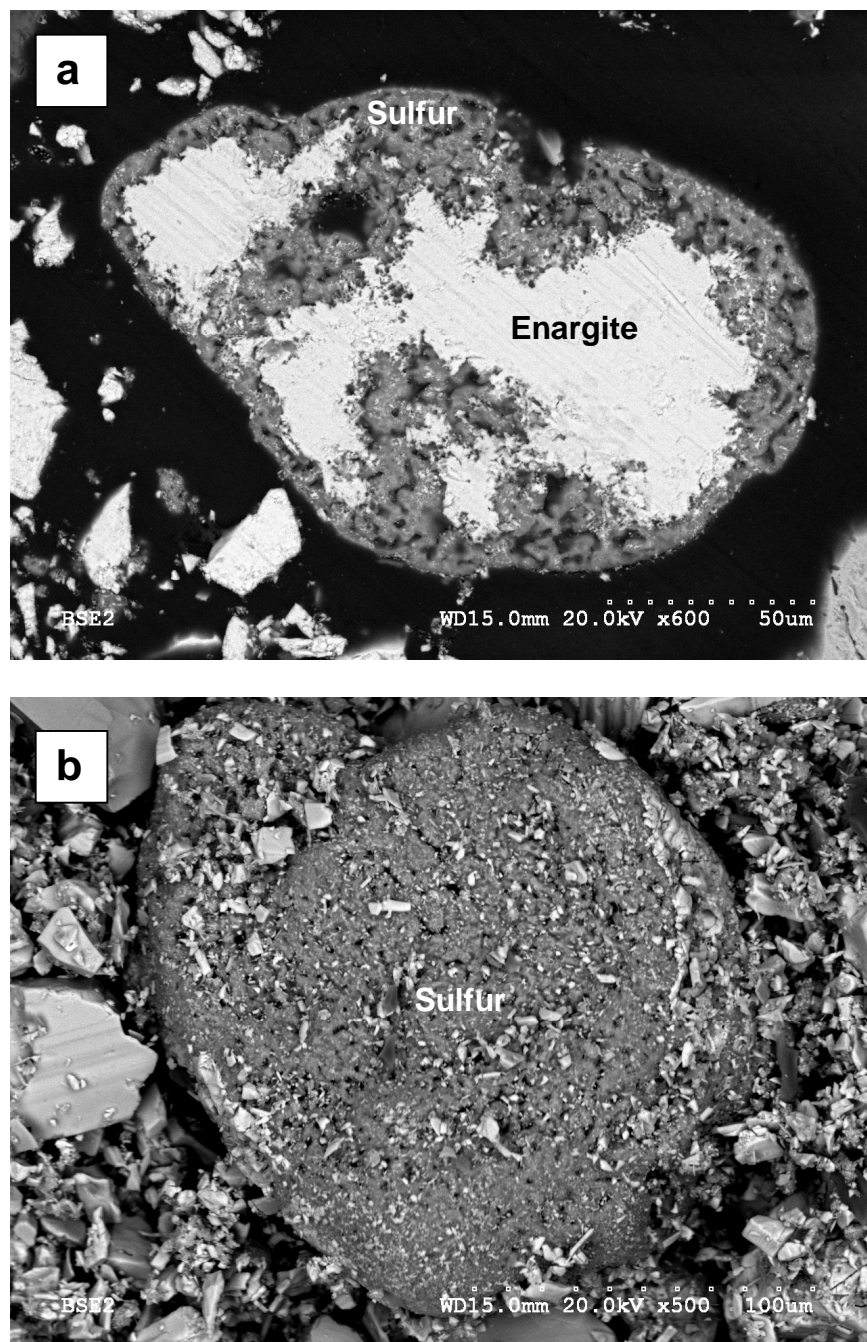
Test R9 was conducted under identical conditions as those of test R1 to study the mineralogical phases of its leach residue. The test was stopped after 54 h and the leach residue was analyzed by XRD. Table 5 displays the results obtained from the XRD analysis of S1 (the enargite sample used in the identical tests R1 and R9), before and after leaching.

**Table 5.** Quantitative phase analysis of enargite sample S1 and its leach residue from test R9.

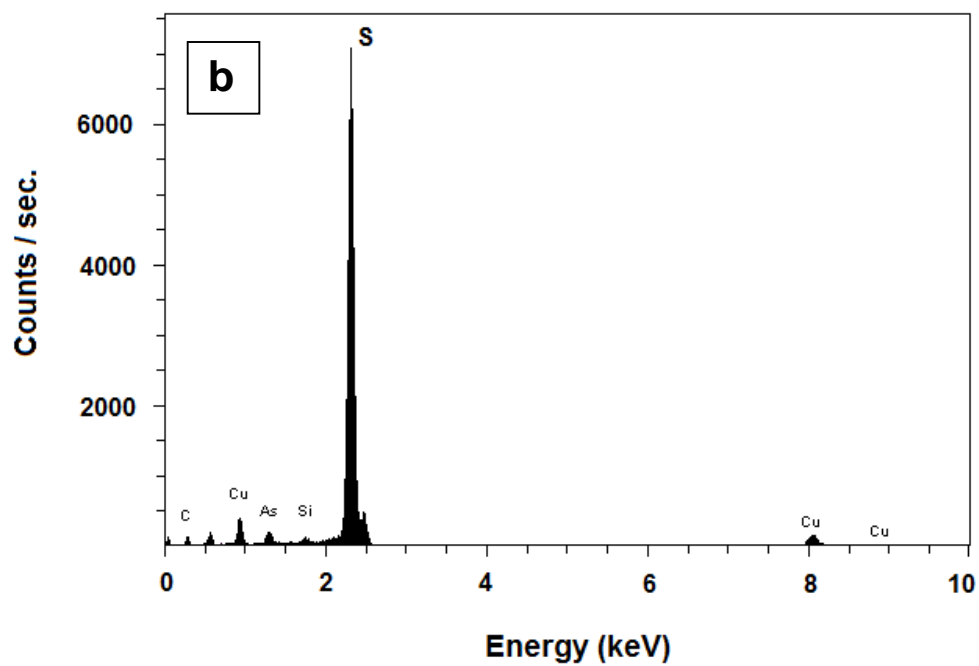
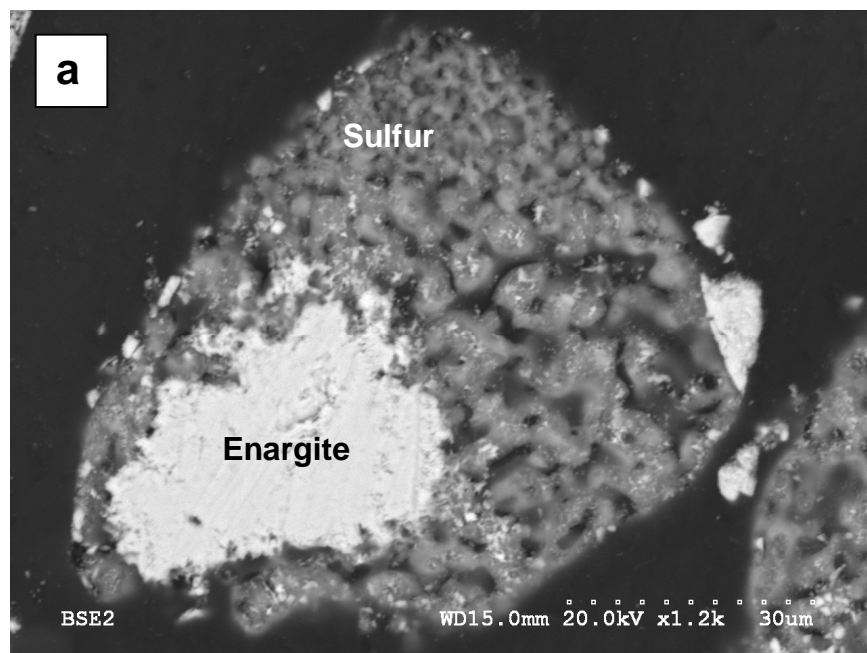
Mineral	Formula	S1 (wt. %)	S1 residue (wt. %)
Enargite	$\text{Cu}_3\text{AsS}_4$	61.7	62.3
Tennantite	$(\text{Cu}, \text{Ag}, \text{Fe}, \text{Zn})_{12}\text{As}_4\text{S}_{13}$	7.0	7.6
Arsenopyrite	$\text{FeAsS}$	0.6	-
Pyrite	$\text{FeS}_2$	15.7	17.9
Covellite	$\text{CuS}$	1.9	-
Chalcocite	$\text{Cu}_2\text{S}$	1.5	-
Bornite	$\text{Cu}_5\text{FeS}_4$	2.0	-
Sphalerite	$(\text{Zn}, \text{Fe})\text{S}$	1.9	-
Sulfur (elemental)	$\text{S}_8$	-	3.8
Quartz	$\text{SiO}_2$	7.7	8.4

It can be seen from the data in Table 5 that covellite, chalcocite and bornite are the copper-containing minerals which were completely leached after 54 h, while enargite and tennantite leaching were incomplete. Moreover,

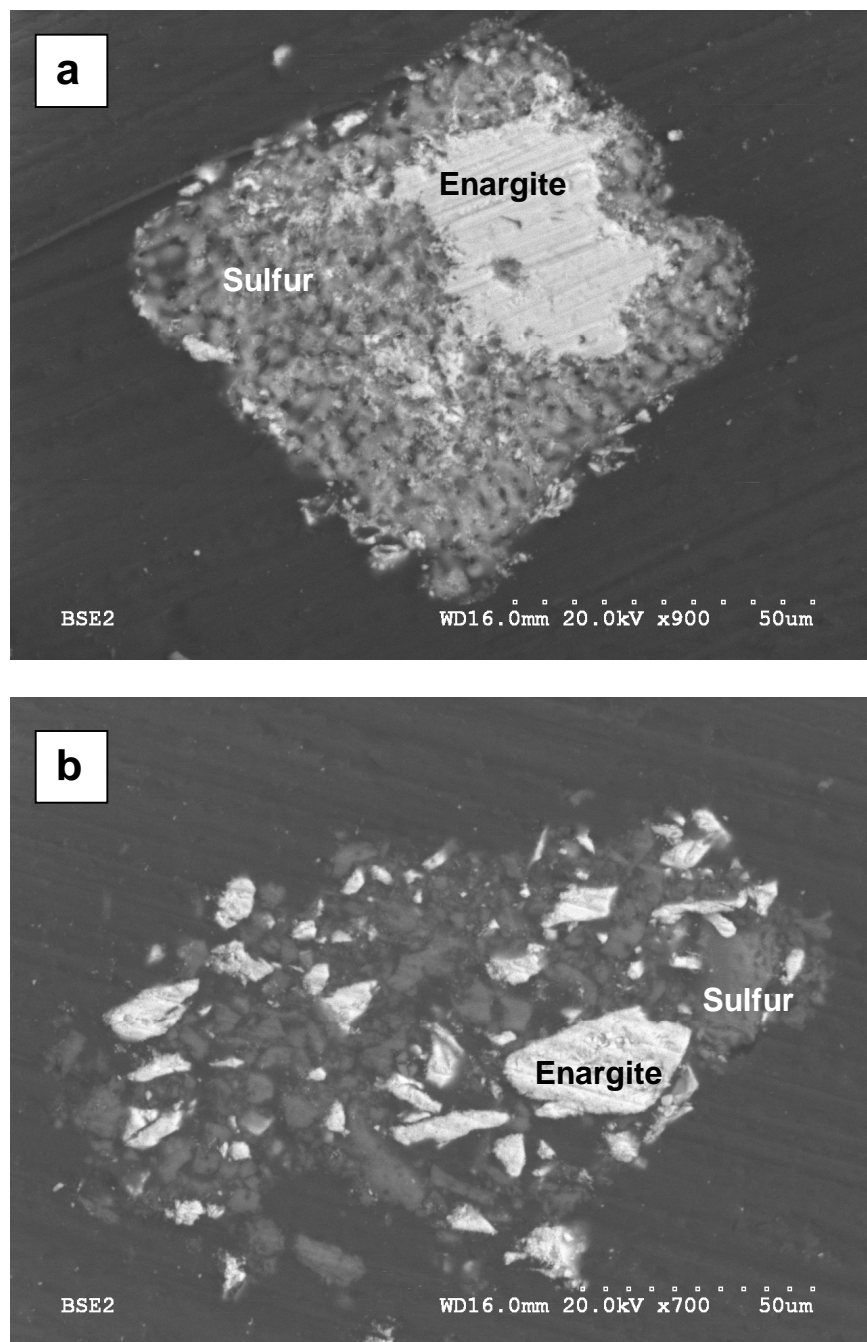
elemental sulfur was formed as a result of leaching. Covellite, chalcocite and bornite accounted for 10 % of the copper extraction value of R1 after 54 h; the other 25 % was from enargite and tennantite leaching. Sulfur formation as a product of leaching reactions of enargite and tennantite retarded their oxidation and caused a plateau in extracted copper. The residue of test R9 was also used for electron microscopy studies. A portion of the residue was mounted in a clear epoxy pellet and polished to expose cross-sections of particles. The obtained specimens were then characterized by SEM and EDX. Partially leached enargite particles were sampled at 7 h and 19 h after test R9 was initiated to study the evolution of the morphology of sulfur layers during leaching. Moreover, test R10 (identical to test R5) was conducted and enargite samples were taken at similar times to investigate the effect of using an activated carbon catalyst on the structure of the sulfur product layer. Figure 6 shows cross-section and external views of a partially leached enargite particle from the residue of test R9. The EDX spectrum of sulfur layer around an enargite particle from the same leach residue is presented in Figure 7. SEM micrographs of particles leached in tests R9 and R10 for 7 h and 19 h are compared in Figures 8 and 9 respectively and the enargite and sulfur species labelled in them were characterized using EDX.



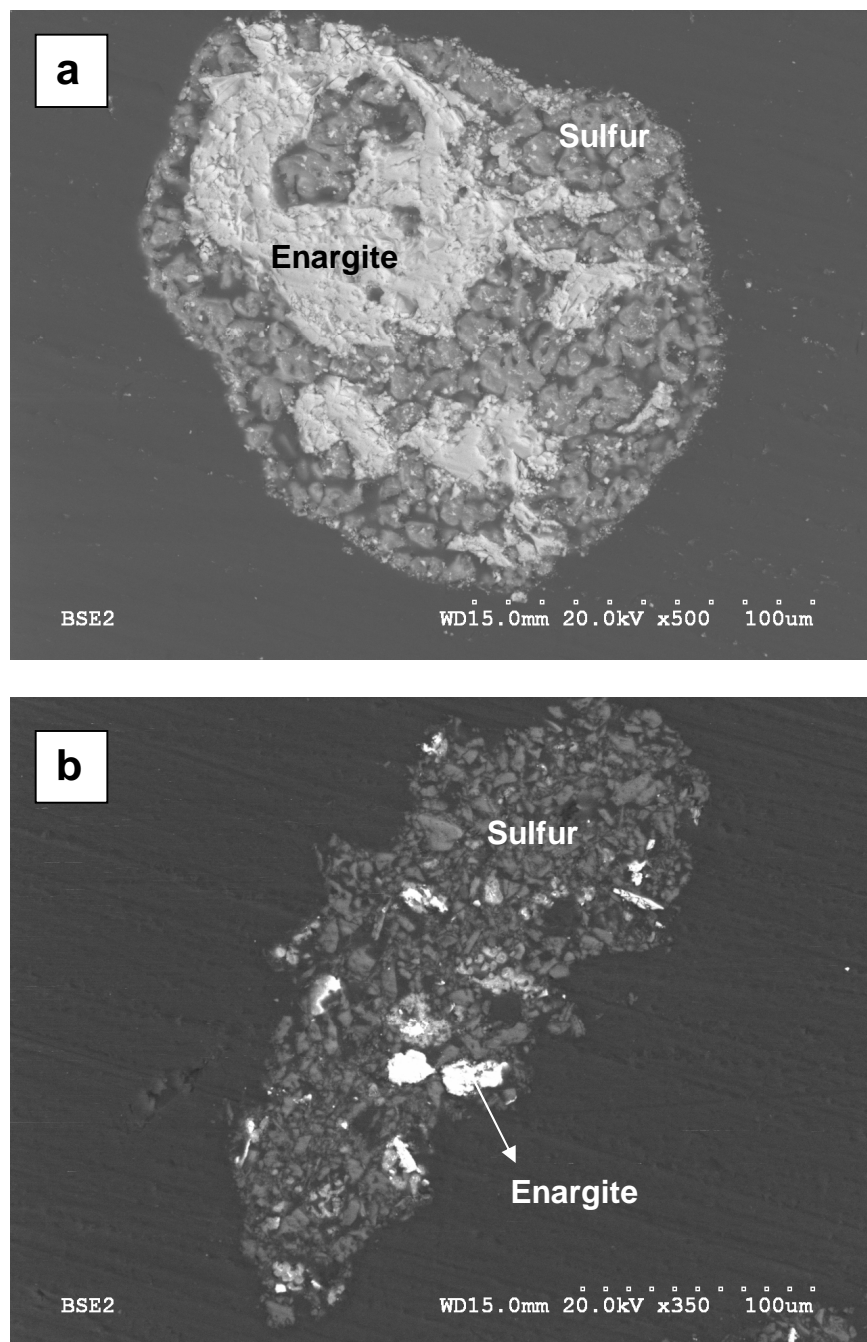
**Figure 6.** SEM micrographs of enargite leached for 54 h in R9 (80 °C, 485 mV vs. Ag/AgCl, 16.3 g/L  $[\text{Fe}]_{\text{total}}$ , 53.3 g/L  $\text{H}_2\text{SO}_4$ ) – a) cross-section of a partially leached enargite particle, b) external view of a sulfur-coated enargite particle.



**Figure 7.** a) SEM cross-section micrograph of an enargite particle leached for 54 h in R9 (80 °C, 485 mV vs. Ag/AgCl, 16.3 g/L [Fe]<sub>total</sub>, 53.3 g/L H<sub>2</sub>SO<sub>4</sub>), b) characteristic EDX spectrum taken from the region labelled “sulfur” in (a).



**Figure 8.** SEM cross-section micrographs of enargite particles leached for 7 h at 80 °C and 485 mV (vs. Ag/AgCl) in an acidic iron sulfate solution (16.3 g/L [Fe]<sub>total</sub> – 53.3 g/L H<sub>2</sub>SO<sub>4</sub>) – a) without an activated carbon catalyst in R9, b) with an activated carbon catalyst in R10.



**Figure 9.** SEM cross-section micrographs of enargite particles leached for 19 h at 80 °C and 485 mV (vs. Ag/AgCl) in an acidic iron sulfate solution (16.3 g/L [Fe]<sub>total</sub> – 53.3 g/L H<sub>2</sub>SO<sub>4</sub>) – a) without an activated carbon catalyst in R9, b) with an activated carbon catalyst in R10.

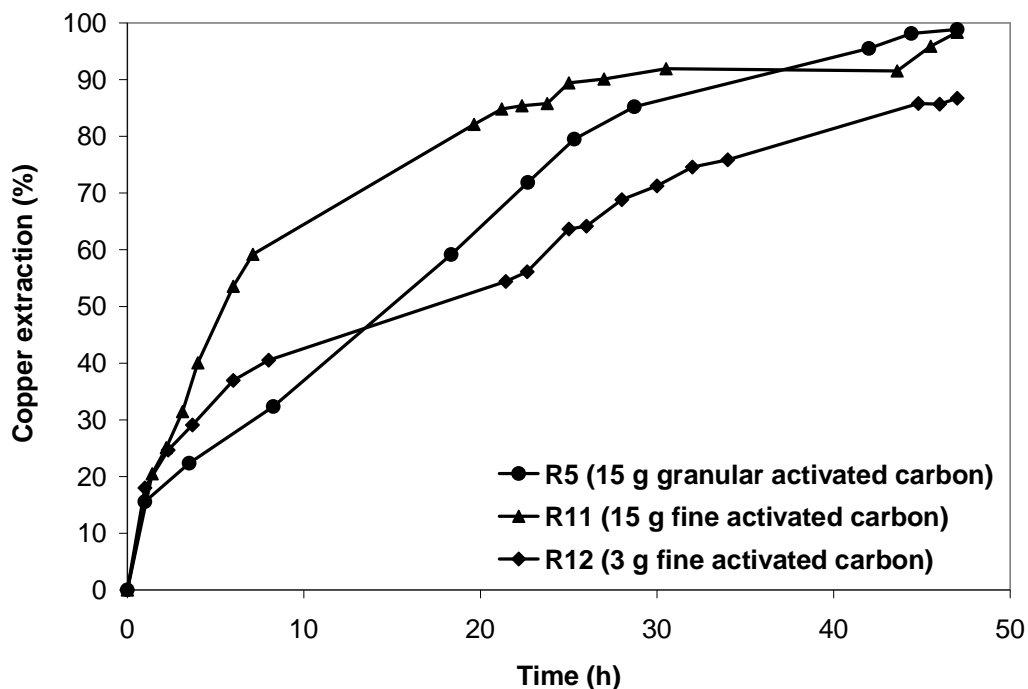
Figures 6 to 9 suggest that leaching of enargite in an iron sulfate solution leads to formation of a protective sulfur layer around enargite particles. This layer is likely the main reason for retardation of enargite leaching in sulfate media and the incomplete extraction of copper from enargite. However, when an activated carbon catalyst is used, the sulfur layer loses its integrity and does not protectively surround enargite particles. Therefore, faster leaching kinetics and complete copper extraction can be achieved. For instance, assuming that test R2 will eventually achieve complete copper extraction, the leaching rate of test R6 is 6 times faster.

Although the mechanistic details of the catalytic behavior of activated carbon catalysts are not well understood, it is believed that the catalytic performance of activated carbon depends on its structure, electronic properties and surface chemistry (Coughlin, 1969). It is probable that a number of factors contribute to the catalysis of enargite leaching in this system. In addition to the change in the sulfur morphology which was demonstrated above, galvanic interactions between activated carbon and enargite particles may take place and increase the rate of enargite oxidation as explained in section 2.3.2. Electron transport through the sulfur product layer, and as a result leaching kinetics, can be improved when fine particles of conductive carbon (sheared from activated carbon granules due to attrition caused by impellers) are embedded in the sulfur product layer structure during its formation. It has been suggested that the addition of carbon particles to sulfur increases its electrical conductivity by as

much as 10 orders of magnitude (Beckman et al., 1980; Wan et al., 1984). Activated carbon may also play a role in catalyzing ferrous ion oxidation by dissolved oxygen in sulfate media, leading to enhancement of ferric ion regeneration. Littlejohn (2008) showed that pyrite had a similar catalytic effect in enhancing ferrous oxidation in sulfate solutions.

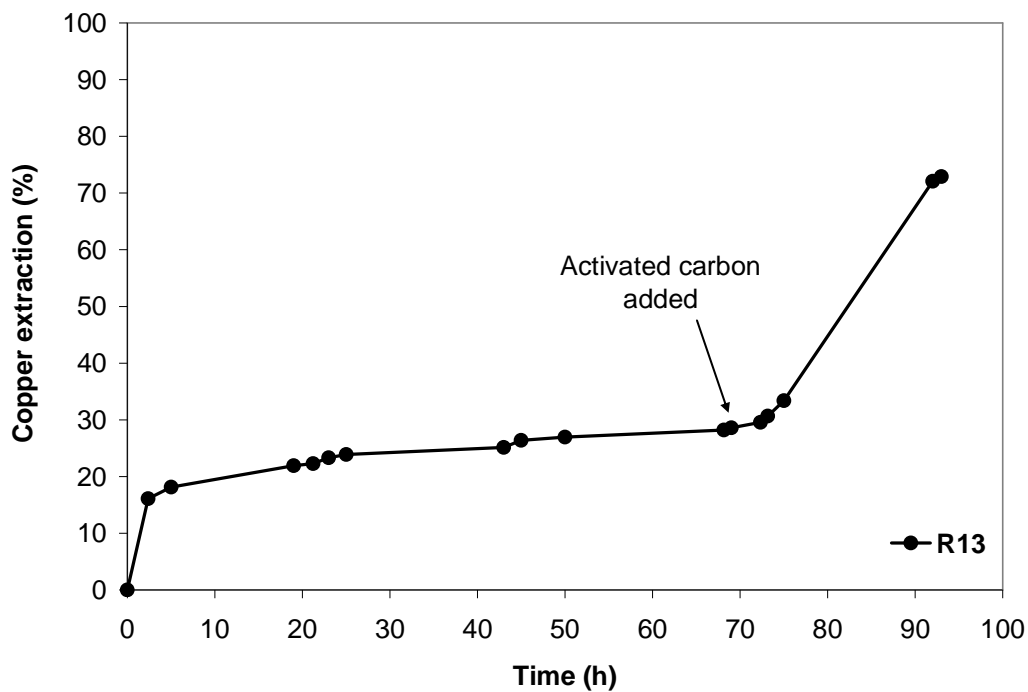
The effect of adding fine particles of activated carbon on the leaching of 15 g of enargite sample S1 was investigated in tests R11 and R12. The leaching conditions were identical to those of R5. A ring mill was utilized to pulverize 20 g of generic activated carbon granules for 10 s, from which 15 g was used in R11 and 3 g in R12. The leaching results of tests R11 and R12, as well as test R5 (for comparison), are presented in Figure 10. Using fine particles of activated carbon provided a better catalytic performance in test R11, probably mainly due to the increase in the available surface area of the catalyst. Although grinding the catalyst leads to a faster leaching kinetics, it potentially can complicate separation of fine carbon particles for recycling to the leaching tanks, such as difficulties with floating the carbon due to the presence of elemental sulfur and unreacted sulfides in leach residue. Therefore, in all of subsequent tests in this research granular activated carbon was used.





**Figure 10.** Effect of fine activated carbon catalyst addition on copper extraction from 15 g of enargite sample S1.

Test R13 was devised to examine the catalytic performance of activated carbon when protective sulfur layers around many enargite particles were already in place. Enargite sample S1 (15 g) was leached at 80 °C and a solution potential of 490 mV (vs. Ag/AgCl) in an acidic iron sulfate solution (16.3 g/L  $[\text{Fe}]_{\text{total}}$  – 53.3 g/L  $\text{H}_2\text{SO}_4$ ) for 69 hours before 15 g of generic activated carbon granules were added. The experiment was ended after 93 h. Figure 11 shows the obtained leaching curve and clearly indicates that activated carbon exhibited a significant catalytic effect in this experiment. At least a three-hour time lag was observed before a distinctively faster leaching rate was achieved in the presence of the carbon catalyst.



**Figure 11.** Effect of activated carbon catalyst addition after 69 h on copper extraction from enargite sample S1.

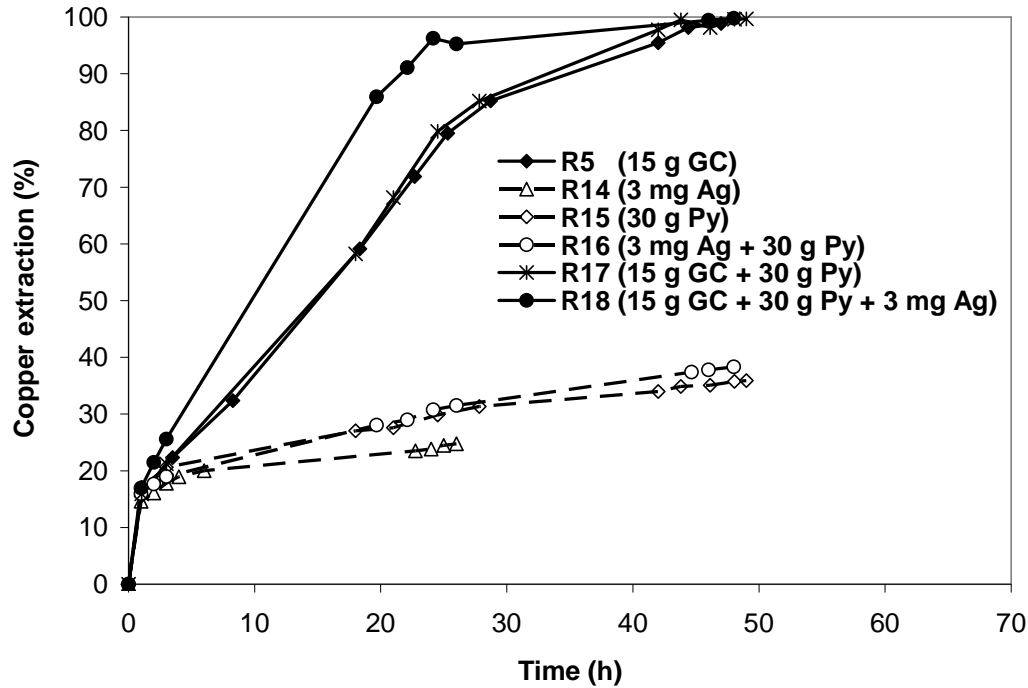
### ***5.3. Synergistic effects of carbon, silver, and pyrite catalysts***

The catalytic behavior of silver (Banerjee et al., 1990) and pyrite (Dixon et al., 2008) for ferric leaching of chalcopyrite has been shown previously. Both of these catalysts were present in the four enargite samples used in this study. Tests R14 to R18 were conducted in order to investigate the probable catalytic roles of silver and pyrite in the leaching of enargite and the possibility of synergy among silver, pyrite, and activated carbon. The leaching conditions for these tests were identical to those of test R5. All catalysts were added at the beginning

of the tests. Silver (3 mg) was added in the form of silver nitrate solution to tests R14, R16 and R18; pyrite (30 g, 93 % purity), which was from Navajún, Spain was ground and used in tests R15 to R18; and generic activated carbon (15 g) was added to tests R17 and R18. The results of tests R14 to R18 (as well as test R5, for comparison) are shown in Figure 12.

As can be seen from Figure 12, the amount of silver that was used in test R14 (which was equivalent to the amount of silver in 15 g of S1) did not have any discernible positive effect on enargite leaching. Results of test R15 suggest that 30 g of Navajún pyrite did not exhibit a strong catalytic effect. Previously, Rivera-Vasquez and Dixon (2009) reported a significant catalytic effect of a pyrite from Huanzala, Peru in leaching of enargite. Differences in catalytic properties of various types of pyrites can probably be attributed to their chemical composition, textures and electrical properties (Abraitis et al., 2004b).

Pyrite and silver together did not have any appreciable synergistic catalytic effect in test R16. The leaching curves of test R5 and R17 are almost identical, indicating that Navajún pyrite did not provide additional benefit to carbon alone. However, a relatively strong synergy was observed in test R18 in which all three catalysts were used. Copper extraction was complete after 24 h in this test. Due to experimental constraints, no test was conducted in this study to investigate the catalytic performance of silver and activated carbon together.

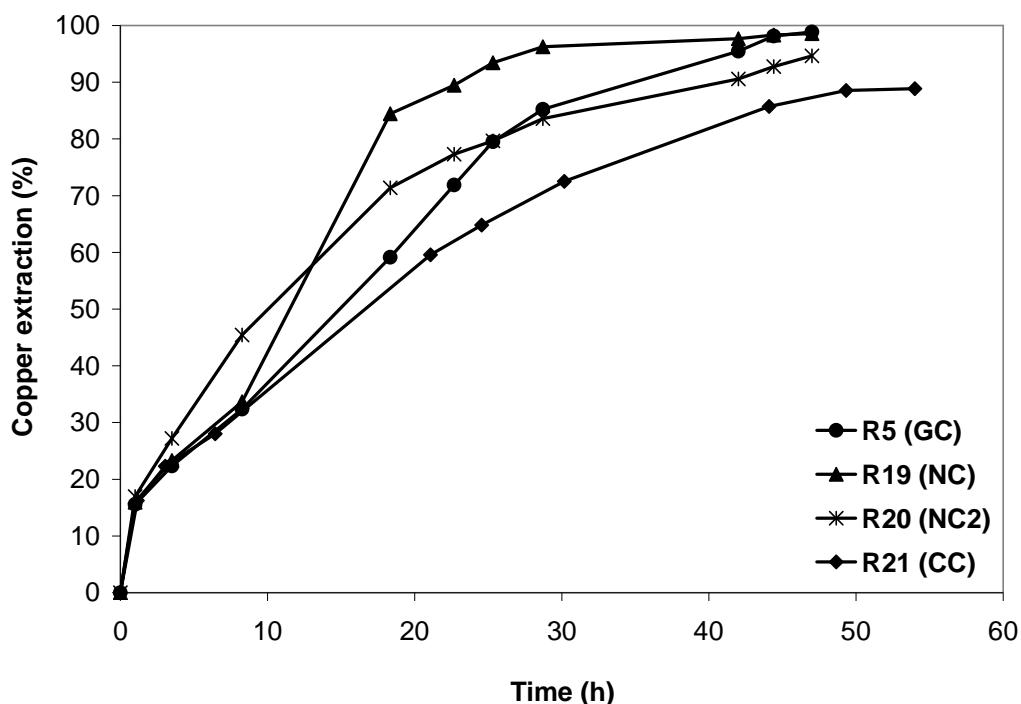


**Figure 12.** Effects of generic activated carbon (GC), silver (Ag), and Navajún pyrite (Py) on copper extraction from 15 g of enargite sample S1.

The leaching curves presented in Figure 12 can be categorized by one characteristic. Those that did not contain activated carbon (tests R14, R15 and R16, illustrated by dashed lines) failed to reach 40 % copper extraction within 50 h. Those containing activated carbon (tests R5, R17 and R18, solid lines) exhibited much faster leaching kinetics and reached complete copper extraction in less than 48 h. This indicates that under the described conditions, activated carbon was by far the most effective catalyst.

#### 5.4. Effect of catalyst type

The catalytic performance of four different types of activated carbon for enargite leaching was tested on sample S1. The leaching conditions were the same as those of R5. A carbon:enargite sample mass ratio of 1 was maintained in all of the experiments. Figure 13 presents the results.



**Figure 13.** Effect of four different types of activated carbon catalysts on copper extraction from enargite sample S1.

All types of activated carbon exhibited excellent catalytic behavior for leaching of enargite. Generic activated carbon (GC) and NORIT® GCA 612 (NC) were particularly effective (tests R5 and R19). These two types were coconut shell-based activated carbons with high carbon content and a high level of hardness. NORIT DARCO® H<sub>2</sub>S (NC2), which was used in test R20, proved to be

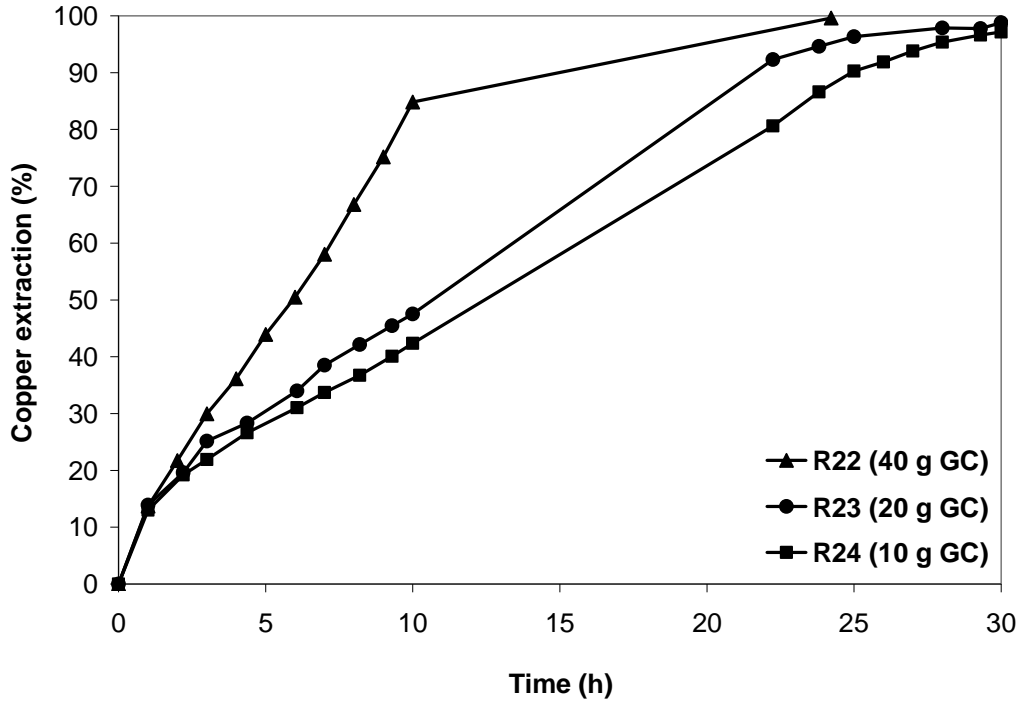
better than GC in the first half of the test but its performance slightly diminished in the rest of the experiment, possibly due to losing its integrity under agitation. CALGON CPG<sup>®</sup> LF 12x40 (CC), which was the least desirable carbon among the four, yielded about 88 % copper extraction in 48 h (test R21).

### ***5.5. Effect of amount of catalyst***

Leaching tests R22, R23 and R24, for which enargite concentrate S2 was used, were conducted at various carbon:concentrate mass ratios. Enargite sample S2 was reground in a ring mill to a P80 of 33  $\mu\text{m}$  and 40 g of it was used in each test. Generic activated carbon (40 g, 20 g and 10 g in tests R22, R23 and R24 respectively) was used as the catalyst. Leaching conditions are presented in Table 2. The results of these experiments are presented in Figure 14.

In test R22, in which the mass ratio of carbon:concentrate was 1 (carbon:copper-arsenic sulfides mass ratio of 4.3), extraction was almost complete after ~ 15 h (based on interpolation of the curve). Test R23, containing a carbon:concentrate mass ratio of 0.5 (carbon:copper-arsenic sulfides mass ratio of 2.2), reached completion within 24 h. Test R24, containing a carbon:concentrate mass ratio of 0.25 (carbon:copper-arsenic sulfides mass ratio of 1.1), concluded after about 30 h. Therefore, acceptable leaching performance

can be achieved at carbon to enargite concentrate (S2) mass ratios as low as 0.25.

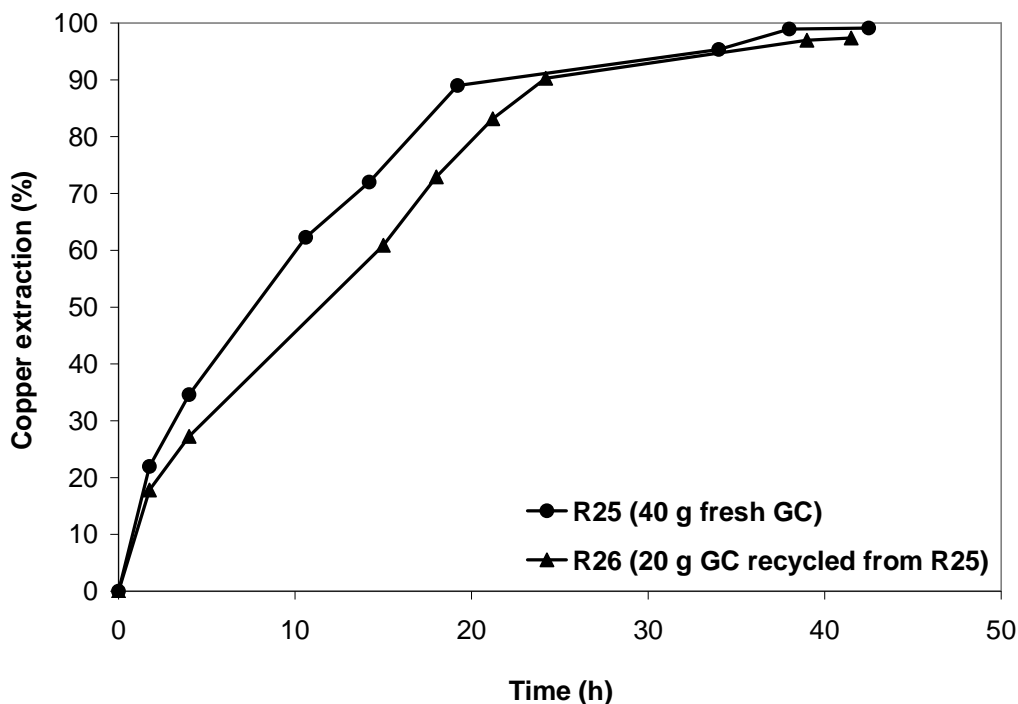


**Figure 14.** Effect of amount of GC on copper extraction from enargite concentrate S2.

### 5.6. Effect of recycling catalyst

Tests R25 and R26 were conducted to investigate the catalytic performance of GC when it was recycled for leaching of reground enargite concentrate S2 (P80 = 33  $\mu\text{m}$ ). A carbon:enargite concentrate mass ratio of 1 was used in both R25 and R26. In test R25, 40 g of both GC and S2, and in test R26, 20 g of both recycled GC from R25 and S2 (after washing and drying) were

used. The leaching conditions can be found in Table 2. Results (Figure 15) suggest that recycled carbon showed only a slightly diminished effect in comparison to fresh carbon catalyst for enargite leaching.

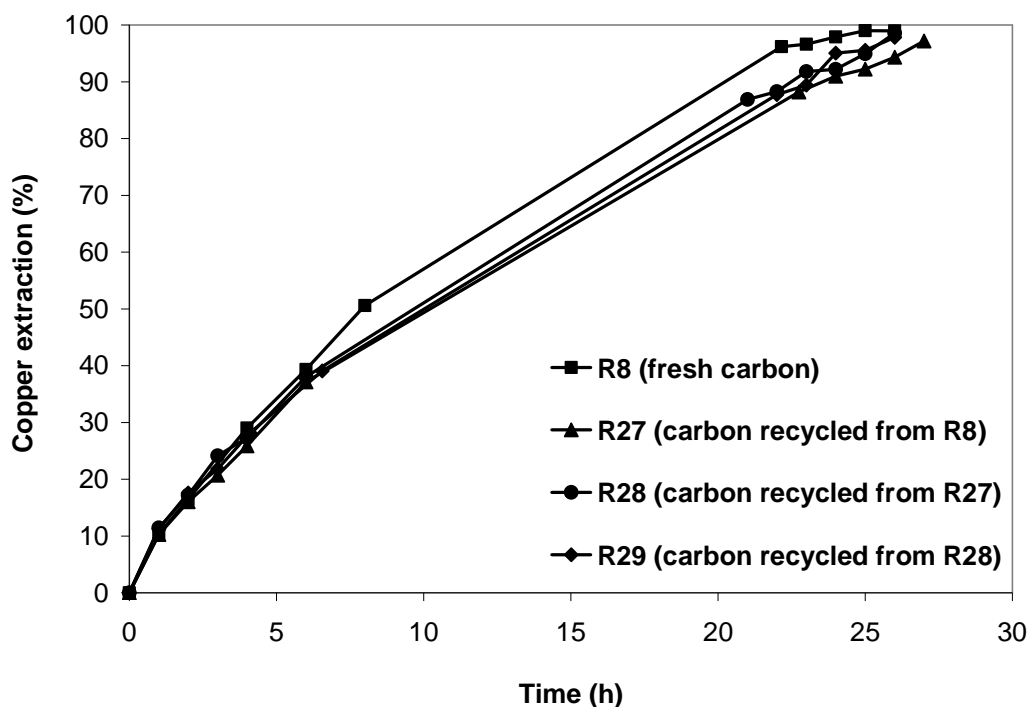


**Figure 15.** Effect of recycling the GC catalyst on copper extraction from enargite concentrate S2.

Effect of recycling the NC catalyst was studied in tests R8, R27, R28 and R29 at a higher potential (515 mV vs. Ag/AgCl) and a lower stirring speed (1000 rpm) in comparison to R25 and R26. Enargite concentrate S4 was used in these tests. The activated carbon particles after each test were separated, dried and weighed. A carbon:concentrate mass ratio of 1 was maintained in these four experiments. Fresh NC was used in test R8 and each subsequent test used the

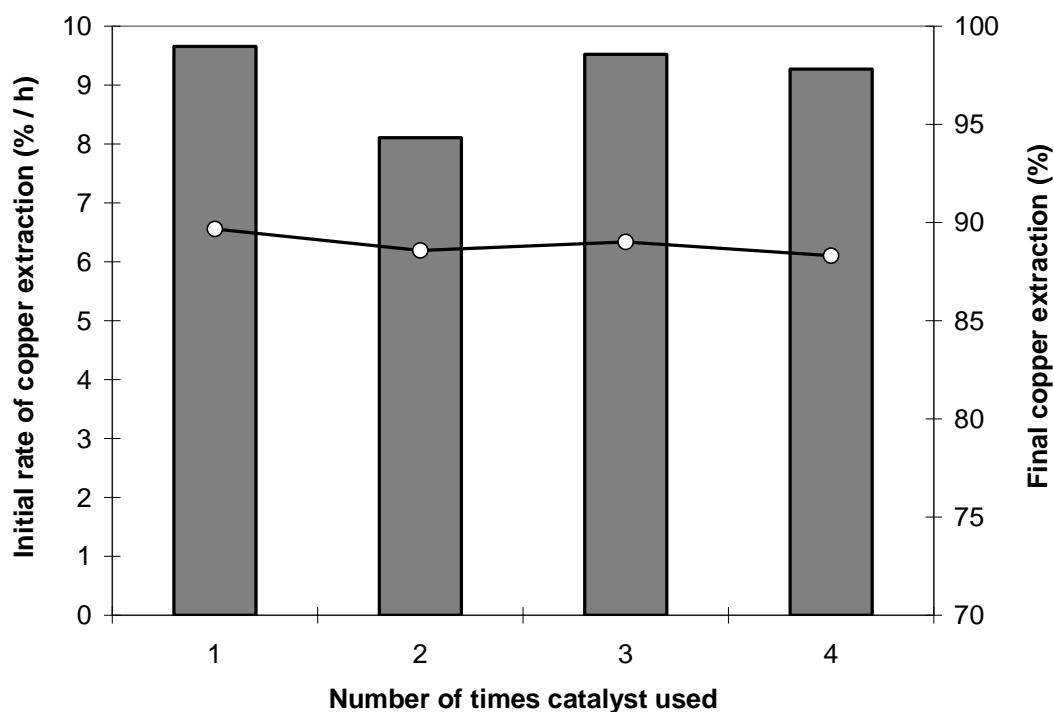


carbon recovered from the previous experiment (i.e. that from R8 was used in R27). The results are presented in Figure 16.



**Figure 16.** Effect of recycling the NC catalyst on copper extraction from enargite concentrate S4.

The NC catalyst exhibited consistent performance for all three recycles. Figure 17 compares initial rates of copper extraction (in the first 6 h of experiments) and final copper extraction values of these tests. The observations suggest that the catalyst showed acceptable levels of stability up to four times of sequential use; therefore, catalyst regeneration may not be necessary in this system.

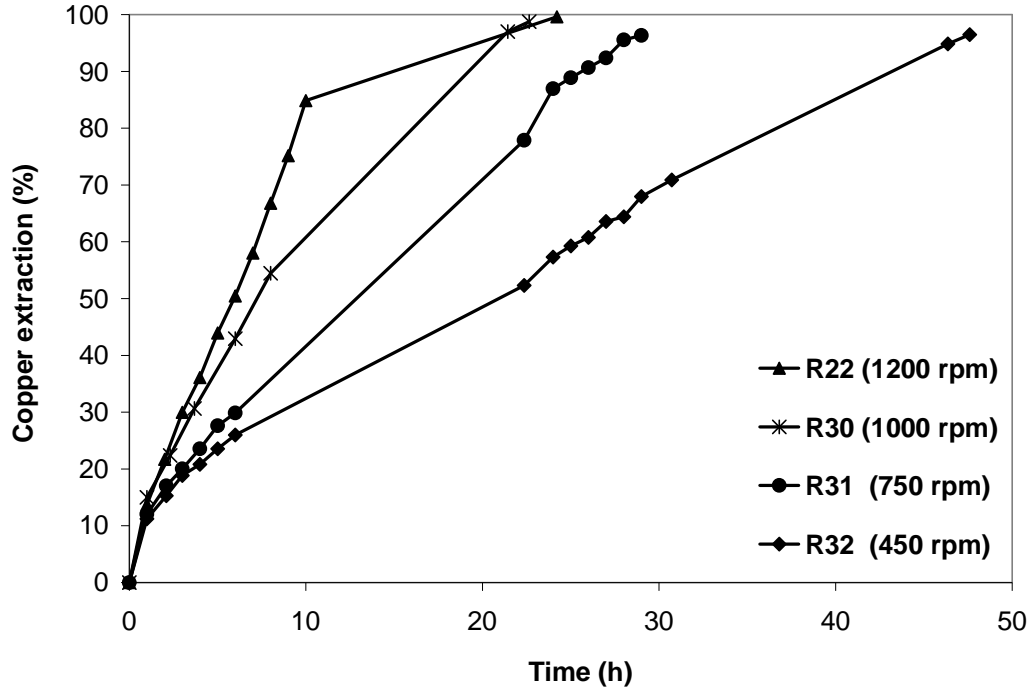


**Figure 17.** Effect of recycling carbon catalyst on the rates of copper extraction in the first 6 h (○) and final copper extractions after 26 h (■) of experiments R8, R27, R28 and R29.

### **5.7. Effect of stirring speed**

Higher stirring speeds increase the surface areas of different phases in the system, shorten diffusion paths and abrade protective layer formed on enargite particles, leading to faster leaching kinetics. However, leaching at a low impeller speed is desirable in order to decrease energy costs and the loss of carbon catalyst by attrition.

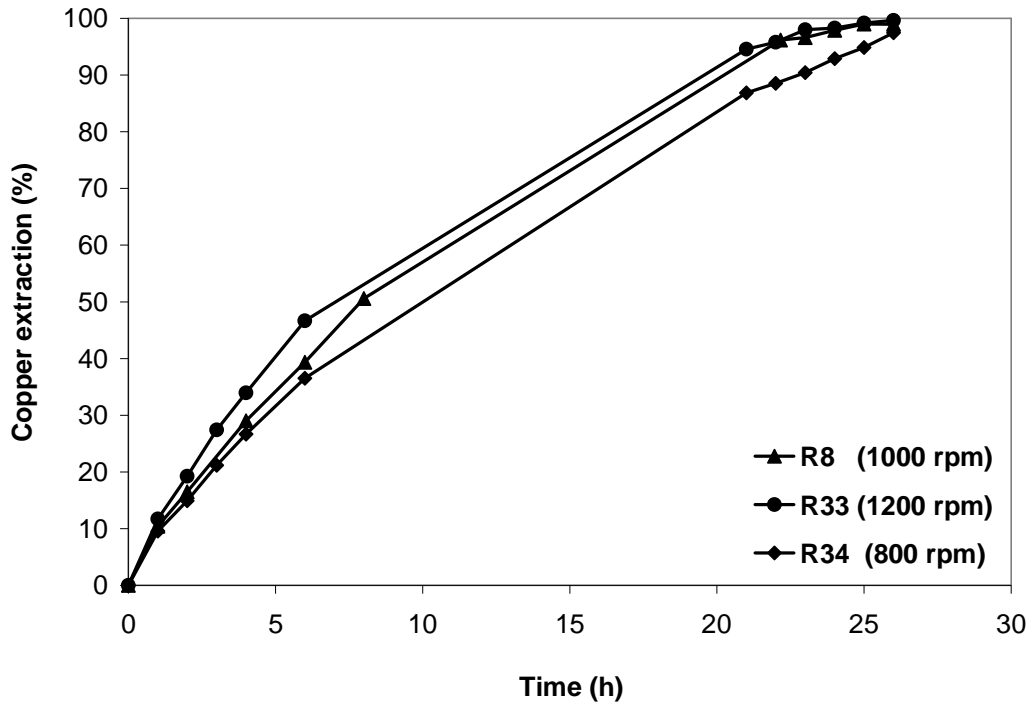
Tests R30, R31 and R32 were conducted using concentrate S2 and under identical conditions as those of R22, but at different impeller speeds respectively. The results can be seen in Figure 18.



**Figure 18.** Effect of stirring speed on copper extraction from enargite concentrate S2.

The amount of time to obtain complete copper extraction from 40 g of concentrate S2 increased from approximately 15 h to 48 h by decreasing the impeller speed from 1200 rpm (R22) to 450 rpm (R32). The impeller was unable to suspend the solids effectively at 450 rpm, resulting in a considerable decrease in leaching kinetics. However, at 1000 rpm (R30) and 750 rpm (R31), complete copper extraction was still attained within 23 h and 30 h respectively.

Tests R33 and R34 were conducted using 60 g of both concentrate S4 and the NC catalyst, under the same leaching conditions as R8 (except for stirring speed). Figure 19 shows the results of experiments R8, R33 and R34.



**Figure 19.** Effect of stirring speed on copper extraction from enargite concentrate S4.

The leaching curves in Figure 19 indicate that increasing the impeller speed from 800 rpm to 1000 rpm had more impact on the leaching kinetics than increasing it from 1000 rpm to 1200 rpm. The effect of stirring speed may be more pronounced at higher pulp densities.

It is worth mentioning that the redox potential of all of the tests shown in Figures 18 and 19 were maintained at 515 mV (vs. Ag/AgCl) throughout the

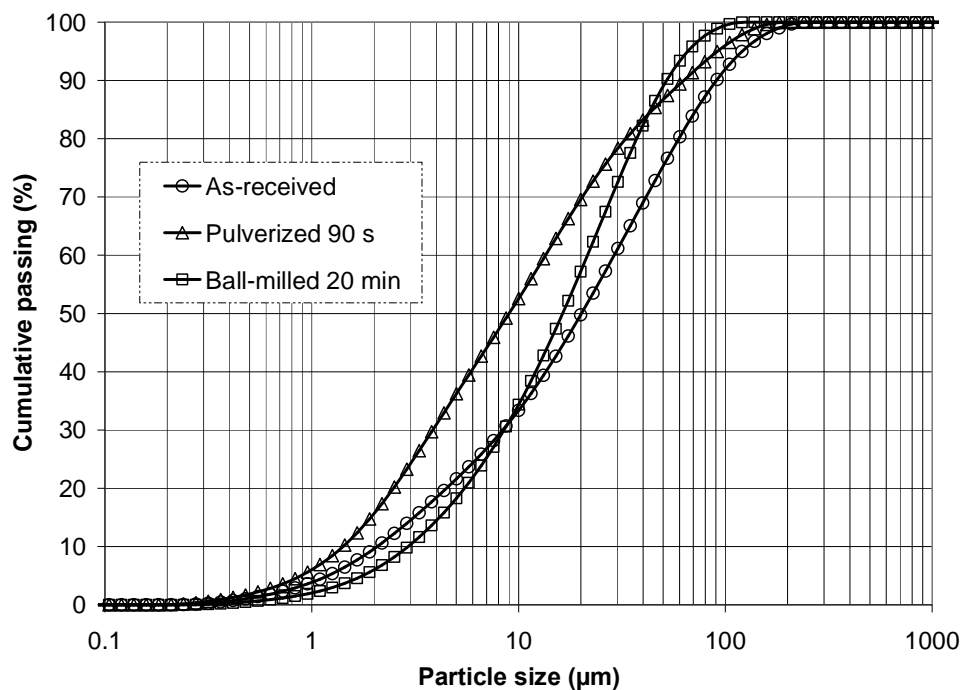
experiments; therefore, the increase in the rate of leaching at higher stirring speeds was not due to the increase in the amount of dissolved oxygen in the solution and the subsequent rise in the redox potential.

### ***5.8. Effect of enargite concentrate grind size***

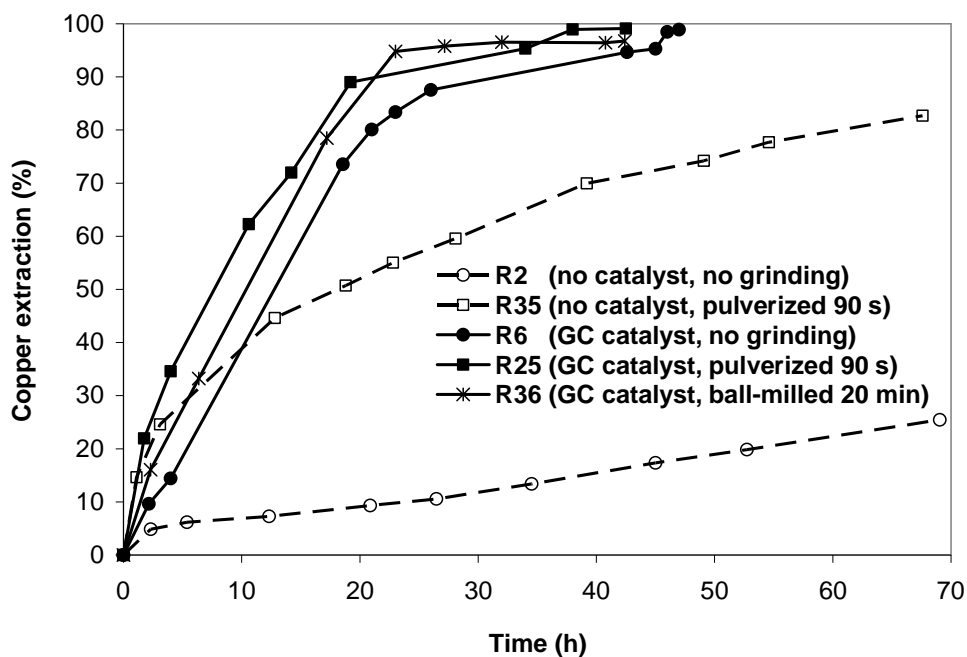
Fine grinding of sulfides can increase their activity and overcome their passivation during leaching. However, fine grinding increases operating costs and can lead to complications in solid/liquid separation.

The importance of the enargite flotation concentrate grind size in this catalytic system was explored. A 200-g portion of S2 (P80 = 59  $\mu\text{m}$ ) was pulverized in a ring mill for 90 s to a P80 of 33  $\mu\text{m}$  and another 400-g portion of S2 was reground in a laboratory-scale ceramic ball mill for 20 min to a P80 of 37  $\mu\text{m}$ . The particle size distributions for as-received and reground materials are shown in Figure 20.

Aside from grinding and catalyst addition, the leaching conditions were identical to those of R2. Figure 21 shows the material used in each test and their corresponding leaching curves. As can be seen from Figure 21, pulverizing and ball-milling gave similar results in the presence of carbon. In the absence of a carbon catalyst, regrinding significantly increased the leaching rate and the final



**Figure 20.** Particle size distributions for as-received and reground concentrate S2.

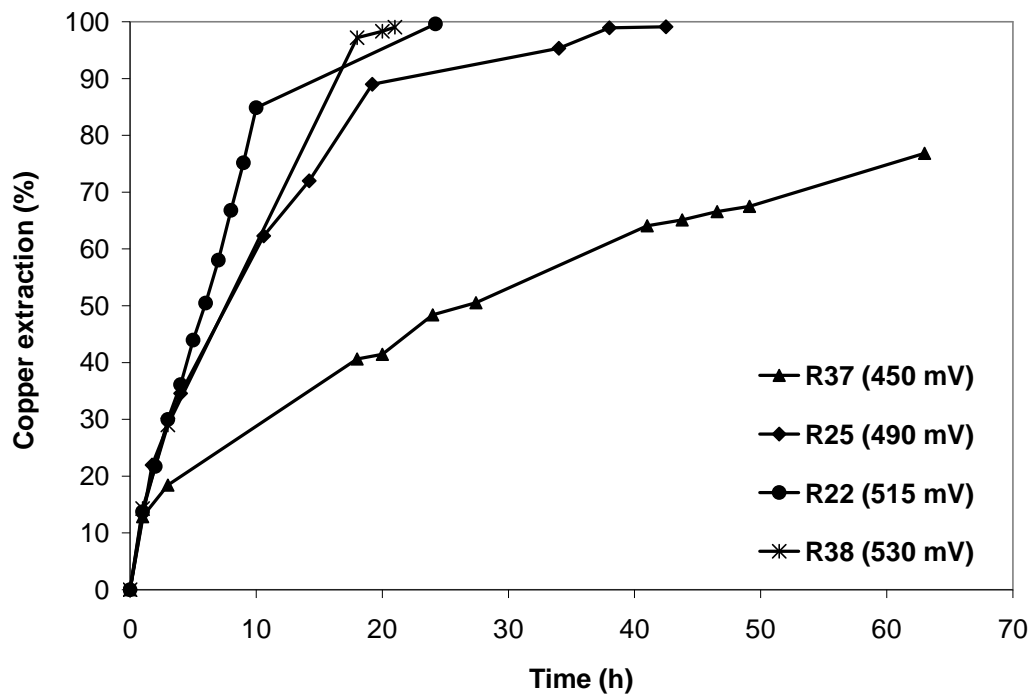


**Figure 21.** Leaching results of as-received and reground concentrate S2 with and without activated carbon.

copper extraction obtained from concentrate S2; but activated carbon catalyzed both as-received and reground concentrate leaching to a similar extent. This may be interesting from an industrial point of view, since using activated carbon may eliminate the need for extra grinding.

### 5.9. Effect of solution redox potential

The results of experiments conducted at different redox potentials are shown in Figure 22.



**Figure 22.** Effect of redox potential on copper extraction from enargite concentrate S2. The potentials are relative to Ag/AgCl reference electrode.

At 450 mV (vs. Ag/AgCl), copper extraction only reached 77 % after 63 h. However, at 490 mV and above, leaching was rapid, achieving practically complete copper extraction within 24 h. The potential of 530 mV was the maximum potential which could be maintained in these tests, probably due to the rapid consumption of oxidant by pyrite oxidation at potentials above this level. The fastest copper extraction rate was obtained at 515 mV.

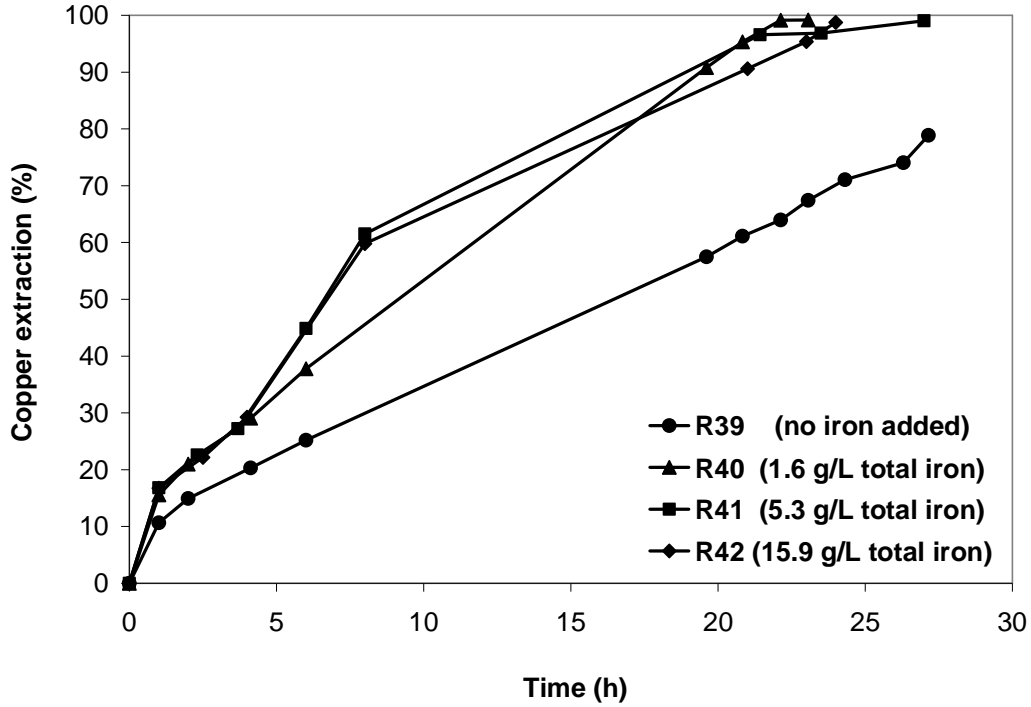
#### ***5.10. Effect of initial total iron concentration***

Tests R39 to R42 were conducted to study the effect of initial total iron concentration on carbon-assisted enargite leaching. A consistent solution redox potential was employed in these tests (515 mV vs. Ag/AgCl). The initial redox potential of the sulfuric acid solution in test R39 was achieved using oxygen sparged into the leaching solution. In order to obtain the same solution potential in tests R40 to R42, iron sulfate salts were added in different amounts but at an identical  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio of 0.97. The results are shown in Figure 23.

All tests containing added iron outperformed test R39. However, elemental analysis of the leach residue of R39 revealed that approximately 0.75 g of iron was leached into the solution during the course of the experiment. The effect of total iron concentration was not as significant as the solution redox potential. The redox potential was mainly governed by the ratio of  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , and not by the



total iron concentration. The results suggest that the initial total iron concentration can be as low as 2 g/L without impeding the leaching behavior.

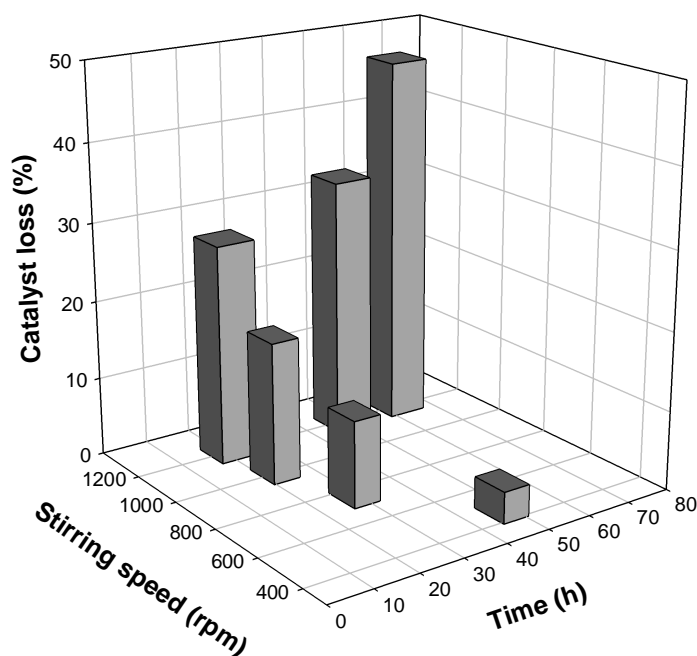


**Figure 23.** Effect of initial total iron concentration on copper extraction from enargite sample S1.

### 5.11. Catalyst loss due to attrition

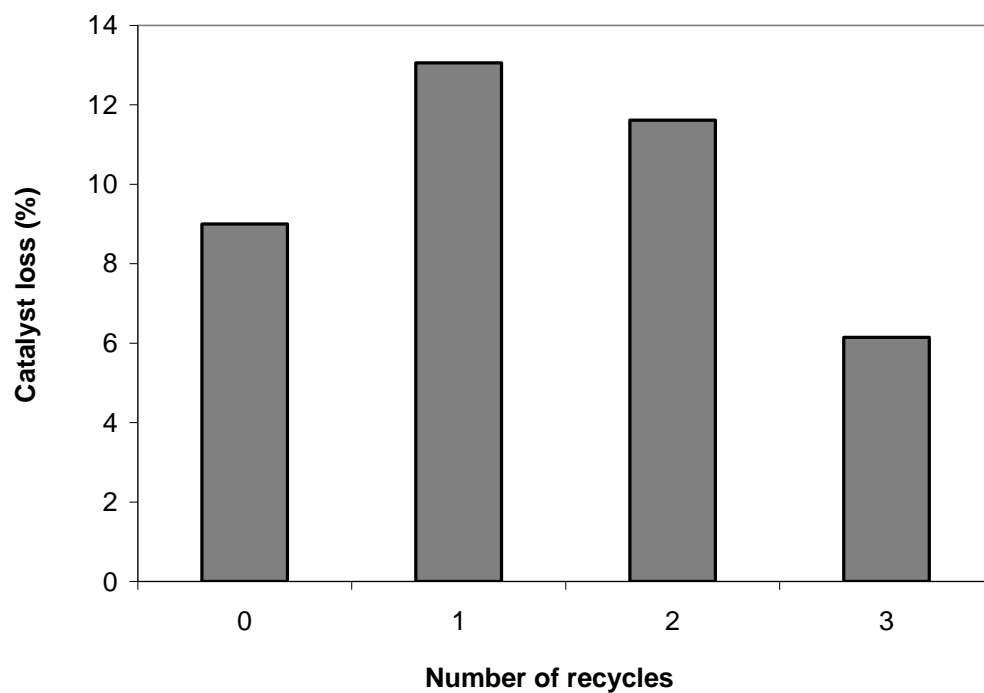
Fine activated carbon particles can be sheared from activated carbon granules due to attrition caused by impellers, resulting in a loss of carbon catalyst. The amount of catalyst loss for a certain type of activated carbon, in a system with a specific reactor and impellers geometry, mainly depends on the

stirring speed of the impellers and the residence time of the catalyst. The coconut shell-based activated carbons tested in this study (GC and NC) exhibited superior catalytic performance as well as higher attrition resistance in comparison to the other products tested. Figure 24 presents the GC catalyst loss values for 6 experiments at different stirring speeds and residence times.

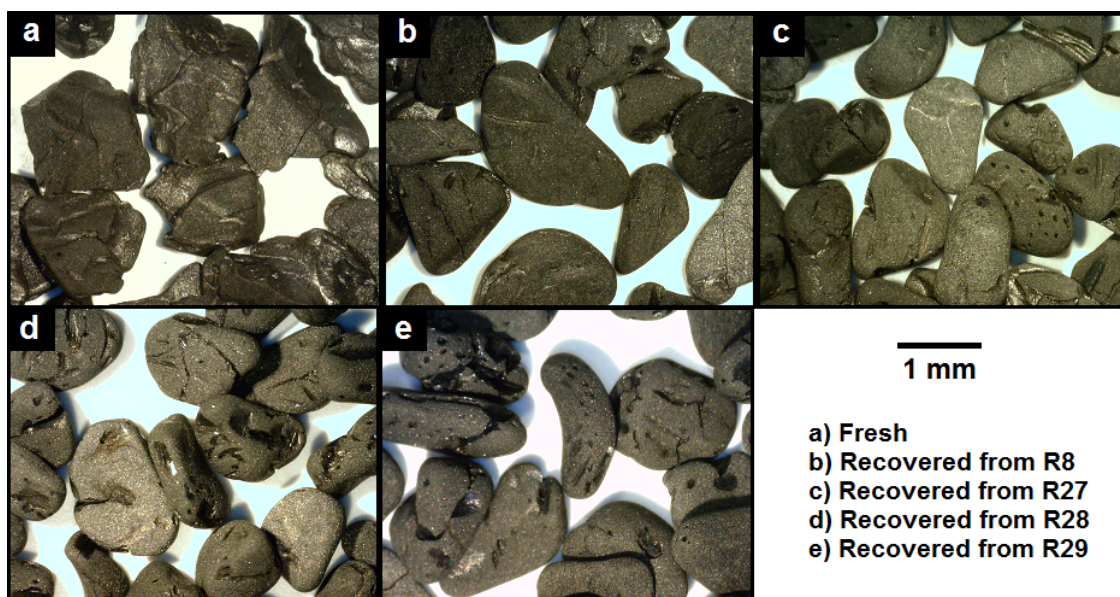


**Figure 24.** The GC catalyst loss as a function of stirring speed and residence time for 6 experiments.

The NC catalyst loss values after use in test R8 and the subsequent recycle tests R27, R28 and R29 (for 26 h at 1000 rpm in each test) can be found in Figure 25. The average amount of loss in each recycle was 10 %, which did not cause a significant decline in leaching kinetics (see Figure 16). Figure 26 shows the morphology of NC granules before and after each recycle test.

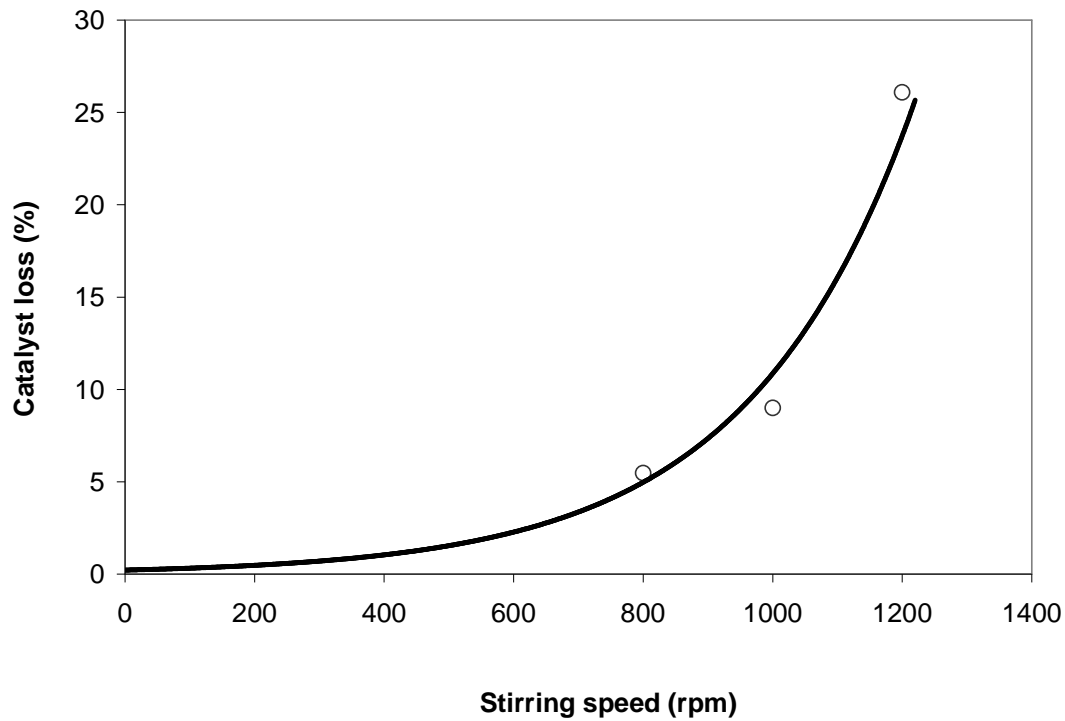


**Figure 25.** The NC catalyst loss in each recycle test, after 26 h at 1000 rpm.



**Figure 26.** The NC catalyst granules morphology before and after each recycle test.

Carbon loss values for fresh NC after 26 h at three different stirring speeds (tests R8, R33 and R34) are shown in Figure 27. Reducing the impeller speed to 800 rpm significantly decreased the carbon loss (from 26 % to 5 % of the initial carbon mass), while having only a minor effect on leaching (see Figure 19).

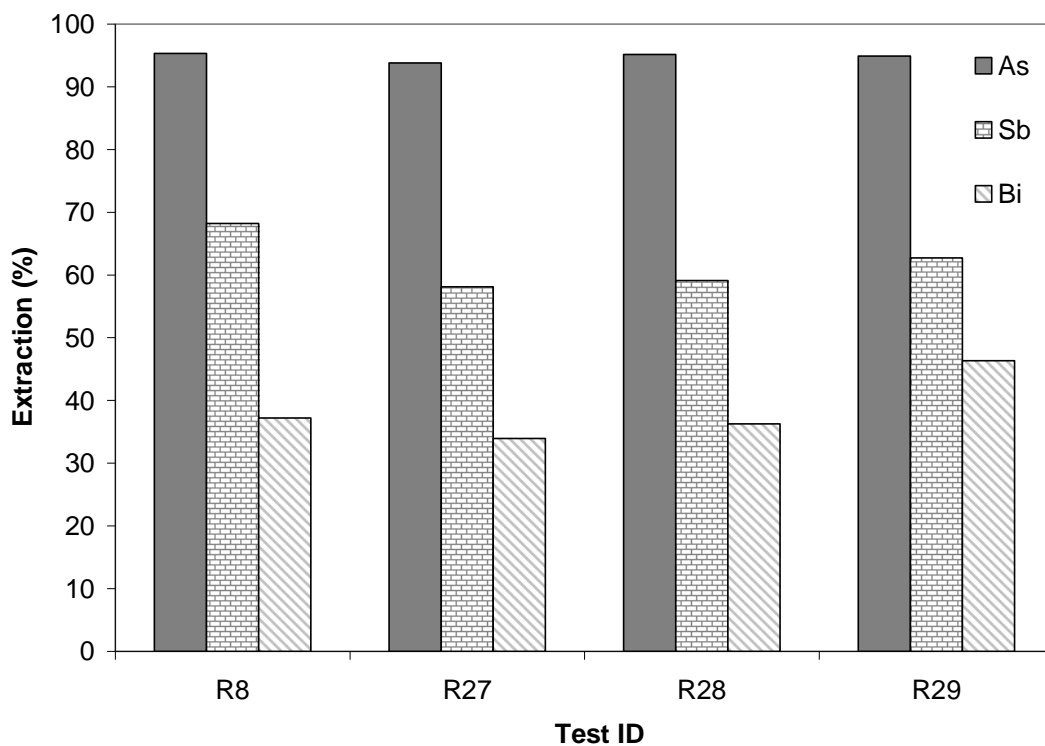


**Figure 27.** The NC catalyst loss after 26 h vs. stirring speed.

### **5.12. Final extractions of As, Sb and Bi**

Arsenic, antimony and bismuth are the most deleterious elements in copper production. Therefore, management of these elements is necessary. Figure 28 shows the final extraction of arsenic, antimony and bismuth from

enargite concentrate S4 into the solution after 26 h for recycle tests R8, R27, R28 and R29. The values were obtained from ICP-MS analysis of the leach residues of these tests. The average copper extraction within this period of time for these four tests was 97.5 %.



**Figure 28.** The final extractions of As, Sb and Bi from enargite concentrate S4 after 26 h in tests R8, R27, R28 and R29.

## 6. Conclusions

This study presents a new process developed for atmospheric leaching of arsenical copper concentrates (i.e. mainly enargite) in iron sulfate solutions. The process utilizes activated carbon as a catalyst. Copper is dissolved along with arsenic and other metals; arsenic is then co-precipitated with iron in a stable form. The simplicity of the process can potentially reduce the risk related to development and implementation of this process at a larger scale.

All four types of activated carbon used in this research successfully catalyzed ferric leaching of enargite. Coconut shell-based activated carbons, which had high carbon content and level of hardness, were particularly effective. A 600 % faster leaching rate was observed using a coconut shell-based activated carbon as a catalyst. SEM studies showed that in the presence of activated carbon, the sulfur product layer loses its integrity and does not protectively surround enargite particles. This may be one of the reasons for the catalytic effect of carbon in enargite leaching. Activated carbon exhibited excellent catalytic behavior even when it was added to the reactor after the formation of protective sulfur layers around enargite particles.

Silver and pyrite did not show strong catalytic activity for enargite leaching; and other than in the presence of silver, pyrite and activated carbon, no synergistic catalytic effect was observed. Investigating the effect of the carbon:concentrate mass ratio on leaching revealed that reducing the ratio to

0.25 (carbon:copper-arsenic sulfides mass ratio of 1.1) still yielded acceptable leaching performance. Activated carbon recovered from one test was recycled to several subsequent tests maintaining virtually the same leaching rate. Lowering the stirring speed from 1200 rpm to 800 rpm had a minor effect on leaching rate at 4 wt. % pulp density, but greatly decreased carbon loss, from 26 % to 5 % of the initial carbon mass, for one of the coconut shell-based activated carbons. It was also observed that activated carbon catalyzed both as-received and reground concentrate leaching to practically the same extent. The solution redox potential was found to be a key factor, therefore the ratio of ferric to ferrous ions was a far more important parameter than the total iron concentration.

Typically, virtually complete copper extraction from the enargite concentrates was achieved in a solution with 53.3 g/L sulfuric acid and 2 g/L initial total iron at 4 wt. % pulp density, 80 °C and 515 mV (vs. Ag/AgCl) in less than 24 h in the presence of activated carbon.

## 7. Recommendations for further work

It is recommended that further research on this subject be undertaken in the following areas:

- Assessment of long-term catalytic activity of an activated carbon catalyst
- Adsorption of various dissolved metals commonly found in arsenical copper concentrates on activated carbon during leaching
- Techno-economic evaluation of the process flowsheet
- Continuous leaching of enargite concentrates in a pilot-scale plant to identify potential technical difficulties and provide better estimates of copper recovery, reagent consumption, build-up of impurities and effluent quality
- Recovery of gold and silver from the leach residue of the process
- A thorough examination of the fate of arsenic and the possibility of precipitating a stable compound of arsenic during leaching at higher pulp densities and lower sulfuric acid concentrations than those used in this research



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