Abstract: In pyrometallurgical processes refining copper, the main source of loss in the conversion stage is from slag. This paper reports on research work treating converter slag containing high percentages of copper (36 wt%) using ammonium hydroxide at room temperature. Variables analyzed are solution pH, agitation, temperature, NH$_4$OH concentration and particle size. Results showed that the hydronium ion resulting from ammonium hydroxide dissociation was the main oxidant of copper compounds in slag, such as CuO, Cu$_2$O and Cu, with the exception of CuFeO$_2$. The particles contain a large amount of microcracks (porosity) in their refractory structure (analyzed by compositional image capture (BSE)). Thus, the diffusion of the leaching solution through the microcracks making contact with the copper oxides would be allowed. Leaching mechanisms were corroborated by X-ray diffraction and scanning electron microscopy analysis. Increasing temperature and NH$_4$OH concentration while decreasing particle size obtained higher copper recoveries, reaching values of 84.8%. Under the same conditions, the main impurity (iron) was minimal (<2%). Solution pH also affected slag leaching. Agitation of the solution positively affected the rate of copper extraction. Leaching kinetics of the leaching solution through the porosity formed in the slag was analyzed under the intraparticle diffusion model. The reaction order was 1.2 with respect to the concentration of ammonium hydroxide and the model was inversely proportional to the square of the particle radius. The activation energy obtained was 42.3 kJ/mol for temperature range 283 to 333 K.

Keywords: converter slag; ammonia leaching; microcracks; kinetics

1. Introduction

Metallurgical treatment of metallic sulfides is generally carried out by means of high temperature methods, usually pyrometallurgy. Conversion stage, there are two sequential stages—the elimination of iron and some other impurities in the so-called "slag blow" stage; and the subsequent stage to convert white metal (Cu$_2$S) to metallic copper (Cu), known as the "copper blow" stage. During the conversion process, highly uncontrolled oxidation occurs, causing chemical copper losses through direct contact of metallic copper with gaseous oxygen (reaction (1)), as well as through direct contact of the white metal with the main constituent of slag, iron oxide (FeO) (reaction (2)).

$$2\text{Cu}_{\text{white metal}} + 1/2\text{O}_2_{\text{gaseous}} = \text{Cu}_2\text{O}_{\text{slag}}$$ \hspace{1cm} (1)

$$\text{Cu}_2\text{S}_{\text{white metal}} + \text{FeO}_{\text{slag}} = \text{Cu}_2\text{O}_{\text{slag}} + \text{FeS}_{\text{white metal}}$$ \hspace{1cm} (2)

Thermodynamically, reaction (1) is very favorable; however and although reaction (2) should not occur because the activity of copper oxide in a slag is on the order of $4.25 \times 10^{-7}$, there is ample
evidence of this oxidized phase. The concentration of copper in slag can vary between grades of 0.68 and 9.13 wt% [1–11].

Slag can be disposed of in landfills as long as it contains less than 1% Cu. Due to the high concentration of useful metal in slag, a proper copper recovery pathway through the use of alternative treatments is attractive. Since this type of copper involves oxidation, one such treatment alternative is hydrometallurgy. Much research has been conducted on copper recovery from converter slags. In the chemical leaching pathway, Anand [1] leached converter slag (4.03% Cu, 1.99% Ni, 0.48% Co) with ferric chloride and obtained extractions of 92%, 28% and 24% copper, nickel and cobalt, respectively, after 10,800 s (3 h). To increase extractions, the same author [2] pre-treated slags with furnace oil (10 wt%) for 10,800 s (3 h). Extraction increased for all three metals, reaching values of 82%, 95% and 80% Cu, Ni and Co, respectively. Then, in a separate study, Anand [3] applied a pressurized leaching solution of dilute sulfuric acid at temperature 403 K (130 °C) and 0.59 MPa O2, yielding recovery of over 90% of the metals of interest (Cu, Ni and Co) and less than 0.8% of Fe (main impurity).

Recoveries of 98% copper, 87% cobalt, 93% nickel and 83% iron were obtained after 7200 s (2 h) of roasting at 423 K (150 °C) and a 3:1 acid/slag ratio. Perederiy [10] applied the High Pressure Oxidative Acid Leaching (HPOXAL) method to extract nickel, cobalt and copper. The work was carried out in a titanium autoclave with oxygen and acid injection. The results obtained at 523 K (250 °C), 90 psi P2O5 and times between 900 and 1200 s (15 to 20 min) yielded between 95–97% extraction of Ni, Co and Cu, each. In another approach, the Taguchi method was used to determine optimum conditions for dissolving copper from converter slags [6] saturated with Cl2 gas. The experimental work was performed in a 0.5 dm3 (500 mL) capacity glass reactor. The results showed 98.35%, 8.79% and 25.17% extraction of Cu, Fe and Zn, respectively, at chlorine gas flow of 3.67 × 10−3 dm3/s (220 mL/min), solid/liquid ratio of 0.1, agitation of 550 rpm and reaction time 5400 s (90 min). Another study [7] used potassium dichromate with sulfuric acid where they found that using the H2SO4-K2Cr2O7 mixture was more advantageous for copper extraction than using H2SO4 alone—using only sulfuric acid, they obtained extractions of 20.5%, 66.6%, 62.1% and 65.7% of Cu, Co, Zn and Fe, respectively; with added potassium dichromate, extractions varied to 81.15%, 12.00%, 3.15% and 10.27% for the same order of metals. The amount of leached copper increased, while the other metals decreased their extractions.

In recent years, Turan [11] leached a mixed slag (BS) generated during flash fusion and conversion using microwaves, hydrogen peroxide and acetic acid. Results showed that the use of microwaves gave shorter leaching times. High copper (95%) and zinc (30%) recoveries were achieved, while iron recoveries were minimal (1.6%). Beşe [8] leached converter slag in a ferric sulfate-sulfuric acid system in the presence and absence of ultrasound. The results showed that ultrasound gave extractions of 89.28%, 51.32%, 69.87% and 13.73% of copper, zinc, cobalt and iron, correspondingly. The absence of ultrasound showed similar extractions.

A different kind of approach from biohydrometallurgy has also been used to recover copper from converter slags. For example, indirect bioleaching, Carranza [9] leached 9 wt% Cu slag with ferric sulfate via the BRISA process (in Spanish—Bioleixiviación Rápida Indirecta con Separación de Acciones; in English-Fast Indirect Bioleaching with Actions Separation). That process gave recovery of nearly 93% copper over 14400 s (4 h) of work. In relation to direct bioleaching, Mehta [4] used bacterium Thiobacillus ferrooxidans and iron oxidizing bacteria to bioleach converter slags at room temperature. High recoveries of 99.0% Copper (over 6912 × 103 s (1920 h)), 22.0% nickel (over 6048 × 103 s (1680 h)) and 30.0% cobalt (over 4320 × 103 s (1200 h)) were obtained.

Of the above works on converter slags using acid systems, none look at alkaline system, that is, basic solutions at pH values above 6. Our research work, then, takes the novel approach to leaching converter slags in ammonia-based systems, with pH values of 6 to 14. Although different copper compounds have already been tested with this leaching alternative in different ammonia media.
such as malachite in ammonia/ammonium carbonate system [12], oxidized copper ore in ammonium chloride solution [13], complex copper in ammonia-ammonium chloride solution [14], malachite ore in ammonium nitrate solutions [15], tenorite and cuprite in ammonium media [16,17]. Ammonia leaching has not been carried out for converter slags.

Therefore, the main objective of this research work is to leach a slag from a Peirce-Smith converter using ammonium hydroxide (NH₄OH) under different working conditions as an alternative to leaching with sulfuric acid (or any other acid).

2. Experimental Design

Codelco Chile’s Ventanas Division provided converter slag specifically from their conversion process in a Peirce-Smith Furnace. In brief, slag is cooled with industrial water to reduce temperature from 1373 K to 293 K, is then crushed, ground and classified into several size fractions, (most frequently −210 + 149, −149 + 105, −105 + 74 and −74 + 53 μm, with average particle sizes of 180, 127, 90 and 64 μm, respectively). Chemical analysis was performed on samples obtained at average sizes of 180 and 64 μm, showing 36% Cu, 19% Fe and the remaining insoluble parts. Converter slag here presented a very high concentration of copper, higher than bibliographically recorded (0.68–9.13% Cu). Therefore, hydrometallurgical treatment of waste (slag) was of interest.

Chemical analyses of the solutions were made by Atomic Absorption Spectroscopy (AAS) with a Hitachi Z-8100 Zeeman kit (Hitachi High-Technologies Corporation, Tokyo, Japan). For the slag characterization in scanning electron microscopy (SEM), the sample was covered with coal to be conductive. Chemical analysis (EDS) and compositional image capture (BSE) and morphological (SEM) were performed using a Tescan® Vega LSH electron microscope, equipped with an EDS Bruker® 6030 detector (TESCAN, Brno, Czech Republic). Solids were determined by X-ray diffraction (XRD), using a Bruker® D4 Endeavor kit, operated with Cu radiation and a Kβ Ni radiation filter (Bruker AXS Advance D8, Bruker, Billerica, MA, USA).

In order to know the chemical species and/or elements present in converter slag, an XRD of the original sample was performed, obtaining the results observed in Figure 1. Here, peaks indicate delafossite (CuFeO₂), cuprite (Cu₂O), tenorite (CuO), metallic copper (Cu), chalcocite (CuS), magnetite (Fe₃O₄) and fayalite (Fe₂SiO₄) compounds—in short, copper present in the converter slag is mainly oxidized.

![Figure 1. X-ray diffraction (XRD) of original converter slag sample.](image-url)
The 180 μm sample was analyzed by SEM to determine the degree of fracture and morphology of the converter slag particles (Figure 2). The particles show an important degree of fracture or porosity (indicated by arrows in the images). This fracturing, called microcracks, could help diffuse leaching solutions through the particle.

![Figure 2. Scanning electron microscopy (SEM) micrograph of original sample of converter slags (264× and 546× magnification.](image)

Leaching experiments began by placing 1 dm$^3$ of ammonium hydroxide leaching solution into a 2 dm$^3$ capacity reactor. This reactor consisted of a heating blanket, condenser (to decrease the evaporation rate), mechanical agitator of the digital type (with a teflon impeller), thermocouple and a tube to extract the liquid samples. Then, 1 × 10$^{-3}$ kg of converter slag sample was introduced. For experiments run at elevated temperature, the solution was first heated to the desired temperature. During the experimental time, liquid samples were extracted and analyzed by AAS for Cu and Fe analysis. In some cases, solid samples were obtained by washing and drying residues and they were analyzed by X-ray diffraction to get the qualitative phase analysis and BSE was used for cross sections of particle morphology.

3. Results and Discussion

Variables that directly affected converter slag dissolution rate, shown below, were NH$_4$OH concentration (mol/dm$^3$), temperature (K), solution pH, particle size (PS, μm), stirring speed (rpm) and liquid/solid ratio (dm$^3$/kg).

3.1. Solution pH

The converter slag dissolution zone in ammonia media at different solution pH values was analyzed. The pH values were 6.0, 10.5 and 14.0. The tests were performed at NH$_4$OH concentration of 0.7 mol/dm$^3$, temperature 298 K, particle size 64 μm, agitation speed 500 rpm and liquid/solid ratio of 1000/1. To maintain the pH value of the solution, sulfuric acid (98% purity) or sodium hydroxide (98.5% purity) was added, as appropriate. Figure 3 shows the results obtained for leaching times up to 2700 s.
Figure 3. Effect of the pH of the leaching solution on copper extraction. Working conditions—[NH$_4$OH] = 0.7 mol/dm$^3$, PS = 64 µm, Agitation = 500 rpm, ratio = 1000/1.

It can be seen in the figure that as the experimental time increases, the extraction of copper from the converter slags increases. Thus, for a pH of 10.5, an extraction of 29.9% Cu was obtained at a time of 600 s, while at 2700 s, extraction reached 69.6%. It should also be noted that copper extractions were lower for pH values of 6.0 and 14.0, reaching extractions of only 7.3% and 15.1%, respectively. This decrease in extraction will be discussed later.

3.2. Effect of Agitating the Solution

The agitation of the leaching solution was varied between a range of 100 and 950 rpm. In addition, an agitation-free test was added. The working conditions used were for pH value 10.5, an ammonium hydroxide concentration of 0.7 mol/dm$^3$, particle size 64 µm, temperature 298 K and a liquid/solid ratio of 1000/1. Figure 4 shows time-dependent copper extractions for the stirring ranges used on the solution.

As can be seen in the figure, a low stirring speed (100 rpm) copper extraction was achieved close to 38.3%. As stirring speed increased, copper extraction increased to 84.8% (at stirring rate 950 rpm). Above 500 rpm, the amount of copper extracted is not highly influenced. This phenomenon is due to the role of mass transfer. Thus, the mass transfer would not be relevant to the flow of ions through the slag particles. It was thus concluded that future experiments would be set at 500 rpm agitation.

It should be noted that working without agitation (0 rpm) an extraction value of 11.1% was achieved. This value is important because copper extraction from converter slag still occurs, even without stirring the solution. This is mainly due to the leaching solution diffusing throughout the slag via microcracks (pores) [18]. These microcracks are produced by the sudden cooling of the slags in the pyrometallurgical process, when water (at 293 K) makes contact with molten slag (1373 K).

Partially leached samples (0 rpm, 2700 s) were analyzed by BSE, which are shown in Figure 5. It can be seen in this figure that the particles contain a large amount of microcracks in their structure, even subdivided inside them generating a greater amount of porosity in the particle. Thus, the diffusion of the leaching solution through the microcracks by contact with the copper oxides would be allowed.

For future work, the study of more detailed analyzes could be evaluated through the use of techniques such as the B.E.T. (Brunauer, Emmett and Teller), which would allow to determine the specific surface area of the solid.
Figure 4. Analysis of the agitation rate of the solution as a function of time. Working conditions: pH = 10.5, [NH₄OH] = 0.7 mol/dm³, T = 298K, PS = 64 µm, ratio = 1000/1.

Figure 5. BSE images of partially leached samples (0 rpm and 2700 s) of converter slag for analysis (455x and 656x magnification). The arrows indicate the microcracks inside the structure.

3.3. Effect of Temperature

The effect of temperature on the leaching rate of converter slag was studied for a range of 283 to 333 K, with NH₄OH concentration constant at 0.7 mol/dm³, particle size at 64 µm and liquid/solid ratio at 1000/1. Figure 6 shows the results of the temperature effect.

As temperature increases, copper extraction is faster. Thus, at time 2700 s and temperature 293 K, copper extraction reached 50%; increasing temperature 1.1 times (323 K), the same extraction was obtained after only 660 s, a reduction of 75.5%.

To determine converter slag leaching mechanisms, samples obtained at a temperature of 298 K, 0.7 mol/dm³ NH₄OH and at times of 2700 and 7200 s (i.e., partially and completely leached) were analyzed. Solid samples were analyzed by XRD. Results for both samples (2700 and 7200 s) were similar. Therefore, only analysis performed for the sample obtained at 7200 s are presented in Figure 7.
Copper extraction, %

Figure 6. Results of copper extraction as a function of time for different temperatures. Working conditions: pH = 10.5, [NH₄OH] = 0.7 mol/dm³, PS = 64 μm, Agitation = 500 rpm, ratio = 1000/1.

Figure 7. Partially reacted sample of converter slag for a time of 7200 s.

Copper compounds can be seen in Figure 7, with strong peaks identifying compound delafossite and a slight presence of cuprite. However, tenorite was not identified in this sample neither metallic copper (Cu). These results indicate that ammonia leaching occurred for oxidized copper species such as Cu₂O and CuO as well as for Cu. Conversely and as confirmed by XRD, CuFeO₂ was not dissolved by NH₄OH. These results are analogous to previous studies [5], in which recoveries over 85% of copper were not possible due to the presence of copper ferrite (CuFeO₂), a ferromagnetic ceramic compound which is very difficult to leach due to its refractory properties.

3.4. Converter Slag Leach Mechanism

Ammonium hydroxide incorporated into the solution was immediately decomposed down to form an ammonium ion (NH₃) and a hydronium ion (H₃O⁺), following reaction (3). In this and previous work [16,17], it was demonstrated that H₃O⁺ is responsible for leaching copper oxides.
through physical and electrochemical processes, while NH$_3$ created copper complexes to maintain cupric ions in the alkaline solution system (constant dissociation of ammonia $= 1.77 \times 10^{-5}$ to 298 K).

$$8\text{NH}_4\text{OH} + 8\text{H}_2\text{O} \rightarrow 8\text{NH}_3 + 8\text{H}_3\text{O}^+ + 8\text{OH}^- \quad (3)$$

Therefore, the leaching mechanism for oxide slags (Cu$_2$O and CuO) in the presence of ammonium hydroxide is given by the following semi-reactions [16,17]:

$$2\text{CuO} + 2\text{H}_3\text{O}^+ \rightarrow \text{Cu}^{2+} + 2\text{H}_2\text{O} + \text{Cu(OH)}_2 \quad (4)$$

$$2\text{Cu}_2\text{O} + 2\text{H}_3\text{O}^+ \rightarrow 3\text{Cu}^{2+} + 2\text{H}_2\text{O} + \text{Cu(OH)}_2 + 4\text{e}. \quad (5)$$

In the case of the reaction (4), the hydronium ion provides protons necessary for the dissolution of CuO (the dissolution of this compound follows a physical process). Reaction (5), in contrast, has the hydronium ion in an electrochemical process to provide the necessary electrons to generate the oxide/reduction pair (using reaction (6)) and thus dissolve the Cu$_2$O.

$$4\text{H}_3\text{O}^+ + 4\text{e} + \text{O}_2 \rightarrow 6\text{H}_2\text{O}. \quad (6)$$

With respect to the compound Cu(OH)$_2$ generated in reactions (4) and (5), this is leached with H$_3$O$^+$ according to reaction (7). The hydronium ion competes to be able to leach cuprite and tenorite (reactions (4) and (5)) and to dissolve Cu(OH)$_2$ (reaction (7)).

$$\text{Cu(OH)}_2 + 2\text{H}_3\text{O}^+ \rightarrow \text{Cu}^{2+} + 4\text{H}_2\text{O}. \quad (7)$$

Copper ions released into the solution (reactions (4) and (5)) are complexed by the ammonium ion to generate copper tetra-amine (Cu(NH$_3$)$_4^{2+}$) according to reaction (8). It should be noted that the tetra-amine formation process is allowed through previous generation of Cu(NH$_3$)$_2^{2+}$; however, that ion is thermodynamically unstable in basic systems [13,15].

$$4\text{Cu}^{2+} + 16\text{NH}_3 \rightarrow 4(\text{Cu(NH}_3)_4^{2+}). \quad (8)$$

To corroborate the formation of copper tetra-amine, a Pourbaix stability diagram (EH-pH) was constructed for the Cu-NH$_4$OH-H$_2$O system for temperature 293 K, copper concentration 0.00236 mol/dm$^3$ and ammonium hydroxide concentrations of 0.1, 0.35 and 0.7 mol/dm$^3$. The thermodynamic data used for the construction of the diagram were extracted from the HSC Chemistry program database [19]. This diagram (Figure 8) shows that solution pH was preponderant vs. potential in obtaining the copper tetra-amine. Thus, for NH$_4$OH concentration 0.1 mol/dm$^3$, Cu(NH$_3$)$_4^{2+}$ was maintained in solution at pH ranging from 7 to 14 for the entire potential range. Outside those pH ranges, copper precipitated as an oxide (CuO), decreasing copper concentration in solution and inhibiting further purification/concentration of this metal. Thus pH effect is shown, here, as in Figure 3. In addition, were copper oxide to form, NH$_3$ consumption (reaction (8)) would stop, NH$_4$OH would not decompose and H$_3$O$^+$ would not be generated (reaction (3)). In short, CuO production directly and negatively affects Cu$_2$O and CuO leaching from the slag.

Tests with NH$_4$OH concentrations (0.35 and 0.70 mol/dm$^3$) show that as concentration of ammonium hydroxide increases, the stability zone of the copper tetra-amine was reduced, yielding for NH$_4$OH 0.7 mol/dm$^3$ a pH range from 8.3 to 13.4.
The formation of the copper tetra-amine generated an imbalance between reactions (4) and (5) (i.e., $Cu^{2+}$ concentration decreased), thus causing a higher dissolution rate for the two copper oxides $CuO$ and $Cu_2O$. These two compounds delivered a greater amount of copper ions to the basic solution, given by reactions (9) and (10).

$$2CuO + 4NH_4OH + 4NH_3 \rightarrow 2(Cu(NH_3)_4^{2+}) + 2H_2O + 4OH^- \quad (9)$$

$$2Cu_2O + 8NH_4OH +8NH_3 + O_2 \rightarrow 4(Cu(NH_3)_4^{2+}) + 4H_2O + 8OH^- \quad (10)$$

It should be noted that if the concentration of ammonia in the solution is reduced, it could lead to the formation of copper oxide.

On the other hand, metallic copper can be dissolved by hydronium ions (coming from the disiation of $NH_4OH$) by an electrochemical process. Then, the dissolution mechanism would be given by the expression 11.

$$Cu + 2NH_4OH + 2NH_3 + 1/2O_2(g) \rightarrow Cu(NH_3)_4^{2+} + H_2O + 2OH^- \quad (11)$$

3.5. Effect of $NH_4OH$ Concentration

Figure 9 shows the results of converter slag copper extraction as a function of $NH_4OH$ concentration. The working temperature was 298 K; particle size, 64 µm; and liquid/solid ratio, 1000:1.

The Figure shows that increased concentration of ammonium hydroxide increased dissolution of converter slag. Thus, at concentration of 0.2 mol/dm$^3$, 36.1% was obtained at a time of 7200 s; at concentration 0.8 mol/dm$^3$, a recovery of 71.3% was obtained after the same amount of time. At the minimum $NH_4OH$ concentration tested (0.1 mol/dm$^3$), copper extraction was 15.6%. Stoichiometric concentrations from reactions (9) and (10) are calculated at 0.5 and 1.0 mol/dm$^3$ of $NH_4OH$, respectively; however, concentrations 5 to 10 times lower than the above still gave significant copper extractions.
Working conditions were similar to previous experiments. The copper extraction curves are given in Figure 10. It is clear that particle size is largely determinant of dissolution rate. For size 180 \( \mu \text{m} \), a recovery of 11.3% was obtained after time 1800 s, while for particle size 64 \( \mu \text{m} \), copper extraction reached 69.9% for the same time. This phenomenon is likely due to two situations, that is, as particle size decreased—1) useful metal was released from the slag and 2) surface area increased.

Figure 9. Effect of \( \text{NH}_4\text{OH} \) concentration on converter slag leach rate. Working conditions: pH = 10.5, \( T = 298 \text{ K} \), PS = 64 \( \mu \text{m} \), Agitation = 500 rpm, ratio = 1000/1.

3.6. Particle Size Analysis

Four different converter slag particle sizes were compared: 64, 90, 127 and 180 \( \mu \text{m} \). Working conditions were similar to previous experiments. The copper extraction curves are given in Figure 10. It is clear that particle size is largely determinant of dissolution rate. For size 180 \( \mu \text{m} \), a recovery of 11.3% was obtained after time 1800 s, while for particle size 64 \( \mu \text{m} \), copper extraction reached 69.9% for the same time. This phenomenon is likely due to two situations, that is, as particle size decreased—1) useful metal was released from the slag and 2) surface area increased.

Figure 10. Evaluation of particle size in copper extraction rate. Working conditions: pH = 10.5, \([\text{NH}_4\text{OH}]=0.7 \text{ mol/dm}^3\), \( T = 298 \text{ K} \), Agitation = 500 rpm, ratio = 1000/1.
3.7. Examination of the Solid-Liquid Ratio

The ratio between leaching solution and slag was examined with the aim of obtaining the highest copper extraction with the lowest amount of solution. Working conditions were similar to those indicated in the previous points. The amount of solution was varied from 0.1 to 1.4 dm³ with amount of slag constant at $1 \times 10^{-3}$ kg. Results are shown in Figure 11.

![Graph showing copper extraction percentage versus dm³ solution/kg particle](image)

**Figure 11.** Effect of liquid/solid ratio on copper extraction. Working conditions: pH = 10.5, $[\text{NH}_4\text{OH}] = 0.7 \text{ mol/dm}^3$, $T = 298 \text{ K}$, PS = 64 µm, Agitation = 500 rpm.

As the liquid/solid ratio decreased, copper extraction decreased. At 100 dm³/kg, an extraction of 9.3% was achieved; at 400 dm³/kg, 60.8%. The highest Cu extractions were at ratio 1000 dm³/kg, which marks the most efficient reaction between diffusion medium NH₄OH and CuO-Cu₂O-Cu.

3.8. Converter Slag Leaching Kinetics

Although and as previously mentioned, converter slag particles have microcracks, Figure 6 shows that slag leaching could also be described by the intraparticle diffusion model, that is, solution leaching through slag porosity. Assuming that constant reactant concentrations and diffusion rate through porous layer of radius $r_o$, the rate equation, described by the shrinking core model, is given by the following expression [20]:

$$1 - 3(1 - x_{CS})^{\frac{3}{2}} + 2(1 - x_{CS}) = k_{app}t.$$  \hspace{1cm} (12)

In Equation (11), $x_{CS}$ is the converted (reacted) fraction of the converter slag; apparent rate constant ($k_{app}$) is a function of temperature, NH₄OH concentration and particle size. Constant $k_{app}$ is directly related to the intrinsic rate constant of the system, given by expression (13):

$$k_{app} = k \frac{C_{\text{NH}_4\text{OH}}^n}{r_o^m} e^{-\frac{E_a}{RT}},$$  \hspace{1cm} (13)

where $k$ is the intrinsic rate constant, $C_{\text{NH}_4\text{OH}}^n$ is the concentration of ammonium hydroxide and $n$ is the reaction order of NH₄OH. Finally, $r_o$ is the initial radius of the slag particle.

A graph of $1 - 3(1 - x_{CS})^{\frac{3}{2}} + 2(1 - x_{CS})$ versus time was constructed for the experimental data obtained in Figure 6 for temperature range 283 to 333 K and for particle size 64 µm. Results are shown
in Figure 12. The same data treatment method was used for the results obtained on the effects of ammonium hydroxide concentration (Figure 9) and particle size (Figure 10).

![Figure 12. Leaching kinetics of converter slag using the data in Figure 6.](image)

The regression lines shown in Figure 12 fit very well to experimental data over the entire temperature range (0.95 > R² > 0.99). These results demonstrate the applicability of this kinetic model for diffusion in a porous layer of radius r₀ (Equation (12)).

Similarly to the above, though to quantify reaction order n, a graph was constructed using kinetic data on the effect of NH₄OH concentrations. Results are shown in Figure 13, where experimental data on all ammonium hydroxide concentrations measured fit very well to Equation (12). Afterwards, the slopes of each adjustment were used for Equation (13) and a graph of ln k app versus ln C NH₄OH was constructed, with initial particle radius and temperature constant, as shown in Figure 14.

![Figure 13. Leaching kinetics of converter slags for different NH₄OH concentrations and particle size of 64 μm.](image)
Figure 14. Analysis of the reaction order in relation to the concentration of ammonium hydroxide.

This figure shows the linear adjustment of the seven $k_{app}$ values (over the whole NH$_4$OH concentration range) with $R^2$ of 0.90. Reaction order $n$ was then calculated using slope values, which resulted in a reaction order $n$ of 1.2 for NH$_4$OH concentration in the solution.

Looking at Equation (13), particle radius squared varied inversely with the apparent kinetic constant. To corroborate this relationship, experimental data obtained from Figure 10 were used and adjusted according to Equation (12), yielding Figure 15. Controlled diffusion through porous layer of radius $r_o$ (Equation (13)), requires that $1/(r_o^2)$ must vary linearly with ln $k_{app}$. Figure 16 shows such variation, where it can be seen that the ln $k_{app}$ data have a very good linear fit to experimental data, $R^2$ of 0.98, indicating that the heterogeneous kinetic model (Equation (12)) models converter slag dissolution very well.

Figure 15. Slag leach kinetics for different particle sizes.
To calculate the activation energy ($E_a$), the intrinsic rate constant (modifying Equation (13)) was first calculated using apparent rate constants (given in Figure 11), at temperature range 283 to 333 K, NH$_4$OH concentration 0.7 mol/dm$^3$, reaction order n of 1.2 and particle size 67 µm ($r_o = 33.5$ µm).

Table 1 shows the $k$-values as a function of the temperature range used in this study.

| T, K  | $T^{-1}/10^3$, K$^{-1}$ | $k_{app}$, s$^{-1}$ | $-\ln (s^{-1} \mu m^2 (mol/dm^3)^{-1})$ |
|-------|--------------------------|----------------------|-----------------------------------------|
| 283   | 3.534                    | $0.30 \times 10^{-5}$ | 5.265                                   |
| 293   | 3.413                    | $1.41 \times 10^{-5}$ | 3.718                                   |
| 298   | 3.356                    | $2.09 \times 10^{-5}$ | 3.324                                   |
| 313   | 3.195                    | $3.93 \times 10^{-5}$ | 2.693                                   |
| 323   | 3.096                    | $4.35 \times 10^{-5}$ | 2.592                                   |
| 333   | 3.003                    | $6.35 \times 10^{-5}$ | 2.213                                   |

After the $k$-values had been obtained, an Arrhenius graph (ln $k$ versus 1/T) was constructed (Figure 17). A good linear adjustment ($R^2 > 0.85$) of the ln $k$ data can be appreciated. The calculated activation energy was 42.3 kJ/mol for the temperature range 283 to 333 K, which is a typical value for a particle diffusion model (Equation (12)). Finally, then, the dissolution rate of converter slag in an ammonia system (NH$_4$OH) can be represented by the following expression:

$$1 - 3(1 - x_{CS})^3 + 2(1 - x_{CS}) = 2.52 \times 10^7 \frac{C_{1.2}^{NH_4OH} r_0^2}{x_{CS}^2} e^{-\frac{42.3}{RT}} t.$$  (14)
The copper oxides

\[ \text{CuFeO} \text{ particle radius}. \]

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