KINETICS AND OPTIMIZATION OF CHALCOPYRITE, SPHALERITE AND ILMENITE LEACHING IN BINARY SOLUTIONS

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OKOYE, CHUKWUNONSO CHUKWUZULOKE 2014217008P

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CERTIFICATION

This is to certify that this dissertation entitled "Kinetics and Optimization of Chalcopyrite, Sphalerite and Ilmenite Leaching in Binary Solutions", submitted by Okoye, Chukwunonso Chukwuzuloke in partial fulfillment of the requirements for the award of Doctor of Philosophy (Ph.D) degree in Chemical Engineering, Faculty of Engineering, Nnamdi Azikiwe University Awka, comprises my original work. No part of this work has been presented as project work, thesis or dissertation in any institution of higher learning.

Okoye, Chukwunonso Chukwuzuloke 2014217008P

Date

APPROVAL PAGE

The Department of Chemical Engineering Nnamdi Azikiwe University, Awka, hereby approves this Dissertation.

Prof. O.D. Onukwuli Supervisor

Prof M. C. Menkiti Head, Dept. of Chemical Engineering

Prof. S. E. Ogbeide External Examiner

Prof. H. C. Godwin Dean, Faculty of Engineering

Prof. P.K. Igbokwe

Dean, School of Post Graduate Studies

Date

Date

Date

Date

Date

DEDICATION

This research work is dedicated to God Almighty, the fountain of all wisdom and knowledge, whose grace has kept me on-going.

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ABSTRACT

Mineral ores are usually processed by means of pyrometallurgical or hydrometallurgical processes. Myriad of deficiencies surrounding pyrometallurgical process have spurred research interests geared toward low temperature and lixiviant concentration hydrometallurgical process. Leaching of copper, zinc and iron from Nigerian chalcopyrite, sphalerite and ilmenite ores using binary solutions (HCl-KCl, HCl-KClO₃ and HCl-NaNO₃) as lixiviants was investigated. The ore samples were characterized using instrumental techniques (scanning electron microscopy, SEM, X-ray diffraction spectroscopy, XRD, energy dispersive x-ray, EDX and X-ray flourescence, XRF). The effect of acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratios on the percentage copper, zinc and iron dissolution was evaluated. The experimental data obtained at various process parameter conditions were fitted in eight kinetics models: diffusion through liquid film model(DTLF), diffusion through product layer model (DTPL), surface chemical reaction model (SCR), mixed kinetics model (MKM), Jander (three dimensional) model, Kröger and Ziegler model, Zhuravlev, Lesokhin and Templeman model and Ginstling-Brounshtein model. Thermodynamic parameters, Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were estimated. Modeling and optimization of the leaching process was achieved using response surface methodology (RSM) and adaptive neuro fuzzy inference system (ANFIS) - Particle swarm optimization technique. The predictive ability of the RSM and ANFIS models were evaluated in terms of root mean square error (RMSE), chi-square (χ^2), model predictive error (MPE) and coefficient of determination (\mathbf{R}^2) . SEM micrographs before and after dissolution displayed modifications in the morphology of the ore samples. XRF results established the dominance of copper, iron and sulphur in chalcopyrite, zinc and sulphur in sphalerite, titanium and iron in ilmenite. XRD revealed that the chalcopyrite, sphalerite and ilmenite exist mainly as CuFeS₂, ZnS and FeTiO₂ respectively confirming the originality of the ores. Results of the leaching studies disclose that all the controllable variables had synergetic effect on the response variable except particle size. HCl-KClO₃ marginally outperformed HCl-KCl and HCl-NaNO₃. The dissolution kinetics of the processes mostly conformed to the diffusion controlled Kröger and Ziegler model. The corresponding activation energy values estimated were generally <21kJ/mol therefore affirming that the processes are diffusion controlled. The average ΔG values of -5.42kJ/mol, -1.25kJ/mol and -4.54Jk/mol; -29.97kJ/mol, -5.23kJ/mol and -27kJ/mol; -1.26kJ/mol, -52.12kJ/mol and -1.30kJ/mol for chalcopyrite, sphalerite and ilmenite dissolution in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants suggest the feasibility and spontaneity of the process. The positive enthalpy values (Δ H) of 10.41 kJ/mol, 5.97 kJ/mol and 9.63 kJ/mol; 45.56 kJ/mol, 10.07 kJ/mol and 42.86 kJ/mol; 6.53 kJ/mol, 67.73 kJ/mol and 6.42 kJ/mol for chalcopyrite, sphalerite and ilmenite dissolution in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants indicate that the reactions were endothermic in nature. RSM model summary results showed that quadratic model compared with linear, 2FI and cubic models, best approximated the experimental data. ANFIS recorded lower values of RMSE, χ^2 , MPE and values closer to unity compared to RSM. The results showed the superiority of ANFIS in capturing the nonlinear behaviour of the leaching systems. The ANFIS-PSO optimal predictions of 96.95%, 97.85% and 95.74%; 95.40%, 97.72% and 90.91%; 98.83%, 95.57% and 92.85% for chalcopyrite, sphalerite and ilmenite in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions were in close agreement with the experimental 95.10%, 95.92% and 94.78%; 93.53%, 96.98% and 88.24%; 96.95%, 96.68% and 90.90% obtained at the same process conditions. The results obtained corroborate the potential capability of HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions as lixiviants for copper, zinc and iron recovery from chalcopyrite, sphalerite and ilmenite ores.

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LIST OF ABBREVIATIONS

ANFIS - Adaptive neuro fuzzy inference system

- ANN Artificial neural network
- CCD Central composite design
- DTLF Diffusion through the liquid film
- DTPL Diffusion through the product layer
- EDX Energy dispersive x-ray
- GUI Graphic user interface
- MKM Mixed kinetics model
- MPE Model predictive error
- OFAT One factor at a time
- RMSE Root mean square error
- RSM Response surface methodology
- SCM Shrinking core model
- SCR Surface chemical reaction
- SEM Scanning electron microscopy
- XRD X-ray diffraction spectroscopy
- XRF X-ray fluorescence

LIST OF SYMBOLS

- C_0 concentration of the penetrating species at the surface
- CAO initial concentration of leaching reagent A
- D Diffusion coefficient
- Ea activation energy
- k_0 pre-exponential factor
- k_1 apparent rate constant for diffusion through the liquid film
- kd apparent rate constant for diffusion through the product layer
- kr apparent rate constant for surface chemical reaction
- R^2 coefficient of determination
- r_o original radius of the ore particle
- t reaction time
- T solution temperature
- x conversion fraction
- β thickness of the product layer
- ΔG Gibbs free energy change
- ΔH Enthalpy change
- ΔS Entropy change
- $\rho_B-molar$ density of the ore particle
- χ^2 Chi-square

CHAPTER ONE INTRODUCTION

1.2 Background of the Study

The increasing demand for metals and metallic compounds in the world has necessitated intensive studies for the extraction of metals from ores (Seyed-Ghasemi and Azizi, *et. al.*, 2017a). Nigeria is one of the richest countries in the world as far as mineral resources are concerned (Baba *et al.*, 2005). Metals play an important role in the industrial development and improved living standards. Society can draw on metal resources from the earth's crust as well as the metals discarded after use. New routes to metal recycling are continually investigated not only for reducing costs but also to prevent the environmental pollution (Seyed-Ghasemi and Azizi, 2017b). Intensive studies on metal extraction from ores are necessary to keep up with the increasing demand for metals (Deng *et al.*, 2015).

Metal production from any metal source, like ore, concentrate, and secondary sources (various industrial wastes containing metals and scrap metals, etc.) is performed by one of the pyrometallurgical and hydrometallurgical methods, or by a combination of both (Ekmekyapar *et al.*, 2015). Pyrometallurgical method emits SO₂ which constitutes serious environmental pollution (Deng *et al.*, 2015; Agacayak *et al.*, 2014). In order to satisfy the environmental regulations, SO₂ need be captured and converted into sulphuric acid which will increase the capital costs for the plants (Xian *et al.* 2012). Hydrometallurgical extraction of metals is a branch of industry for which the research work is ongoing to develop processes which are less costly, more environmentally friendly and acceptable economically (Habbache *et al.*, 2009). Hydrometallurgical technique process train consists of three sections: leaching, leacheate purification and electrowining (Baba and Adekola, 2013).

Leaching is one of the central unit operations in the hydrometallurgical processes (Coruh *et al.*, 2012; Hu *et al.*, 2011). Often, a leaching stage is one of the initial operations in the processes (Crundwell, 2013; Abdel-Aal, 2000), and as a result, the efficiency of leaching has a primary effect on the technical and economic success of a hydrometallurgical business. For this reason, a

great deal of attention has been focused on the study of dissolution reactions, and particularly on the kinetics of these reactions (Crundwell, 2013).

Leaching kinetics plays an important role in the extraction of metals and compounds (Seyed-Ghasemi and Azizi, 2017b). An accurate understanding of the kinetics of dissolution is required in order to interpret the complex behaviour of leaching reactors, and to optimise the performance of a hydrometallurgical operation (Crundwell, 2013). The dissolution of mineral ore takes place through the following stages: (1) diffusion of reactant through the diffusion layer, (2) adsorption of the reactant on the solid, (3) chemical reaction between the reactant and the solid, (4) desorption of the product from the solid and (5) diffusion of the product through the diffusion layer. Any of these stages (1) - (5) may be the rate controlling step depending on its relative speed to the others (Baba *et al.*, 2012).

In the leaching step, the metal is leached using a suitable lixiviant (Ekmekyapar *et al.*, 2015). Leaching is generally carried out by adding an effective oxidant to an acid solution (Xian *et al.*, 2012). The redox potential of sulphur / metal sulphide pair is less than that of the selected oxidants, so that the oxidation of sulphide to sulphur (Adebayo *et al.* 2006), sulfate (Tian *et al.*, 2017), ferric hydroxysulfates or polysulfides (Shiers *et al.*2015) is possible. The redox reaction can proceed and an oxidant considered effective only when its electrode potential is higher than that of sulfur. The addition of oxidant can significantly increase the leaching rate and shorten the leaching time (Tian *et al.*, 2017). The structures of mineral ores are strongly held by covalent bonds and usually need to be leached in a strong oxidizing environment. The electrode potential of an oxidant is directly proportional to its efficiency (Córdoba *et al.*, 2008). By reducing the resistance of electron transfer during oxidation of ores, the leaching rate is increased (Dakubo *et al.*, 2012). Some of the widely used oxidants in leaching are hydrogen peroxide, ferric sulphate, ferric chloride, etc. There are two main groups of metal-bearing ores: sulphide and oxide ores (Cao and Orrù, 2014).

Sulfide minerals are compounds in which sulphur is combined as an anion with a metal (or semimetal) cation or cations (Bowles *et al.*, 2011). Sulphide mineral ores are refractory and difficult to leach (Agacayak *et al.*, 2014; Chojnacka *et al.*, 2007) due to the strong sulfur binding to these

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minerals hence metals are usually extracted by chemical oxidation (Pedroza *et al.*, 2012). Several hundred sulfide minerals are known, but only five are sufficiently abundant accessory minerals to have been categorized as 'rock forming' (Bowles *et al.*, 2011). These five are pyrite, pyrrhotite, galena, sphalerite and chalcopyrite (Vaughan and Corkhill, 2017).

Chalcopyrite (CuFeS₂) is the most important commercial copper sulphide mineral and is the principal source of commercially produced copper (Agacayak *et al.*, 2014). It occurs in igneous and metamorphic rock and in metalliferous veins. Chalcopyrite is the most stable of the copper sulfide minerals because of its structural configuration (Baba *et al.*, 2012). Among the non-ferrous metals, copper is one of the most important metals used in the industry because of its electrical, thermal, optical and catalytic properties (Ekmekyapar *et al.*, 2015).

Sphalerite (ZnS) is the most important zinc sulphide minerals (Sokić *et al.*, 2012). Zinc sulfide is a predominant form of zinc in the earth crust (Guler, 2015). Zinc is one of the most important base metals in the galvanizing, cosmetic, die casting and manufacturing industries (Irannajad *et al.*, 2012). To by-pass the challenge of high energy cost associated with the roasting stage in the conventional RLE (roasting, leaching and electro-winning) method of zinc production, a number of researchers have been trying to develop alternative methods such as the direct leaching of sphalerite at the atmospheric pressure in the presence of oxidants (Hasani *et al.*, 2016).

Oxide minerals class comprises of those minerals in which the oxide anion (O^{2-}) is bonded to one or more metal ions. The hydroxide-bearing minerals are typically included in the oxide class. Within the oxide class are several minerals of great economic importance. These include the chief ores of iron, chromium, manganese, tin, and aluminium. Examples of oxide minerals include the cassiterite, hematite, ilmenite, columbite, zincite, etc. The selected mineral from this class, ilmenite or titanic iron ore (FeTiO₃), is widespread in igneous rocks as an accessory mineral, but is seldom concentrated or found in large crystals except in pegmatites and large bodies of plutonic rock. There are publications on leaching of titanium from ilmenite, however, very limited reports have been published on leaching of iron from ilmenite ore. Hence, there is a lack of information on leaching mechanism of iron from ilmenite ore in mineral acid. In recent times, response surface methodology (RSM), artificial neural networks (ANN) and more recently adaptive neuro fuzzy inference systems (ANFIS) are applied for modeling and optimization of various processes thus covering up for the lapses of OFAT. RSM is a collection of statistical techniques for designing experiments, building models, evaluating the effects of factors and searching for the optimum conditions (Kalil *et al.*, 2000). The most extensive application of RSM can be found in the industrial world in situations where a number of input variables affect some performance measures (responses), which are not easy or feasible to depict with a rigorous mathematical formulation (Fan *et al.*, 2017). The most popular and often used form of RSM is the central composite design (CCD) and it could be used in many fields of research for the optimization of different processes (Amin *et al.*, 2010).

Nowadays, ANFIS (a combination of fuzzy logic and neural network), developed by Jang, 1993, has also been employed as a modelling (Mehrabi and Pesteei, 2010) and predictive tool in a wide range of disciplines, including engineering. The main reason for using this technique is to accurately find relationships between the parameters of input and output even for nonlinear functions due to its ability to employ learning algorithms (Akbari *et al.*, 2018). A neuro-fuzzy system uses learning methods derived from artificial neural network in order to find the parameters of fuzzy system which includes appropriate membership functions and fuzzy rules. This combination creates an efficient approach for various modelling systems, so that each of these two methods may recover the weakness of another and increase the efficiency of the neuro-fuzzy system (Mehrabi and Pesteei, 2010). Although the technique has been employed in modeling various systems, its application to leaching processes is still very scarce.

This research intends to ascertain the effectiveness of non-conventional HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions as lixiviants in the recovery of copper, zinc and iron from uninvestigated chalcopyrite, sphalerite and ilmenite of Nigerian origin. The completion of this study will provide characterization, optimization, kinetics and thermodynamics data for the leaching systems.

1.2 Statement of the Problem

At the present, Nigeria's revenue is majorly dependent on crude oil thus a mono-economy nation. Before the discovery of the black gold in the 1970's, agriculture and mining were the major drivers of the economy. Owing to the adverse effect of dwindling oil price, there is a current drive to diversify the Nigerian economy. Government is therefore poised to strengthen investments in agriculture, power, solid minerals, manufacturing and service sectors. There is no gainsaying the fact that under the Nigerian soil are abundant untapped mineral resources. The Nigerian Extractive Industries and Transparency Initiative (NEITI) report reveals that there are about forty different kinds of solid minerals and precious metals buried in Nigerian soil waiting to be explored. Some are molydenite, chalcopyrite, galena, sphalerite, quatz, pyrite, ilmenite, etc.

Among the classification of mineral ores, leaching of valuable metals from sulphide ores is known to be difficult owing to their stable and recalcitrant nature. Myriad of deficiencies surrounding the conventional pyrometallurgical process such as high energy cost, shortage of high grade ores and emission of SO₂, an environmental pollutant have spurred research interest geared towards development of low temperature hydrometallurgical process for the extraction of base metals from sulphide mineral ores. The slow dissolution rate in extraction of base metals from sulphide ores usually attributed to passivation on the surface of the mineral ore during the hydrometallurgical process is still under investigation. For ores belonging to both the sulphide and oxide families, development of lixiviants for efficient leaching of some precious metals is a subject of research to date as researchers have not exhausted all possible formulations. HCl-KClO₃, HCl-KCl and HCl-NaNO₃ binary solution formulations have not been used in the recovery of copper, zinc and iron from chalcopyrite, sphalerite and ilmenite ores, therefore, the choice of the selected solutions for this current study.

1.3 Aim and Objectives

The aim of this research is to study the kinetics and optimization of chalcopyrite, sphalerite and ilmenite leaching in binary solutions. The objectives are:

- 1 To characterize the mineral ores using some instrumental techniques such as X-Ray fluorescence, X-ray diffraction and scanning electron microscopy techniques.
- 2 To investigate the influence of batch leaching process parameters, such as acid concentration, oxidant concentration, particle size, solution temperature, stirring speed, contact time and liquid-to-solid ratio on the percentage of copper, zinc and iron dissolved from chalcopyrite, sphalerite and ilmenite respectively.
- 3 To study the kinetics of leaching of copper, zinc and iron from chalcopyrite, sphalerite and ilmenite ores using various kinetic models such as shrinking core model's diffusion through the liquid film, diffusion through product layer, surface chemical reaction; mixed kinetic model, Jander (three-dimensional), Kröger and Ziegler, Zhuravlev, Lesokhin and Templeman, Ginstling-Brounshtein models.
- 4 To develop statistical models establishing relationship between the process variables and the response variable using response surface methodology (central composite design).
- 5 To predict and optimize the leaching processes using the RSM and adaptive neuro-fuzzy inference system (ANFIS)-particle swarm techniques.
- 6 To determine the thermodynamic leaching parameters such as ΔG , ΔH and ΔS .

1.4 Significance of the Study

Revitalization of Nigeria's mining industry is an issue of national interest. A research geared towards proffering solutions to the challenges militating the optimal productivity in the mining industry is immensely timely. The paradigm shift from pyrometallurgy to hydrometallurgy in leaching of valuable metals from refractory mineral ores will contribute in no small measure in ameliorating the level of pollutants in our environment. Results from credible researches show that life expectancy in Nigeria is low. Undoubtedly, pollution contributes in no small measure to this fact. The successful completion of this research will furnish kinetics, thermodynamic and optimization data for the leaching of copper, zinc and iron from Nigerian chalcopyrite, sphalerite and ilmenite mineral ores. Also, empirical equations relating the dependent and independent variables for the leaching process will be established.

1.5 Scope of the Study

This research is limited to leaching of copper, zinc and iron from Nigerian chalcopyrite, sphalerite and ilmenite, respectively using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions. The study covers kinetics, thermodynamics and optimization of the leaching process using RSM and ANFIS-PSO techniques.

CHAPTER TWO LITERATURE REVIEW

2.1 Mineral Ores

Minerals and metals are one of the essential components for the growth of human society. Needs of survival taught the prehistoric Paleolithic men the uses of stones as tools even before 20,000 years ago. The discovery of minerals, its exploitation and uses became many folds with the advent of civilization and is continuing till date (Haldar, 2013). The crust of the earth and underlying relatively rigid mantle make up the lithosphere. The crust is composed of a great variety of minerals and rocks. More than 80% of all raw materias that are used in various sectors of economy, society and the environment are of mineral origin, and demand for them is greater every day. In most countries, the values of raw materials used for the metal industry and building materials exceed the value of the funds allocated for oil and gas, although, we hear more about oil and gas (Halda and Tisljar, 2014).

A mineral is a naturally occurring crystalline, inorganic substance that has a specific chemical formula and a crystal structure. Mineral resources are essentially the accumulation of natural occurring materials or commodity found on or in the earth that can be extracted profitably (Lar, 2018), or with hope of profit. The latter part of the definition implies that what was not ore yesterday may become ore today as a result of the exhaustion of richer sources of a metal or the development of large scale and low-cost production methods (Dunham, 1981).

Hibashi (2017) also defined a mineral as a naturally occurring substance having a definite chemical composition, constant physical properties, and a characteristic crystalline form. Ores are a mixture of minerals: they are processed to yield an industrial mineral or treated chemically to yield a single or several metals. In order to exploit the different elements, it is best to produce the elements from places where different processes have led to their enrichment. In nature, such a place is called a mineral deposit or an ore deposit. An ore deposit usually includes naturally occurring materials which can be subjected to mining with economical profit. "Ore" is in the English language also used about such materials even if they cannot be exploited with a profit (Segalst, 1997).

A mineral reserve is the economically mineable part of a measured and/or indicated mineral resource. Measured mineral resource refers to part of a mineral resource for which quantity, grade or quality, densities, shape, and physical characteristics are estimated with confidence sufficient to allow the application of modifying factors to support detailed mine planning and final evaluation of the economic viability of the deposit (Ashanti, 2016). Most of the rock deposits contain metals or minerals. When the concentration of valuable minerals or metals is too low to justify for mining, it is considered to be a waste or gangue material. Within an ore body, the valuable minerals are surrounded by gangue minerals (Balasubramanian, 2015). Ore deposits are rarely comprised of 100% ore-bearing minerals, but usually associated with rock forming minerals (RFM) during mineralization process. These associated minerals or rocks, having no significant or least commercial value, are called "gangue" minerals (Haldar, 2013).

Ores undergo a beneficiation process by physical methods before being treated by chemical methods to recover the metals. Beneficiation processes involve liberation of minerals by crushing and grinding then separation of the individual mineral by physical methods (gravity, magnetic, etc.) or physicochemical methods (flotation). Chemical methods involve hydrometallurgical, pyrometallurgical, and electrochemical methods (Habashi, 2017). Minerals as integral part of the rocks are forming in different ways by complex processes such as: crystallization of magma (pyrogenesis), crystalization from gases and vapours (pneumatolysis), crystalization from the hot solution (hydrothermal), crystalization and deposition of minerals from aqueous solutions (hydatogenesis), vapourization of highly concentrated aqueous solutions due to the strong evaporation, dynamic metamorphism, contact metamorphism, life process of organisms (biochemical processes), etc (Halda and Tisljar, 2014).

2.1.1 Historical background of mineral ores

Mining may well have been the second of humankind's earliest endeavours— granted that agriculture was the first. The two industries ranked together as the primary or basic industries of early civilization. Little has changed in the importance of these industries since the beginning of civilization. If we consider fishing and lumbering as part of agriculture and oil and gas production as part of mining, then agriculture and mining continue to supply all the basic

resources used by modern civilization (Rodiwal, 2015). Table 2.1 shows the uses of mineral ores from prehistoric to modern age.

Need or Use	Purpose	Age
Tools and utensils	Food, shelter	Prehistoric
Weapons	Hunting, defense, warfare	Prehistoric
Ornaments and decoration	Jewelry, cosmetics, dye	Ancient
Currency	Monetary exchange	Early
Structures and devices	Shelter, transport	Early
Energy	Heat, power	Medieval
Machinery	Industry	Modern
Electronics	Computers, communications	Modern
Nuclear fission	Power, warfare	Modern

Table 2.1: Humans' Uses of Mineral ores

Source: Rodiwal (2015)

2.1.2 Classification of mineral ores

There are many schemes for classifying mineral ores. Some have an economic basis linked to the end use of the metal or mineral; others depend partly or entirely on geologic factors. Some scholars grouped ores based on the use of the mineral ores, type of the mineral ore, etc. These notwithstanding, mineral ores may be generally classified into two groups: metallic and non metallic.

1. Metallic minerals are the chief raw materials for the manufacture of metals. Metallic mineral ores, which include ferrous metals such as iron and its associates, manganese, molybdenum and tungsten, the non-ferrous metals such as lithium, bismuth, the base metals (copper, lead, zinc, and tin, nickel, chromium, arsenic, cadmium), the precious metals (gold, silver, tin, the platinum group metals) and the radioactive minerals such as uranium, thorium and radium. (Lar 2018, Habashi 2017, Rodiwal 2015).

 Non metallic minerals (industrial minerals) are so-called because they are not used for the manufacture of metals and also because of their lack of metallic lustre. They constitute about 75% of all the minerals. These minerals include construction materials such as stone aggregates, limestone, clay and many others (Lar 2018, Habashi 2017, Rodiwal 2015).

Classifications based on the type of mineral provide the basis for another system of classification as displayed in Table 2.2:

Classification	Minerals	
Sulfides and sulfosalts	Covellite - CuS, Chalcocite - Cu ₂ S, Chalcopyrite - CuFeS ₂ ,	
	Bornite - Cu ₈ FeS ₄ , Tetrahedrite - (Cu, Ag) ₁₂ Sb ₄ S ₁₃ , Galena -	
	PbS, Sphalerite - (Zn, Fe)S, Cinnabar – HgS, Cobaltite - (Co,	
	Fe)AsS, Molybdenite - MoS ₂ , Pentlandite - (Fe, Ni) ₉ S ₈ , Millerite	
	– NiS, Realgar – AsS, Stibnite - Sb ₂ S ₃ , Sperrylite - PtAs ₂ ,	
	Laurite - RuS ₂	
Oxides and hydroxides	Bauxite Gibbsite - $Al(OH)_3$, Boehmite - (γ -AlO(OH)), Diaspore	
	- (α -AlO(OH)), Cassiterite -SnO ₂ , Cuprite - Cu ₂ O, Chromite -	
	(Fe, Mg)Cr ₂ O ₄ , Columbite - Tantalite or coltan (Fe, Mn)(Nb,	
	Ta) ₂ O ₆ , Hematite - Fe ₂ O ₃ , Ilmenite - FeTiO ₃ , Magnetite - Fe ₃ O ₄ ,	
	Pyrolusite - MnO_2 , Rutile -TiO ₂ , Uraninite (pitchblende) - UO ₂	
Oxysalts	Calcite - CaCO ₃ , Rhodochrosite - MnCO ₃ , Smithsonite - ZnCO ₃ ,	
	Malachite - Cu ₂ CO ₃ (OH) ₂ , Barite - BaSO ₄ , Gypsum -	
	CaSO ₄ .2H ₂ O, Scheelite - CaWO ₄ , Wolframite - (Fe, Mn)WO ₄ ,	
	Apatite - Ca ₈ (PO ₄) ₃ (F,Cl, OH)	
Halides	Halite – NaCl, Sylvite – KCl, Fluorite - CaF ₂	
Metals and native elements	Gold Au, Silver - Ag, Platinum-group metals - Pt, Pd, Ru,	
	Copper – Cu, Carbon - C (diamond, graphite)	
Silicates	Beryl - Be ₃ Al ₂ (SiO ₃) ₆ , Garnet - Silicate of Al, Mg, Fe,	
	Garnierite - Mixture of the Ni-Mg-hydrosilicates, Kaolinite -	

Table 2.2: Mineral ore classification based on type of mineral

Source: Arndt et al. (2015)

2.1.3 Selected minerals under study

The current study investigated chalcopyrite, sphalerite and ilmenite.

2.1.3.1 Chalcopyrite

Chalcopyrite (CuFeS₂) is the most abundant copper mineral, comprising roughly 70% of the world reserves, therefore its relevance to the copper industry is evident (Veloso *et al.*, 2016). Table 2.3 presents the elemental composition of select chalcopyrite samples from different parts of the globe. It is a brassy to golden yellow colour mineral and was first discovered in Polk country in 1847. Chalcopyrite occurs in igneous and metamorphic rock and in metalliferous veins. It is not only the most abundant copper sulfides, but also the most stable minerals because of its structural configuration (Baba *et al.*, 2012). Figures 2.1 and 2.2 show the unit cell structure of chalcopyrite and the physical appearance of chalcopyrite ore.



Plate 2.1: Unit cell of chalcopyrite
A structure. Atoms are represented by circles as follows: dark grey (copper), light grey

- e (iron), white (sulfur).
- F Source: Khoshkhoo (2016)



Plate 2.2: Physical appearance of chalcopyrite ore. Source: ScienceMall (2019)

copper extraction as compared to pyrometallurgical processes (Qian *et al.*, 2014). Hydrometallurgical methods can treat low grade complex ores at comparatively lower cost, and therefore, are gaining importance over the years. Hydrometallurgical methods also offer other
potential advantages, such as that the final product is electrolytic copper and the size of leaching residue is smaller comparing that produced by pyrometallurgy, which is easier for further treatment (Xian *et al.*, 2012; Yoo *et al.*, 2010). However, chalcopyrite is refractory with regards to hydrometallurgical processing (Veloso *et al.*, 2016).

According to several investigations, the chalcopyrite leaching rates are generally slow during leaching, which may be caused by passivation formed on the chalcopyrite surface attributed to three 'sulfur-containing' compounds (a layer of elemental sulphur, ferric hydroxysulfates or polysulfides) (Shiers *et al.*, 2016; Xian *et al.*, 2012). This limitation of the poor dissolution kinetics of chalcopyrite drives the search for innovative ways to increase dissolution kinetics using different oxidants (Shiers *et al.*, 2016; Agacayak *et al.*, 2014), or with the help of bacteria from the genus *Acidithiobacillus* (formerly *Thiobacillus*), which are isolated from mine water (Bogdanovic *et al.*, 2016). Many oxidants have been applied to the leaching of chalcopyrite, including hypochlorite, nitrate, oxygen, ferric ion and cupric ion and dichromate ion. (Agacayak *et al.*, 2014).

In conventional technology, copper is recovered from chalcopyrite concentrates (Agacayak *et al.*, 2014). Copper is one of the "base metals", a term that refers to a group of common metals, dominated by the transition elements, which are widely used in industry (Arndt *et al.*, 2015). Copper (atomic number 29) is one of the first metals used by humans for items such as coins and ornaments at least 10 000 years ago in western Asia. Since the prehistoric chalcolithic period and bronze age, copper has been prominent in the development of human civilization (Khoshkhoo, 2016). The elemental composition chalcopyrite collected from different parts of the world is presented in Table 2.3. Copper is characterized by high ductility, and electrical and thermal conductivity. Unlike metals with incomplete d-shells, metallic bonds in copper are lacking a covalent character and are relatively weak. This observation explains the low hardness and high ductility of single crystals of copper (Trigg and Immergut, 1992). The softness of copper partly explains its high electrical conductivity (59.6×10⁶ S/m) and high thermal conductivity, second highest (second only to silver) among pure metals at room temperature (Hammond, 2004). This is because the resistivity to electron transport in metals at room temperature

originates primarily from scattering of electrons on thermal vibrations of the lattice, which are relatively weak in a soft metal (Trigg and Immergut, 1992).

Major elemental composition (%)										Ref
Cu	Fe	S	Pb	Mg	Al	Zn	Κ	As	_	
32.5	29.3	34.1	0.30	0.01	0.04	0.50	0.02	0.06	Sonora,	Qian et
									Mexico	al., 2014
27.2	27.2	NA	2.6	NA	NA	3.8	NA	NA	Sivas,	Aydogan
									Turkey	et al.,
										2006
30.2	28.7	25.1	NA	0.51	0.65	NA	0.099	NA	Australia	Shier ser
										al., 2016
23.52	23.17	27.27	1.13	NA	NA	1.01	NA	NA	Sivas,	Agacayak
									Turkey	et al.,
										2013
33.25	31.06	34.11	NA	NA	NA	NA	NA	NA	Chile	Xian <i>et</i>
										al., 2012

Table 2.3: Elemental composition of chalcopyrite from different parts of the world

NA - Not Analyzed

2.1.3.2 Sphalerite

Zinc sulfide is a predominant form of zinc in the earth crust and sphalerite (ZnS) is the most important mineral among them (Guler, 2015). The elemental composition of sphalerite from different parts of the world (Table 2.4) buttresses Guler's stance. The name sphalerite is from the Greek word "sphaleros" which means deceiving or treacherous. This name is in response to the many different appearances of sphalerite and because it can be challenging to identify in hand specimens. Names for sphalerite used in the past or by miners include "zinc blende," "blackjack," "steel jack," and "rosin jack." The appearance and properties of sphalerite are variable. It occurs in a variety of colours, and its luster ranges from nonmetallic to submetallic and resinous to adamantine (King, 2018).

It is commonly associated with other sulphide minerals, such as chalcopyrite, galena and pyrite, in disseminated form with complex mineralogical composition and fine-grained structures (Sokić *et al.*, 2012). It is found in metamorphic, igneous, and sedimentary rocks in many parts of the



Plate 2.3: Unit cell of sphalerite structure. Atoms are represented by circles as follows: brown (zinc), purple (sulfur). Source: King (2018a)



Plate 2.4: Physical appearance of sphalerite ore Source: Mele (2018)

Both pyrometallurgical and hydrometallurgical processes are applied for processing zinc sulphide ores and concentrates (Sokić *et al.*, 2012). A variety of problems such as high energy cost, shortage of high grade ores, processing of lean and complex ores and exploitation of smaller deposits have prompted the development of low temperature hydrometallurgical processes for the extraction of base metals from their sulphide ores and concentrates (Adebayo *et al.*, 2012). Many processes have been developed over decades and at present, nearly 80–85% of total zinc production is carried out by hydrometallurgical processes (Guler, 2015).

Zinc is the fourth most widely used metal after iron, aluminium, and copper with an annual production of about 13 million tones (Tolcin, 2015). Zinc is used as corrosion-protection coatings on steel (galvanized metal), as diecastings, as an alloying metal with copper to make brass, and as chemical compounds in rubber, ceramics, paints, and agriculture. It is also an essential element for proper growth and development of humans, animals, and plants (Adebayo *et al.*, 2012; Emsley, 2011). The elemental composition of sphalerite is shown in Table 2.4.

Major elemental composition (%)										Ref
Zn	Fe	S	Pb	Cu	Ca	Ag	Mn	Sb	-	
42.71	11.21	34.26	2.39	0.18	0.18	NA	0.10	NA	Western,	Guler,
									Turkey	2015
16.40	7.12	29.20	0.78	NA	NA	NA	NA	NA	Ebonyi,	Adebayo
									Nigeria	et al.,
										2006
32.70	21.00	27.20	1.19	0.67	NA	NA	NA	NA	Namibia	Merwe,
										2003
58.73	1.94	18.58	0.49	NA	NA	NA	NA	NA	Isfahan,	Hasani
									Iran	et al.,
										2015
50.00	7.00	31.00	3.00	0.80	0.02	0.01	NA	0.14	India	Peng et
										al., 2005

Table 2.4: Elemental composition of sphalerite from different parts of the world

NA - Not Analyzed

2.1.3.3 Ilmenite

Ilmenite is a common accessory mineral in igneous rocks, sediments, and sedimentary rocks in many parts of the world. Ilmenite is a black iron-titanium oxide with a chemical composition of FeTiO₃ (King, 2018). It is a weakly magnetic black or steel-gray solid. From a commercial perspective, ilmenite is the most important ore of titanium (Sibum *et al.*, 2005), a metal needed to make a variety of high-performance alloys. Most of the ilmenite mined worldwide is used to manufacture titanium dioxide, TiO_2 , an important pigment, whiting, and polishing abrasive (King, 2018). Ilmenite occurs associated with cassiterite, columbite, tantalite, wolframite, zircon and monazite in the younger granites of Northern Nigeria. The ilmenite is mined principally from the alluvial deposits derived from these granites. More than 90% of the ilmenite produced in Nigeria is mined in the Jos Plateau and in outlying younger granite masses in Bauchi, Zaria, Kano and Benue zones (Olanipekun, 1999).

Ilmenite is a minor ore of iron as the magnetite and ilmenite are processed for their iron contents (Samal, 2017). Raw ilmenite is refined by decreasing the iron content (Baba *et al.*, 2012). Ilmenite, by virtue of being rich in iron, often presents a big difficulty in the production of TiO_2 pigment. Because of the growing scarcity of the world's natural rutile resources, many studies

are being focused on the beneficiation of ilmenite into synthetic rutile (Yuanboa *et al.*, 2010). Table 2.5 shows that titanium and iron are the dominant metals present in ilmenite ore sourced from various parts of the world. This present research on ilmenite seeks to propose a veritable condition for the leaching of iron from ilmenite ore and also suggest ilmenite as an alternative source of iron.



Plate 2.5: Unit cell of Ilmenite structure. Source: Wilson *et al.*, (2005)



Plate 2.6: Physical appearance of ilmenite ore. King (2018b)

Plates 2.5 and 2.6 represent unit cell and physical appearance of ilmenite ore respectively. In ilmenite, there are two types of metal ions, which form alternating bilayers of Fe and Ti ions perpendicular to the c axis. The Fe and Ti ions are octahedrally coordinated to O ions with three octahedral edges shared between cation octahedra of the same type (Wilson *et al.*, 2005).

Major elemental composition (%)										Ref
Ti	Fe	Si	Mn	Mg	Pb	S	Cu	Ca	-	
30.1	30.0	0.22	0.60	1.29	NA	NA	NA	NA	Australia	Das <i>et</i>
										al., 2013
33.1	29.1	0.26	1.06	0.12	NA	NA	NA	NA	Australia	Das <i>et</i>
										al., 2013
42.06	27.43	11.24	0.079	0.035	0.14	3.14	2.79	0.86	Kwara,	Baba et
									Nigeria	al., 2011

Table 2.5: Elemental composition of ilmenite from different parts of the world

50.21	48.84	0.43	0.82	0.48	NA	NA	NA	0.06	China	Wang et
										al., 2011
44.50	46.10	2.57	0.83	3.76	NA	NA	NA	0.61	Sichuan,	Li et al.,
									China	2008

NA - Not Analyzed

2.2 Characterization Techniques of Mineral Ores

The identification and characterization of ores and the minerals that make up those ores is of fundamental importance in the development and operation of mining and mineral-processing operations (Fennel et al., 2018). The characterization of minerals in terms of their size, habit, chemical composition, morphology, texture, association with other minerals and other physical attributes is important in studies of mineral deposits of all types (Cook, 2000). The characterization of solid is most important since the process selection is closely linked to the nature of minerals/ores resulting from geological formation. The mineralogical characterisation may involve identification of minerals (crystal structure and chemistry), minerals fabric/association of minerals, quantification of phases, elemental associations and, occurrence of minor/trace minerals/elements (Kumar, 2017). The growing need for detailed information about the mineralogical composition of a mineral deposit determines that mineral characterization studies form an integral and often critical part of investigations of deposits (Cook, 2000). X-ray diffraction (XRD), x-ray fluorescence (XRF), scanning electron microscopy (SEM), fourier transform infrared (FTIR), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), etc are some of the techniques employed for characterization of mineral ores. A brief overview of the characterization methods employed in this research is described below.

2.2.1 XRD

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. X-ray diffractometers consist of three basic elements: an x-ray tube, a sample holder, and an x-ray detector (Dutrow and Clark, 2018). X-ray diffraction (XRD) analysis is a mineralogical identification method that permits semi- to full-quantitative assessment of the minerals present in a given sample and in what relative proportions they occur. The sample may be a pulverised bulk

sample, a processing product or a pure, separated mineral fraction. The method is especially suitable for the study of material containing significant small-scale variation in mineralogy (e.g., carbonates), or in mineral chemistry of component minerals or an exceptionally coarse-grained sample, inhibiting the reliability of image analysis studies of thin-sections. The XRD method has its advantage in being a rapid technique involving only minimal sample preparation and is therefore a convenient starting point in mineral characterization procedures. It may be used to complement microscopic study of thin-sections and may be followed up by other supplementary techniques where more information is required (Cook, 2000).

2.2.2 XRF

An x-ray fluorescence (XRF) spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. It works on wavelength-dispersive spectroscopic principles that are similar to an electron probe microanalyzer (EPMA). However, an XRF cannot generally make analyses at the small spot sizes typical of EPMA work (2-5 microns), so it is typically used for bulk analyses of larger fractions of geological materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) x-ray emitted from a sample when it is excited by a primary x-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent x-rays ("a fingerprint") that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition.

X-Ray fluorescence is used in a wide range of applications, including research in igneous, sedimentary, and metamorphic petrology, soil surveys, mining (e.g., measuring the grade of ore), cement production, ceramic and glass manufacturing, metallurgy (e.g., quality control), etc. The relative ease and low cost of sample preparation, and the stability and ease of use of x-ray spectrometers make XRF one of the most widely used methods for analysis of major and trace elements in rocks, minerals, and sediment (Wirth and Barth, 2018).

2.2.3 SEM

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive

from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD) (Swapp, 2018).

2.2.4 EDX

Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample (Goldstein, 2003). It is often an attachment to scanning electron microscopy instruments. Typically scanning electron microscopy provides the visual analysis and energy dispersive x-ray provides the elemental analysis (Gossman Forensics, 2019). It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum. EDS can be used to determine which chemical elements are present in a sample, and can be used to estimate their relative abundance (Goldstein, 2003).

2.3 Mineral Ore Deposit

Mineral deposits refer to a place where a few elements of interest have been concentrated by nature above the average crustal geochemical abundance for commercial exploitation. They can be classified into metallic mineral deposits, nonmetallic (or industrial) deposits, and building or ornamental stones (Boni, 2005).

In order for a mineral crystal to grow, the elements needed to make it must be present in the appropriate proportions, the physical and chemical conditions must be favourable, and there must be sufficient time for the atoms to become arranged. Physical and chemical conditions include factors such as temperature, pressure, presence of water, pH, and amount of oxygen available. Time is one of the most important factors because it takes time for atoms to become ordered. If time is limited, the mineral grains will remain very small. The presence of water enhances the mobility of ions and can lead to the formation of larger crystals over shorter time periods.

Most of the minerals that make up the rocks around us formed through the cooling of molten rock, known as magma. At the high temperatures that exist deep within earth, some geological materials are liquid. As magma rises up through the crust, either by volcanic eruption or by more gradual processes, it cools and minerals crystallize. If the cooling process is rapid (minutes, hours, days, or years), the components of the minerals will not have time to become ordered and only small crystals can form before the rock becomes solid. The resulting rock will be fine-grained (i.e., crystals less than 1 mm). If the cooling is slow (from decades to millions of years), the degree of ordering will be higher and relatively large crystals will form. In some cases, the cooling will be so fast (seconds) that the texture will be glassy, which means that no crystals at all form. Minerals can also form in several other ways:

- Precipitation from aqueous solution (i.e., from hot water flowing underground, from evaporation of a lake or inland sea, or in some cases, directly from seawater).
- Precipitation from gaseous emanations.
- Metamorphism: formation of new minerals directly from the elements within existing minerals under conditions of elevated temperature and pressure.
- Weathering: during which minerals unstable at earth's surface may be altered to other minerals.
- Organic formation: formation of minerals within shells (primarily calcite) and teeth and bones (primarily apatite) by organisms (these organically formed minerals are still called minerals because they can also form inorganically) (Earle, 2018).

2.3.1 Mineral ore deposits in Nigeria

Nigeria lies approximately between latitudes 4°N and 15°N and Longitudes 3°E and 14°E, within the Pan African mobile belt in between the West African and Congo cratons (Lar, 2018). Nigeria is enriched with abundant minerals resources. However, less than 5% of these minerals are currently being mined, processed and marketed. These include coal, kaolin, barite, limestone, dolomite, gypsum, feldspar, gold, iron ore, lead-zinc, tin, niobium and tantalum ores. The remaining 95% mineral ores, though in demand are untapped (Lar, 2018). Today, the mining sector accounts for 0.3% of national employment, 0.02% of exports and about USD1.40billion to the Nigerian GDP. As part of the strategies to reform the sector, the ministry has identified seven (7) strategic minerals, namely, coal, bitumen, limestone, iron ore, barites, gold and lead/ zinc for priority development (FGN, 2016). Table 2.6 is a tabulation of Nigerian mineral resources and locations.

Table 2.6: Nigerian mineral re	esources and	their locations
--------------------------------	--------------	-----------------

S/No.	States	Potential minerals in commercial quantities per state
1	Abia	Glass sand limestone, salt shale, ball day, granite galena, marble laterite,
		bentonite, phosphate, kaolin, pyrite, feldspar, petroleum, lignite, gypsum,
		sphalerite, clay
2	Adamawa	Feldspars, fluorspar, marble, gypsum, magnesite, tantalite, rock crystal,
		laterites, topas, sandstones, mercury, glass sand, zircon, spinel, emerald,
		graphite, beryil, tourmaline, mica, iron ore, clay minerals, diatomite, coal,
		garnet, aquamarine, gold dust, zoisite, cassaterine, agates, amethyst
		chalcopyrite, kaolin, limestone, chalcedony, onyx, barytes, zinc, tin,
		uranium, quartz, mica, wolframite, columbite, platinum, ruby
3	Akwa	Clay, glass sand, salt, silica, granite, coal, petroleum, natural gas, kaolin,
	Ibom	limestone, lignite
4	Anambra	Clay, iron stone, natural gas, petroleum, sand stone, kaolin, pytrite, lignite
5	Bauchi	Kaolin, trona, gypsum, cassiterite, mica, clay, tantalite, galena, iron ore,
		gemstone, sphalerite, silica sand, barite, columbite, zinc, lead, muscovite,
		quartz, tin, glass sand, monazite, feldspar, graphite, wolfram, coal, agate,
		rutile, tungsten, copper, talc, limonite, ziron
6	Beyelsa	Salt, petroleum, natural gas, silica sand, bentonite, petroleum, limestone,
		glass sand
7	Benue	Gemstone, barites, feldspar, marble, mica, quartz, galena, lead, zinc ore,
		silica sand, clay, crushed and dimension stone, fluorspar, wolframite,
		bauxite, shale, magnesite, illmenite

8	Borno	Silica sand, natural gas, sapphire, topaz, mica, quartz, gypsum, uranium, iron
		ore, megnesite, feldspar, granite, aquamarine, nepheline, limestone, kaolin,
		bentonite, laterite, refractory clay, trona, gold, tin, potash
9	Cross	Salt limestone, coal, magenese, mica, limenite, gold, quartz, glass sand,
	Rivers	tourmaline, petroleum, natural gas, kaolin, tin ore, sharp sand, spring water,
		salt deposite, talc, granite, galena, lead, zinc, tin ore, muscovite, uranium,
		barite
10	Delta	Kaolin, lateritic clay, gravel, silica sand, natural gas, petroleum, ball clay,
		bauxite, granite, river sand, clay, spring water
11	Ebonyi	Lead, zinc ore, salt, limestone, ball clay, refractory clay, gypsum, granite
12	Edo	Charonokite, copper, gold, marble, granite, gypsum, petroleum, dorite,
		lignite, limestone, ceramic clay
13	Ekiti	Clay, chamokite, quartz, lignite, limestone, granite, gemstone, bauxite,
		cassiterite, clumbite, tantalite, feldspar, kaolin
14	Enugu	Leterite clay, crude oil, kaolinitic clay, iron ore, glass sand, petroleum,
		gypsum, coal, silica sand, ceramics
15	Gombe	Graphite, kaolin, limestone, silica sand, uranium, coal, halites, clay, gypsum,
	_	diatomite, granite
16	Imo	Crude oil, shale, natural gas, kaolin, laterite sand, limestone, salt, marble
17	Jigawa	Glass sand, granite, laterite clay, silica, kaolin, iron ore, quartz, potash, talc,
10	T T 1	illmenite, gemstone, columbite
18	Kaduna	Muscovite, granite, gold, manganese, clay, graphite, sand, zircon, kyanite,
10	17	tin ore, illmenite, gemstone, columbite
19	Kano	Clay, laterite, cassitertrite, columbite, illmenite, galena, phyrochlorite,
		kaonne, gemstone, sinca, un ore, monazite, wonramite, thorium, granite,
20	Voteino	Gold manganasa lateritia alay faldanar black tourmaling amothyst
20	Katsilla	Gold, manganese, lateritic, clay, leidspai, black tourmanne, ametryst,
		asbestos tourmalin chromites illmenite diamond graphite iron ore
		notash silica sand
21	Kebbi	Salt iron ore gold feldspar limestone quartz bauxitic clay manganese.
		kaolin. mica
22	Kogi	Clay, iron ore, gemstone, marble, limestone, feldspar, dolomite, phosphate,
	C	mica, cassiterite, granite, ornamental stone, coal, kwara, clay, kaolin, silica
		sand, quartz, dolomite, marble, feldspar, gold, tantalite, cassiterite, granite,
		limestone
23	Lagos	Silica sand, bitumen, sharp sand, gravel, petroleum, laterite
24	Nassarawa	Cassiterite, gemstone, amethyst, beryl, chrysolite, emerald, gamet, sapphire,
		topaz, barites, galena, monazite, zicron, glass sand, coal
25	Niger	Bell clay, kaolin, limestone, granite, glass sand iron ore, red clay, feldspar,

silica sand, quartz, asbestos, marble, talc, gemstone, gold, manganese and tantalite

26	Ogun	Kaolin, feldspar, silica sand, mica, granite, clay, phosphate, gypsum,
	<u> </u>	innestone, quartz, tar sand
27	Ondo	Marble, gold, gemstone, diorite, lignite
28	Osun	Clay, granite, talc, dolomite, feldspar, quartz, limestone, mica, gold
29	Oyo	Clay, feldspar, granite, limonite, iron ore, kaolin, quartz, talc, marble,
		dolomite, tourmaline, aquamarine, amethyst, gemstone
30	Plateau	Monazite, columbite, feldspar, clay, cassisterite, gemstone, kaolin, dolomite,
		mica, zicron, marble, limonite, barite, quartz, talc, galena
31	Rivers	Petroleum, natural gas, silica sand, glass sand, clay
32	Sokoto	Silica sand, clay, salt, limestone, phosphate, gypsum, kaolin, latente, potash,
		granite
33	Taraba	Fluorspar, gamet, tourmaline, sapphire, zicron, tantalite, columbite,
		cassiterite, barite, galena, limestone, latente, calcite, bentonic clay,
34	Yobe	Salt, trona, diatomite, clay, gypsum, kaolin, silica sand, limestone, epsomite,
		iron ore, shale uranium, granite, bentonic clay,
35	Zamfara	Gold, alluvia gold, granite, chromites, chamorckite, clay, feldspar, spring
		water
36	FCT	Limestone, kaolin, granite, feldspar, mica, dolomite clay, sand, talc, lead,
		zinc and gold

Source: Investment Promotion Brochure August 2016

2.4 Hydrometallurgy

Hydrometallurgy is a method for obtaining metals from their ores. It is a technique within the field of extractive metallurgy involving the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials (Hiskey, 2000; Habashi, 2009). This plays an integral role in the multi-billion dollar minerals processing industry (Bhargava *et al.*, 2016). The hydrometallurgical route for the recovery of a metal, where dissolution (leaching), separation, concentration and metal recovery is carried out at near ambient temperature, is becoming more competitive with the conventional high temperature processes (pyrometallurgy) used in the smelting of metals. The more general characteristics of hydrometallurgy, which differ from pyrometallurgy are parameters such as low operating temperatures, more environmental friendly, larger plant size for a given throughput of material, low unit costs and selective chemical reactions (Smith, 2018).

Hydrometallurgy is typically divided into three general areas: leaching, solution concentration and purification and metal recovery. The most important operation in hydrometallurgy is leaching of properly prepared raw material (Ochromowicz and Chmielewski, 2011). After leaching, some of the techniques that may be applied in concentrating the metal ions in the leachate include: precipitation, cementation, solvent extraction, ion exchange, electrowinning, etc.

2.4.1 Leaching

The encyclopedia of science and technology describes "leaching" as the removal of a soluble fraction, in the form of a solution, from an insoluble permeable solid with which it is associated. In this sense, leaching is a macroscopic process in which the mass of a substance passes through boundaries of the permeable solid in question (Van der Sloot *et al.*, 2009). Leaching is concerned with the extraction of a soluble constituent from a solid by means of a solvent. The process may be used either for the production of a concentrated solution of a valuable solid material, or in order to remove an insoluble solid, such as a pigment, from a soluble material with which it is contaminated (Richardson, 2002). Describing leaching by a very simple equation:

material (leachee) + leachant
$$\rightarrow$$
 leachate (2.1)

Leaching from a porous material is an integrated process of mass transport due to gradients in concentration, chemical potential or pressures, combined with all chemical interactions between the solid phase and the pore solution. The release from the solid into the pore water, at every point in time and space, is controlled by a complex set of interactions which include: dissolution-precipitation, adsorption-desorption, cation exchange, incorporation into solid solutions, and complexation within the aqueous phase (Van der Sloot *et al.*, 2009).

Leaching involves the use of aqueous solutions to extract metal from metal bearing materials which is brought into contact with a material containing a valuable metal (Um, 2017). The most efficient leaching agents are acids, due to their ability to leach both base and precious metals (Kaŵberović *et al.*, 2018). In recent times researchers have used sulfuric, nitric, hydrochloric acids, etc, as leaching agents. In addition to inorganic acids, organic acids have also been

employed as leaching reagents (Deng *et al.*, 2015). Leaching is generally carried out by adding an effective oxidant to an acid solution (Xian *et al.*, 2012).

There are two key types of chemical reactions: oxidation and reduction. Oxidation does not necessarily have anything to do with oxygen. Oxidation occurs when an atom, molecule, or ion loses one or more electrons in a chemical reaction. When oxidation occurs, the oxidation state of the chemical species (an atom, molecule, or ion) increases. The opposite process is called reduction, which occurs when there is a gain of electrons or the oxidation state of an atom, molecule, or ion decreases (Helmenstine, 2018). An oxidizer, also known as an oxidant or oxidizing agent, is a reactant that removes electrons from other reactants during a redox reaction. It may also be considered to be a chemical species that transfers electronegative atoms to a substrate. The oxidizing agent typically takes these electrons for itself, thus gaining electrons and being reduced. An oxidizing agent is thus an electron acceptor (Smith and Jerry, 2007).

Oxidants facilitates the leach process by acting as the electron carrier during oxidation (Venter and Boylett, 2009). From the redox point of view, the selection of oxidants for sulfide ores is based on the standard electrode potential. An oxidizing agent will be effective if its standard electrode potential is higher than that of sulfur (Tian *et al.*, 2017). Watling (2013) hinted that ferric ion is commonly employed oxidant in hydrometallurgical process for oxidation of sulfide ores. However, the oxidizing potential of ferric ion is not particularly high consequently several stronger oxidants have been tested. The development of processes using inorganic acid as lixiviant and oxidants other than ferric ions is an interesting research area. The alternative oxidants selected for this study are stronger oxidizing agents than ferric ions. Li *et al* (2010) reported that a high solution redox potential would result in an increased leach rate. Table 2.7 presents the standard electrode potential values of the selected oxidants and sulfur. The oxidants selected for this study are readily commercially available. They include:

- a. Chlorate based KClO₃
- b. Chloride based KCl
- c. Nitrate based NaNO₃

Oxidant	Oxidation-reduction reaction	Standard reduction	Ref.
		potential ($E^{\Theta}V$)	
Sulfur	$S^{2-} - 2e^- \leftrightarrow S$	0.480	Tian <i>et al.</i> , 2017
Ferric ion	$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	0.771	Watling, 2013
Nitrate	$NO_3^- + 2H^+ + e^- \leftrightarrow NO_2 + H_2O$	0.800	Tian et al., 2017
Chlorate	$\text{ClO}_3^- + \ \text{6H}^+ + \ \text{5e}^- \ \rightarrow \ \text{3H}_2\text{O} + \ \text{0.5Cl}_2$	1.458	Harris, 2007
	$ClO_3^- + 6H^+ + 6e^- \rightarrow 3H_2O + Cl^-$	1.451	Shierset al., 2016
Chloride	$Cl_2(aq) + 2e^- \rightarrow 2Cl^{-1}$	1.396	Harris, 2007

Table 2.7: Standard reduction potential for ferric ion and chlorate

Sulphide ores are oxidized to elemental sulphur (S°) and eventually to sulphates $(SO_4^{2^-})$, polysulphides $(S_n^{2^-})$, etc depending on the redox potential of the oxidant (Adebayo *et al*, 2006, Li *et al*, 2010). The leaching of a sulphide concentrate in an acidic solution in the presence potassium chlorate, potassium chloride and sodium nitrate can be expressed as:

$$3MeS + 2ClO_3^- + 12H^+ \leftrightarrow 3Me^{2+} + (3S^{\circ} \text{ or } 3S_n^{2-} \text{ or } SO_4^{2-}) + Cl_2 + 6H_2O$$
(2.2)

$$3MeS + 2Cl^{-} + 2H^{+} \leftrightarrow 3Me^{2+} + (3S^{\circ} \text{ or } 3S_{n}^{2-} \text{ or } SO_{4}^{2-}) + Cl_{2} + H_{2}$$
(2.3)

$$3MeS + 2Cl^{-} + 6H^{+}$$

$$\leftrightarrow 3Me^{2+} + Cl_{2} + 3H_{2}S \qquad (2.4)$$

$$3MeS + 2NO_{3}^{-} + 8H^{+} \leftrightarrow 3Me^{2+} + (3S^{\circ} \text{ or } 3S_{n}^{2-} \text{ or } SO_{4}^{2-}) + 2NO + 4H_{2}O$$
(2.5)

Me: Divalent metal ions: Zn, Cu, Fe

2.4.1.1 Leaching process variables

Efficient and effective leaching of mineral ores basically requires a strict consideration of the enlisted important parameters below:

- (a) Particle size: Particle size influences the extraction rate in a number of ways. The ore or concentrate particles must be small enough for the valuable metals they contain to be exposed physically to the leach solution (Smith, 2018). The smaller the size, the greater is the interfacial area between the solid and liquid, and therefore the higher is the rate of transfer of material and the smaller is the distance the solute must diffuse within the solid as already indicated. On the other hand, the surface may not be so effectively used with a very fine material if circulation of the liquid is impeded, and separation of the particles from the liquid and drainage of the solid residue are made more difficult. It is generally desirable that the range of particle size should be small so that each particle requires approximately the same time for extraction and, in particular, the production of a large amount of fine material should be avoided as this may wedge in the interstices of the larger particles and impede the flow of the solvent.
- (b) Solvent: The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low for it to circulate freely. Generally, a relatively pure solvent will be used initially, although as the extraction proceeds the concentration of solute will increase and the rate of extraction will progressively decrease, first because the concentration gradient will be reduced, and secondly because the solution will generally become more viscous (Richardson *et al.*, 2002). Other criteria that are likely to be considered on solvent selection include:

(i) Solubility of the specific substances in the solvent: For example, vegetable oils consisting of triglycerides of fatty acids are normally extracted with hexane, whereas for free fatty acids extraction, more polar alcohols are used.

(ii) Physical properties such as low interfacial tension and viscosity: The solvent should be capable of wetting the solids and penetrating through pores and capillaries in the matrix. Also, its low viscosity assists diffusion rates in the solvent phase.

(iii) Recovery: The capacity of the solvent to be reused in subsequent subsequent extractions should be considered. If distillation or evaporation is used, the solvent should not form azeotropes and the latent heat of vaporization should be small.

(iv) Hazards and cost: Ideally the solvent should be nontoxic, nonhazardous, nonreactive, nonflammable, harmless to the environment, and cheap. Avoidance of solvent losses may be obtainable through a better process design (Varzakas and Tzia, 2015).

- (c) Temperature: In most cases, the solubility of the material which is being extracted will increase with temperature to give a higher rate of extraction. Further, the diffusion coefficient will be expected to increase with rise in temperature and this will also improve the rate of extraction. In some cases, the upper limit of temperature is determined by secondary considerations, such as, for example, the necessity to avoid enzyme action during the extraction of sugar.
- (d) Agitation of the fluid: Agitation of the solvent is important because this increases the eddy diffusion and therefore the transfer of material from the surface of the particles to the bulk of the solution, as discussed in the following section. Further, agitation of suspensions of fine particles prevents sedimentation and more effective use is made of the interfacial surface (Richardson *et al.*, 2002).
- (e) Pulp density: The rate of leaching increases with decreasing pulp density. In the case of high pulp densities, low quantities of solution and high concentrations exist, this will cause the equilibrium to shift and reaction rates will decrease (Smith, 2018).

2.4.2 Leaching kinetics

The kinetics of leaching process is very important for process design, optimization and control. A careful kinetic study concerning the controlling reaction step(s), the factors kinetically influencing the metal extraction yield and the estimation of the modeling parameters is particularly important for an efficient design process of hydrometallurgical operations (Veglio *et* *al.*, 2001). The kinetics of dissolution of sulphide minerals in chloride media has received considerable attention recently. There are several justifications for this interest; among them is the availability of materials for construction with improved resistance to chloride attack. Most importantly, however, is the substantially faster dissolution rate exhibited by sulphides in chloride media, as well as the potential application of such electrolytes in the treatment of complex sulphides (Baba and Adekola, 2010). Leaching kinetics is controlled either by the diffusional mass transfer of the reactant through a liquid boundary layer or ash layer or chemical reaction at the ore surface (Levenspiel, 1999).

Kinetics information can only be derived from experimentation and observation and is influenced by a number of factors such as mineralogy, surface area, reactant concentrations, product layer formation and temperature (Yevenes, 2009). The dissolution of minerals is of importance to a number of fields of endeavour. In particular, it is the rate of dissolution that is important. Knowledge of the kinetics might allow the rate to be accelerated or retarded, depending on the field of endeavour. The kinetics of dissolution of minerals are frequently found to be close to one-half order in the oxidant (Crundwell, 2013b). The observable parameters that describe the kinetics of a reaction are the orders of reaction and the activation energy. Of these two parameters, it is the orders of reaction that are paramount for the development of a reaction mechanism (Crundwell 2015).

The term mechanism can be construed to mean the pathway by which the reaction occurs. Also, reaction mechanism study reveals the rate-controlling step, thus mechanism of the reaction is more accurately described by the term 'kinetic mechanism'. In order to determine the mechanism, a researcher needs kinetic parameters therefore, to propose the mechanism of dissolution, the mechanism must be supported by measured kinetic parameters (Crundwell, 2013b). The dissolution of mineral ore takes place through the following stages: (1) diffusion of reactant through the diffusion layer, (2) adsorption of the reactant on the solid, (3) chemical reaction between the reactant and the solid, (4) desorption of the product from the solid and (5) diffusion of the product through the diffusion layer. Any of these stages (1) - (5) may be the rate controlling step depending on its relative speed to the others (Baba *et al.*, 2012).

Leaching is in general a slow process. Consequently, the extent to which the targeted mineral is leached, is determined not only by the thermodynamics of the system, but by kinetic factors as well. What becomes important is how long it takes for the leaching system to approach the equilibrium condition, and how much time the operation allows for it to do so. In some cases, equilibrium is not possible. Based on an understanding of kinetics, decisions about the most suitable operating conditions can be made in a rational manner (Smith, 2018).

The leaching of liberated mineral particles from ores such as chalcopyrite, sphalerite, ilmenite by lixiviants is a true example of a heterogeneous liquid-solid reaction that often leads to formation of solid products which form on the unreacted core. For reactions involving solid-state, a model can describe a particular reaction type and translate that matimatically into a rate equation. A model is a theoretical, mathematical description of what occurs experimentally. Many models have been developed based on certain mechanistic assumptions. Other models are more empirically based, and their mathematics facilitates data analysis with little mechanistic meaning. Therefore different rate expressions are produced from these models. In solid-state kinetics, mechanistic interpretations usually involve identifying a reasonable reaction model because information about individual reaction steps is often difficult to obtain (Khawam and Flanagan, 2006). The kinetics analysis of heterogeneous liquid-solid reaction is commonly described shrinking core model

2.4.2.1 Shrinking core model

This model was first developed by Yagi and Kunii (Levenspiel, 1999). The shrinking core model (SCM) has been extensively applied in the kinetics analysis of particulate systems. This is because in its classical form it is one of the simplest models developed for fluid–solid reactions (Veloso *et al.*, 2016). The shrinking core model is used to describe situations in which solid particles are being consumed either by dissolution or reaction and, as a result, the amount of the material being consumed is "shrinking" (Fogler, 1999).

This model assumes that the reaction between the solid and liquid reactants occurs on the outer surface of the solid particle. As the reaction proceeds, the unreacted core of the solid particles shrinks toward the center of the solid (Ekmekyapar *et al.*, 2015), leaving behind completely

converted material and inert solid. We refer to these as "ash." Thus, at any time there exists an unreacted core of material which shrinks in size during reaction (Levenspiel, 1999). According to shrinking core model postulation, the dissolution process is controlled by either diffusion through the solution boundary, diffusion through the solid product layer, or surface chemical reaction (Feng *et al.*, 2015). The integrated equation derived for a condition where the dissolution rate is controlled by the diffusion through the liquid film (DTLF) is given as:

$$k_1 t = x$$
(2.6)

If the process is controlled by diffusion through the product layer (DTPL), the integrated equation of the shrinking-core model can be described as:

$$k_{d}t = 1 - 3(1 - x)^{2/3} + 2(1 - x)$$
where $k_{d} = \frac{6bD_{e}C_{A}}{\rho_{B}R^{2}}$
(2.7)

If the process is controlled by surface chemical reaction, (SCR), the integrated equation of the shrinking-core model can be described as:

$$k_{r}t$$

$$= 1 - (1 - x)^{1/3}$$
(2.8)
where $k_{r} = \frac{bk'C_{AO}}{a\rho_{B}r_{o}}$

where x is the conversion fraction of solid particles, k_1 , k_d and k_r are the apparent rate constants for diffusion through the liquid film, diffusion through the product layer and surface chemical reaction respectively, t is the reaction time (Feng *et al.*, 2015). k' is the apparent speed constant, C_{AO} is the initial concentration of leaching reagent A, ρ_B is the molar density of the ore particle, r_o is the original radius of the ore particle, a and b are the reaction coefficient of the leaching agent A and the ore B, respectively (Deng *et al.*, 2015).

Mixed kinetic process is a hybrid of diffusion through the product layer and surface chemical reaction models. Chemical and diffusion rates are of the same magnitude. Equation (2.9) summarizes the mechanism where 'b' is a direct function of surface reaction.

$$\left(1 - \frac{2x}{3}\right) - (1 - x)^{\frac{2}{3}} + \frac{1}{b} \left[1 - (1 - x)^{\frac{1}{3}}\right] = Kt$$
(2.9)

For practical purposes, b is always equal to 1 and x is the fraction of the ore dissolved at a given leaching time (Baba *et al.*, 2012).

Asides the shrinking core model, the experimental data were also evaluated with kinetic models postulated by other scholars.

In diffusion controlled reactions, the thickness of the product layer, β , is related to reaction time, t, by the well known parabolic rate law:

$$\beta^2 = 2kt \tag{2.10}$$

Where k is the proportionality constant.

A number of modifications of equation (2.10) have been suggested in terms of the fraction of the sample reacted. Of these, the Jander, Kröger-Ziegler, Zhuravlev, Lesokhin and Templeman and Ginstling-Broushtein models were selected for the current study.

2.4.2.2 Jander's three-dimensional diffusion controlled model

The assumptions used in Jander's model were: (a) The chemical reaction at the phase boundary is considerably faster than the transport process and thus, the reaction is diffusion-controlled (diffusion of reactant through a continuous product layer). (b) The product is not miscible with

any of the reactants. (c) The reacting particles are all sphere of uniform radii. (d) The ratio of the volume of the product to the reactant is unity. (e) The increase in thickness of the product layer follows the parabolic law; i.e. the reaction interface is a plane. (f) The diffusion coefficient of the species is not a function of time (Dickinson and Heal, 2000).

The Jander's diffusional model is based on the assumption of spherical solid particles of uniform radii and is surrounded by other reactant. This is illustrated schematically in plate 2.7. This type of model applies to reactions between solids and gases, solids and liquid and in certain solid-solid reactions if one of the reactants is considered as a continuous medium. In the diffusion controlled process one of the reactants must penetrate through the layer dividing the two reactants A and B.



Plate 2.7: Spherical solid particles of uniform radii and is surrounded by other reactant

Let the original radius be R. At time t the interface has spread inwards a distance β , leaving sphere of reactant A of radius r:

$$r = R - \beta$$
Volume of original sphere
$$= \frac{4}{3} n \rho \pi R^{3}$$
(2.11)
(2.12)

The conversion fraction for a reaction involving n spherical particles can be written as:

$$=\frac{\frac{4}{3}n\rho\pi R^{3}-\frac{4}{3}n\rho\pi (R-\beta)^{3}}{\frac{4}{3}n\rho\pi R^{3}}$$
(2.14)

Where β is the thickness of the reaction zone. Equation (2.14) can be simplified to become:

$$x = 1 - \left(\frac{R-\beta}{R}\right)^3$$
(2.15)

Rearranging:

$$\beta = R(1 - (1-x)^{1/3})$$
(2.16)
$$\frac{d\beta}{dx} = \frac{1}{3}R(1-x)^{-2/3}$$
(2.17)

If the model is a diffusion controlled mechanism, a number of possible assumptions can be made to derive further rate equations. The time dependence of the gradual build up of the layer can be described by the parabolic law. Rate varies inversely with β .

From parabolic law:

$$\beta^2 = 2DV_m C_o t$$

$$= kt$$
(2.18)

$$2\frac{\beta d\beta}{dt} = k_1 \text{ or } \frac{d\beta}{dt} = \frac{k_1}{2\beta}$$
$$= \frac{DV_m C_o}{\beta}$$
(2.19)

Where β is thickness of product layer, D the diffusion coefficient (slowest transport), V_m the volume of product AB formed from 1 mol of the slowest penetrating component, and C_o the concentration of the penetrating species at the surface. Substituting equation (2.16) in (2.18)

$$R^{2} (1 - (1 - x)^{1/3})^{2} = kt$$
(2.20)

Assuming $k' = \frac{k}{R^2}$

$$(1 - (1 - x)^{1/3})^2 = k't$$
(2.21)

Equation (2.21) is Jander model equation.

2.4.2.3 Kroger and Ziegler model

There are some weaknesses in Jander's model because of some assumptions made in his analysis. Jander's equation was verified preferentially for small degrees of conversion of the reagents. The deviation between experimental data and theoretical value becomes larger at large conversion thus indicating that a more complicated situation actually exists.

Kroger and Ziegler, indicated that Jander's assumption of a constant diffusion coefficient was not applicable to all solid systems, particularly during the early stage of a reaction. They used most of the Jander's geometry and improved Jander's equation by assuming that the diffusion coefficient of the transported species was inversely proportional to time. This is equivalent to assuming that rate of change of product layer thickness is inversely proportional to time which is known as the Tammann theory (Tammann, 2019).

If the diffusion equation is:

$$\frac{d\beta}{dt} = \frac{V_m C_o k_2}{\beta t}$$
(2.22)

Diffusion constant inversely proportional to t. Integrate back again:

$$\int 2\beta d\beta$$

$$= \int 2V_m C_o k_2 \frac{dt}{t} \qquad (2.23)$$

$$\beta^2$$

$$= 2V_m C_o k_2 lnt \qquad (2.24)$$
Therefore, $R^2 (1 - (1 - x)^{1/3})^2 = 2V_m C_o k_2 lnt \qquad (2.25)$
Or

$$\binom{(1 - (1 - x)^{1/3})^2}{k_3 lnt} =$$
(2.26)

where

$$k_3 = \frac{2V_m C_o k_2}{R^2}$$

Equation (2.26) is the Kroger and Ziegler Model equation (Dickson and Heal, 1999).

2.4.2.4 Zhuravlev, Lesokhin and Templeman model

Zhuravlev, Lesokhin and Templeman modified the Jander's equation by assuming that the activity of the reacting substances was proportional to the fraction of the unreacted material (1 - x) (Zhuravlev *et al*, 2019). In other words they submitted that the concentration C_o is not a constant, but a factor of reactant activity varying with (1 - x):

$$\frac{d\beta}{dt} = \frac{DV_m C_o(1-x)}{\beta}$$
$$= \frac{k_4(1-x)}{\beta}$$
(2.27)

Where, $k_4 = DV_m C_o$ Therefore, $\frac{\beta d\beta}{1-x} = k_4 dt$ (2.28)

Substitute for β and $d\beta$ from equations (2.16) and (2.17):

$$\frac{R\left(1-(1-x)^{1/3}\right)\times(1/3)R(1-x)^{-2/3}}{1-x}dx$$

$$=k_4dt$$
(2.29)
$$\frac{\left(\frac{1}{3}\right)R^2\left((1-x)^{-2/3}-(1-x)^{-1/3}\right)dx}{1-x}$$

$$=k_4dt$$
(2.30)

$$\binom{1}{3} R^2 \left((1-x)^{-5/3} - (1-x)^{-4/3} \right) dx$$

= $k_4 dt$ (2.31)

Integrating

$$\binom{1}{3}R^{2}\left(\frac{3}{2}(1-x)^{-2/3} - 3(1-x)^{-1/3} + c\right)dx$$

$$= k_{4}dt$$
(2.32)

At t = 0, x = 0 then c = 3/2

$$R^{2}\left(\frac{1}{2}(1-x)^{-2/3} - (1-x)^{-1/3} + \frac{1}{2}\right)$$

= $k_{4}dt$ (2.33)

$$\frac{1}{2}R^{2}\left((1-x)^{-2/3}-2(1-x)^{-1/3}+1\right)$$

= $k_{4}dt$ (2.34)

$$\begin{pmatrix} (1-x)^{-1/3} - 1 \end{pmatrix}^2 \\ = k_5 t$$
 (2.35)

Where

$$k_5 = \frac{2k_4}{R^2}$$

Equation (2.35) is the Zhuravlev Lesokhin and Templeman model equation (Dickson and Heal, 1999).

2.4.2.5 Ginstling-Brounshtein model

A modified form of the shrinking core model for product ash layer diffusion control was developed by Ginstling and Brounshtein (1950). They have shown that the Jander model (equation 2.17) which used the parabolic law (derived for a plane surface) is oversimplified and holds only at low conversion values (i.e. low β/R values), the steady-state solution of Fick's law for radical diffusion in a sphere is:

$$C_{(r)} = \frac{aC_1(b-r) + bC_2(r-a)}{r(b-a)}$$
(2.36)

Where $C_{(r)}$ is the reactant concentration at a particular value of r(a < r < b), C_1 is the concentration of the diffusing species at surface r = a, and C_2 is the concentration of the diffusing species at surface r = b. The reaction at the interface is assumed to occur at a much faster rate than diffusion, therefore, $C_1 \approx 0$. Therefore equation (2.36) becomes:

$$C_{(r)} = \frac{bC_2(r-a)}{r(b-a)}$$
(2.37)

Taking the derivative of the above equation with respect to r at r = a gives

$$\frac{dC}{dr} = \frac{(b-a)bC_2}{a(b-a)^2}$$
(2.38)

From Plate 2.7, $r = R - \beta$, b = R and a = r, so equation (2.38) becomes:

$$\frac{dC}{dr} = \frac{RC_2}{(R-\beta)\beta}$$
(2.39)

The rate of reaction zone, $d\beta/dt$ can be related to dC/dr by:

$$\frac{dx}{dt} = \frac{D}{\frac{dC}{\epsilon} \frac{dC}{dr}}$$
(2.40)

Where D is the diffusion coefficient, \in is a proportionality constant equal to $\rho n/\mu$ (ρ and μ are the specific gravity and molecular weight of the product, respectively, and n is the stoichiometric coefficient of the reaction). Substituting equation (2.39) into equation (2.40) gives:

$$\frac{d\beta}{dt} = \frac{D}{\epsilon} \frac{RC_2}{(R-\beta)\beta}$$
(2.41)

Which can be rewritten as:

$$\frac{d\beta}{dt} = k \frac{R}{(Rx - x^2)}$$
(2.42)

Where $k = DC_2/\in$. Separating variables and integrating equation 2.38 gives:

$$kt = 1 - \left(\frac{2}{3}\right)x - \left(1 - x\right)^{2/3}$$
(2.43)

Equation 2.43 is the *Gingstling-Brounshtein* model equation (Khawam and Flanagan2006).

2.5 Leaching Thermodynamics

Changes in reaction that may be expected during a leaching process require an idea of the thermodynamic parameters of the system. The thermodynamic characteristics of the reaction system will indicate the maximum possible extent to which the value-bearing mineral can be converted to a soluble species, as well as the solubility of that species in the aqueous solution. It is important to note that the extent to which the targeted mineral is leached, is determined not only by the thermodynamics of the system, but by kinetic factors as well (Smit, 2001). The three main thermodynamic parameters include free energy change (Δ G), enthalpy (Δ H) and entropy (Δ S) of leaching.

The Gibbs free energy (ΔG) is the fundamental criterion for spontaneity of a process and can be determined using the relationship:

$$\Delta G = \Delta H - T\Delta S \tag{2.44}$$

The enthalpy and entropy values were computed from the slope and intercept of the van't Hoff equation, which is given by:

$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(2.45)

The ΔG tells about the overall spontaneity of the process which depends upon the actual change in entropy and enthalpy. Negative ΔG indicates that the reaction is spontaneous while positive ΔG explains that the reaction is non-spontaneous (requires energy to go from reactants to products). Spontaneity is not synonymous with speed. The ΔH indicates the nature of the process, whether it is endothermic or exothermic. R is the universal gas constant $(8.314 \text{Jmol}^{-1}\text{K}^{-1})$ and T is temperature (K).

If pressure is held at the reference pressure, then the van't Hoff equation states (White, 2000):

$$\begin{pmatrix} \frac{\partial \ln k}{\partial T} \end{pmatrix} = \frac{-\Delta H}{RT^2}$$
(2.46)

Integrating

$$lnk = \frac{-\Delta H}{RT} + \ln A \tag{2.47}$$

$$\frac{k_{1}}{k_{-1}} = \frac{A_{1}e^{-E_{1}}/RT}{A_{-1}e^{-E_{-1}}/RT}$$
(2.48)

$$K = A e^{-(E_1 - E_{-1})/RT} = A e^{-\Delta H/RT}$$
(2.49)

Where
$$\Delta H^{\circ} = E_1 - E_{-1}$$

 $\frac{A_1}{A_{-1}} = A =$
 $e^{\Delta S/R}$
(2.50)

2.6 Experimental Design

The word experiment is used in a very precise form to indicate an investigation where the system under study is under control of the investigator. On the contrary, for an observational study, some characteristics will be out of the control of the investigator. (Cox and Reid 2000). According to Montgomery (2001), the experiment can be seen as a test, or as a series of tests, in which the proposed changes are applied on the input variables of a process or system, to, then, observe and identify the changes occurred on the output variables. Still according to Montgomery (2001), the design of experiments refers to the process of planning of experiments in a way that appropriate data can be analyzed through statistical methods, resulting in valid and objective conclusions. According to Kelton (1999), one of the main goals of the experimental design is to estimate how changes in input factors affect the results, or answers of the experiment.

Design of experiments is a series of tests in which purposeful changes are made to the input variables of a system or process and the effects on response variables are measured. Design of experiments is applicable to both physical processes and computer simulation models. Experimental design is an effective tool for maximizing the amount of information gained from a study while minimizing the amount of data to be collected (Telford, 2007).

Some terms are commonly used in design of experiments. Mason *et al.* (2003) define "factor" as a controllable experimental variable, which variation influences the response variable. Each factor must assume some values, defined as levels. The changes occurred on the mean of the values of the response variable correspond to the effects. Besides the effects caused by the factors, the effects created by the interaction of the factors can be determined. According to Telford, (2007), interaction occurs when the effect on the response of a change in the level of one factor from low to high depends on the level of another factor. In other words, when an interaction is present between two factors, the combined effect of those two factors on the response variable cannot be predicted from the separate effects. The effect of two factors acting in combination can either be greater (synergy) or less (interference) than would be expected from each factor separately.

The main uses of design of experiments are:

- Discovering interactions among factors
- Screening many factors

- Establishing and maintaining quality control
- Optimizing a process
- Designing robust products

Reliability of results, depiction of the combined effects of all the independent variables at a single time and lesser time consumption are some among many other advantages attached to the employment of the services of statistical experimental design method in optimizing all the affecting parameters of an experiment. Design of experiment methods include Combined, Mixture, Response surface, factorial, etc.

2.6.1 Response surface methodology (RSM)

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for developing, improving and optimizing processes. It can be used to define the relationships between the response and the independent variables with a minimum number of trials according to special experimental designs based on factorial designs. The main advantages of RSM lie in the fact that this method is less expensive and time consuming to classical methods (Silva *et al*, 2004)

RSM can be used to optimize any process in which response of interest is influenced by several variables (Sahu *et al*, 2009). Primarily, this optimization is done by the following three major steps viz., performing the statistically designed experiments, estimating the coefficients in a mathematical model and predicting the responses and examining the adequacy of the model (Myers and Montgomery, 1995). RSM helps to enumerate the relationships between output variables called responses (Y) and input variables called factors (X_i s) (Sahu *et al*, 2009).

$$Y = f(X_1, X_2, X_3, ..., X_n)$$
(2.51)

Response surface methodology (RSM) was used as a statistical tool for the purpose of this research project considering the fact that one of the cardinal objectives of this research is to determine precise conditions required to achieve optimal leaching efficiency of the chalcopyrite,

sphalerite and ilmenite ores in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions used as lixiviants.

Central composite design, Box-Benhken, one factor, miscellaneous, optimum (Custom), userdefined, historical data design are all types of the Response Surface Methodology.

2.6.1.1 Central composite design (CCD)

The fractional central composite design technique is a standard RSM design which was applied in this research work. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters. Generally, the CCD consists of a 2^n factorial runs with 2n axial runs and n_c central runs (Hameed *et al*, 2008). The centre points are utilized to evaluate the experimental error and the reproducibility of the data. Thus, for a leaching process having five (5) independent parameters, the total number of experiments required is:

$$N = 2^{n-1} + 2n + n_c = 2^4 + (2x5) + 6 = 32$$
(2.52)

2.7 Artificial Neuro Fuzzy Inference System (ANFIS)

The most well-known artificial intelligent systems are the artificial neural network (ANN), the adaptive neuro-fuzzy interference system (ANFIS) and the support vector machine (SVM). The ANFIS is a powerful predicting or estimating method, which is capable of producing accurate results for a given problem, and it has the advantages of the learning property of ANNs and the expert knowledge of the fuzzy inference systems (FISs) (Ahmet and Ali, 2015). ANFIS is a hybrid intelligent system (combination of two or more intelligent technologies). This combination is done usually to overcome single intelligent technology (Azeez et al., 2013). This marriage of learning capability of neural network and knowledge representation ability of fuzzy logic has given birth to fuzzy neural networks. As a result, the drawback of neural network black box inability to explain decision (lack of transparency), and weakness of learning in fuzzy logic have been conquered (Ahmet and Ali, 2015). ANFIS corresponds to a set of fuzzy IF–THEN rules that have learning capability to approximate nonlinear functions (Abraham, 2005). Hence, ANFIS is considered to be a universal estimator (Jang, 1997). According to literature, fuzzy neural networks are able to approximate any plant with high degree of accuracy; be it

engineering, medicine, transportation, or business and economics, etc (Deshmukh, and Kumar, 2007). Bodyanskiy and Dolotov (2010) affirmed that ANFIS is one of the best solutions in data modeling and capable of reasoning and learning in an uncertain and imprecise environment. Unlike ANN, Fuzzy Neural Network (FNN) also referred to as fuzzy inference system maps inputs through input membership functions to the desired output(s) via output membership functions, and this mapping generates rule-base in the course of learning (Talpur *et al.*, 2017).

These rules in FNN are directly mapped into the neural structure of the network. The accuracy of rules depends on appropriateness of type and parameters of membership functions. ANFIS is based on Takagi-Sugeno-Kang model (TSK), or simply Sugeno fuzzy model, where a rule R_k can be represented as:

$$R_k: IF \ \mu A_i(x) AND \ \mu B_i, (y) THEN f$$

= $p_k x + q_k y + r_k$ (2.53)

where k is the number of rules, A_i and B_i are n fuzzy membership functions of any shape i.e., gaussian, triangular, trapezoidal, etc., denoted by μ in the antecedent part of the rule R_k , and p_k , q_k , r_k are the linear parameters of consequent part of the k_{th} rule. The parameters of membership functions (antecedent or premise parameters) and consequent part of the rule (consequent parameters) are tuned during the training process (Talpur *et al.*, 2017).

2.8 **Review of Related Literature**

Khawassek *et al* (2016) studied the kinetics of leaching process using sulfuric acid for Sella uranium ore material, south eastern desert, Egypt. Their results showed uranium dissolution efficiency of 91.5 % was obtained for Sella ore particle size 150- 63µm after 4 hours contact time leaching using 1.0 M sulfuric acid and liquid/ solid mass ratio, ml/ g of 3 at 40 °C with 400 rpm mechanical stirring speed. The kinetic data showed that the leaching process can be described by a shrinking-core model with apparent activation energy equals to 10.13 kJ/mol. The low activation energy supported the findings that the Sella ore leaching rate is controlled by diffusion-controlled process.

Sahu *et al* (2011) investigated the dissolution kinetics of nickel laterite ore in aqueous acid solutions of three metabolic acids, i.e., citric acid, oxalic acid and acetic acid were investigated in a batch reactor individually. The researchers determined that the experimental data comply with a shrinking core model. The diffusion coefficients for citric acid, oxalic acid and acetic acid were found to be 1.99×10^{-9} cm²/s, 2.59×10^{-8} cm²/s, and 1.92×10^{-10} cm²/s respectively. The leaching ability of each acid was observed and it was found that oxalic acid was better than the other two.

Baba *et al* (2011) studied the dissolution kinetics of a Nigerian galena ore in hydrochloric acid. The XRD analysis result showed that galena is the dominant mineral phase, with the presence of associated minerals, such as a-quartz (SiO₂), sphalerite (ZnS), cassiterite (SnO₂), pyrite (FeS₂) and manganese oxide (MnO₂). Results of leaching studies showed that galena dissolution in HCl solution increases with increasing acid concentration and temperature; while it decreases with particle diameter and solid/liquid ratio at a fixed stirring rate of 450 rpm. The researchers reported that 94.8% of galena was dissolved by 8.06 M HCl at 80°C within 120 min with initial solid/liquid ratio of 10 g/L. Activation energy, reaction order, Arrhenius constants, reaction and dissociation constants were calculated to be 38.74 kJ/mol, 0.28, 73.69s⁻¹, 1.73 ± 0.13 x 10³ and 1.37 ± 0.024 x 10⁴ mol L⁻¹s⁻¹, respectively. The mechanism of dissolution of galena was established to follow the shrinking core model for the diffusion controlled mechanism with surface chemical reaction as the rate controlling step for the dissolution process. The XRD analysis of the postleaching residue showed the presence of elemental sulphur, lead chloride and quartz.

A kinetic study of the leaching of manganese mining residue by sulfuric acid and potassium oxalate was conducted by Abdallah *et al* (2015). The study observed that the leaching rates are significantly influenced by the reaction temperature, to both concentration oxalate and acid. The observed effects of the relevant operating variables on the leaching rates are consistent with a kinetic model for chemical control. The apparent activation energy for the leaching of pyrolusite has been calculated using the Arrhenius expression and was found to be (63.7 ± 2.9) kJ/mol. The experimental results indicate a reaction order of 1.07 for [H₂SO₄] concentration and 0.96 for [K₂C₂O₄]. It is concluded that the reductive leaching of pyrolusite with potassium oxalate in acid

medium is controlled by chemical reaction. The rate expression associated with the dissolution rate of pyrolusite depending on the parameters chosen may be summarized as follows:

$$1 - (1 - x)^{1/3} = \frac{1.45 \ 10^7}{r_0^{0.82}} \cdot [H_2 S O_4]^{1.07} [K_2 C_2 O_4]^{0.96} \exp\left(-\frac{63735}{RT}\right) \cdot t$$
(2.50)

Olubambi *et al* (2006) studied the leaching of zinc and copper from Nigeria bulk sulfide ore with sulfuric acid in the presence of hydrogen peroxide (H_2O_2), with the aim to investigate the effectiveness of hydrogen peroxide as an oxidant for the sulfuric acid. The results of this study have shown that sulfuric acid leaching in the presence of hydrogen peroxide is an effective route for copper and zinc recovery from Nigerian complex sulfide ore.

2.8.1 Chalcopyrite leaching

According to Xian *et al* (2012) research on leaching chalcopyrite with sodium chlorate in hydrochloric acid solution, stirring speed has a negligible effect on copper dissolution, suggesting that the reaction is not controlled by liquid phase diffusion. Their results indicate that the leaching process is highly dependent on temperature for the range of 25–65°C. This result is consistent with the values for the activation energy at 25–45°C (60.0 kJ mol). Within these temperature ranges, the leaching process is controlled by a chemical reaction. However, at temperatures of 65–85°C, the activation energy in (0–180 min) is 28.17 kJ mol⁻¹) and 45–65°C (57.7 kJ mol⁻¹, which suggests that the reaction is diffusion and chemically controlled during this stage. During the last stage (180–300 min) of the process at 65–85°C, the activation energy is only 0.55 kJmol⁻¹. At this point, it appears that diffusion predominates.

Hernandez, *et al.*, (2015) experimented the usage of seawater in leaching of the chalcopyrite ore samples with copper grade of 1.6% in acidic media. They prepared different leach solutions using different acids (H₂SO₄, HCl and HNO₃) with and without seawater. Cupric chloride and ferric chloride were added as oxidant in the leaching process. Leaching tests were conducted in the agitated leaching reactors with 400 rpm using 100 g of the representative ore sample and 1L of leach solution at 45°C, with duration of 7 days. The ore was ground to P₈₀ of 62.5 μ m. The maximum copper extraction of 37.7% was obtained in the test performed using hydrochloric acid in the seawater-based media and in the presence of cupric chloride. In the leaching test
conducted using sulfuric acid in the seawater-based media and in the presence of sodium chloride and cupric chloride, the maximum copper recovery of 34.2% was obtained. In all of the different designed leaching approaches, the highest copper extraction was obtained in the tests performed with addition of the cupric ions (Cu²⁺). In general, copper extraction in the leaching tests performed using seawater-based acidic media, were higher than those conducted in the pure water-based leaching media. Only exceptions observed when chloride ions (sodium chloride) were added externally. This indicated the importance of chloride ions presence in the leach solution.

The leaching conditions of chalcopyrite (CuFeS₂) concentrate in a hydrogen peroxide medium were investigated by Agacayak *et al* (2014). The effects of the leaching parameters, such as stirring speed, temperature, hydrogen peroxide concentration and the particle size of the concentrate on Cu extraction were studied. It was found that stirring speed has no effect on the leaching. Copper extraction from chalcopyrite is directly proportional to hydrogen peroxide concentration, but the extraction decreases at temperatures above 60°C. The maximum copper extraction was obtained with the following conditions without stirring: 240 min of leaching time, 3.0 M hydrogen peroxide concentration, 40°C leaching temperature and 53-75 μ m particle size fraction.

Bogdanović *et al* (2016) dealt with the investigation of column leaching of low-grade ores from the copper mine Cerovo, Serbia (the approximate Cu content in the ore ranges from 0.2 - 0.3 % with >10 % copper in the form of oxide minerals). The leaching experiments were performed using sulphuric acid solutions The copper concentration in the leach solution ranged from 0.80 to 1.75 g dm⁻³. The total Cu recovery rate ranged from 30 to 56 %, whereas the recovery rate of copper oxide minerals ranged from 67 to 100 %. They observed that increasing the amount of liquid phase, copper recovery increases as well, and copper oxide minerals were completely leached out. According to their findings, the concentration of copper ions was sufficiently high for the use of either solvent extraction or ion exchange techniques or both for further treatment of the leach solution.

Tian *et al* (2017) reported research progress of chalcopyrite leaching at ambient temperature and atmospheric pressure with various oxidants such as Fe³⁺, NaClO₃, KMnO₄, Na₂S₂O₈, O₃ and

NaNO₃. The research highlighted the merits of the usage of oxidants in the leaching of chalcopyrite and also analyzed the leaching mechanisms. It was found that O_3 would be the best oxidant for oxidative leaching of chalcopyrite in acid leaching medium, due to its high oxidation potential and no other by-products or impurities generated except water during leaching process.

Aydogan *et al* (2006) studied the dissolution of chalcopyrite in acidic potassium dichromate solution. The effects of sulphuric acid and potassium dichromate concentrations were investigated by changing stirring speed, leaching temperature and particle size. It was determined that dissolution rate increased with increasing sulphuric acid concentration, potassium dichromate concentration and temperature. A particle size below 75 μ m was required to leach 80% copper in 150 min at 90 °C. The kinetic study showed that the dissolution of chalcopyrite is represented by shrinking core model with diffusion through a porous product layer of sulphur. The activation energy (Ea) for the dissolution reaction was calculated as 24 kJ/mol.

Adebayo *et al* (2003) investigated the kinetics of dissolution of chalcopyrite with hydrogen peroxide in sulphuric acid solution. The influence of temperature, stirring speed, concentrations of hydrogen peroxide and sulphuric acid as well as particle size, were studied. The dissolution kinetics was found to follow a shrinking- core model, with surface chemical reaction as the rate-determining step. This is in agreement with activation energy of 39 kJ mol⁻¹ and a linear relationship between the rate constant and the reciprocal of particle size. Increasing the H₂O₂ and H₂SO₄ concentrations has a positive effect on the oxidation of sulphide. The reaction orders recorded were 1.45 and 0.77 with respect to concentration of H₂O₂ and H₂SO₄, respectively.

Petrović *et al* (2018) researched on the leaching of chalcopyrite concentrate in hydrochloric acid with hydrogen peroxide as a strong oxidizing agent. The effects of the leaching variables on metal extraction, such as stirring speed, solid-to-liquid ratio, temperature and HCl and H_2O_2 concentrations, were studied. The maximum final copper extraction of 33% was attained with 3.0 mol/L H_2O_2 in 0.5 mol/L HCl at room temperature after 180 min of the reaction. The results showed that the copper extraction was increased in the first 60 min of reaction, after which it essentially ceased due to the fast catalytic decomposition of hydrogen peroxide. The dissolution process was described by the first order kinetics equation. The apparent activation energy of 19.6 kJ/mol suggested that the dissolution process was under diffusion control. The reaction orders for HCl and H_2O_2 were established to be 0.30 and 0.53, respectively.

Murray *et al* (2006) reported that both NaCl and KCl improve chalcopyrite leaching at pH 2.0 and 28°C. The researchers submitted that KCl enhances chalcopyrite leaching, but attributed the effect to potassium rather than chloride. The scientists also reported that the over potential (a measure of resistance to oxidation) developed during oxidation of sulfides in a sulfate system is not observed in chloride system. The reason for this could be attributed to chloride functioning as an electron transfer agent. Such behaviour was concluded to enhance leaching in an oxidation - reduction reaction by facilitating transfer of the electron from the species being oxidized.

Hundstrom *et al* (2005) investigated chalcopyrite (CuFeS₂) dissolution in cupric chloride solutions. The results obtained determined that the dissolution of a stationary chalcopyrite sample was controlled by diffusion in the reaction product layer at pH 3 and changing to chemical rate control at pH 1. The FeOOH formation in addition to the elemental sulphur favours chalcopyrite dissolution.

2.8.2 Sphalerite leaching

Adebayo *et al* (2006) examined the leaching of powdered sphalerite using hydrogen peroxide and nitric acid. The important variables such as temperature, concentrations of hydrogen peroxide and nitric acid as well as stirring speed and particle size were investigated. The hydrogen peroxide and nitric acid concentrations have significant effects on the leaching of sphalerite. The leaching of sphalerite is dependent on temperature and stirring speed and inversely proportional on the ore particle size. The apparent activation energy is found to be 28.7kJmol⁻¹ suggesting that the reaction is chemical - control at the surface of the particles.

Sokić, *et al* (2012) investigated the application of hydrometallurgical method in processing complex sulphide ores and concentrates. The outcome of their findings reveals the influences of temperature and time on the leaching degree of zinc. With temperature increasing from 60 to 90°C, the zinc leaching increased from 25.23% to 71.66% after 2 hours and. from 59.40% to

99.83% after 4 hours. The selected kinetic model indicated that the diffusion through the product layer was the rate-controlling step during the sphalerite leaching. The activation energy was determined to be 55 kJ/mol in the temperature range 60°C -90°C. XRD, light microscopy and SEM/EDX analyses of the complex concentrate and leach residue confirmed formation of elemental sulphur and diffusion-controlled leaching mechanism.

Hasani *et al* (2015) investigated the extraction of zinc from a sphalerite concentrate using sodium nitrate as an oxidant in a sulfuric acid solution. They reported that dissolution rate increased with increase in the sulfuric acid and sodium nitrite concentrations and temperature but decreased with increase in the particle size and S/L ratio. Moreover, the stirring speed had a significant effect on the leaching rate. Under the optimum conditions, 74.11% of zinc was obtained. A new shrinking core model (SCM) variant presented in their work captured the kinetic data more appropriately. Based on this model, the activities of the reactants control the diffusion but the two concentrations affect the second order reaction rate or diffusion in both directions. At 75 °C, the R² values in the surface chemical reactions and diffusion were 0.78 and 0.89, respectively. Using the new model, however, the R² value 0.989 was obtained. The reaction orders with respect to (H₂SO₄), (NaNO₃), S/L ratio, and particle size were 1.603, 1.093, -0.9156, and -2.177, respectively. The activation energy for the dissolution was 29.23 kJ/mol.

Deng *et al* (2015) researched on the dissolution kinetics of smithsonite as an alternative zinc source in trichloroacetic acid (TCA) solution. TCA was derived from industrial waste acid in the pharmaceutical, biotechnology and chemical fields. The outcome of their investigation showed that the dissolution kinetics conformed to the shrinking core model controlled by surface chemical reaction. The apparent activation energy of the reaction was calculated as 47.61 kJ/mol, indicating the obvious effect of temperature on the reaction rate. The reaction kinetic equation associated with the main influencing factors was eventually established as 1-(1-x)-1/3=[0.0002 (C)0.384 (P)0.969 exp(-5726T)] t. The high reaction speed of smithsonite in TCA solution shows that TCA has a dissolution effect on zinc oxide ores; thus, it can be employed as an advantageous environmentally friendly organic leaching reagent.

Seyed-Ghasemi and Azizi (2017b) studied the leaching kinetics of a low-grade zinc oxide ore in different acid media. The results obtained showed that the leaching reagent concentration and the reaction temperature exerted significant effects on the extraction of zinc, whereas the L/S ratio and stirring speed exhibited a relatively moderate effect on the leaching rate. The maximum leaching rate with inorganic acids was obtained to be 90.76%, while the maximum zinc recovery with citric acid was determined to be 88.68%. It was found that the zinc leaching process followed the kinetic law of the shrinking core model. It was distinguished that the dissolution rate was controlled by diffusion through the fluid film in the HNO₃ medium with the activation energy of 4.38 kJ/mol, whereas when dissolution was performed in the presence of HCl, H₂SO₄, and citric acid, an intermediate process (i.e. a physico-chemical process) was the rate-controlling step.

Aydogan (2006) studied the kinetics of dissolution of sphalerite with hydrogen peroxide in sulphuric acid solution. The researcher considered the influence of stirring speed (0–600rpm), dissolution temperature (10–60°C), sulphuric acid concentration (0.5–6.0 M), hydrogen peroxide concentration (0.1–6 M), and particle size on dissolution of sphalerite. The dissolution kinetics was found to follow a shrinking-core model, with the surface chemical reaction as the rate determining step. The research recorded activation energy of 43 kJ/mol and also reported that increasing concentrations of sulphuric acid and hydrogen peroxide have positive effect on the dissolution of sphalerite while stirring speed had no effect on the rate of sphalerite dissolution.

Uçar (2009) studied the extraction of zinc from a sphalerite concentrate using sodium chlorate as an oxidant in hydrochloric acid solutions. The results from this research reveal that stirring speed did not significantly affect zinc extraction compared with other experimental parameters. The dissolution rate increased with increasing sodium chlorate and hydrochloric acid concentrations and temperature, but decreased with increasing particle size. The kinetic study showed that the dissolution of zinc could be represented by a shrinking core model with surface chemical reaction. The activation energy (*Ea*) for the dissolution reaction was calculated as 41.1 kJ/mol.

Baba *et al* (2000) evaluated the dissolution kinetics of a Nigerian sphalerite in HCl. The effects of HCl concentration, temperature, particle diameter, stirring speed, solid/liquid ratio on the leaching of sphalerite were investigated. The XRF analysis showed that the sphalerite mineral consists of zinc and sulphur as major elements. The leaching experiments showed that sphalerite dissolution in HCl increases with acid concentration and temperature, but decreases with particle diameter and solid/liquid ratio. In HCl 4 M and at 80 °C, about 91.80% of sphalerite was dissolved within 120 min using $-112 + 63 \mu$ m particle diameter and solid/liquid ratio of 10 g/L. The activation energy, reaction order, Arrhenius constant and reaction constant calculated from the experimental data were 39.09 kJ/mol, 0.24, 13.46 s⁻¹ and 2.21 ± 0.4 × 10³. Kinetic data analysis indicated that the rate determining step for the dissolution process followed a surface chemical reaction. XRD analysis of the post-leaching residue provided evidence for the presence of silica and traces of sulphur in the residual solid.

Babu *et al* (2002) investigated the recovery of zinc from sphalerite concentrate by oxidative leaching with ammonium, sodium and potassium persulphates in sulphuric acid media. The outcome of their research revealed that leaching of 95% zinc was extracted from the concentrate of particle size $-150 \mu m$ at a temperature of 333 K for 5 h in the presence of 20% (w/v) ammonium persulphate (APS) with 5% (v/v) sulphuric acid concentration. The research reported that diffusion through the product layer was the rate-controlling step during the dissolution. The activation energy was determined to be $41\pm 2 \text{ kJ/mol}$ in the temperature range 308-333 K which was also an indication of the diffusion-controlled process.

In 2005, Aydogan *et al.* published their findings for leaching kinetics of sphalerite concentrate in FeCl₃–HCl solution. The effects of stirrer speed of 200–600 rpm, ferric ion concentration in range of 0–1 M, solid/liquid ratio in range of 1/100–1/5, leaching temperature range of 40–80 °C and particle size on zinc dissolution rate were studied. The activation energy for the leaching process was found to be 45.30 kJ/mol and the Arrhenius constant was calculated to be 5.454 s⁻¹. The rate of the reaction based on reaction-controlled process was written as,

 $[1-(1-\alpha)^{1/3}]=k_0(Fe^{3+})0.36(\rho_{S/L})^{-0.33}r_0-0.97exp(-45300/RT)t$. The dissolution of sphalerite with acidic ferric chloride solution was found to be controlled by reaction-controlled process.

2.8.3 Ilmenite leaching

Das *et al* (2013) studied the direct leaching of Australian ilmenite ore samples with HCl. They reported the effectiveness of leaching at high chloride (Cl⁻) concentration (~500 g/L) in the feed solution. They also reported that the presence of CaCl₂ was more effective for leaching than that of MgCl₂ and NaCl due to its higher solubility. The optimum conditions for leaching ilmenite in this study were found to be 5–7.5 M HCl solution with a total Cl⁻ concentration of ~500 g/L, 3.3% (w/w) pulp density, 70–80 °C solution temperature and 4–6 h retention time. Under these conditions, the optimum leaching efficiencies were ~98–99% Ti and 96% Fe for ilmenite ore A and 94% Ti and 93% Fe for ilmenite ore B.

Wang *et al* (2010) studied the use of oxalic acid for the removal of iron from the intermediates of ilmenite leached by KOH liquor. They investigated the effects of pH, temperature, initial oxalate concentration, and illumination on ilmenite leaching. The results presented reveal that orthorhombic crystal $Ti_2O_2(OH)_2(C_2O_4).H_2O$ formed as the leaching proceeded. Scanning electronic microscope (SEM) images implied that the formation of $Ti_2O_2(OH)_2(C_2O_4).H_2O$ with good crystallinity proceeded through three stages. Calcining $Ti_2O_2(OH)_2(C_2O_4).H_2O$, anatase (350°C) or rutile (550°C) type TiO₂ was obtained, respectively. Elemental analysis found that the calcined product contained 94.9% TiO2 and 2.5% iron oxide, but only about 1600 ppm dissolvable iron oxide was left, which indicates that oxalic acid was comparatively effective on iron oxide removal from the intermediates. Finally, an improved route was proposed for the upgrading of ilmenite into rutile.

Baba *et al* (2011) studied the leaching and solvent extraction of total iron and titanium from ilmenite. From their findings, the experimental results indicate that the dissolution rate is by diffusion control. The calculated activation energy, reaction order and Arrhenius constant were 38.4 kJ/mol, 0.85 and 11.8s-1, respectively. The mineralogical purity by X-ray diffraction (XRD) showed that apart from prominent ilmenite, (FeTiO₃) peaks, the following compounds: ZnSO₄, SiO₂, CaFeO₇, Fe₂(SO₄)₃, CaTiO₄ and Mn₅O₈ were also present. An extraction efficiency of 97% total titanium was obtained by 1.5 M TBP in kerosene from initial 10g/L ilmenite leach liquor at $25 \pm 2^{\circ}$ C in a single extraction stage. Iron was effectively eliminated using 3M ammoniacal solution at pH 3.5.

Olanipekun (1999) researched on kinetic study of the leaching of powdered ilmenite ore by hydrochloric acid. He investigated the effects of stirring speed ranging from 100 to 500 min⁻¹, particle size ranging from 20 to 74 μ m, acid concentration ranging from 7.2 to 9.6M and temperature ranging from 70 to 90°C on titanium and iron dissolution. Findings show that the dissolution rates are significantly influenced by the temperature and concentration of the acid solutions. The experimental data for the dissolution rates of titanium and iron were analyzed with the shrinking-core model for reaction control. The apparent activation energy for the dissolution of titanium and iron were evaluated using the Arrhenius expression.

Sasikumar *et al* (2004) reported the effect of mechanical activation, particle size and distribution, surface area, unit cell parameters, crystallite size and strain of a beach sand ilmenite concentrate from Chatrapur, Orissa, India on the kinetics of sulfuric acid leaching. It was observed that mechanical activation significantly enhances the dissolution of both iron and titanium in sulfuric acid. The kinetic parameters for leaching of the activated samples were determined using a nonlinear least squares minimization procedure. The activation energy for leaching of iron was marginally higher than that of titanium.

Ramadan *et al* (2016) studied the leaching kinetics of Abu-Ghalaga ilmenite ore. The study reported 93.21% TiO₂ assaying and iron dissolution 96.62% assaying at an optimum leaching condition of 20% acid concentration, 63 μ m particle size, 1:6 solid/liquid ratio, 400 r.p.m. agitation speed, 110°C reaction temperature, and 300 minutes agitation time. The leaching kinetics of ilmenite ore showed that the rate of dissolution using HCl acid is a diffusion controlled and follows the shrinking core model, [1-2(1-X)2/3+2(1-X)]= K_dt with an apparent activation energy of 17.607KJ/mol.

2.9 Summary of Literature review and knowledge gap

A critical review of existing literature reveals that there is no published data on recovery of copper, zinc and iron from chalcopyrite, sphalerite and ilmenite ores sourced from Ohankwu Ikwo mine, Ebonyi state, Ihetutu mine, Ebonyi state and Egon mine, Nassarawa state

respectively. There exist gaps in furnishing holistic leaching study data of these ores. Formulation of binary solutions as lixiviants for efficient leaching of ores is a subject of research to date as researchers have not exhausted all possible formulations thus there are gaps in the usage of binary solutions in the recovery of metals from ores. For example, HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions used in the current research have not been tested for the chalcopyrite, sphalerite and ilmenite leaching. Generally, it is pertinent to note that in leaching studies, limited data has been published for ores from Nigerian origin.

Literature also show some published one-factor at a time (OFAT), kinetics and thermodynamics data for the oxidative leaching of copper, zinc and iron from chalcopyrite, sphalerite and ilmenite minerals respectively. Pedroza *et al* (2012) studied the oxidative leaching of chalcopyrite and pyrite in sulphuric acid-ozone media, Xian *et al* 2012 investigated with hydrochloric-sodium chlorate solution. Sokić *et al* (2012) examined the oxidative leaching of sphalerite in sulphuric acid-sodium nitrate solution. Das *et al* (2012) also conducted a research of leaching of ilmenite in hydrochloric-calcium chloride medium. The scope of these investigations in most cases fails to cover the effect of the interaction of dissolution process variables and also, optimization of the leaching process. Desai *et al* (2008) opined that the conventional "one-factor-at-a-time" approach is laborious and time consuming. Moreover, it seldom guarantees the determination of optimal conditions. This research will seek to address this gap using RSM and ANFIS-PSO techniques. To the best of my knowledge, there is no published data on the use of statistical tool such as RSM to study the interactive effects; optimization tools like the RSM and ANFIS-PSO technique in the optimization of leaching process variables of metals from mineral ores using HCI-KCIO₃, HCI-KCI and HCI-NaNO₃ binary solutions as lixiviants.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Raw Materials: Mineral Ores

The raw materials used for this study are chalcopyrite sphalerite and ilmenite. The raw materials were sourced from eastern and northern parts of Nigeria. Chalcopyrite and sphalerite were sourced from Ohankwu Ikwo mine, Ikwo LGA and Ihietutu mine, Ivo LGA respectively from Ebonyi state (geographical location shown in appendix G) while ilmenite was sourced from a mine in Egon town, Egon Local Government Area, Nassarawa state.

The mineral ores were properly washed with water. This ensured the removal of unwanted materials, sand, dirt, etc. The washed materials (chalcopyrite, sphalerite and ilmenite) underwent sorting (separation of the desired ore from other overlying materials by physical examination of its physical appearance). This was done to increase the percentage of the desired mineral ore.

3.2 Chemicals and Equipments Used

Majority of the chemicals for this research were purchased from a chemical vendor at Head Bridge Onitsha Chemicals market in Anambra state, Nigeria. The chemicals used in the cause of the experiments for this research were all of analytical grade.

Chemicals used in this study are hydrochloric acid (HCl), potassium chloride (KCl), potassium chlorate (KClO₃), sodium nitrate (NaNO₃) and distilled water.

The equipments used for this research are presented in Table 3.1:

No	Name	Model	Uses
1.	Atomic Absorption Spectrophotometer (AAS)	FS 240 AA	For heavy metal analysis
2.	X-Ray Fluorescence (XRF)	EDX3600B	For elemental composition analysis
3.	X-Ray Diffractometer	ARL X'TRA	For mineralogical constituent evaluation
4.	Scanning Electron Microscopy (SEM)	Phenom Prox.	For Surface morphology analysis.
5.	Magnetic stirrer with Hot plate.	B.Bran Scientific model 78HW-1	For homogenization of the content of the reactor and determination of thermodynamic parameters
6.	Digital Weighing balance	BL 3002	To measure mass of materials/reagents.
7.	Two-neck flat bottom conical flask	Pyrex	Reactor for the leaching experiments
8.	Micro pipette		For collection of samples
9.	Spatula		Collection of samples and scraping material out of beakers
10.	Funnel		For easy transferring of liquids

Table 3.1: List of equipments, models and uses

11	Measuring cylinder (1000ml, 500ml, 100ml)		To measure different volumes of samples
12	Condenser	Pyrex	To return the vapourized fluid to the reactor
13	Beakers (250ml)	Pyrex	For mixing of samples
14.	Sieve		For size reduction
15.	Syringe (5ml, 10ml).		For supernatant solution withdrawal
16.	Stop watch		For time regulation
17.	Filter paper	What man	For filtration
18	Nose mask		For protection against inhaling poisonous gases and perceiving pungent smell
19	Hand Gloves		For hand covering

3.3 Characterization of the Mineral Ores

3.3.1 X-Ray Diffraction (XRD)

The X-ray diffraction (XRD) analyses were performed using a CuK α (0.15418 nm) source (40 kV, 40 mA) from a Siemens D-501, with a graphite secondary monochromator and a scintillation counter detector. The powdered sample was placed on a flat plastic plate, which was rotated at 30 r/min. The scans were performed at 25°C in 20 steps of 0.04°, with a 2 s recording time for each step. Where accurate 20 values were required, Si was added as internal 20 standard (Verryn, 2002).

3.3.2 Scanning electron microscopy (SEM)

Samples for scanning electron microscopy (SEM) were prepared by placing the powder samples on conductive carbon tape, which was in turn fixed to an aluminium plate. Scanning Electron Microscopy uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. In most SEM microscopy applications, data is collected over a selected area of the surface of the sample and a two-dimensional image is generated that displays spatial variations in properties including chemical characterization, texture and orientation of materials.

3.3.3 Energy dispersive x-ray (EDX) spectroscopy

The generation of the X-rays in a SEM is a two-step process. In the first step, the electron beam hits the sample and transfers part of its energy to the atoms of the sample. This energy can be used by the electrons of the atoms to "jump" to an energy shell with higher energy or be knocked-off from the atom. If such a transition occurs, the electron leaves behind a hole. Holes have a positive charge and, in the second step of the process, attract the negatively-charged electrons from higher-energy shells. When an electron from such a higher-energy shell fills the hole of the lower-energy shell, the energy difference of this transition can be released in the form of an X-ray. This X-ray has energy which is characteristic of the energy difference between these two shells. It depends on the atomic number, which is a unique property of every element. In this way, X-rays are a *"fingerprint"* of each element and can be used to identify the type of elements that exist in a sample.

3.3.4 X-ray fluorescence (XRF)

A pre-fired sample of 1g and 6g of lithium tetra-borate flux was mixed in a 5% Au/Pt crucible and fused at 1000°C in a muffle furnace with occasional swirling. The glass disk was transferred into a preheated Pt/Au mould and the bottom surface was analyzed. (Landman, 2003).

3.4 Leaching Test

Leaching experiments were performed in a 500ml two-neck flask glass reactor coupled with a reflux condenser equipped with a magnetic stirring system with hot plate. To study the effects of particle size, acid concentration, oxidant concentration, solution temperature, stirring speed and liquid-to-solid ratio on leaching process, experiments were carried out in batches. 2g of the ores (chalcopyrite, sphalerite and ilmenite) were introduced into the reactor containing 100ml of leachant placed on a magnetic stirrer. The magnetic stirrer agitated the solution at a fixed temperature (60 ± 2^{0} C), except for the study on effect of temperature where temperature ranged from 30^{0} C - 90^{0} C for 3 hours. At the end of the set time, the solution was filtered using Whatman No. 1 filter paper. Metal ion concentrations in the supernatant solutions were analyzed using atomic absorption spectrometer (model FS 240AA) after suitable dilutions of the leach liquor.

The percentage of metal dissolution into the solution from the mineral ore was calculated by the formula given in Equation (3.1):

% metal dissolved =
$$\frac{\text{Amount ofmetal passing into the solution}}{\text{Amount of metal in the original sample}} \times \frac{100}{1}$$
 (3.1)

3.4.1 Effect of acid concentration

The effect of concentration of hydrochloric acid on the leaching efficiency was investigated at different concentrations (1, 2, 3 and 4M) at temperature 60 ± 2^{0} C, 75µm particle size of the mineral ores, 300rpm and 2g/100ml liquid-to-solid ratio.

3.4.2 Effect of oxidant concentration

At an acid concentration of 1M, temperature 60 ± 2^{0} C, 75µm particle size of the mineral ores, 300rpm stirring speed and 2g/100ml liquid-to-solid ratio, the effect of oxidant concentration (0.15, 0.3, 0.45 and 0.6M) on the leaching efficiency was investigated.

3.4.3 Effect of particle size

The effect of particle size on the percentage copper, zinc and iron dissolved respectively in HCl-KClO₃, HCl-KCl and HCl-NaNO₃ binary solutions was studied by changing the particle size in the range of $75\mu m$ -600 μm of the mineral ores (chalcopyrite, sphalerite and ilmenite) at temperature 60 ± 2^{0} C.

3.4.4 Effect of temperature

The effect of temperature on the leaching performance of acid-oxidant solutions was studied. At temperature 30°C, the percentage of metal ion dissolved in the leachant was evaluated. 2g of the ore was dispersed in 100ml of 1M HCl - 0.6M oxidant at a stirring speed of 300rpm for 3 hours. The same process was repeated for temperatures 45, 60, 75 and 90°C. With the aid of an atomic absorption spectrophotometer (FS 240AA), the concentration of the metal dissolved in the supernatant solution at the end of each leaching time was measured.

3.4.5 Effect of stirring speed

The stirring speed of the content of the two-neck flask reactor was varied between 100rpm and 500rpm. The effect of the variation on leaching performance of the system was studied.

3.4.6 Effect of liquid/solid ratio

To study the effect of liquid-to-solid ratio on copper, zinc and iron extraction, the amount of chalcopyrite, sphalerite and ilmenite ores respectively were varied from 1 to 3g/100ml solution of the lixiviant while keeping other parameters such as solution temperature 75^{0} C, 300rpm stirring speed, 75 µm particle size constant.

3.5 Leaching Kinetic Studies

The rate at which the metallic ions were dissolved into the lixiviants was studied at varying temperatures (30, 45, 60 and 90°C), 75µm particle size, 300rpm stirring speed, 2g of the mineral ore and 100ml of the lixiviant. At predefined times (30, 60, 90, 120, 150 and 180 mins) about 3ml of the solution was withdrawn. The withdrawn solution was filtered and the concentration of the supernatant solution was measured using atomic absorption spectrometer (model FS 240AA) after suitable dilutions of the leach liquor. The Jander, Kroger and Ziegler, Zhuravlev, Lesokhin

and Templeman, Ginstling-Brounshtein and shrinking core kinetic model equations were evaluated to study the leaching kinetics process.

3.6 Dissolution Thermodynamics

The thermodynamic characteristics of the reaction system will indicate the maximum possible extent to which the value-bearing mineral can be converted to a soluble species, as well as the solubility of that species in the aqueous solution. The degree to which such a transfer can be achieved is determined by the rate at which the reaction proceeds.

To properly deduce the changes during the leach process and to rightfully conclude whether the process is spontaneous or not, thermodynamics parameters of the leaching process was studied. Equations (3.2) and (3.3) were employed to determine the thermodynamic parameters (Gibbs free energy change Δ G, enthalpy change Δ H and entropy change Δ S).

$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(3.2)

$$\Delta G = \Delta H - T\Delta S \tag{3.3}$$

The values of ΔS and ΔH can be calculated from the intercept and slope of the plot of ln k Vs. 1/T.

3.7 Design of Experiment for the Optimization of the Leaching Process

A fractional central composite factorial design was employed to study the effect of the interaction of five independent variables (factors) and also to generate a model. The independent variables studied were solution temperature, liquid-to-solid ratio, stirring speed, acid concentration and time. For the study of the combined interaction of the five factors, 32 runs of experiments were performed which was generated thus: $N = 2^{n-1} + 2n + n_c = 2^4 + (2x5)$ axial or star points + 6 (center points) = 32. The matrix for the five variables was varied at five levels (- α , -1, 0, +1, and + α). The lower level of variable was designated as "-1", intermediate lower level as "- α ", medium level as "0", intermediate higher level as "+ α ", and higher level as "+1".The

experiments were performed in random order to avoid systematic error. Tables 3.2 and 3.3 display the factor levels with their corresponding real values and the design matrix respectively.

Independent variable	Symbol			Range and	l levels	
		-α	-1	0	+1	$+\alpha$
Temperature (⁰ C)	А	30	45	60	75	90
Liquid-to-solid ratio (L/g)	В	10	15	20	25	30
Stirring Speed (rpm)	С	100	200	300	400	500
Acid Conc. (M)	D	1	2	3	4	5
Contact time (mins)	E	30	60	90	120	150

Table 3.2: Experimental range of the independent variables at different levels, to examine the interaction of different factors on the % metal dissolution on different lixiviants

Run	Temp. (K)		Liquid-t	o-solid	Stirring	speed	Acid con	c. (M)	Contact	time
order	A	L	ratio (g/L)	(rpı	n)	D		Ε	
			В		C					
	Coded	Real	Coded	Real	Coded	Real	Coded	Real	Coded	Real
1	+1	75	-1	15	-1	200	1	4	1	120
2	-1	45	-1	15	-1	200	1	4	-1	60
3	-1	45	1	25	-1	200	-1	2	-1	60
4	0	60	0	20	0	300	0	3	0	90
5	1	75	1	25	-1	200	1	4	-1	60
6	-1	45	-1	15	1	400	-1	2	-1	60
7	1	75	-1	15	-1	200	-1	2	-1	60
8	0	60	0	20	0	300	0	3	0	90
9	-1	45	1	25	-1	200	1	4	1	120
10	0	60	0	20	0	300	0	3	0	90
11	0	60	-α	10	0	300	0	3	0	90
12	0	60	0	20	0	300	0	3	0	90
13	-α	30	0	20	0	300	0	3	0	90
14	-1	45	1	25	1	400	-1	2	1	120
15	0	60	0	20	0	300	0	3	0	90
16	0	60	0	20	-α	100	0	3	0	90
17	0	60	0	20	0	300	0	3	0	90
18	0	60	0	20	0	300	0	3	- α	30
19	0	60	0	20	$+ \alpha$	500	0	3	0	90
20	0	60	0	20	0	300	$+ \alpha$	5	0	90
21	0	60	0	20	0	300	- α	1	0	90
22	1	75	-1	15	1	400	1	4	-1	60
23	0	60	$+ \alpha$	30	0	300	0	3	0	90
24	$+\alpha$	90	0	20	0	300	0	3	0	90
25	1	75	1	25	-1	200	-1	2	1	120
26	-1	45	1	25	1	400	1	4	-1	60
27	-1	45	-1	15	-1	200	-1	2	1	120
28	1	75	1	25	1	400	1	4	1	120
29	0	60	0	20	0	300	0	3	$+ \alpha$	150
30	1	75	-1	15	1	400	-1	2	1	120
31	-1	45	-1	15	1	400	1	4	1	120
32	1	75	1	25	1	400	-1	2	-1	60

Table 3.3 Experimental design for dissolution studies using different lixiviants

The dependent and independent variables are related by a second order quadratic model. The second order model is represented in equation (3.4).

$$Y = \beta_{0} + \beta_{1}x_{1} + \beta_{2}x_{2} + \beta_{3}x_{3} + \beta_{4}x_{4} + \beta_{5}x_{5} + \beta_{6}x_{1}x_{2} + \beta_{7}x_{1}x_{3} + \beta_{8}x_{1}x_{4} + \beta_{9}x_{1}x_{5} + \beta_{10}x_{2}x_{3} + \beta_{11}x_{2}x_{4} + \beta_{12}x_{2}x_{5} + \beta_{13}x_{3}x_{4} + \beta_{14}x_{3}x_{5} + \beta_{15}x_{4}x_{5} + \beta_{16}x_{1}^{2} + \beta_{17}x_{2}^{2} + \beta_{18}x_{3}^{2} + \beta_{19}x_{4}^{2} + \beta_{20}x_{5}^{2}$$

$$(3.4)$$

3.8 Modelling with ANFIS

Adaptive neuro fuzzy inference system is an intelligent model that comprises of ANN and fuzzy logic which is very efficient in modeling and gives a very high degree of prediction when utilized. Figure 3.1 is the flow chart of modeling with ANFIS



承 Neuro-Fuzzy Designer: Untitled File Edit View ANFIS Info 1 # of inputs: 1 # of outputs: 1 # of input mfs: 3 0.5 0 0 0.2 0.4 0.6 0.8 1 Clear Plot Load data Generate FIS Train FIS Test FIS Optim. Method: Type From: Load from file hybrid -Plot against: Training file Load from worksp. Error Tolerance: Training data Testing 0 Grid partition Testing data Checking worksp. Epochs: Sub. clustering Checking data 3 Demo Load Data... Clear Data Generate FIS Train Now Help Close

ANFIS graphic user interface is shown in Plate 3.1. The input variable, the experimental output, the membership function models and the number of epochs are selected in this GUI.

Plate 3.1: ANFIS GUI before selecting the required parameters

Plate 3.2 shows the GUI after selecting the required parameters and training.

承 Neuro-Fuzzy Designer: Untit	led	
File Edit View		
20 -	Training Error	ANFIS Info.
20 - 20 - 10 - *******	** ^{***********************************}	# of inputs: 5 # of outputs: 1 # of input mfs: 7 7 7 7 7
0 ** · 0 5	10 15 20 25	30 Clear Plot
	Epochs	
Load data	Generate FIS Train FIS	Test FIS
Training Tresting Checking Demo Load Data Clear Data	Load from file Load from worksp. Grid partition Sub. clustering Generate FIS	 Plot against: Training data Test Now
a new fis generated	Не	Ip Close

Plate 3.2: ANFIS GUI after selecting the parameters and simulating.

The fuzzy logic input and output parameters are shown in Plate 3.3.

👞 Fuzzy Logic Desig	gner: Untitled			
File Edit View				
	\leq			
		Untitled (sugeno	,	f(u)
input4				output
FIS Name:	Untitled		FIS Type:	sugeno
And method	prod	-	current Variable	
Or method	probor	- N	lame	input1
Implication	min	- T	ype	input
Aggregation	max	- L		[505 565]
Defuzzification	wtaver	•	Help	Close
System "Untitled": 5 i	inputs, 1 output, and 1680	7 rules		

Plate 3.3: Fuzzy logic Input and output parameters

Plate 3.3 shows that there are five inputs and one output. The membership function used for the variables is displayed in Plate 3.4.



Plate 3.4: Membership function

The type of membership function used in this study is the triangular membership function which is seven in number for each model.

承 I	Rule Edit	or: Untitl	ed										×
File	e Edit	View	Options										
1.	lf (input1	is in1mf1)) and (input2 i	s in2mf1)	and (in	iput3 is	in3mf1)	and	(input4	is in4mf1)	and (inp	out5 is inf	
2.	lf (input1 lf (input1	is in1mf1) is in1mf1)	and (input2 is) and (input2 is)	s in2mf1) s in2mf1)	and (in and (in	iput3 is iput3 is	in3mf1) in3mf1)	and (and ((input4 (input4	is in4mf1) is in4mf1)	and (inp and (inp	out5 is info out5 is info	im 🔤 📗
4. 5.	lf (input1 lf (input1	is in1mf1) is in1mf1)	and (input2 is) and (input2 is)	s in2mf1) s in2mf1)	and (in and (in	iput3 is iput3 is	in3mf1) in3mf1)	and and	(input4 (input4	is in4mf1) is in4mf1)	and (inp and (inp	out5 is in5 out5 is in5	im
6. 7.	If (input1 If (input1	is in1mf1) is in1mf1)	and (input2 is and (input2 is	s in2mf1) s in2mf1)	and (in and (in	iput3 is iput3 is	in3mf1) in3mf1)	and and	(input4 (input4	is in4mf1) is in4mf1)	and (inp and (inp	out5 is in5 out5 is in5	im
8. 9.	If (input1 If (input1	is in1mf1) is in1mf1)	and (input2 is and (input2 is	s in2mf1) s in2mf1)	and (in and (in	iput3 is iput3 is	in3mf1) in3mf1)	and and	(input4 (input4	is in4mf2) is in4mf2)	and (inp and (inp	out5 is in5 out5 is in5	im im +
•													•
lf	input1	is	and input2 is		and in	put3 is		and	input4 i	s	and inc	out5 is	Th
in1 in1 in1 in1 in1 in1	1mf1 1mf2 1mf3 1mf4 1mf5 1mf6	4 III +	in2mf1 in2mf2 in2mf3 in2mf4 in2mf5 in2mf6	4	in3mf1 in3mf2 in3mf3 in3mf4 in3mf5 in3mf6		• III •	in4m in4m in4m in4m in4m	11 12 13 14 15 16	4 III +	in5mf2 in5mf2 in5mf3 in5mf4 in5mf5 in5mf6		
	not Connecti or and	on –	not Weight:	Delete	rule not	A	dd rule		ot Change	rule	not	<<	>>
FIS	S Name: U	Intitled								Help		Close	;

The rules arrangement embedded in the Sugeno model is shown in Plate 3.5

Plate 3.5: ANFIS Sugeno model rules

A total of 16,807 rules were generated in the Sugeno model. The rules are further enhanced as shown in table 3.4

Runs	Input1	Input2	Input3	Input4	Input5	Output
1	In1mf1	In2mf1	In3mf1	In4mf1	In5mf1	Out1mf1
2	In1mf1	In2mf1	In3mf1	In4mf1	In5mf2	Out1mf2
3	In1mf1	In2mf1	In3mf1	In4mf1	In5mf3	Out1mf3
4	In1mf1	In2mf1	In3mf1	In4mf1	In5mf4	Out1mf4
5	In1mf1	In2mf1	In3mf1	In4mf1	In5mf5	Out1mf5
6	In1mf1	In2mf1	In3mf1	In4mf1	In5mf6	Out1mf6
7	In1mf1	In2mf1	In3mf1	In4mf1	In5mf7	Out1mf7
8	In1mf1	In2mf1	In3mf1	In4mf2	In5mf1	Out1mf1
9	In1mf1	In2mf1	In3mf1	In4mf2	In5mf2	Out1mf2
10	In1mf1	In2mf1	In3mf1	In4mf2	In5mf3	Out1mf3
11	In1mf1	In2mf1	In3mf1	In4mf2	In5mf4	Out1mf4
12	In1mf1	In2mf1	In3mf1	In4mf2	In5mf5	Out1mf5
13	In1mf1	In2mf1	In3mf1	In4mf2	In5mf6	Out1mf6
14	In1mf1	In2mf1	In3mf1	In4mf2	In5mf7	Out1mf7
15	In1mf1	In2mf1	In3mf1	In4mf3	In5mf1	Out1mf1
16	In1mf1	In2mf1	In3mf1	In4mf3	In5mf2	Out1mf2
17	In1mf1	In2mf1	In3mf1	In4mf3	In5mf3	Out1mf3
18	In1mf1	In2mf1	In3mf1	In4mf3	In5mf4	Out1mf4
19	In1mf1	In2mf1	In3mf1	In4mf3	In5mf5	Out1mf5
20	In1mf1	In2mf1	In3mf1	In4mf3	In5mf6	Out1mf6
21	In1mf1	In2mf1	In3mf1	In4mf3	In5mf7	Out1mf7
22	In1mf1	In2mf1	In3mf1	In4mf4	In5mf1	Out1mf1
23	In1mf1	In2mf1	In3mf1	In4mf4	In5mf2	Out1mf2
24	In1mf1	In2mf1	In3mf1	In4mf4	In5mf3	Out1mf3
25	In1mf1	In2mf1	In3mf1	In4mf4	In5mf4	Out1mf4
26	In1mf1	In2mf1	In3mf1	In4mf4	In5mf5	Out1mf5
27	In1mf1	In2mf1	In3mf1	In4mf4	In5mf6	Out1mf6
28	In1mf1	In2mf1	In3mf1	In4mf4	In5mf7	Out1mf7
29	In1mf1	In2mf1	In3mf1	In4mf5	In5mf1	Out1mf1
30	In1mf1	In2mf1	In3mf1	In4mf5	In5mf2	Out1mf2
31	In1mf1	In2mf1	In3mf1	In4mf5	In5mf3	Out1mf3
32	In1mf1	In2mf1	In3mf1	In4mf5	In5mf4	Out1mf4
33	In1mf1	In2mf1	In3mf1	In4mf5	In5mf5	Out1mf5
34	In1mf1	In2mf1	In3mf1	In4mf5	In5mf6	Out1mf6
35		In2mf1	In3mf1	In4mf5	In5mf7	Out1mf/
36		In2mf1	In3mf1	In4mf6	In5mf1	OutImfl
37		In2mf1	In3mf1	In4mf6	In5mf2	Out1mf2
38		In2mf1	In3mf1	In4mf6	In5mf3	Out1mf3
39		$\ln 2mfl$	In3mf1	In4mf6	In5mf4	Out1mf4
40	In Imf I	$\ln 2m \Gamma$	$1n_{3}mf_{1}$	In4mf6	Inomio	Out1mf5
41		In2mII	103m11	In4mI6		Out1mf6
42		1n2m1	103m1	104m16	Inomi /	Out1mf/
43	Inimfi	In2mf1	in3mf1	In4mf /	Insmfl	OutImfl

Table 3.4: Rules for the Sugeno model

44	In1mf1	In2mf1	In3mf1	In4mf7	In5mf2	Out1mf2
45	In1mf1	In2mf1	In3mf1	In4mf7	In5mf3	Out1mf3
46	In1mf1	In2mf1	In3mf1	In4mf7	In5mf4	Out1mf4
47	In1mf1	In2mf1	In3mf1	In4mf7	In5mf5	Out1mf5
48	In1mf1	In2mf1	In3mf1	In4mf7	In5mf6	Out1mf6
49	In1mf1	In2mf1	In3mf1	In4mf7	In5mf7	Out1mf7
50	In1mf1	In2mf1	In3mf2	In4mf1	In5mf1	Out1mf1
51	In1mf1	In2mf1	In3mf2	In4mf1	In5mf2	Out1mf2
52	In1mf1	In2mf1	In3mf2	In4mf1	In5mf3	Out1mf3
53	In1mf1	In2mf1	In3mf2	In4mf1	In5mf4	Out1mf4
54	In1mf1	In2mf1	In3mf2	In4mf1	In5mf5	Out1mf5
55	In1mf1	In2mf1	In3mf2	In4mf1	In5mf6	Out1mf6
56	In1mf1	In2mf1	In3mf2	In4mf1	In5mf7	Out1mf7

Where In1mf1 is input 1 membership function 1 and out1mf1 is output 1 membership function 1. Table 3.4 is the first 56 rules of the model.

The architecture of the artificial neural network is displayed in Plate 3.6



Plate 3.6: ANFIS structure

3.9 Particle Swarm Optimization (PSO)

The algorithm for PSO is shown in figure 3.2



Figure 3.2: Particle swarm optimization format.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Characterization of Chalcopyrite, Sphalerite and Ilmenite

X-ray fluorescence (XRF), scanning electron microscopy (SEM), energy dispersive x-ray (EDX) spectroscopy and X-ray diffractometry results displayed the elemental compositions, morphology and mineralogy of the investigated ores.

4.1.1 X-ray fluorescence (XRF)

The results of the elemental composition of the Nigerian sourced chalcopyrite, sphalerite and ilmenite using the X-ray fluorescence technique are presented in Tables 4.1, 4.2 and 4.3, respectively. The results reveal that copper, iron and sulphur are the dominant elements in chalcopyrite; zinc and sulphur are dominant in sphalerite while titanium and iron are dominant in ilmenite ore. Other elements occurred in traces as it is evident in Tables 4.1, 4.2 and 4.3. The dominance of copper, iron and sulphur in chalcopyrite from Ohankwu Ikwo mine, Ikwo LGA, Ebonyi state (Table 4.1) is similar to the characterization result presented in Table 2.3 for chalcopyrite ore from Sonora Mexico, Sivas Turkey and Chile. Zinc and sulphur dominated the elemental compositions of sphalerite from Western Turkey, Isfahan Iran and India (Table 2.4). This is similar to the findings from sphalerite sourced from Ihietetu mine, Ivo LGA, Ebonyi state (Table 4.2). Table 2.5 shows that titanium and iron were major elements in Australian and Chinese ilmenite. This is similar to result presented for Egon, Nassarawa ilmenite in Table 4.3. In addition to titanium and iron, the presence of silicon was appreciable for Kwara, Nigerian ilmenite (Table 2.5).

Table 4.1: XRF result for chalcopyrite

				-							
Majo	r eleme	ental co	ompositi	ion (%)						
Al	Si	Р	S	Κ	Ca	Fe	Cu	As	s Pb	Au	
2.20	5.46	0.59	41.31	0.35	0.16	16.85	24.22	2 0.6	6 6.27	0.73	
											_
Table	e 4.2: X	KRF res	sult for s	sphaler	ite						
Majo	r eleme	ental co	ompositi	ion (%)						
Al	Si	Р	S	Ca	Co	Fe	Ni	Cu	Zn	Sn	Sb
0.72	0.32	0.32	23.44	0.01	0.04	1.19	0.05	0.04	57.56	0.02	0.04

Table 4.3: XRF result for ilmenite

Major	Major elemental composition (%)													
Al	Si	Р	S	Ca	Ti	Mn	Co	Fe	Ni	Cu	Zn	Nb	Mo	Sn
2.80	5.06	1.72	2.98	1.98	37.46	1.23	0.56	29.28	0.06	0.13	0.16	0.95	0.24	15.06

4.1.2 Scanning electron microscopy (SEM) and Energy Dispersive X-Ray (EDX) Spectroscopy

The morphologies of the ores were pictured using the scanning electron microscopy. There is a visible modification between the raw samples (Plates 4.1, 4.3 and 4.5) and their corresponding residues (Plates 4.7, 4.9 and 4.11). The particles seen in the micrographs for the raw samples have irregular shapes with rough edges and seem to be highly crystalline. The reduction in crystallinity of the particles observed in the residues as compared with the appearances in the raw samples may be due to the attack of the lixiviants on the ores (Nnanwube and Onukwuli, 2018). It can be observed that smaller particles in the submicron range aggregated to form particle sizes in range of several microns. Hence, powders adhere together and agglomerated due to the leaching treatment (Zarib *et al* 2019).

The observed shifts in peaks of the elemental compositions of the raw samples (Plates 4.2, 4.4 and 4.6) and their corresponding residues (4.8, 4.10 and 4.12) suggest interactions between the binary solutions and mineral ores. The energy dispersive x-ray (EDX) spectra of the residues of chalcopyrite, sphalerite and ilmenite ores obtained from HCl-KClO₃ media leaching and presented in Plates 4.8, 4.10 and 4.12 show the presence of sulphur, lead and iron with traces of copper, manganese and zinc; lead, zinc and copper; tin and vanadium respectively. The y-axis of the EDX spectra depicts the number of counts (number of x-rays received and processed by the detector) and x-axis, the energy of the X-rays. The position of the peaks leads to the identification of the elements and the peak height helps in the qualitative analysis of each element's concentration in the sample. Similar findings were observed in chalcopyrite, sphalerite and ilmenite residues from HCl-KCl and HCl-NaNO₃ media. Their micrographs and elemental compositions from EDX spectra are presented in Appendix A.





Plate 4.1: SEM micrograph for raw chalcopyrite sample

Plate 4.2: EDX spectrum for raw chalcopyrite sample



Plate 4.3: SEM micrograph for raw sphalerite sample







Plate 4.5: SEM micrograph for raw ilmenite sample



Plate 4.6: EDX spectrum for raw ilmenite sample



Plate 4.7: SEM micrograph for Chalcopyrite residue leached with HCl-KClO₃



Plate 4.8: EDX spectrum for chalcopyrite residue leached with HCl- $\ensuremath{\mathsf{KClO}_3}$



Plate 4.9: SEM micrograph for Sphalerite residue leached with HCl-KClO₃



Plate 4.10: EDX spectrum for Sphalerite residue leached with HCl-KClO₃



Plate 4.11: SEM micrograph for Ilmenite residue leached with HCl-KClO₃



Plate 4.12: EDX spectrum for Ilmenite residue leached with HCI-KCIO₃

4.1.3 X-ray diffraction analysis

Tables 4.4 to 4.6 display the x-ray diffractograms of the mineralogical compositions of raw samples of chalcopyrite, sphalerite and ilmenite. The results show that chalcopyrite exist mainly as CuFeS₂, sphalerite as ZnS and ilmenite as FeTiO₃. Table 4.4 recorded that chalcopyrite ore gave three major peaks at 2.9967, 2.9024 and 2.6174Å respectively. Also, Table 4.5 and 4.6 recorded that sphalerrite and ilmenite ores gave three major peaks each at 3.1274, 1.6332, 2.7078Å and 2.7310, 2.7563 and 2.2407 Å respectively. Chalcopyrite, sphalerite and ilmenite diffractograms are displayed in Figures A1 – A3 in Appendix A. similar observations were made by Baba *et al* (2014), Sokić *et al* (2012), Hasani *et al* 2015 and Li *et al* 2008.

20	d-value (Å)	Compound	I/Io	JCPDS file no
29.82	2.9967	Chalcopyrite (CuFeS ₂)	1000.00	96-101-0941
30.81	2.9024	Chalcopyrite (CuFeS ₂)	651.41	96-101-0941
34.26	2.6174	Chalcopyrite (CuFeS ₂)	342.65	96-101-0941
58.66	1.5738	Chalcopyrite (CuFeS ₂)	71.99	96-101-0941

Table 4.4: X-ray diffraction data for raw chalcopyrite sample

JCPDS File No: Joint Committee on Power Diffraction Standards File Number

Table 4.5: X-ray diffraction data for raw sphalerite sample

20	d-value (Å)	Compound	I/Io	JCPDS file no
33.05	2.7078	Sphalerite (ZnS)	115.76	96-110-1051
56.28	1.6332	Sphalerite (ZnS)	682.62	96-110-1051
28.52	3.1274	Sphalerite (ZnS)	1000.00	96-110-1051
59.03	1.5637	Sphalerite (ZnS)	39.95	96-110-1051

JCPDS File No: Joint Committee on Power Diffraction Standards File Number

Table 4.6: X-ray diffraction data for raw ilmenite sample

		-		
20	d-value (Å)	Compound	I/Io	JCPDS file no
32.48	2.7563	Ilmenite (FeTiO ₃)	704.93	96-900-8036
32.79	2.7310	Ilmenite (FeTiO ₃)	909.80	96-900-8036
40.25	2.2407	Ilmenite (FeTiO ₃)	134.78	96-900-8036
50.32	1.8132	Ilmenite (FeTiO ₃)	62.49	96-900-8036

4.2 Batch Leaching Studies

4.2.1 Effect of Acid Concentration

The influence of hydrochloric acid concentrations on the dissolution rates of ores under investigation were illustrated in Figure 4.1. The results indicated that copper, zinc and iron dissolved up to about 77.46%, 80.61% and 67.22% in 180 minutes at concentration as low as 1M while at the same residence time and 4M, the minerals dissolved up to about 96.75%, 88.73% and 80.11%, respectively (Table B1). It is evident from the plots that the percentage of copper, zinc and iron dissolved increases with increasing acid concentration. It was observed that there was less than 4% increment when the acid concentration was increased from 3M to 4M. The observation within this region according to Olanipekun, 1999 could among other things be attributed to precipitation phenomena. Hence, concentration of the leachant has a significant effect on the leaching of ores. The higher the concentration of HCl, the higher the percentage of the mineral ore dissolved trend followed possibly reveal that the rate of minerals dissolution is

affected directly by the hydrogen ion $[H^+]$ concentration. Similar findings were reported by Adekola *et al.* (2018) and Baba *et al.* (2005).



Figure 4.1: Effect of acid concentration on %yield

4.2.2 Effect of Oxidant Concentration

Figures 4.2 to 4.4 reveal the effect of oxidants (KCl, KClO₃ and NaNO₃) on the leaching efficiencies of chalcopyrite, sphalerite and ilmenite. The oxidants were varied between 0.15M to 0.60M in 1M acid concentration, 60°C solution temperature, 75µm particle size, 2g/100ml liquid-to-solid ratio and 300rpm stirring speed. A relatively low leaching efficiency of 77.46%, 80.61% and 67.22% were observed for chalcopyrite, sphalerite and ilmenite ores respectively prior to the addition of the oxidants. At 0.6M KCl, KClO₃ and NaNO₃, 93.75%, 92.16% and 85.67%; 87.95%, 91.22% and 86.13%; 81.83%, 81.09% and 76.62% respectively were recorded for chalcopyrite, sphalerite and ilmenite respectively (Tables B2 - B4). The visible difference in the leaching efficiency observed suggests that addition of the oxidants under investigation to hydrochloric acid have synergetic effect on the leaching rates of chalcopyrite, sphalerite and ilmenite. This may be due to the high oxidation potential of the selected oxidants (Table 2.7) which considerably contributes to increasing the dissolution of the ore by partially converting the sulfide to elemental sulphur and subsequently to sulphates, polysulphides, etc. Xian et al. (2012) recorded similar observations in their research, leaching chalcopyrite with sodium chlorate, and therefore concluded that leaching efficiency increases with increase in the NaClO₃ concentration. The results obtained as presented in Figures 4.2 to 4.4 and also Tables B2 to B4 in Appendix B depict that the leaching efficiencies of chalcopyrite, sphalerite and ilmenite are dependent on concentration of the leaching solution. At room temperature, the solubility of potassium chlorate is 8.15g/100ml. Concentration above 0.6M will produce a supersaturated solution therefore 0.6M concentration was not exceeded.





Figure 4.2: Effect of oxidant conc. on %Cu dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution

4.2.3

Effect of part

Figure 4.3: Effect of oxidant conc. on %Zn dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution



Figure 4.4: Effect of oxidant conc. on %Fe dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution

The results on the effect of particle size on chalcopyrite, sphalerite and ilmenite dissolution in 1M HCl-0.6M KCl, 1M HCl-0.6M KClO₃ and 1M HCl-0.6M NaNO₃ leaching media were investigated in the range of 75 μ m to 600 μ m at a temperature of 60°C, 300rpm stirring speed and 2g/100ml liquid-to-solid ratio. The percentage mineral dissolved is plotted against different

particle sizes for various leachants under investigation as shown in Figures 4.5 to 4.7. The trend followed by the plots reveal an inversely proportional relationship between particle size and percentage copper, zinc and iron dissolved. The better performance recorded at finer particle sizes can be explained by the fact that smaller (finer) particles of the ground samples are associated with larger specific active surface area, thereby enhancing the samples' exposure to the lixiviants. The results suggest that for larger particle sizes of the ores, the lixiviant molecules did not completely penetrate into the particle. Therefore, 75µm is the preferred chalcopyrite, sphalerite and ilmenite particle size for further experiments conducted (Tables B5 to B7 in Appendix B). The findings indicated that the smaller particle size fraction result in a faster dissolution rate, which is consistent with the report presented by Feng *et al.* (2015).



Figure 4.5: Effect of particle size on %Cu dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution



Figure 4.6: Effect of particle size on %Zn dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution



4.2.4 Effect of solution temperature

The results obtained as presented in Figures 4.8 to 4.10 and also Tables B8 to B10 in Appendix B depict that the dissolution percentage of copper, zinc and iron is dependent on the lixiviant temperature. While the leaching fraction of copper, zinc and iron were generally below 50% at 30 °C after 180 minutes, it was increased to above 90% at about 75 °C. As the reaction temperature was further increased to 90 °C a negligible effect on the leaching fractions of copper, zinc and iron was observed. In a similar research, Feng *et al.* (2015) concluded in their research that the reaction temperature significantly affected the dissolution rate at a lower temperature range. At a higher temperature the difference was not so great as to justify the greater energy consumption. To determine the other leaching parameters, 75 °C was chosen as the optimum leaching temperature. The selection of 75 °C is also advantageous since it is lower than the boiling point of solution. By this way the leaching process will be more economical by preventing loss of the lixiviant through evaporation.



Figure 4.8: Effect of solution temperature on %Cu dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution



Figure 4.9: Effect of solution temperature on %Zn dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution



Figure 4.10: Effect of solution temperature on %Fe dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution

4.2.5 Effect of stirring speed

The effect of stirring speed on the percentage leaching efficiency of lixiviants was investigated in the range of 100 - 500 rpm at 75µm particle size of the ores, 75°C solution temperature and 1M HCl/0.6M oxidant. Figures 4.11 to 4.13 show that leaching efficiency generally increased with increase in stirring speed. The increase in leaching efficiency observed was more pronounced between 100 - 300 rpm above which the effect of further increase in stirring speed was marginal. The observation between 100 - 300 rpm might be as a result of enhanced diffusion of liquid reactants (Wang *et al.*, 2017). Agitation reduces the liquid film thickness formed around the ore particles thus the diffusion through the boundary layer of the leaching reagent toward the external surface of the particles eases (Ekmekyapar*et al.*, 2014). Therefore, increasing the stirring speed promotes reactants diffusion from bulk solution to mineral surface and improves the leaching rate (Ghasemi and Azizi, 2017). Above 300rpm, dissolution rate became almost independent of the stirring speed. This implies that the leaching process within this stirring speed (300 – 500rpm) is not controlled by film diffusion (Xian *et al.*, 2012) but by chemical reaction



also reported by Baba et al. (2005).

Figure 4.11: Effect of stirring speed on %Cu dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution



Figure 4.12: Effect of stirring speed on %Zn dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution



(Deng et al., 2015). The stirring speed was then kept constant at 300rpm. Similar findings was

4.2.6 Effect of

Figure 4.13: Effect of stirring speed on %Fe dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution

Results of fraction of copper, zine and non-ore disported as a function of inquit to solid ratios are displayed in Figures 14 to 16. It is clear from the displayed Figures that the more liquid-to-solid ratio was increased from 10 g/l to 30 g/l, the more chalcopyrite, sphalerite and ilmenite dissolution. Chalcopyrite, sphalerite and ilmenite in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions recorded an increase from 79.08%, 84.91% and 78.39% to 97.76%, 93.99% and
91.14%; 79.47%, 84.72% and 73.42% to 94.85%, 96.72% and 93.98%; 81.17%, 88.02% and 79.86% to 97.03%, 96.08%, 92.17% at 180 minutes residence time (Tables 14 to 16). The selected liquid-to-solid ratios selected for the study did not saturate the lixiviant hence the trend followed by the plots. Upward review of the liquid-to-solid ratio is tantamount to increase in leachable particles per unit of the lixiviant. Similar finding was reported by Khawassek *et al.*, 2016.



Figure 4.14: Effect of liquid-to-solid ratio on %Cu dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution



Figure 4.15: Effect of liquid-to-solid ratio on %Zn dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution



Figure 4.16: Effect of liquid-to-solid ratio on %Fe dissolved in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solution

4.3 Leaching Kinetics

Eight kinetics models were investigated at different contact times for better understanding of the dissolution of chalcopyrite, sphalerite, ilmenite ores in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media. The experimental data in Figures 4.17 to 4.22 were correlated with the selected kinetic models (Equations 4.1 to 4.8) for solid-liquid reactions to determine the mechanics of the reaction, evaluate apparent activation energy and derive a semi-empirical model - model in which calculations are based on a combination of observed associations between variables and theoretical considerations relating variables through fundamental principles (IPCC, 2013) governing the kinetics process. The models include: shrinking core models (diffusion through liquid film model(DTLF), diffusion through product layer model (DTPL), surface chemical reaction model (SCR)), mixed kinetics model (MKM), Jander (three dimensional) model, Kröger and Ziegler model, Zhuravlev, Lesokhin and Templeman model and Ginstling-Brounshtein model. The selected model equations are tabulated in Table 4.7.

Model	Equation	Plot made	Equation
			number
DTLF	$k_1 t = x$	x vs t	(4.1)
DTPL	$k_d t = 1 - 3(1 - x)^{2/3} + 2(1 - x)$	$1 - 3(1 - x)^{2/3} + 2(1 - x) vs t$	(4.2)
SCR	$k_r t = 1 - (1 - x)^{1/2}$	$1-(1-x)^{1/2} vs t$	(4.3)
МКМ	$\left(1 - \frac{2x}{3}\right) - (1 - x)^{\frac{2}{3}} + \frac{1}{b} \left[1 - (1 - x)^{\frac{1}{3}}\right] = Kt$	$\left(1 - \frac{2x}{3}\right) - (1 - x)^{\frac{2}{3}} + \frac{1}{b} \left[1 - (1 - x)^{\frac{2}{3}}\right] vs t$	(4.4)
Jander (three dimensional)	$(1 - (1 - x)^{1/3})^2 = k't$	$(1 - (1 - x)^{1/3})^2 vs t$	(4.5)
Kröger and Ziegler	$(1 - (1 - x)^{1/3})^2 = k_3 lnt$	$(1 - (1 - x)^{1/3})^2$ vs lnt	(4.6)
Zhuravlev, Lesokhin and Templeman	$\left((1-x)^{-1/3}-1\right)^2 = k_5 t$	$((1-x)^{-1/3}-1)^2 vs t$	(4.7)
Ginstling-	$kt = 1 - {\binom{2}{2}}x - (1 - x)^{2/2}$	$1 - \left(\frac{2}{2}\right)x - (1 - x)^{2/2} vs t$	(4.8)
Brounshtein	(3)	(3/	

Table 4.7: Leaching kinetic model equations

4.3.1 Leaching kinetics for chalcopyrite using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions as lixiviants

4.3.1.1 HCl-KCl

In order to study the reaction mechanism and kinetics of the dissolution of chalcopyrite ore in HCl-KCl lixiviant, the process variables (acid concentration, oxide concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio) were plotted against time as shown in Figures 4.17 - 4.22, respectively.



Figure 4.17: Effect of acid conc. on %Cu dissolved using HCI-KCI



Figure 4.18: Effect of oxidant concentration on %Cu dissolved using



Figure 4.19: Effect of particle size on %Cu dissolved using HCI-KCI



Figure 4.20: Effect of solution temperature on %Cu dissolved using HCl-



Figure 4.21: Effect of stirring speed on %Cu dissolved using HCI-KCI



Figure 4.22: Effect of liquid-to-solid ratio on %Cu dissolved using HCl-KCl

The experimental data plotted in Figures 4.17 to 4.22 were fitted into equations (4.1) to (4.8) to ascertain the kinetic equation that best described the dissolution kinetics of chalcopyrite in HCl-KCl solution at various acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio. From Table 4.8, Kröger and Ziegler kinetic model's correlation coefficient (\mathbb{R}^2) values showed excellent linearity ($\mathbb{R}^2 > 0.9$) for the

dissolution of chalcopyrite ore in HCl-KCl binary solution. The higher coefficient of determination reported for Kröger and Ziegler diffusion controlled kinetic reaction model when compared with other models investigated show higher favourability of the Kröger and Ziegler kinetic model in describing the kinetics of the process. Therefore, the overall rate is diffusion controlled and adequately described by the Kröger and Ziegler kinetic model equation. The fitted plots are displayed in Figures 4.23 to 4.28. The ill-fitted plots are shown in Figures D1 to D36 in Appendix D.

Process parameters				R ² (Chalcor	oyrite-HCl-KCl)			
L	DTLF	DTPL	SCR	MKM	JANDER	KROGER	ZLT	GINSTLING
Acid Conc								
1	0.692	0.857	0.778	0.854	0.873	0.988	0.903	0.857
2	0.717	0.906	0.860	0.905	0.924	0.990	0.938	0.906
3	0.731	0.916	0.873	0.914	0.942	0.990	0.959	0.916
4	0.750	0.923	0.894	0.923	0.946	0.991	0.923	0.923
Ox. Conc								
0.15	0.816	0.966	0.923	0.966	0.978	0.988	0.965	0.966
0.3	0.768	0.949	0.895	0.947	0.964	0.994	0.958	0.949
0.45	0.734	0.923	0.871	0.922	0.939	0.993	0.926	0.923
0.6	0.739	0.937	0.894	0.936	0.963	0.992	0.961	0.937
Particle Size								
75	0.739	0.937	0.894	0.936	0.963	0.992	0.961	0.937
150	0.794	0.98	0.935	0.985	0.982	0.998	0.894	0.986
300	0.82	0.983	0.939	0.983	0.976	0.997	0.892	0.983
600	0.829	0.98	0.916	0.979	0.989	0.985	0.969	0.98
Temperature								
30	0.991	0.946	0.995	0.957	0.941	0.878	0.922	0.946
45	0.883	0.984	0.947	0.984	0.987	0.950	0.960	0.984
60	0.729	0.911	0.870	0.911	0.931	0.991	0.926	0.911
75	0.640	0.899	0.848	0.896	0.954	0.981	0.956	0.899
90	0.688	0.913	0.869	0.911	0.951	0.988	0.962	0.913
Stirring Speed								
100	0.674	0.852	0.786	0.850	0.873	0.986	0.904	0.852
200	0.656	0.871	0.809	0.868	0.906	0.984	0.952	0.871
300	0.640	0.899	0.848	0.896	0.954	0.981	0.956	0.899
400	0.659	0.893	0.849	0.891	0.934	0.984	0.950	0.893
500	0.663	0.919	0.891	0.918	0.971	0.984	0.904	0.919
Solid –Liquid								
10	0.873	0.925	0.915	0.926	0.928	0.943	0.919	0.925
15	0.786	0.926	0.901	0.925	0.941	0.984	0.944	0.926
20	0.640	0.899	0.848	0.896	0.954	0.981	0.956	0.899
25	0.560	0.846	0.794	0.843	0.921	0.961	0.899	0.846
30	0.502	0.796	0.735	0.792	0.909	0.941	0.911	0.796

Table 4.8: Coefficient of determination values for investigated kinetic models at various process variables





Figure 4.23: Kroger and Ziegler kinetic plots for chalcopyrite at different acid concentrations



Figure 4.24: Kroger and Ziegler kinetic plots for Chalcopyrite in HCl-KCl at different oxide concentrations



Figure 4.25: Kroger and Ziegler kinetic plots for chalcopyrite in HCl-KCl at different Particle



Figure 4.27: Kroger & Ziegler Kinetic plots for chalcopyrite in HCl-KCl at diff. stirring speed



Figure 4.26: Kroger & Ziegler plots for chalcopyrite in HCl-KCl at different Solution Temperatures



Figure 4.28: Kroger & Ziegler kinetic plots for chalcopyrite in HCl-KCl at diff. liquid-solid ratio

The apparent rate constants, k, were derived from the slope of the plots of the left side of Equation (4.6) against the natural logarithm of reaction time for each parameter (acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio) as presented in Figures 4.23 to 4.28 and tabulated in Table 4.9.

Process parameters		Krögler and Ziegler kinetic model
Acid concentration (M)	$K_k (min^{-1})$	\mathbb{R}^2
1	0.171	0.988
2	0.189	0.990
3	0.193	0.990
4	0.197	0.991
Oxide concentration (M)		
0.15	0.183	0.988
0.30	0.185	0.994
0.45	0.189	0.993
0.60	0.193	0.992
Particle size (µm)		
75	0.193	0.992
150	0.183	0.998
300	0.178	0.997
600	0.168	0.985
Solution temperature (°C)		
30	0.093	0.878
45	0.167	0.950
60	0.192	0.991
75	0.196	0.981
90	0.196	0.988
Stirring speed		
100	0.183	0.986
200	0.192	0.984
300	0.196	0.981
400	0.196	0.984
500	0.199	0.984
Liquid-to-solid ratio		
10	0.172	0.943
15	0.193	0.984
20	0.196	0.981
25	0.197	0.961
30	0.195	0.941

Table 4.9: Apparent rate constants k_k and coefficient of determination (R^2) values for Krögler and Ziegler kinetic model

To establish the effects of the reaction parameters on the apparent rate constant, the following equation may be suggested (Ekmekyapar *et al.*, 2015):

$$k = k_o (AC)^{\alpha} (OC)^{\beta} (PS)^{\gamma} (SS)^{\theta} (LS)^{\varphi} exp(-E_a/RT)$$

$$\tag{4.9}$$

Where the constants α , β , γ , θ and φ are the reaction orders for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) respectively. Ea, R, T and k_o represent activation energy, universal gas constant, solution temperature and frequency or pre-exponential factor. The kinetic equation expressed in Equation (4.10) for the dissolution process was obtained by combining Equations (4.6) and (4.9).

$$\left(1 - (1 - x)^{1/3}\right)^2 = k_o (AC)^{\alpha} (OC)^{\beta} (PS)^{\gamma} (SS)^{\theta} (LS)^{\varphi} exp(-E_a/RT) lnt$$
(4.10)

From Figures 4.29 to 4.33, the values of the constants, α , β , γ , θ and ϕ , were estimated from the slope of the plots of the natural logarithm of apparent rate constants versus natural logarithm of the parameters given in Table 4.9.



Figure 4.29: Plot of ln K vs ln AC for Chalcopyrite in HCl





Figure 4.30: Plot of ln K vs ln OX for Chalcopyrite in HCl-KCl







Figure 4.33: Plot of ln K vs ln SL for Chalcopyrite in HCl-KCl

Figure 4.34: Plot of ln K vs 1000/T for Chalcopyrite in HCl-KCl

The reaction orders recorded for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) from Figures 4.29 to 4.33 are 0.049, 0.050, -0.064, 0.072, 0.729, respectively. The activation energy was calculated from the slope of the Arrhenius plot on Figure 4.34. The Arrhenius equation is expressed as:

$$k = Aexp\left(\frac{-E_a}{RT}\right) \tag{4.11}$$

Where k is the overall rate constant $(m^2.min^{-1})$, A is the pre-exponential factor (min^{-1}) , E_a is the activation energy (J/mol), R is the universal gas constant (8.314J/mol.K) and T is the reaction temperature (K). Activation energy and pre-exponential factor values of 10.41kJ/mol and 0.118s⁻¹ respectively were derived from Arrhenius plot (Figure 4.34). According to Abdallah *et*

al. (2015), the activation energy of a diffusion controlled process is usually 21kJ/mol or less, when chemical reaction is the rate controlling step, the activation is between 40-100kJ/mol. Activation energy of 10.41kJ/mol calculated for dissolution of chalcopyrite in HCl-KCl confirms that the dissolution process within the scope of investigation is diffusion controlled. The equation describing the dissolution kinetics of chalcopyrite in HCl-KCl medium can be written as:

$$\left(1 - (1 - x)^{1/3}\right)^2 = 0.118(AC)^{0.049}(OC)^{0.050}(PS)^{-0.064}(SS)^{0.072}(LS)^{0.729}exp(-10.41/RT)lnt$$
(4.12)

4.3.1.2 HCl-KClO₃

The process variables: acid concentration, oxide concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio were plotted against time as shown in Figures 4.35 to 4.40 respectively in order to investigate the reaction mechanism and dissolution kinetics of chalcopyrite ore in HCl-KClO₃ lixiviant.



Figure 4.35: Effect of acid conc. on %Cu dissolved using HCl



Figure 4.37: Effect of particle size on %Cu dissolved using HCl-KClO₃



Figure 4.36: Effect of oxidant concentration on %Cu dissolved using HCI-KCIO₃



Figure 4.38: Effect of solution temperature on %Cu dissolved using HCI-KCIO₃



Figure4.39: Effect of stirring speed on %Cu dissolved using HCl-KClO₃



Figure 4.40: Effect of liquid-to-solid ratio on %Cu dissolved using HCl-KClO₃

The experimental data plotted in Figures 4.35 to 4.40 were tested in the eight dissolution kinetics models under investigation to deduce the model that fitted best the kinetics experimental data for chalcopyrite leaching in HCl-KClO₃ binary solution. The adequacy of the models in describing the system was adjudged with the correlation of determination. From Table 4.10, the correlation coefficient (R²) values for Zhuravlev, Lesokhin and Templeman diffusion equation and Kröger and Ziegler diffusion equation were closest to unity. However, the Kröger and Ziegler diffusion equation were closest to unity. However, the Kröger and Ziegler diffusion equation, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio. The higher coefficient of determination reported for Kröger and Ziegler diffusion investigated confirm higher suitability of the Kröger and Ziegler kinetic model over the other models investigated. Therefore, the overall rate is diffusion controlled and adequately described by the Kröger and Ziegler kinetic model equation. The fitted plots are displayed in Figures 4.41 to 4.46. The ill-fitted plots are shown in Figures D37 to D66 in Appendix D.

Process paramete	rs			R ² (Chal	copyrite-HCl-KClO	3)		
-	DTLF	DTPL	SCR	MKM	JANDER	KROGER	ZLT	GINSTLING
Acid Conc								
1	0.692	0.857	0.778	0.854	0.873	0.988	0.903	0.857
2	0.717	0.906	0.860	0.905	0.924	0.990	0.938	0.906
3	0.731	0.916	0.873	0.914	0.942	0.990	0.959	0.916
4	0.750	0.923	0.894	0.923	0.946	0.991	0.923	0.923
Ox. Conc								
0.15	0.749	0.964	0.858	0.961	0.966	0.989	0.929	0.964
0.3	0.742	0.971	0.861	0.968	0.983	0.991	0.967	0.971
0.45	0.705	0.955	0.847	0.952	0.977	0.991	0.979	0.955
0.6	0.477	0.669	0.593	0.665	0.727	0.933	0.825	0.669
Particle Size								
75	0.477	0.699	0.593	0.665	0.727	0.933	0.825	0.669
150	0.510	0.724	0.608	0.719	0.776	0.942	0.899	0.724
300	0.552	0.783	0.650	0.726	0.826	0.956	0.924	0.783
600	0.630	0.883	0.727	0.875	0.915	0.975	0.978	0.883
Temperature	01000	01000	0	01070	000 10	01370	01770	01000
30	0.724	0.876	0.776	0.872	0.886	0.992	0.908	0.876
45	0.603	0.821	0.709	0.817	0.884	0.972	0.920	0.821
60	0.549	0.789	0.702	0.785	0.842	0.958	0.923	0.789
75	0.569	0.838	0.746	0.834	0.897	0.963	0.955	0.838
90	0.571	0.817	0.711	0.813	0.865	0.963	0.944	0.817
Stirring Speed	01071	01017	01711	01010	01000	01200	0.7	01017
100	0.675	0.923	0.835	0.920	0.943	0.986	0.926	0.923
200	0.639	0.893	0.802	0.890	0.925	0.978	0.949	0.893
300	0.542	0.756	0.678	0.752	0.794	0.956	0.821	0.756
400	0.556	0.818	0.729	0.814	0.877	0.959	0.961	0.818
500	0.553	0.780	0.692	0.776	0.847	0.952	0.970	0.780
Solid –Liquid	0.000	0.700	0.072	0.770	0.017	0.952	0.970	0.700
10	0.712	0.907	0.831	0.905	0.923	0.992	0.920	0.907
15	0.610	0.884	0.768	0.879	0.926	0.972	0.963	0.884
20	0.542	0.756	0.678	0.752	0.794	0.956	0.821	0.756
25	0.543	0.848	0.729	0.842	0.916	0.945	0.948	0.848
30	0.526	0.040	0.709	0.042	0.883	0.940	0.940	0.811

Table 4.10: Coefficient of determination values for investigated kinetic models at various process variables



Figure 4.41: Kroger kinetic plots for chalcopyrite at different acid concentration



Figure 4.43: Kroger kinetic plots for chalcopyrite in HCl-KClO₃ at different particle Size



Figure 4.45: Kroger Kinetic kinetic plots for chalcopyrite in HCl-KClO₃ at different stirring speed



Figure 4.42: Kroger kinetic plots for chalcopyrite in HCl-KClO₃ at different Oxidant



Figure 4.44: Kroger kinetic plots for chalcopyrite in HCl-KClO₃ at different solution temperature



Figure 4.46: Kroger kinetic plots for chalcopyrite in HCl-KClO₃ at different liquid-to-solid ratio

The apparent rate constants, k, were derived from the slope of the plots of $(1 - (1 - x)^{1/3})^2$ against the natural logarithm of reaction time for each parameter (acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio). The derived apparent rate constants, k, data were presented in Table 4.11.

Process parameters	Krögler and Zie	gler kinetic model
Acid concentration (M)	$K_k (min^{-1})$	\mathbf{R}^2
1	0.171	0.988
2	0.189	0.990
3	0.193	0.990
4	0.197	0.991
Oxide concentration (M)		
0.15	0.158	0.989
0.30	0.165	0.991
0.45	0.176	0.991
0.60	0.188	0.933
Particle size (µm)		
75	0.188	0.933
150	0.174	0.942
300	0.168	0.956
600	0.157	0.975
Solution temperature (°C)		
30	0.140	0.992
45	0.173	0.972
60	0.189	0.958
75	0.190	0.963
90	0.183	0.963
Stirring speed		

Table 4.11: Apparent rate constants k_k and coefficient of determination (\mathbb{R}^2) values for Krögler and Ziegler kinetic model

100	0.184	0.986
200	0.186	0.978
300	0.189	0.956
400	0.190	0.959
500	0.190	0.952
Liquid-to-solid ratio		
10	0.179	0.992
15	0.182	0.972
20	0.189	0.956
25	0.185	0.945
30	0.187	0.940

To appreciate the relationship between the reaction process parameters on the rate constant, the proposed semi-empirical model was substituted in Krögler and Ziegler kinetic model equation. The resultant equation is expressed as:

$$\left(1 - (1 - x)^{1/3}\right)^2 = k_o (AC)^{\alpha} (OC)^{\beta} (PS)^{\gamma} (SS)^{\theta} (LS)^{\varphi} exp(-E_a/RT) lnt$$
(4.13)

The reaction order with respect to acid concentration, oxidant concentration, particle size, stirring speed and liquid-to-solid ratio for equation 4.13 were obtained from the slope of the plots of the natural logarithm of apparent rate constants versus logarithm of the parameters presented in Figures 4.47 to 4.51.



Figure 4.47: Plot of ln k vs ln AC for chalcopyrite in $KClO_3$



Figure 4.49: Plot of ln K vs ln PS for chalcopyrite in $HCl-KClO_3$



Figure 4.51: Plot of ln K vs ln SL for chalcopyrite in HCl-KClO $_3$



Figure 4.48: Plot of ln k vs ln OC for chalcopyrite in HCl-KClO $_3$



Figure 4.50: Plot of ln K vs ln SS for chalcopyrite in HCl-KClO $_3$



Figure 4.52: Plot of ln K vs 1000/T for chalcopyrite in HCl-KClO $_3$

The reaction orders recorded for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) from Figures 4.47 to 4.51 are 0.049, 0.121, -0.083, 0.024, 0.038, respectively. The slope and intercept of the linearized form of the Arrhenius plot gave the activation energy and pre-exponential factor respectively. Activation energy and pre-exponential factor values of 5.97kJ/mol and 0.026s⁻¹, respectively, were recorded from the computations. The activation energy of 5.97kJ/mol for dissolution of chalcopyrite in HCl-KClO₃ suggests that the process is diffusion controlled within the scope of investigation. Equation (4.14) which describes the dissolution kinetics of chalcopyrite in HCl-KClO₃ medium was obtained by substituting the derived reaction order values for the process parameters in equation (4.13).

$$\left(1 - (1 - x)^{1/3}\right)^2 = 0.026(AC)^{0.049}(OC)^{0.121}(PS)^{-0.083}(SS)^{0.024}(LS)^{0.038}exp(-5.97/RT)lnt$$
(4.14)

4.3.1.3 HCl-NaNO₃

To study the reaction mechanism and dissolution kinetics of chalcopyrite ore in $HCl-NaNO_3$ solution, plots of acid concentration, oxide concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio against time were graphed and presented in Figures 4.53 to 4.58.



Figure 4.53: Effect of acid conc. on %Cu dissolved using HCl



Figure 4.54: Effect of oxidant concentration on %Cu dissolved using



Figure 4.55: Effect of particle size on %Cu dissolved using HCl-NaNO₃



Figure 4.57: Effect of stirring speed on %Cu dissolved using HCl-NaNO₃



Figure 4.56: Effect of solution temperature on %Cu dissolved using HCl-NaNO₃



Figure 4.58: Effect of liquid-to-solid ratio on %Cu dissolved using HCl-NaNO₃

The suitability of the selected dissolution kinetics models in fitting the experimental data plotted in Figures 4.53 to 4.58 at various acid concentrations, oxidant concentrations, particle sizes, solution temperatures, stirring speed and liquid-to-solid ratio were examined for chalcopyrite leaching in HCl-NaNO₃ solution. The suitability of the models in fitting the experimental data was determined based on the closeness of the correlation coefficient (\mathbb{R}^2) values to unity. Investigation of the coefficient of determination data presented for the model equations under consideration depicts that Equations (4.7) and (4.6) (Zhuravlev, Lesokhin and Templeman diffusion equation and Kröger and Ziegler diffusion equation) gave higher linearity compared to other models. A closer examination of the two models reveal that the Kröger and Ziegler diffusion equation showed more excellent linearity compared to Zhuravlev, Lesokhin and Templeman diffusion equation. On this note, the overall rate is diffusion controlled and adequately described by the Kröger and Ziegler kinetic model equation. The fitted plots are displayed in Figures 4.59 to 4.64. The ill-fitted plots are shown in Figures D67 to D94 in Appendix D.

Process parameter	rs	R^2 (Chalcopyrite-HCl-NaNO ₃)						
	DTLF	DTPL	SCR	MKM	JANDER	KROGER	ZLT	GINSTLING
Acid conc								
1	0.692	0.857	0.778	0.854	0.873	0.988	0.903	0.857
2	0.717	0.906	0.860	0.905	0.924	0.990	0.938	0.906
3	0.731	0.916	0.873	0.914	0.942	0.990	0.959	0.916
4	0.750	0.923	0.894	0.923	0.946	0.991	0.923	0.923
Ox. conc								
0.15	0.788	0.937	0.868	0.936	0.950	0.991	0.970	0.937
0.3	0.749	0.936	0.848	0.934	0.954	0.995	0.981	0.936
0.45	0.720	0.911	0.829	0.909	0.933	0.992	0.966	0.911
0.6	0.641	0.900	0.785	0.896	0.941	0.980	0.992	0.900
Particle size								
75	0.641	0.900	0.785	0.896	0.941	0.980	0.992	0.900
150	0.701	0.885	0.802	0.882	0.898	0.990	0.906	0.885
300	0.700	0.898	0.798	0.895	0.916	0.990	0.942	0.898
600	0.740	0.954	0.831	0.949	0.970	0.996	0.994	0.954
Temperature								
30	0.919	0.989	0.939	0.989	0.989	0.944	0.988	0.989
45	0.698	0.915	0.779	0.909	0.936	0.991	0.977	0.915
60	0.641	0.900	0.785	0.896	0.941	0.980	0.992	0.900
75	0.634	0.908	0.797	0.903	0.950	0.978	0.994	0.908
90	0.629	0.822	0.756	0.877	0.918	0.977	0.974	0.882
Stirring speed								
100	0.620	0.841	0.726	0.836	0.870	0.976	0.919	0.841
200	0.622	0.862	0.745	0.867	0.896	0.976	0.950	0.862
300	0.634	0.908	0.797	0.903	0.950	0.978	0.994	0.908
400	0.612	0.907	0.800	0.902	0.957	0.972	0.976	0.907
500	0.619	0.908	0.810	0.904	0.957	0.975	0.959	0.908
Solid –liquid								
10	0.688	0.920	0.802	0.914	0.946	0.989	0.985	0.920
15	0.681	0.928	0.815	0.924	0.956	0.988	0.987	0.928
20	0.634	0.908	0.797	0.903	0.950	0.978	0.994	0.908
25	0.610	0.874	0.770	0.870	0.917	0.973	0.967	0.874
30	0.606	0.888	0.785	0.883	0.937	0.971	0 984	0.888

Table 4.12: Coefficient of determination values for investigated kinetic models at various process variables



Figure 4.59: Kroger kinetic plots for chalcopyrite at different acid concentration



Figure 4.61: Kroger kinetic plots for chalcopyrite in HCl-NaNO₃ at different particle size



Figure 4.63: Kroger kinetic plots for chalcopyrite in HCl-NaNO₃ at different stirring speed



Figure 4.60: Kroger kinetic plots for chalcopyrite in HCl-NaNO₃ at different oxidant concentrations



Figure 4.62: Kroger kinetic plots for chalcopyrite in HCl-NaNO₃ at different solution temperature



Figure 4.64: Kroger Kinetic plots for chalcopyrite in HCl-NaNO₃ at different liquid-to-solid ratio

The slope of the plots of $(1 - (1 - x)^{1/3})^2$ against the reaction time gave the apparent rate constants, k, for each parameter (acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio). The values for the apparent rate constants for chalcopyrite dissolution in HCl-NaNO₃ medium are tabulated in Table 4.13.

Process parameters	Krögler and Zieg	gler kinetic model
Acid concentration (M)	$k_k (min^{-1})$	R^2
1	0.171	0.988
2	0.189	0.990
3	0.193	0.990
4	0.197	0.991
Oxide concentration (M)		
0.15	0.167	0.991
0.30	0.170	0.995
0.45	0.176	0.992
0.60	0.179	0.980
Particle size (µm)		
75	0.179	0.980
150	0.173	0.990
300	0.167	0.990
600	0.155	0.996
Solution temperature (°C)		
30	0.100	0.944
45	0.150	0.991
60	0.179	0.980
75	0.183	0.978
90	0.174	0.977
Stirring speed		

Table 4.13: Apparent rate constants k_k and coefficient of determination (R^2) values for Krögler and Ziegler kinetic model

100	0.172	0.976
200	0.176	0.976
300	0.183	0.978
400	0.187	0.972
500	0.188	0.975
Liquid-to-solid ratio		
10	0.169	0.989
15	0.175	0.988
20	0.183	0.978
25	0.185	0.973
30	0.187	0.971

The values of the constants, α , β , γ , θ and ϕ , in the proposed semi-empirical model published by Ekmekyapar *et al.* (2015) were estimated from the slope of the plots of the natural logarithm of apparent rate constants versus logarithm of the parameters (Figures 4.65 to 4.69). The activation energy (E_a) and pre-exponential factor were computed from the slope and intercept of the Arrhenius plot in Figure 4.70.



Figure 4.65: Plot of ln k vs ln AC for chalcopyrite in HCl





Figure 4.66: Plot of ln k vs ln OC for chalcopyrite in HCl-NaNO_3 $\,$





Figure 4.69: Plot of ln k vs ln LS for chalcopyrite in HCl-NaNO $_3$



Figure 4.70: Plot of ln k vs 1000/T for chalcopyrite in HCl-NaNO $_3$

The reaction orders recorded for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) from Figures 4.65 to 4.69 are 0.049, 0.050, -0.067, 0.059, 0.096 respectively. Activation energy and pre-exponential factor values of 9.63kJ/mol and 0.086s⁻¹ respectively were derived from the plot of natural logarithm of k against the inverse of temperature presented in Figure 4.70. Activation energy of 9.63kJ/mol calculated for dissolution of chalcopyrite in HCl-NaNO₃ confirms that the dissolution process within the scope of investigation is diffusion controlled. The equation describing the dissolution kinetics of chalcopyrite in HCl-NaNO₃ medium can be written as:

$$\left(1 - (1 - x)^{1/3}\right)^2 = 0.086(AC)^{0.049}(OC)^{0.05}(PS)^{-0.067}(SS)^{0.059}(LS)^{0.096}exp(-9.63/RT)lnt$$
(4.15)

4.3.2 Dissolution kinetics for sphalerite using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions as lixiviants

4.3.2.1 HCl-KCl

Sphalerite leaching reaction mechanisms can be influenced by varying acid concentrations, oxidant concentrations, particle sizes, solution temperatures, stirring speed, etc. The overall effects of these process variables determine the pattern of dissolution of zinc. To study the reaction mechanism and kinetics of the dissolution process, the process variables were plotted against time. Figures 4.71, 4.72, 4.73, 4.74, 4.75 and 4.76 depict the effects of acid concentrations, oxidant concentrations, particle sizes, solution temperatures, stirring speed and liquid-to-solid ratio respectively on sphalerite dissolution.



Figure 4.71: Effect of particle size on %Zn dissolved using HCl



Figure 4.72: Effect of oxidant concentration on %Zn dissolved using HCI-KCI



Figure 4.73: Effect of particle size on %Zn dissolved using HCI-KCI



Figure 4.74: Effect of solution temperature on %Zn dissolved using HCI-KCI



Figure 4.75: Effect of stirring speed on %Zn dissolved using HCI-KCI



Figure 4.76: Effect of liquid-to-solid ratio on %Zn dissolved using HCl-KCl

The yield (% Zn dissolved) results for different acid concentrations, oxidant concentrations, particle sizes, solution temperatures, stirring speed and liquid-to-solid ratio were fitted into the eight kinetic models under review with the correlation coefficient being the determining factor for a best fit in describing the kinetics of sphalerite dissolution in HCl-KCl. Table 4.14 displays the correlation coefficient for the reviewed kinetics models. It was observed that Zhuravlev, Lesokhin and Templeman diffusion equation best fitted well to the experimental data. The fitted plots are presented in Figures 4.77, 4.78, 4.79, 4.80, 4.81 and 4.82 for process parameters - acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and

liquid-to-solid ratio, respectively. The result obtained therefore posits that the overall rate for the dissolution of sphalerite in HCl-KCl medium is diffusion controlled and can be suitably be described by the Zhuravlev, Lesokhin and Templeman diffusion model equation. The ill-fitted plots are shown in Figures D137 to D164 in Appendix D.

Process parameters			U	R ² (Sphale	erite-HCl-KCl)			
L	DTLF	DTPL	SCR	MKM	JANDER	KROGER	ZLT	GINSTLING
Acid conc								
1	0.722	0.940	0.839	0.937	0.962	0.994	0.986	0.940
2	0.704	0.919	0.825	0.916	0.943	0.992	0.971	0.919
3	0.716	0.943	0.855	0.940	0.970	0.993	0.987	0.943
4	0.690	0.913	0.832	0.911	0.949	0.988	0.988	0.913
Ox. conc								
0.15	0.649	0.893	0.746	0.886	0.923	0.981	0.980	0.893
0.3	0.717	0.943	0.840	0.940	0.962	0.993	0.973	0.943
0.45	0.724	0.974	0.875	0.971	0.993	0.994	0.972	0.974
0.6	0.720	0.958	0.872	0.955	0.979	0.994	0.974	0.958
Particle size								
75	0.720	0.958	0.872	0.955	0.979	0.994	0.974	0.958
150	0.804	0.945	0.897	0.946	0.941	0.989	0.912	0.945
300	0.798	0.943	0.875	0.942	0.942	0.990	0.925	0.943
600	0.840	0.971	0.905	0.970	0.970	0.991	0.954	0.971
Temperature								
30	0.922	0.966	0.942	0.968	0.966	0.860	0.963	0.966
45	0.757	0.915	0.834	0.912	0.926	0.994	0.939	0.915
60	0.720	0.958	0.872	0.955	0.979	0.994	0.974	0.958
75	0.642	0.941	0.832	0.937	0.982	0.979	0.968	0.941
90	0.675	0.956	0.858	0.953	0.975	0.981	0.931	0.956
Stirring speed								
100	0.686	0.941	0.824	0.937	0.967	0.988	0.973	0.941
200	0.645	0.926	0.807	0.921	0.966	0.980	0.987	0.926
300	0.642	0.941	0.832	0.937	0.982	0.979	0.968	0.941
400	0.659	0.944	0.850	0.940	0.982	0.984	0.942	0.944
500	0.641	0.917	0.809	0.913	0.958	0.980	0.988	0.917
Solid –liquid								
10	0.644	0.898	0.798	0.893	0.931	0.980	0.984	0.898
15	0.652	0.925	0.804	0.921	0.962	0.982	0.994	0.925
20	0.642	0.941	0.832	0.937	0.982	0.979	0.968	0.941
25	0.588	0.900	0.794	0.895	0.962	0.966	0.978	0.900
30	0.578	0.895	0.764	0.891	0.963	0.964	0.954	0.895

Table 4.14: Coefficient of determination values for investigated kinetic models at various process variables



Figure 4.77: ZLT Plots for sphalerite at different acid concentration



Figure 4.79: ZLT kinetic plots for sphalerite in HCl-KCl at different particle size



Figure 4.81: ZLT kinetic plots for sphalerite in HCl-KCl at different stirring speed



Figure 4.78: ZLT kinetic plots for sphalerite in HCl-KCl at different oxidant concentrations



Figure 4.80: ZLT kinetic plots for sphalerite in HCl-KCl at different solution temperature



Figure 4.82: ZLT kinetic plots for sphalerite in HCl-KCl at different liquid-to-solid ratio

The apparent rate constants, k, presented in Table 4.15 were derived from the slope of the plots of $(1/(1-x)^{1/3}-1)^2$ against the reaction time for each parameter (acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio).

Process parameters	Zhuravlev, Lesokhin and	Fempleman kinetic model
Acid concentration (M)	$K_z (min^{-1})$	R^2
1	0.003	0.986
2	0.004	0.971
3	0.006	0.987
4	0.007	0.988
Oxide concentration (M)		
0.15	0.001	0.980
0.30	0.003	0.973
0.45	0.005	0.972
0.60	0.007	0.974
Particle size (µm)		
75	0.007	0.974
150	0.003	0.912
300	0.001	0.925
600	0.001	0.954
Solution temperature (°C)		
30	0.000	0.963
45	0.001	0.939
60	0.007	0.974
75	0.010	0.968
90	0.090	0.931
Stirring speed		
100	0.004	0.973
200	0.006	0.987

Table 4.15: Apparent rate constants k_z and coefficient of determination (R^2) values for Zhuravlev, Lesokhin and Templeman kinetic model

300	0.010	0.968
400	0.012	0.942
500	0.008	0.988
Liquid-to-solid ratio		
10	0.002	0.984
15	0.005	0.994
20	0.010	0.968
25	0.015	0.978
30	0.020	0.954

To evaluate the effect of acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS) and liquid-to-solid ratio (LS) on the dissolution of sphalerite in HCl-KCl lixiviant, a semi-emperical model is postulated as:

$$\left(\frac{1}{(1-x)^{1/3}} - 1\right)^2 = k_o (AC)^{\alpha} (OC)^{\beta} (PS)^{\gamma} (SS)^{\theta} (LS)^{\varphi} exp(-E_a/RT)t$$
(4.16)

From Figures 4.83 to 4.87, the values of the constants, α , β , γ , θ and ϕ , were estimated from the slope of the plots of the natural logarithm of apparent rate constants versus logarithm of the parameters given in Table 4.16.



Figure 4.83: Plot of ln K vs ln AC for Sphalerite in acid concentrations



Figure 4.84: Plot of ln K vs ln OC for Sphalerite in HCl-KCl



Figure 4.85: Plot of ln k vs ln PS for sphalerite in HCl-KCl



Figure 4.87: Plot of ln k vs ln LS for sphalerite in HCl-KCl



Figure 4.86: Plot of ln K vs ln SS for sphalerite in HCl-KCl



Figure 4.88: Plot of ln k vs 1000/T for sphalerite in HCl-KCl

The reaction orders recorded for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) from Figures 4.83 to 4.87 are 0.630, 1.410, -1.000, 0.818, 2.128, respectively. Activation energy and pre-exponential factor values of 45.57kJ/mol and 850.36s⁻¹ respectively were calculated from the slope of the Arrhenius plot on Figure 4.88. Activation energy of 45.57kJ/mol derived from Arrhenius plot computations which followed diffusion control model suggests surface chemical reaction control. Zhou *et al.* (2004), reported that it sometimes better to predict the rate controlling mechanism of heterogeneous dissolution reactions from plots of the kinetic equation rather than from the value of activation energy (E_a). Therefore, the dissolution process of sphalerite in HCl-KCl medium within the experimental conditions investigated is still considered as being diffusion controlled. The derived

semi-empirical equation describing the dissolution kinetics of sphalerite in HCl-KCl medium can be written as:

$$\left(\frac{1}{(1-x)^{1/3}} - 1\right)^2$$

= 850.36(AC)^{0.630}(OC)^{0.1.410}(PS)^{-1.000}(SS)^{0.818}(LS)^{2.128}exp(-45.57/RT)t (4.17)

4.3.2.2 HCl-KClO₃

To study the reaction mechanism and kinetics of the dissolution of sphalerite ore in $HCl-KClO_3$ at various process variables: acid concentrations, oxidant concentrations, particle sizes, solution temperatures, stirring speed and liquid-to-solid ratios were plotted against time. Figures 4.89 to 4.94 show the plots of individual effects of each of the process variables as a function of time.



Figure 4.89: Effect of particle size on %Zn dissolved using HCl



Figure 4.91: Effect of particle size on %Zn dissolved using HCl-KClO₃



Figure 4.90: Effect of oxidant concentration on %Zn dissolved using HCl-KClO₃



Figure 4.92: Effect of solution temperature on %Zn dissolved using HCI-KClO₃



Figure 4.93: Effect of stirring speed on %Zn dissolved using HCI-KCIO₃



Figure 4.94: Effect of liquid-to-solid ratio on %Zn dissolved using HCl-KClO₃

The experimental data of Figures 4.89 to 4.94 were examined with equations (4.1) to (4.8) to ascertain the equation that best described the reaction kinetics of sphalerite dissolution in HCl-KClO₃ binary solution. It was glaring that whole experimental data fitted very well to Equations 4.6, 4.7 and 4.8 (Kröger and Ziegler diffusion model, Zhuravlev, Lesokhin and Templeman diffusion equation and Ginstling-Brounshtein model). Amongst the three kinetics models, the experimental data best fitted the Kröger and Ziegler diffusion model as adjudged by the coefficient of determination presented on Table 4.16. The fitted plots are presented in Figures 4.95 to 4.100 representing data for process parameters: acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio, respectively. The poorly fitted plots are shown in Figures D95 to D136 in Appendix D.
Process paramete	R^2 (Sphalerite-HCl-KClO ₃)								
	DTLF	DTPL	SCR	MKM	JANDER	KROGER	ZLT	GINSTLING	
Acid conc									
1	0.722	0.940	0.839	0.937	0.962	0.994	0.986	0.940	
2	0.704	0.919	0.825	0.916	0.943	0.992	0.971	0.919	
3	0.716	0.943	0.855	0.940	0.970	0.993	0.987	0.943	
4	0.690	0.913	0.832	0.911	0.949	0.988	0.988	0.913	
Ox. conc									
0.15	0.735	0.935	0.833	0.932	0.954	0.995	0.982	0.935	
0.3	0.727	0.947	0.852	0.944	0.968	0.995	0.985	0.947	
0.45	0.697	0.914	0.826	0.911	0.939	0.991	0.972	0.914	
0.6	0.704	0.950	0.878	0.948	0.980	0.992	0.956	0.950	
Particle size									
75	0.704	0.950	0.878	0.948	0.980	0.992	0.956	0.950	
150	0.783	0.973	0.897	0.972	0.972	0.992	0.932	0.973	
300	0.817	0.978	0.907	0.978	0.976	0.993	0.945	0.978	
600	0.867	0.966	0.935	0.966	0.956	0.985	0.911	0.966	
Temperature									
30	0.736	0.905	0.776	0.897	0.914	0.994	0.938	0.905	
45	0.664	0.862	0.747	0.857	0.885	0.985	0.934	0.862	
60	0.704	0.950	0.878	0.948	0.980	0.992	0.956	0.950	
75	0.713	0.954	0.909	0.953	0.981	0.993	0.926	0.954	
90	0.744	0.925	0.881	0.924	0.936	0.994	0.920	0.925	
Stirring speed	01711	019 20	0.001	0.72	0.700	0.777	0.720	0.720	
100	0.706	0.946	0.863	0.943	0.977	0.992	0.983	0.946	
200	0.698	0.941	0.867	0.938	0.974	0.991	0.976	0.941	
300	0.713	0.954	0.909	0.953	0.981	0.993	0.926	0.954	
400	0.701	0.931	0.887	0.930	0.952	0.991	0.901	0.931	
500	0.717	0.959	0.929	0.958	0.977	0.993	0.891	0.959	
Solid –liquid	0.717	0.959	0.727	0.950	0.977	0.775	0.071	0.707	
10	0.702	0.899	0.819	0.897	0.920	0.991	0.946	0.899	
15	0.700	0.908	0.842	0.906	0.935	0.990	0.965	0.908	
20	0.713	0.954	0.909	0.953	0.981	0.993	0.926	0.954	
25	0.686	0.914	0.969	0.933	0.945	0.989	0.926	0.934	
30	0.654	0.914	0.864	0.912	0.955	0.983	0.930	0.914	

Table 4.16: Coefficient of determination values for investigated kinetic models at various process variables





Figure 4.95: Kroger plots for sphalerite at different acid concentration



Figure 4.97: Kroger kinetic plots for sphalerite in HCl-KClO₃ at different particle size



Figure 4.99: Kroger kinetic plots for sphalerite in HCl-KClO₃ at different stirring speed



Figure 4.96: Kroger kinetic plots for sphalerite in HCl-KClO₃ at different oxidant concentrations



Figure 4.98: Kroger kinetic plots for sphalerite in HCl-KClO₃ at different solution temperature



Figure 4.100: Kroger kinetic plots for sphalerite in HCl-KClO₃ at different liquid-to-solid ratio

The values of the apparent rate constants, k, derived from the slope of the plots of $(1 - (1 - x)^{1/3})^2$ against the natural logarithm of reaction time for each parameter (acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio) were tabulated in Table 4.17.

Process parameters	Kröger and Zi	egler kinetic model
Acid concentration (M)	$K_k (min^{-1})$	R^2
1	0.173	0.994
2	0.176	0.992
3	0.182	0.993
4	0.185	0.988
Oxide concentration (M)		
0.15	0.166	0.995
0.30	0.176	0.995
0.45	0.180	0.991
0.60	0.189	0.992
Particle size (µm)		
75	0.189	0.992
150	0.166	0.992
300	0.156	0.993
600	0.151	0.985
Solution temperature (°C)		
30	0.117	0.994
45	0.160	0.985
60	0.189	0.992
75	0.195	0.993
90	0.190	0.994
Stirring speed		

Table 4.17: Apparent rate constants k_k and coefficient of determination (R^2) values for Kröger and Ziegler kinetic model

100	0.186	0.992
200	0.189	0.991
300	0.195	0.993
400	0.195	0.991
500	0.196	0.993
Liquid-to-solid ratio		
10	0.179	0.991
15	0.188	0.990
20	0.195	0.993
25	0.194	0.989
30	0.195	0.983

The constants on the semi-empirical model were calculated from the slope of the plots of ln k vs ln of the individual process parameters in Figures 4.101 - 4.105 to determine the effect of acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) on the rate constant for dissolution of sphalerite in HCl-KClO₃ leaching system. Substituting the derived constants, these effects can be expressed as:

$$k = 0.11(AC)^{0.049}(OC)^{0.088}(PS)^{-0.106}(SS)^{0.035}(LS)^{0.077}exp(-10.07/RT)lnt$$
(4.18)



Figure 4.101: Plot of ln k vs ln AC for sphalerite in acid concentrations





Figure 4.102: Plot of ln k vs ln OC for sphalerite in HCl-KClO $_3$





Figure 105: Plot of ln k vs ln LS for sphalerite in HCl-KClO $_3$

Figure 106: Plot of ln k vs 1000/T for sphalerite in HCl-KClO₃

The reaction orders recorded for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) from Figures 4.101 to 4.105 are 0.049, 0.088, -0.106, 0.035, 0.077, respectively. The activation energy of 10.07 kJ/mol was calculated from the slope of the Arrhenius plot on Figure 4.106. Also from the intercept of the same plot, the pre-exponential factor of 0.11s⁻¹ was computed. According to Abdallah*et al.* (2015), the activation energy of a diffusion controlled process is usually 21kJ/mol or less, when chemical reaction is the rate controlling step, the activation is between 40-100kJ/mol. Activation energy of 10.07kJ/mol calculated for dissolution of sphalerite in HCl-KClO₃ confirms that the dissolution

process within the scope of investigation is diffusion controlled. The equation describing the dissolution kinetics of sphalerite in HCl-KClO₃ medium can be written as:

$$((1-x)^{1/3} - 1)^2 = 0.11(AC)^{0.049}(OC)^{0.088}(PS)^{-0.106}(SS)^{0.035}(LS)^{0.077}exp(-10.07/RT)lnt$$
(4.19)

4.3.2.3 HCl-NaNO₃

The experimental data for the process variables: acid concentration, oxide concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio were plotted as a function time respectively as shown in Figures 4.107 - 4.112 in order to investigate the reaction mechanism and dissolution kinetics of sphalerite ore in HCl-NaNO₃ lixiviant.



Figure 4.107: Effect of particle size on %Zn dissolved using HCl





Figure 4.108: Effect of oxidant concentration on %Zn dissolved using HCI-NaNO₃



Test for linearity of the experimental data plotted in Figures 4.113 to 4.118 and Figures D165 to D192 on equations 4.1 to 4.8 were conducted to deduce the kinetics equation that best explained the behaviour of the dissolution of sphalerite in HCl-NaNO₃. The recorded correlation coefficient as seen in Table 4.18, shows that Kröger and Ziegler diffusion model, Zhuravlev, Lesokhin and Templeman diffusion equation and Jander three dimensional kinetics model fitted the experimental data. Comparing the linearity displayed by the three models, it is clear that Zhuravlev, Lesokhin and Templeman diffusion model best fitted the experimental data. The fitted plots are presented in Figures 4.113 to 4.118 representing data for process parameters: acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio, respectively. The poorly fitted plots are shown in Figures D165 to D192 in Appendix D.

Process parameter	ters R^2 (Sphalerite-HCl-NaNO ₃)							
	DTLF	DTPL	SCR	MKM	JANDER	KROGER	ZLT	GINSTLING
Acid Conc								
1	0.722	0.940	0.839	0.937	0.962	0.994	0.986	0.940
2	0.704	0.919	0.825	0.916	0.943	0.992	0.971	0.919
3	0.716	0.943	0.855	0.940	0.970	0.993	0.987	0.943
4	0.690	0.913	0.832	0.911	0.949	0.988	0.988	0.913
Ox. Conc								
0.15	0.731	0.947	0.817	0.942	0.964	0.995	0.991	0.947
0.3	0.680	0.917	0.794	0.913	0.940	0.986	0.970	0.917
0.45	0.640	0.904	0.779	0.899	0.942	0.979	0.986	0.904
0.6	0.617	0.894	0.773	0.890	0.940	0.974	0.990	0.894
Particle Size	0.017	0.07 .	0	0.020			0.770	
75	0.617	0.894	0.773	0.890	0.940	0.974	0.990	0.894
150	0.611	0.843	0714	0.838	0.879	0 974	0.956	0.843
300	0.683	0.932	0.786	0.926	0.955	0.985	0.990	0.932
600	0.697	0.938	0.792	0.932	0.957	0.985	0.986	0.932
Temperature	0.097	0.750	0.772	0.752	0.007	0.905	0.700	0.950
30	0.925	0.963	0 947	0.965	0.962	0.916	0 956	0.963
45	0.796	0.903	0.889	0.975	0.983	0.988	0.978	0.977
60	0.617	0.894	0.773	0.890	0.940	0.974	0.990	0.894
75	0.594	0.888	0.765	0.883	0.941	0.967	0.979	0.888
90	0.576	0.846	0.703	0.805	0.899	0.967	0.985	0.846
Stirring Speed	0.570	0.010	0.712	0.010	0.077	0.902	0.705	0.010
100	0.642	0.911	0.783	0 906	0.950	0.980	0 998	0.911
200	0.672	0.907	0.781	0.902	0.946	0.974	0.966	0.907
300	0.594	0.888	0.765	0.883	0.941	0.967	0.979	0.888
400	0.571	0.880	0.756	0.875	0.941	0.958	0.940	0.880
500	0.529	0.823	0.705	0.817	0.899	0.945	0.940	0.800
Solid –Liquid	0.527	0.025	0.705	0.017	0.077	0.775	0.717	0.025
10	0.678	0 924	0 782	0.918	0 949	0.986	0.986	0.924
15	0.647	0.924	0.782	0.918	0.959	0.978	0.987	0.924
20	0.047	0.924	0.765	0.910	0.939	0.978	0.907	0.924
20	0.394	0.000	0.703	0.005	0.941	0.907	0.979	0.000
20 20	0.571	0.847	0.742	0.842	0.905	0.902	0.975	0.822
30	0.554	0.832	0.740	0.828	0.902	0.958	0.990	0.832

Table 4.18: Coefficient of determination values for investigated kinetic models at various process variables



Figure 4.113: ZLT plots for sphalerite at different acid concentration



Figure 4.115: ZLT kinetic plots for sphalerite in HCl-NaNO₃ at different particle size



Figure 4.117: ZLT kinetic plots for sphalerite in HCl-NaNO₃ at different stirring speed



Figure 4.114: ZLT kinetic plots for sphalerite in HCI-NaNO₃ at different oxidant concentrations



Figure 4.116: ZLT kinetic plots for sphalerite in HCl-NaNO₃ at different solution temperature



Figure 4.118: ZLT kinetic plots for sphalerite in HCl-NaNO₃ at different liquid-to-solid ratio

The apparent rate constants, k, were derived from the slope of the plots of $(1/(1-x)^{1/3}-1)^2$ against the reaction time for each parameter (acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio). The results of the plots are presented in Table 4.19.

, I		
Process parameters	Zhuravlev, Lesokhin and Temp	pleman diffusion kinetic model
Acid concentration (M)	$K_z (min^{-1})$	R^2
1	0.003	0.986
2	0.004	0.971
3	0.006	0.987
4	0.007	0.988
Oxide concentration (M)		
0.15	0.001	0.991
0.30	0.002	0.970
0.45	0.004	0.986
0.60	0.006	0.990
Particle size (µm)		
75	0.006	0.990
150	0.002	0.956
300	0.001	0.990
600	0.001	0.986
Solution temperature (°C)		
30	0.000	0.956
45	0.002	0.978
60	0.006	0.990
75	0.008	0.979
90	0.004	0.985

Table 4.19: Apparent rate constants k_k and coefficient of determination (R^2) values for Zhuravlev, Lesokhin and Templeman diffusion Kinetic Model

Stirring speed		
100	0.004	0.998
200	0.005	0.966
300	0.008	0.979
400	0.009	0.940
500	0010	0.919
Liquid-to-solid ratio		
10	0.001	0.986
15	0.003	0.987
20	0.008	0.979
25	0.010	0.975
30	0.016	0.990

To further understand the contributory effect of the studied process parameters on the dissolution kinetics of sphalerite in HCl-NaNO₃ solution, a semi empirical model postulated as:

$$\left(\frac{1}{(1-x)^{1/3}} - 1\right)^2 = k_o (AC)^{\alpha} (OC)^{\beta} (PS)^{\gamma} (SS)^{\theta} (LS)^{\varphi} exp(-E_a/RT)t$$
(4.20)

is derived. Substituting the values of the constants, α , β , γ , θ and ϕ estimated from the slope of the plots of the natural logarithm of apparent rate constants versus logarithm of the parameters in Figures 4.119 to 4.123, we have:



In OC -1 -0.5 0 -2 -1.5 -5 = 1.302x - 4.50 -5.4 $R^2 = 0.984$ -5.8 \leq 2 -6.2 -6.6 -7

Figure 4.119: Plot of ln k vs ln AC for sphalerite in acid concentrations

Figure 4.120: Plot of ln k vs ln OC for sphalerite in HCl-NaNO $_3$



Figure 4.121: Plot of ln k vs ln PS for sphalerite in HCl-NaNO_3 $\,$



Figure 4.123: Plot of ln k vs ln LS for sphalerite in $HCl-NaNO_3$



Figure 4.122: Plot of ln k vs ln SS for sphalerite in HCI-NaNO3



Figure 4.124: Plot of ln k vs 1000/T for sphalerite in HCl-NaNO $_3$

The reaction orders recorded for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) from Figures 4.119 to 4.123 are 0.630, 1.302, -0.875, 0.609, 2.529, respectively. The activation energy and pre-exponential factor calculated from the slope and intercept of the Arrhenius plot on Figure 4.124 are given as 42.86 kJ/mol and 409.79s⁻¹, respectively. It is not common to report high activation energy process as diffusion controlled, however, Zhou *et al.* (2004) highlighted the preference of adjudging rate limiting step of heterogenous dissolution reactions from kinetic equation rather than from the activation energy value. Therefore, it is upheld that for dissolution of sphalerite in HCl-NaNO₃ medium within the scope of investigation is diffusion controlled. The equation describing the dissolution kinetics of sphalerite in HCl-NaNO₃ medium can be written as:

$$\left(\frac{1}{(1-x)^{1/3}} - 1\right)^2$$

= 409.79(AC)^{0.630}(OC)^{1.302}(PS)^{-0.875}(SS)^{0.609}(LS)^{2.529}exp(-42.86/RT)lnt (4.21)

4.3.3 Dissolution kinetics for ilmenite using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions as lixiviants

4.3.3.1 HCI-KCI

The process variables (acid concentration, oxide concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio) were plotted against time as shown in Figures 4.125 to 4.130 respectively to investigate the reaction mechanism and kinetics of the dissolution ilmenite ore in HCl-KCl lixiviant.



Figure 4.125: Effect of acid conc. on %Fe dissolved using HCl



Figure 4.127: Effect of particle size on %Fe dissolved using HCI-KCI



Figure 4.126: Effect of oxidant concentration on %Fe dissolved using HCI-KCI



Figure 4.128: Effect of solution temperature on %Fe dissolved using HCI-KCI



Figure 4.129: Effect of stirring speed on %Fe dissolved using HCI-KCI



Figure 4.130: Effect of liquid-to-solid ratio on %Fe dissolved using HCl-KCl

The experimental data plotted in Figures 4.125 to 4.130 were fitted into equations 4.1 - 4.8 to ascertain the kinetic equation that best described the dissolution kinetics of ilmenite in HCl-KCl solution at various acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio. From Table 4.20, Kröger and Ziegler kinetic model's correlation coefficient (R^2) values showed excellent linearity ($R^2 > 0.9$) for the dissolution of ilmenite ore in HCl-KCl solution. The higher coefficient of determination reported for Kröger and Ziegler diffusion controlled kinetic reaction model equation when compared with other models investigated confirm higher favourability of the Kröger and Ziegler kinetic model over the other models investigated in this research. Therefore, the overall rate is diffusion controlled and adequately described by the Kröger and Ziegler kinetic model equation. The fitted plots are displayed in Figures 4.131 to 4.136. The ill-fitted plots are shown in Figures D193 to D234 in Appendix D.

Process parameters	5	R ² (Ilmenite-HCl-KCl)									
1	DTLF	DTPL	SCR	MKM	JANDER	KROGER	ZLT	GINSTLING			
Acid conc											
1	0.625	0.880	0.713	0.872	0.910	0.971	0.971	0.880			
2	0.645	0.895	0.748	0.889	0.922	0.976	0.964	0.895			
3	0.631	0.893	0.750	0.887	0.925	0.972	0.966	0.893			
4	0.626	0.894	0.754	0.888	0.929	0.972	0.973	0.894			
Ox. conc											
0.15	0.617	0.858	0.695	0.849	0.886	0.969	0.949	0.858			
0.3	0.657	0.914	0.758	0.907	0.940	0.978	0.979	0.914			
0.45	0.590	0.855	0.703	0.848	0.899	0.964	0.978	0.855			
0.6	0.521	0.753	0.627	0.746	0.809	0.945	0.936	0.753			
Particle size											
75	0.521	0.753	0.627	0.746	0.809	0.945	0.936	0.753			
150	0.527	0.747	0.621	0.741	0.795	0.948	0.913	0.747			
300	0.596	0.861	0.705	0.853	0.902	0.964	0.977	0.861			
600	0.596	0.846	0.687	0.838	0.881	0.964	0.956	0.846			
Temperature											
30	0.577	0.779	0.620	0.767	0.799	0.962	0.854	0.779			
45	0.525	0.724	0.589	0.716	0.759	0.946	0.853	0.724			
60	0.521	0.753	0.627	0.746	0.809	0.945	0.936	0.753			
75	0.550	0.808	0.695	0.803	0.865	0.956	0.960	0.808			
90	0.616	0.929	0.817	0.924	0.975	0.972	0.930	0.929			
Stirring speed											
100	0.559	0.810	0.687	0.804	0.862	0.958	0.958	0.810			
200	0.549	0.791	0.679	0.786	0.842	0.956	0.930	0.791			
300	0.550	0.808	0.695	0.803	0.865	0.956	0.960	0.808			
400	0.547	0.818	0.703	0.813	0.882	0.954	0.980	0.818			
500	0.546	0.827	0.715	0.822	0.896	0.954	0.972	0.827			
Solid –liquid											
10	0.520	0.749	0.623	0.743	0.805	0.945	0.934	0.749			
15	0.531	0.774	0.651	0.768	0.831	0.949	0.948	0.774			
20	0.550	0.808	0.695	0.803	0.865	0.956	0.960	0.808			
25	0.572	0.868	0.763	0.863	0.929	0.961	0.981	0.868			
30	0.596	0.929	0.853	0.925	0.985	0.968	0.916	0.929			

Table 4.20: Coefficient of determination values for investigated kinetic models at various process variables



Figure 4.131: Kroger and Ziegler kinetic plots for ilmenite in HCI-KCl at different acid conc.



Figure 4.133: Kroger and Ziegler kinetic plots for ilmenite in HCl-KCl at different particle sizes



Figure 4.135: Kroger & Ziegler kinetic plots for ilmenite in HCl-KCl at diff. stirring speed



Figure 132: Kroger and Ziegler kinetic plots for ilmenite in HCI-KCl at different oxidant concentrations



Figure 4.134: Kroger & Ziegler plots for ilmenite in HCl-KCl at different solution temperatures



Figure 4.136: Kroger & Ziegler kinetic plots for ilmenite in HCl-KCl at diff. liquid-to-solid ratio

The apparent rate constants, k, were derived from the slope of the plots of the left side of Equation (4.6) against the natural logarithm of reaction time for each parameter (acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio) as presented in Table 4.21.

Process parameters		Krögler and Ziegler kinetic model
Acid concentration (M)	$K_k(\min^{-1})$	R^2
1	0.151	0.971
2	0.159	0.976
3	0.166	0.972
4	0.170	0.972
Oxide concentration (M)		
0.15	0.146	0.969
0.30	0.156	0.978
0.45	0.166	0.964
0.60	0.173	0.945
Particle size (µm)		
75	0.173	0.945
150	0.170	0.948
300	0.164	0.964
600	0.156	0.964
Solution temperature (°C)		
30	0.123	0.962
45	0.152	0.946
60	0.173	0.945
75	0.183	0.956
90	0.186	0.972
Stirring speed		
100	0.178	0.958
200	0.181	0.956
300	0.183	0.956
400	0.185	0.954
500	0.186	0.954
Liquid-to-solid ratio		
10	0.173	0.945
15	0.178	0.949
20	0.183	0.956
25	0.189	0.961
30	0.194	0.968

Table 4.21: Apparent rate constants k_k and coefficient of determination (R^2) values for Krögler and Ziegler kinetic model

The kinetic equation expressing the behavior of the dissolution process was obtained by combining equation (4.6) (Krögler and Ziegler kinetic model) and equation (4.9) (effects of the reaction parameters on the apparent rate constant). The outcome of these combinations is expressed as:

$$\left(1 - (1 - x)^{1/3}\right)^2 = k_o (AC)^{\alpha} (OC)^{\beta} (PS)^{\gamma} (SS)^{\theta} (LS)^{\varphi} exp(-E_a/RT) lnt$$
(4.22)

From Figures 4.137 to 4.141, the values of the constants, α , β , γ , θ and ϕ , were estimated from the slope of the plots of the natural logarithm of apparent rate constants versus natural logarithm of the parameters.



Figure 4.137: Plot of ln k vs ln AC for ilmenite dissolution



Figure 4.139: Plot of ln k vs ln PS for ilmenite in HCl-KCl



Figure 4.138: Plot of ln k vs ln OC for ilmenite in HCl-KCl



Figure 4.140: Plot of ln k vs ln SS for ilmenite in HCl-KCl



Figure 4.141: Plot of ln k vs ln LS for ilmenite in HCl-KCl



Figure 4.142: Plot of ln K vs 1000/T for ilmenite in HCl-KCl

The reaction orders recorded for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) from Figures 4.137 to 4.141 are 0.086, 0.122, -0.05, 0.027, 0.104 respectively.. Activation energy and pre-exponential factor values of 6.29kJ/mol and 0.026s⁻¹ respectively were derived from Arrhenius plot (Figure 4.142). Activation energy of 6.29kJ/mol calculated for dissolution of ilmenite in HCl-KCl confirms that the dissolution process within the scope of investigation is diffusion controlled. The equation describing the dissolution kinetics of chalcopyrite in HCl-KCl medium can be written as:

$$\left(1 - (1 - x)^{1/3}\right)^2 = 0.026(AC)^{0.086}(OC)^{0.122}(PS)^{-0.050}(SS)^{0.027}(LS)^{0.104}exp(-6.29/RT)lnt$$
(4.23)

4.3.3.2 HCl-KClO₃

The experimental data for the process variables: acid concentration, oxide concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio were plotted as a function time as shown in Figures 4.143 - 4.148 respectively in order to investigate the reaction mechanism and dissolution kinetics of sphalerite ore in HCl-KClO₃ lixiviant.



Figure 4.143: Effect of acid concentration on %Fe dissolved using HCl



Figure 4.144: Effect of oxidant concentration on %Fe dissolved using HCI-KCIO₃



Figure 4.145: Effect of particle size on %Fe dissolved using HCl-KClO $_3$



Figure 4.147: Effect of stirring speed on %Fe dissolved using HCI-KCIO₃



Figure 4.146: Effect of solution temperature on %Fe dissolved using HCl-KClO₃



Figure 4.148: Effect of liquid-to-solid ratio on %Fe dissolved using HCI-KCIO₃

Test for linearity of the experimental data was investigated by fitting the experimental data plotted in Figures 4.143 to 4.148 on equations (4.1) to (4.8) to deduce the kinetics equation that best explained the behaviour of the dissolution of ilmenite in HCI-KCIO₃. The recorded correlation coefficient as seen in Table 4.22, shows that Kröger and Ziegler diffusion model, Zhuravlev, Lesokhin and Templeman diffusion equation and Jander three dimensional kinetics model fitted the experimental data. Comparing the linearity displayed by the three models, Zhuravlev, Lesokhin and Templeman diffusion model best fitted the experimental data. The fitted plots are presented in Figures 4.149 to 4.154 representing data for process parameters: acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio, respectively. The poorly fitted plots are shown in Figures D235 to D272 in Appendix D.

Process parameter	ters R^2 (Ilmenite-HCl-KClO ₃)							
-	DTLF	DTPL	SCR	MKM	JANDER	KROGER	ZLT	GINSTLING
Acid Conc								
1	0.625	0.880	0.713	0.872	0.910	0.971	0.971	0.880
2	0.645	0.895	0.748	0.889	0.922	0.976	0.964	0.895
3	0.631	0.893	0.750	0.887	0.925	0.972	0.966	0.893
4	0.626	0.894	0.754	0.888	0.929	0.972	0.973	0.894
Ox. Conc								
0.15	0.664	0.912	0.744	0.903	0.935	0.980	0.980	0.912
0.3	0.708	0.942	0.808	0.936	0.960	0.990	0.982	0.942
0.45	0.633	0.901	0.743	0.894	0.934	0.971	0.985	0.901
0.6	0.598	0.884	0.735	0.878	0.931	0.964	0.985	0.884
Particle Size								
75	0.598	0.884	0.735	0.878	0.931	0.964	0.985	0.884
150	0.592	0.860	0.705	0.853	0.902	0.961	0.972	0.860
300	0.576	0.826	0.668	0.818	0.866	0.958	0.955	0.826
600	0.606	0.860	0.693	0.851	0.892	0.965	0.958	0.860
Temperature	0.000	01000	0.070	01001	0.07	0.000	0.700	0.000
30	0.648	0.859	0.695	0.848	0.875	0.980	0.915	0.859
45	0.672	0.916	0.764	0.909	0.940	0.983	0.981	0.884
60	0.598	0.884	0.735	0.878	0.931	0.964	0.985	0.916
75	0.556	0.851	0.733	0.846	0.919	0.955	0.994	0.851
90	0.513	0.813	0.735	0.809	0.906	0.933	0.981	0.813
Stirring Speed	0.010	0.015	0.720	0.009	0.900	0.912	0.901	0.015
100	0.636	0.917	0.804	0.912	0.955	0.977	0.981	0.917
200	0.580	0.879	0.758	0.874	0.939	0.962	0 994	0.879
300	0.556	0.851	0.733	0.846	0.919	0.955	0.994	0.851
400	0.530	0.819	0.702	0.813	0.895	0.935	0.972	0.819
500	0.510	0 771	0.762	0.015	0.847	0.941	0.972	0 771
Solid –Liquid	0.510	0.771	0.000	0.705	0.077	0.771	0.751	0.771
10	0.632	0.925	0.801	0.920	0.965	0.975	0.981	0.925
15	0.568	0.925	0.729	0.920	0.905	0.959	0.992	0.925
20	0.556	0.851	0.723	0.846	0.910	0.955	0.992	0.851
25	0.536	0.825	0.755	0.040	0.919	0.955	0.994	0.825
25	0.550	0.825	0.720	0.019	0.901	0.950	0.992	0.023
30	0.550	0.805	0.709	0.039	0.934	0.940	0.923	0.805

Table 4.22: Coefficient of determination values for investigated kinetic models at various process variables



Figure 4.149: ZLT plots for ilmenite at different acid concentration



Figure 4.151: ZLT kinetic plots for ilmenite in HCl-KClO₃ at different particle size



Figure 4.153: ZLT kinetic plots for ilmenite in HCl-KClO₃ at different stirring speed



Figure 4.150: ZLT kinetic plots for ilmenite in $HCl-KClO_3$ at different oxidant concentrations



Figure 4.152: ZLT kinetic plots for ilmenite in HCl-KClO₃ at different solution temperature



Figure 4.154: ZLT kinetic plots for ilmenite in HCl-KClO₃ at different liquid-to-solid ratio

The apparent rate constants, k, were derived from the slope of the plots of $(1/(1-x)^{1/3}-1)^2$ against the reaction time for each parameter (acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio). The derived apparent rate constants are presented in Table 4.23.

Process parameters	Zhuravlev, Lesokhin and Temp	bleman diffusion kinetic model
Acid concentration (M)	$K_z (min^{-1})$	R^2
1	0.0012	0.971
2	0.0018	0.964
3	0.0026	0.966
4	0.0032	0.973
Oxide concentration (M)		
0.15	0.0009	0.980
0.30	0.0017	0.982
0.45	0.0019	0.985
0.60	0.0037	0.985
Particle size (µm)		
75	0.0037	0.985
150	0.0024	0.972
300	0.0016	0.955
600	0.0012	0.958
Solution temperature (°C)		
30	0.0003	0.915
45	0.0013	0.981
60	0.0037	0.985
75	0.0102	0.994
90	0.0273	0.981
Stirring speed		
100	0.0076	0.981
200	0.0094	0.994
300	0.0102	0.994
400	0.0104	0.972
500	0.0107	0.957
Liquid-to-solid ratio		
10	0.0068	0.981
15	0.0073	0.992
20	0.0102	0.994
25	0.0141	0.992
30	0.0284	0.923

Table 4.23: Apparent rate constants k_k and coefficient of determination (R^2) values for Zhuravlev, Lesokhin and Templeman diffusion Kinetic Model

A semi-emperical model to show the relationship between the reaction process parameters on the rate constant is expressed in Equation (4.24). The reaction orders recorded for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) from Figures 4.155 to 4.159 are 0.714, 0.921, -0.545, 0.212, 1.205 respectively.

$$k = 409.79(AC)^{0.714}(OC)^{0.921}(PS)^{-0.545}(SS)^{0.212}(LS)^{1.205}exp(-67.73/RT)$$
(4.24)

The activation energy of 67.73 kJ/mol and pre-exponential factor of 409.79s⁻¹were calculated from Figure 4.160.



Figure 4.155: Plot of ln k vs ln AC for ilmenite in acid concentrations



Figure 4.157: Plot of ln k vs ln PS for ilmenite in HCl-KClO $_3$



Figure 4.156: Plot of ln k vs ln OC for ilmenite in $HCl-KClO_3$



Figure 4.158: Plot of ln k vs ln SS for ilmenite in HCl-KClO $_3$





Figure 4.159: Plot of ln k vs ln LS for ilmenite in $HCl-KClO_3$

Figure 4.160: Plot of ln k vs 1000/T for ilmenite in HCl-KClO $_3$

Activation energy of 67.73kJ/mol calculated for dissolution of ilmenite in HCl-KClO₃ seems high for a diffusion controlled process as suggested by the kinetics plots. Ajemba and Onukwuli, 2012 clearly noted that in recent studies, diffusion controlled reactions could have unusually high activation energy. Buttressing their position, they cited instances such as, the activation energy for the diffusion controlled dissolution of Nigerian cassiterite ore in hydrochloric acid was reported to be 50.05kJ/mol (Alafara, 2009) and that for diffusion controlled hydrochloric acid leaching of iron from bauxite varied from 62kJ/mol to 79kJ/mol for different particle size fractions (Paspaliaris, et al, 1987); while that for diffusion control through the product layer using hydrochloric and nitric acids were determined to be 40.8 and 38.3kJ/mol, respectively, for dissolution of sepiolite (Ozdemir et al, 2005).The equation describing the dissolution kinetics of ilmenite in HCl-KClO₃ medium can be written as:

$$\left(\frac{1}{(1-x)^{1/3}}-1\right)^2 = 409.79(AC)^{0.714}(OC)^{0.921}(PS)^{-0.545}(SS)^{0.212}(LS)^{1.205}exp(-67.73/RT)t \quad (4.25)$$

4.3.3.3 HCl-NaNO3

To study the reaction mechanism and kinetics of the dissolution of ilmenite ore in HCl-NaNO₃ at various process variables: acid concentrations, oxidant concentrations, particle sizes, solution temperatures, stirring speed and liquid-to-solid ratios against time. Figures 4.161 to 4.166 show the plots of individual effects of each of the process variables as a function of time.



Figure 4.161: Effect of acid conc. on %Fe dissolved using HCl



Figure 4.162: Effect of oxidant concentration on %Fe dissolved using HCl-NaNO₃



Figure 4.163: Effect of particle size on %Fe dissolved using HCl-NaNO₃



Figure 4.164: Effect of solution temperature on %Fe dissolved using HCl-NaNO₃



Figure 4.165: Effect of stirring speed on %Fe dissolved using HCl-NaNO₃



Figure 4.166: Effect of liquid-to-solid ratio on %Fe dissolved using HCI-NaNO₃

The experimental data of Figures 4.161 to 4.166 were examined with equations (4.1) to (4.8) to ascertain the equation that best described the reaction kinetics of ilmenite dissolution in HCl-NaNO₃. It was glaring that whole experimental data fitted very well to Equations (4.6) and (4.7) (Kröger and Ziegler diffusion model and Zhuravlev, Lesokhin and Templeman diffusion equation). Amongst the two kinetics models, the experimental data best fitted the Kröger and Ziegler diffusion model as adjudged by the coefficient of determination presented on Table 4.24. The fitted plots are presented in Figures 4.167 to 4.172 representing data for process parameters acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio respectively. The poorly fitted plots are shown in Figures D273 to D308 in Appendix D.

Process paramete	ers R ² (Ilmenite-HCl-NaNO ₃)							
-	DTLF	DTPL	SCR	MKM	JANDER	KROGER	ZLT	GINSTLING
Acid Conc								
1	0.625	0.880	0.713	0.872	0.910	0.971	0.971	0.880
2	0.645	0.895	0.748	0.889	0.922	0.976	0.964	0.895
3	0.631	0.893	0.750	0.887	0.925	0.972	0.966	0.893
4	0.626	0.894	0.754	0.888	0.929	0.972	0.973	0.894
Ox. Conc								
0.15	0.691	0.902	0.759	0.895	0.919	0.990	0.956	0.902
0.3	0.571	0.705	0.619	0.701	0.713	0.963	0.716	0.705
0.45	0.596	0.828	0.684	0.821	0.859	0.967	0.926	0.828
0.6	0.568	0.815	0.670	0.807	0.858	0.959	0.952	0.815
Particle Size								
75	0.568	0.815	0.670	0.807	0.858	0.959	0.952	0.815
150	0.518	0.716	0.686	0.709	0.754	0.943	0.855	0.716
300	0.573	0.805	0.656	0.797	0.840	0.960	0.922	0.805
600	0 574	0 798	0.641	0 789	0.828	0.959	0.903	0.798
Temperature	01071	01170	01011	01107	0.020	0.707	017 02	0.170
30	0.711	0.905	0.758	0.896	0.916	0.992	0.942	0.905
45	0.615	0.859	0.694	0.850	0.887	0.970	0.951	0.859
60	0 568	0.815	0.670	0.807	0.858	0.959	0.952	0.815
75	0.502	0.727	0.611	0.721	0.788	0.938	0.927	0.727
90	0.483	0.727	0.598	0.695	0.711	0.931	0.932	0.700
Stirring Speed	0.105	0.700	0.570	0.075	0.711	0.951	0.952	0.700
100	0.521	0.750	0.625	0.744	0.804	0.944	0.919	0.750
200	0.509	0.731	0.612	0.725	0.786	0.940	0.910	0.731
300	0.502	0.727	0.611	0.721	0.788	0.938	0.927	0.727
400	0.496	0.716	0.607	0.711	0.799	0.935	0.918	0.716
500	0.492	0.711	0.600	0.706	0.776	0.934	0.930	0.711
Solid –Liquid	0.172	0.711	0.000	0.700	0.770	0.951	0.950	0.711
10	0.470	0.638	0.540	0.632	0.684	0.926	0.819	0.638
15	0.489	0.686	0.578	0.680	0.739	0.934	0.877	0.686
20	0.102	0.000	0.611	0.000	0.788	0.938	0.927	0.000
25	0.502	0.756	0.641	0.751	0.831	0.936	0.964	0.756
20	0.504	0.750	0.041	0.751	0.031	0.950	0.904	0.750

Table 4.24: Coefficient of determination values for investigated kinetic models at various process variables



Figure 4.167: Kroger plots for ilmenite at different acid concentration



Figure 4.169: Kroger kinetic plots for ilmenite in HCl-NaNO₃ at different particle size



Figure 4.171: Kroger kinetic plots for ilmenite in The *i* HCl-NaNO₃ at different stirring speed



Figure 4.168: Kroger kinetic plots for ilmenite in $HCl-NaNO_3$ at different oxidant concentrations



Figure 4.170: Kroger kinetic plots for ilmenite in HCl-NaNO₃ at different solution temperature



Figure 4.172: Kroger kinetic plots for ilmenite in HCl-NaNO₃ at different liquid-to-solid ratio

against the natural logarithm of reaction time for each parameter (acid concentration, oxidant concentration, particle size, solution temperature, stirring speed and liquid-to-solid ratio). The derived apparent rate constants presented in Table 4.25.

Drogog peromotors		Vräger and Ziegler kingtig model
A sid sequenties (NO)	\mathbf{V} (, :, -1)	$rac{1}{2}$
Acid concentration (M)	$\mathbf{K}_k(\min)$	K
1	0.151	0.971
2	0.159	0.976
3	0.166	0.972
4	0.170	0.972
Oxide concentration (M)		
0.15	0.141	0.990
0.30	0.148	0.963
0.45	0.158	0.967
0.60	0.166	0.959
Particle size (µm)		
75	0.166	0.959
150	0.157	0.943
300	0.156	0.960
600	0.144	0.959
Solution temperature (°C)		
30	0.119	0.992
45	0.147	0.970
60	0.166	0.959
75	0.177	0.938
90	0.182	0.931
Stirring speed		
100	0.173	0.944
200	0.175	0.940
300	0.177	0.938
400	0.179	0.935
500	0.178	0.934
Liquid-to-solid ratio		
10	0.170	0.926
15	0.174	0.934
20	0.177	0.938
25	0.182	0.936
30	0.189	0.951

Table 4.25: Apparent rate constants k_k and coefficient of determination (R^2) values for Kröger and Ziegler kinetic model

A semi-emperical model to show the relationship between the reaction process parameters on the rate constant combined with the Kröger and Ziegler kinetic model can be expressed as:

$$(1 - (1 - x)^{1/3})^2 = k_o (AC)^{\alpha} (OC)^{\beta} (PS)^{\gamma} (SS)^{\theta} (LS)^{\varphi} exp(-E_a/RT) lnt$$
(4.26)

From Figures 4.173 to 4.177, the values of the constants, α , β , γ , θ and ϕ , were estimated from the slope of the plots of the natural logarithm of apparent rate constants (Table 4.25) versus natural logarithm of the process parameters.



Figure 4.173: Plot of ln k vs ln AC for ilmenite in acid concentrations



Figure 4.175: Plot of ln k vs ln PS for ilmenite in HCl-NaNO $_3$



Figure 4.177: Plot of ln k vs ln LS for ilmenite in $HCl-NaNO_3$



Figure 4.174: Plot of ln k vs ln OC for ilmenite in $HCl-NaNO_3$



Figure 4.176: Plot of ln k vs ln SS for ilmenite in HCl-NaNO3



Figure 4.178: Plot of ln k vs 1000/T for ilmenite in HCl-NaNO_3 $\,$

The reaction orders recorded for acid concentration (AC), oxidant concentration (OC), particle size (PS), stirring speed (SS), liquid-to-solid ratio (LS) from Figures 4.173 to 4.177 are 0.086, 0.116, -0.062, 0.020, 0.090 respectively. The activation energy was calculated from the slope of the Arrhenius plot on Figure 4.178. The activation energy of the leaching process and the value of constant A were calculated and found to be equals 6.42 kJ/mol and 0.03s⁻¹, respectively. The value of activation energy in the dissolution process may be characterized to predict the controlling step. The activation energy of a diffusion controlled process is usually 21kJ/mol or less, when chemical reaction is the rate controlling step, the activation is between 40-100kJ/mol. Activation energy of 6.42kJ/mol calculated for dissolution of ilmenite in HCl-NaNO₃ confirms that the dissolution process within the scope of investigation is diffusion controlled. The equation describing the dissolution kinetics of ilmenite in HCl-NaNO₃ medium can be written as:

 $\left((1-x)^{1/3} - 1 \right)^2$ = 0.03(AC)^{0.086}(OC)^{0.116}(PS)^{-0.062}(SS)^{0.020}(LS)^{0.090}exp(-6.42/RT)lnt (4.27)

4.4 Dissolution Thermodynamics

In order to evaluate the feasibility and, also, further elucidate the temperature effect on the leaching of copper, zinc and iron from chalcopyrite, sphalerite and ilmenite, respectively, thermodynamic parameters such as standard free energy (ΔG), standard enthalpy change (ΔH) and standard entropy change (ΔS) were obtained. The Gibbs free energy (ΔG) is the fundamental criterion for spontaneity of a process and can be determined using the relationship:

 $\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$

(4.28)

The enthalpy and entropy values were computed from the slope and intercept of the van't Hoff equation, which is given by:

$$=\frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(4.29)

where R is the universal gas constant (8.314Jmol⁻¹K⁻¹), T is solution temperature (K) and k is apparent rate constant. Figure 4.179 to 4.181 represent plots of natural logarithm of k against inverse values of temperature.



Figure 4.179 : Thermodynamic plot for chalcopyrite leaching



Figure 4.180 : Thermodynamic plot for sphalerite leaching



Figure 4.181 : Thermodynamic plot for ilmenite leaching

From the slopes and intercepts the change in enthalpy and change in entropy were obtained. The values of the standard Gibb's free energy computed using equation (4.28), enthalpy and entropy change are tabulated in Tables 4.26 to 4.28. The negative ΔG reveals the spontaneous nature of leaching. Also, the adopted sign convention, confirms the feasibility of the leaching process. Positive enthalpy values recorded in this research indicates that the reactions are endothermic. The positive entropy values suggest increased randomness at the solid/solution interface.

Lixiviants	T(K)	ΔG	ΔS	ΔH
HCl-KCl	303	-4.93		
	318	-5.17		
	333	-5.42	16.29	10.41
	348	-5.66		
	363	-5.90		
HCl-KClO ₃	303	-1.13		
	318	-1.19		
	333	-1.25	3.76	5.97
	348	-1.30		
	363	-1.36		
HCl-NaNO ₃	303	-4.13		
	318	-4.34		
	333	-4.54	13.67	9.63
	348	-4.75		
	363	-4.95		

Table 4.26: Thermodynamic parameters for the leaching of chalcopyrite

 Table 4.27: Thermodynamic parameters for the leaching of sphalerite

Lixiviants	T(K)	ΔG	ΔS	ΔH	
HCl-KCl	303	-27.26			
	318	-28.61			
	333	-29.97	90.12	45.56	

	348	-31.32		
	363	-32.67		
HCl-KClO ₃	303	-4.80		
	318	-5.04		
	333	-5.28	15.88	10.07
	348	-5.52		
	363	-5.75		
HCl-NaNO ₃	303	-25.43		
	318	-26.69		
	333	-27.95	84.05	42.86
	348	-29.21		
	363	-30.47		

Table 4.28: Thermodynamic parameters for the leaching of ilmenite

Lixiviants	T(K)	ΔG	ΔS	ΔH
HCl-KCl	303	-1.15		
	318	-1.21		
	333	-1.26	3.82	6.53
	348	-1.32		
	363	-1.38		
HCl-KClO ₃	303	-47.42		
	318	-49.77		
	333	-52.12	156.72	67.73
	348	-54.47		
	363	-56.82		
HCl-NaNO ₃	303	-1.18		
	318	-1.24		
	333	-1.30	3.92	6.42
	348	-1.36		
	363	-1.42		

4.4 Design and Statistical Analysis of Leaching Experiments Using Response Surface Methodology

Design of experiments was used in planning the experiments so that the dependent variable obtained can be investigated to give valid and objective conclusions. A-32 experimental run generated by 2^5 fractional factorial central composite design technique of the response surface methodology were performed to evaluate the combined effect of the independent variables (solution temperature, liquid-to-solid ratio, stirring speed, acid concentration and
contact time) on the response (% Yield). The experimental matrix and analyses were computed using the Design Expert software trial version 11.0. The low and high levels of the controllable variables were chosen on the basis of preliminary experiments.

Solution temperature of 318 and 348K, liquid-to-solid ratio of 15 and 25 l/g, steering speed of 200 and 400rpm and contact time of 60 and 120 minutes were marginal conditions of effective variables which were fed to the software. Each variable was varied over five levels: low level (code:-1), high level (code: +1), central level (code: 0), and two other levels – axial (codes: $-\alpha$ and $+\alpha$). Original values of the variables are presented in Tables E1 to E9 in Appendix E.

4.4.1 RSM modeling of the leaching process of chalcopyrite using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions as lixiviants

The interaction of the controllable leaching process variables and the corresponding independent variables were tabulated in Tables E1 to E9 in appendix E for chalcopyrite ore in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants. The experimental data was fitted to the linear, 2FI, quadratic and cubic models to generate regression models. The adequacy of each type of model under investigation was evaluated using analysis of variance (ANOVA). In Tables 4.29, 4.30 and 4.31 presented least values for standard deviation, mean square error and F-values for quadratic model. This suggests that the quadratic model better fitted the experimental data. Also, the predicted R^2 values of 0.799, 0.9636 and 0.9099 for the leaching of chalcopyrite in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions for the quadratic model are closest to unity when compared with the values presented for cubic, 2FI and linear models. This corroborates the submission that the quadratic model best correlates the actual and predicted data for the leaching process. The predicted R^2 considers all effects and adjusted R² considers only square effects and interaction effects between two input variables (Jie et al., 2014). Predicted R² values of 0.799, 0.9636 and 0.9099 are in reasonable agreement with the adjusted R^2 values of 0.9760, 0.9878 and 0.9892 (the difference is <0.2). The coefficient of determination, R^2 , was recorded to be 0.9915, 0.9957 and 0.9962 indicating that only 0.85%, 0.43% and 0.38% of the total variations could not be explained by the models.

As shown in Tables 4.29 to 4.31, the quadratic model has the lowest prediction error sum of squares (PRESS) values (2711.24, 108.80 and 603.5) for the three lixiviants used for the

leaching of chalcopyrite when compared with the linear (6133.91, 1997.42 and 2458.52), 2FI (43800, 6405.68 and 8982.26) and cubic (92592.4, 153.46 and 13366.28) models. The smaller the PRESS value, the better the model's predictability (Okoye *et al.*, 2019). Based on these findings, quadratic model was chosen and further computations on experimental data were done using the quadratic model.

Source	Std.	MSE	F-Value	Lack of Fit	\mathbf{R}^2	Adjusted \mathbf{P}^2	Predicted \mathbf{P}^2	PRESS
	Dev.			p-value		ĸ	K	
Linear	12.79	202.62	1006.9	< 0.0001	0.684	0.6238	0.5452	6133.9
			7		4			1
2FI	14.91	323.47	1607.5	< 0.0001	0.736	0.4887	-2.2475	43800
			7		1			
Quadrati	3.23	18.94	94.13	< 0.0001	0.991	0.976	0.799	2711.2
с					5			4
Cubic	3.79	85.31	423.95	< 0.0001	0.993	0.9669	-5.8651	92592.
					6			4

Table 4.29: Model summary for Chalcopyrite in HCl-KCl

Table 4.30: Model summary for Chalcopyrite in HCl-KClO₃

Source	Std. Dev.	MSE	F- Value	Lack of Fit p-value	\mathbf{R}^2	Adjusted R^2	Predicted R ²	PRESS
Linear	7.21	63.84	34.17	0.0005	0.5481	0.4612	0.3315	1997.42
2FI	8.70	109.18	58.44	0.0001	0.5949	0.2151	-1.1440	6405.68
Quadratic	1.08	0.60	0.32	0.9013	0.9957	0.9878	0.9636	108.80
Cubic	1.26	0.13	0.07	0.8030	0.9968	0.9836	0.9486	153.46

Table 4.31: Model summary for Chalcopyrite in HCl-NaNO₃

					2			
Source	Std.	MSE	F-	Lack of Fit	R^2	Adjusted	Predicted	PRESS
	Dev.		Value	p-value		\mathbf{R}^2	\mathbf{R}^2	
Linear	7.93	77.72	286.41	< 0.0001	0.7562	0.7093	0.633	2458.52
2FI	9.56	132.93	489.87	< 0.0001	0.7815	0.5767	-0.3409	8982.26
Quadratic	1.53	4.04	14.89	0.0047	0.9962	0.9892	0.9099	603.5
Cubic	1.51	12.31	45.38	0.0011	0.998	0.9895	-0.9954	13366.28

Table 4.32 tabulates ANOVA for chalcopyrite leaching using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃. The models' F-values 64.15, 126.60 and 143.33 imply that the models are significant. Model F-value is calculated as a ratio of mean square regression and mean square residual (Khataee *et al.*, 2010). Values of P-value less than 0.0500 indicate model terms are significant. In general, it can be considered that higher Fisher's F-test values and lower p-values indicate the relative significance of each term. In this case A, B, C, D, E, AB, AC, BE,

 A^2 , B^2 , C^2 , D^2 , E^2 ; A, B, D, E, AB, AC, AD, AE, BC, BE, A^2 , E^2 ; A, B, D, E, AD, BC, A^2 , E^2 are significant model terms for chalcopyrite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media respectively.

		F-value			P-value	
Source	Chale-	Chalc-HCl-	Chalc-HCl-	Chalc-	Chalc-HCl-	Chalc-HCl-
Model	64.15	126.60	143.33	< 0.0001	< 0.0001	< 0.0001
A-Temperature	628.9	865.93	1502.36	< 0.0001	< 0.0001	< 0.0001
B-L/S	49	99.54	127.96	< 0.0001	< 0.0001	< 0.0001
C-Stirring Speed	9.08	0.88	4.58	0.0118	0.3685	0.0557
D-Acid Conc.	11.15	38.90	135.51	0.0066	< 0.0001	< 0.0001
E-Time	187.57	388.61	405.59	< 0.0001	< 0.0001	< 0.0001
AB	22.32	6.27	3.58	0.0006	0.0293	0.0850
AC	7.19	28.29	0.01	0.0213	0.0002	0.9400
AD	0.051	12.55	13.90	0.8247	0.0046	0.0033
AE	2.87	8.58	1.30	0.1184	0.0137	0.2790
BC	2.94E-05	26.83	48.52	0.9958	0.0003	< 0.0001
BD	4.81	12.88	0.12	0.0508	0.0043	0.7313
BE	28.51	19.65	0.00	0.0002	0.0010	0.9834
CD	4.97E-03	2.23	0.44	0.9451	0.1632	0.5206
CE	0.82	1.38	1.24	0.3847	0.2643	0.2896
DE	0.29	0.23	3.86	0.6032	0.6408	0.0752
A^2	261.44	906.07	591.50	< 0.0001	< 0.0001	< 0.0001
B^2	27.85	3.69	0.50	0.0003	0.0812	0.4951
C^2	19.94	0.59	3.15	0.001	0.4572	0.1036
D^2	7.29	0.20	2.99	0.0207	0.6644	0.1114
E^2	72.61	153.92	37.01	< 0.0001	< 0.0001	< 0.0001
Adeq Precision						
Chalc-Hcl-KCl		29.995				
Chalc-HCl-KClO ₃		45.550				
Chalc-NaNO ₃		54.569				

Table 4.32: ANOVA for response surface quadratic model for chalcopyrite leaching

Adeq Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratios 29.995, 45.550 and 54.569 recorded for HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media respectively indicate an adequate signal thus the models generated can be used to navigate the design space.

Response surface methodology generated second-order empirical model showing the relationship between linear, interaction and quadratic effects of the controllable factors and the response in generalized form (equation 3.4) was subjected to factor screening. From the ANOVA results, variables or interaction of variables whose p-value (probability value) is greater than 0.05 (i.e. 5% level of significance) is eliminated from the model equation generated. The final equations for chalcopyrite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media in coded values can be expressed as:

$$Y_{\text{HCl-KCl}} = 89.19 + 16.53\text{A} + 4.61\text{B} + 1.99\text{C} + 2.20\text{D} + 9.03\text{E} + 3.81\text{AB} - 2.16\text{AC} - 4.31\text{BE} - 9.64\text{A}^2 - 3.15\text{B}^2 - 2.66\text{C}^2 - 1.61\text{D}^2 - 5.08\text{E}^2$$
(4.30)

 $Y_{\text{HCl-NaNO3}} = 79.13 + 12.07\text{A} + 3.52\text{B} + 3.63\text{D} + 6.27\text{E} + 1.42\text{AD} - 2.66\text{BC} - 6.85\text{A}^{2} - 1.71\text{E}^{2}$ (4.32)

In Equations (4.30), (4.31) and (4.32) all the linear factors (solution temperature (A), liquidto-solid ratio (B), steering speed (C), acid concentration (D) and contact time (E)) were significant except for steering speed (C) in Equations (4.31) and (4.32) (p-values < 0.05). The effect of the linear interactions AD, AE, BC, BD; BD; AB, AC, AE, BD, BE, in Equations (4.30), (4.31) and (4.32) respectively are insignificant (p-values > 0.05) therefore are not present in the equation. In the same vein, the quadratic effects of liquid-to-solid ratio, steering speed and acid concentration (B², C² and D²) did not appear in Equations (4.31) and (4.32) respectively. The positive sign in front of the terms indicates synergetic effect while the negative sign implies antagonistic effect of the factor on the response. Equations (4.30), (4.31) and (4.32) show that the linear effects of all the factors have synergetic effect on the dependent variable.

The normal probability versus residual plots (Figures 4.182, 4.184 and 4.186) show whether the residuals follow a normal distribution. When the plotted points follow a straight line it implies that there is a good relationship between the experimental and the predicted values of response. In some cases moderate scatter are expected. Tables E1, E2 and E3 in appendix E show the predicted and experimental data for the leaching of chalcopyrite in HCl-KCl, HClKClO₃ and HCl-NaNO₃ lixiviants. The results obtained present that the selected quadratic model was adequate in predicting the response variables for the experimental data.





Figure.4.182: Normal plot of residuals for leaching of chalcopyrite in HCl-KCl solution

Figure.4.183: Plot of predicted versus actual experimental values for leaching of chalcopyrite in HCl-KCl solution



Figure.4.184: Normal plot of residuals for leaching of chalcopyrite in HCl-KClO₃ solution



Figure.4.185: Plot of predicted versus actual experimental values for leaching of chalcopyrite in HCl-KClO₃ solution



The predicted vs actual plots (Figures 4.183, 4.185 and 4.187) depict how the models predict over the range of data under study. It also reveals values not properly predicted by the model. For robust correlation to be established between the actual and predicted values, it is expected that the plots should scatter around the 45° line. It was observed in Figures 4.183, 4.185 and 4.187 that the actual response values closely aligned to the predicted (Okoye *et al.*, 2019).

4.4.2: Three dimensional surface Plots for chalcopyrite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants

Figures 4.188, 4.189 and 4.190 illustrate the effects of the interaction of time an acid concentration on leaching process response. It is observed that the yield (%Cu dissolved) increases as time increases for HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants at all acid concentrations indicating high rate of %Cu dissolution. Upward review of time above 105 minutes for HCl-KCl and HCl-KClO₃ lixiviants displayed a mild observable effect on the response. For HCl-NaNO₃ lixiviant, a steady increase in the response was observed as time increased. A steady increase on yield was displayed as acid concentrations was reviewed upward for HCl-KClO₃ and HCl-NaNO₃ lixiviants at all interaction points within the design space. This behaviour slightly different for HCl-KCl lixiviant. Above 3.50M acid concentration, there seems to be no observable effect on the response.

Figures 4.191, 4.192 and 4.193 displays the 3D plots of the interactive effects of contact time and stirring speed for chalcopyrite leaching process using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ as lixiviants. Figure 4.191 shows initial synergetic effect of stirring speed on the response. Above 300rpm, there was no observable effect on the yield regardless of time increase. In Figure 4.192, steering speed had synergetic effect on the response over the range of values under investigation. Above 105 minutes the interactive effects of steering speed and contact time was insignificant on the response. Figure 4.193 displayed antagonistic behaviour on the response as stirring speed was increased over time.



PO 6725 84 12000 E: Time 7500 6000 200 D: Acid Conc

Figure.4.188: 3D Plot of the effect of time and acid conc for chalcopyrite leaching with HCl-KCl solution

Figure.4.189: 3D Plot of the effect of time and acid conc for chalcopyrite leaching with HCl-KClO₃ solution



Figure.4.190: 3D Plot of the effect of time and acid conc for chalcopyrite leaching with HCl- NaNO₃ solution



Figure.4.191: 3D Plot of the effect of time and stirring speed for chalcopyrite leaching with HCl-KCl solution





Figure.4.192: 3D Plot of the effect of time and stirring speed for chalcopyrite leaching with HCl- $KClO_3$ solution

Figure.4.193: 3D Plot of the effect of time and stirring speed for chalcopyrite leaching with

3-D surface plots pictured in Figures 4.194, 4.195 and 4.196 followed a similar trend for the interactive effects of time and liquid-to-solid ratio for the leaching of chalcopyrite on HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solutions. The yield increased as liquid-to-solid ratio increased over the time of the study. This could be as a result of unsaturation of the lixiviants. Figures 4.197, 4.198 and 4.199 depict the interaction between contact time and solution temperature. It is seen from the plots that upward review of time and solution temperature resulted to increase in Yield (%Cu dissolved). Approaching 348K for Figures 4.197 – 4.199, a milder effect on the response was observed. The directly proportional relationship of solution temperature on the response may be as a result of

increase in kinetic energy of the system which in-turn increased the rate of collision (molecular interactions) of the reacting molecules.



Figure.4.194: 3D Plot of the effect of time and L/S ratio for chalcopyrite leaching with HCl- KCl solution



Figure.4.195: 3D Plot of the effect of time and L/S ratio for chalcopyrite leaching with HCl-KClO₃ solution



Figure.4.196: 3D Plot of the effect of time and L/S ratio for chalcopyrite leaching with HCl- NaNO₃ solution



Figure.4.197: 3D Plot of the effect of time and contact temperature for chalcopyrite leaching with HCl-KCl solution





Figure 4.198: 3D Plot of the effect of time and contact temperature for chalcopyrite leaching with HCl- KClO₃ solution

Figure.4.199: 3D Plot of the effect of time and contact temperature for chalcopyrite leaching with HCl-NaNO₃ solution

4.4.3 RSM modeling of the leaching process of sphalerite using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants

Tables E4 to E6 in Appendix E display the interaction of the independent and dependent variables for the leaching of sphalerite using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions as lixiviants. The adequacy of linear, 2FI, quadratic and cubic models to describe the experimental data was evaluated using analysis of variance (ANOVA). Quadratic model has the lowest values for standard deviation, mean square error and F-values (Tables 4.33, 4.34 and 4.35). The predicted R² values of 0.7766, 0.7829 and 0.8799 for the leaching of sphalerite in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media for the quadratic model are closest to unity when compared with the values presented for cubic, 2FI and linear models. The results obtained confirm that quadratic model best fitted the experimental data. Predicted R² values of 0.7766, 0.7829 and 0.8799 are in reasonable agreement with the adjusted R² values of 0.9753, 0.9754 and 0.9861 (the difference is <0.2). The coefficient of determination, R², was recorded to be 0.9912, 0.9913 and 0.9951 indicating that only 0.88%, 0.87% and 0.49% of the total variations could not be explained by the models.

Tables 4.33 to 4.35 reveal that quadratic model has the lowest prediction error sum of squares (PRESS) values (1682.2, 1129.39 and 682.45) for the three lixiviants used for the leaching of sphalerite when compared with the linear (3623.51, 1918.08 and 2003.84), 2FI (15550.2, 12450.22 and 7867.62) and cubic (15044.5, 9570.07 and 5042.69) models. The higher a

model's PRESS value the farther its predictive capability. Based on these findings, quadratic model was chosen and further computations on experimental data were done using the quadratic model.

Source	Std.	MSE	F-	Lack of Fit	\mathbf{R}^2	Adjusted	Predicted	PRESS
	Dev.		Value	p-value		\mathbf{R}^2	\mathbf{R}^2	
Linear	9.57	113.37	409.46	< 0.0001	0.6836	0.6228	0.5188	3623.51
2FI	9.61	134.20	484.68	< 0.0001	0.8038	0.6198	-1.065	15550.2
Quadratic	2.45	10.78	38.94	0.0005	0.9912	0.9753	0.7766	1682.22
Cubic	1.59	13.868	50.05	0.0009	0.9980	0.9895	-0.9979	15044.5

Table 4.33: Model summary for sphalerite in HCl-KCl

Table 4.34: Model summary for sphalerite in HCl-KClO₃

Source	Std.	MSE	F-	Lack of Fit	\mathbf{R}^2	Adjusted	Predicted	PRESS
	Dev.		Value	p-value		\mathbf{R}^2	\mathbf{R}^2	
Linear	7.21	64.20	150.55	< 0.0001	0.7383	0.6880	0.6283	1918.08
2FI	8.78	111.88	262.36	< 0.0001	0.7611	0.5371	-1.4126	12450.22
Quadratic	2.02	7.16	16.79	0.0036	0.9913	0.9754	0.7829	1120.41
Cubic	1.35	8.81	20.67	0.0061	0.9979	0.9890	-0.8545	9570.07

Table 4.35: Model summary for sphalerite in HCl-NaNO₃

Source	Std.	MSE	F-	Lack of Fit p-	R^2	Adjusted	Predicted	PRESS
	Dev.		Value	value		\mathbf{R}^2	\mathbf{R}^2	
Linear	7.12	62.74	151.96	< 0.0001	0.7677	0.7230	0.6472	2003.84
2FI	7.30	77.33	187.29	< 0.0001	0.8499	0.7092	-0.3850	7867.62
Quadratic	1.60	4.34	10.50	0.0104	0.9951	0.9861	0.8799	682.45
Cubic	1.06	4.64	11.25	0.0203	0.9988	0.9939	0.1123	5042.69

Table 4.36 tabulates ANOVA for sphalerite leaching using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃. The models' F-values 62.13, 62.15 and 110.70 imply that the models are significant. Model F-value is calculated as a ratio of mean square regression and mean square residual (Khataee *et al.*, 2010). Values of P-value less than 0.0500 indicate model terms are significant. In general, it can be considered that higher Fisher's F-test values and lower p-values indicate the relative significance of each term. In this case A, B, D, E, AD, AE, BC, BD, BE, CE, DE, A², B², C², D², E²; A, B, D, E, AE, A², B², D², E²; A, B, C, D, E, AB, AE, BD, CD, CE, A², B², D², E² are significant model terms for sphalerite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media respectively.

Table 4.36: ANOVA for response surface quadratic model for sphalerite leaching

		F-value			P-value	
Source	Chalc-	Chalc-HCl-	Chalc-HCl-	Chalc-	Chalc-HCl-	Chalc-HCl-
	HCl-KCl	KClO ₃	NaNO ₃	HCl-KCl	KClO ₃	NaNO ₃
Model	62.13	62.15	110.70	< 0.0001	< 0.0001	< 0.0001
A-	493.77	540.30	871.55	< 0.0001	< 0.0001	< 0.0001
Temperature						
B-L/S	51.70	18.55	204.23	< 0.0001	0.0012	< 0.0001
C-Stirring	1.68	0.08	11.58	0.2215	0.7821	0.0059
Speed				0.0001	0.0004	0.0004
D-Acid	151.33	85.78	320.67	< 0.0001	< 0.0001	< 0.0001
Conc.	150 50	290 64	200.01	< 0.0001	< 0.0001	< 0.0001
E-Time	158.52	280.04	300.01	< 0.0001	< 0.0001	< 0.0001
AB	1.02	0.01	12.94	0.3347	0.9214	0.0042
AC	2.23	1.86	4.13	0.1638	0.1999	0.0669
AD	23.48	0.42	0.07	0.0005	0.5307	0.8021
AE	7.62	14.43	20.84	0.0185	0.0030	0.0008
BC	47.23	4.18	0.07	< 0.0001	0.0655	0.7904
BD	39.93	1.75	121.50	< 0.0001	0.2122	< 0.0001
BE	12.18	1.03	0.74	0.0051	0.3323	0.4082
CD	3.20	0.29	9.84	0.1011	0.6006	0.0095
CE	6.26	4.47	10.21	0.0295	0.0581	0.0085
DE	7.45	0.04	2.57	0.0196	0.8512	0.1374
A^2	204.00	209.25	281.71	< 0.0001	< 0.0001	< 0.0001
\mathbf{B}^2	7.51	13.62	17.84	0.0192	0.0036	0.0014
C^2	14.20	0.29	0.78	0.0031	0.5998	0.3965
D^2	9.19	23.81	38.91	0.0114	0.0005	< 0.0001
E^2	36.13	85.31	25.68	< 0.0001	< 0.0001	0.0004
Adeq Precisio	n					
Sphalerite-HC	l-KCl	29.64				
Sphalerite -HO	Cl-KClO ₃	32.49				
Sphalerite -Na	NO ₃	37.44				

Adequacy Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratios 29.64, 32.49 and 37.44 recorded for HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media respectively indicate an adequate signal thus the models generated can be used to navigate the design space.

Response surface methodology generated second-order empirical model showing the relationship between linear, interaction and quadratic effects of the controllable factors and the response in generalized form (equation (3.4)) was subjected to factor screening. From the ANOVA results, variables or interaction of variables whose p-value (probability value) are

greater than 0.05 (i.e. 5% level of significance) are eliminated from the model equation generated. The final equations for sphalerite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media in coded values can be expressed as:

$$\begin{split} Y_{\text{HCI-KCI}} &= 83.74 + 11.12\text{A} + 3.60\text{B} + 6.15\text{D} + 6.30\text{E} + 2.97\text{AD} - 1.69\text{AE} - 4.21\text{BC} - 3.87\text{BD} \\ &+ 2.14\text{BE} + 1.53\text{CE} + 1.67\text{DE} - 6.46\text{A}^2 - 1.24\text{B}^2 - 1.71\text{C}^2 - 1.37\text{D}^2 - 2.72\text{E}^2 \end{split}$$

$$\end{split}$$

$$\begin{aligned} Y_{\text{HCI-KCIO3}} &= 85.48 + 9.62\text{A} + 1.79\text{B} + 3.84\text{D} + 6.95\text{E} + 1.93\text{AE} - 5.40\text{A}^2 - 1.39\text{B}^2 - 0.21\text{C}^2 \\ &- 1.83\text{D}^2 - 3.47\text{E}^2 \end{aligned}$$

$$\begin{aligned} Y_{\text{HCI-NaNO3}} &= 78.45 + 9.63\text{A} + 4.66\text{B} + 1.11\text{C} + 5.84\text{D} + 5.65\text{E} + 1.44\text{AB} - 1.82\text{AE} - 4.40\text{BD} \end{split}$$

$$Y_{\text{HCl-NaNO3}} = 78.45 + 9.63\text{A} + 4.66\text{B} + 1.11\text{C} + 5.84\text{D} + 5.65\text{E} + 1.44\text{AB} - 1.82\text{AE} - 4.40\text{BD} - 1.25\text{CD} - 1.28\text{CE} - 4.95\text{A}^2 - 1.25\text{B}^2 - 1.84\text{D}^2 - 1.49\text{E}^2$$
(4.35)

In Equations (4.33), (4.34) and (4.35) all the linear factors (solution temperature (A), liquidto-solid ratio (B), steering speed (C), acid concentration (D) and contact time (E)) were significant except for steering speed (C) in Equations (4.33) and (4.34) (p-values < 0.05). The effect of the linear interactions AB, AC, CD; AB,AC, AD, BC, BD, BE, CD, CE, DE; AC, AD, BE, DE in Equations (4.33), (4.34) and (4.35) respectively are insignificant (pvalues > 0.05) therefore are not present in the equation. In the same vein, the quadratic effect of steering speed (C^2) did not appear in Equation (4.35). The positive sign in front of the terms indicates synergetic effect while the negative sign implies antagonistic effect of the factor on the response. Equations (4.33), (4.34) and (4.35) show that the linear effect of all the factors has synergetic effect on the dependent variable.

The normal probability versus residual plots (Figures 4.200, 4.202 and 4.204) show whether the residuals follow a normal distribution. When the plotted points follow a straight line it implies that there is a good relationship between the experimental and the predicted values of response. In some cases moderate scatter are expected. Tables E4, E5 and E6 in appendix E show the predicted and experimental data for the leaching of sphalerite in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants. The results obtained show that the selected quadratic model was adequate in predicting the response variables for the experimental data.







Figure 4 202. Normal plot of residuals for Normal Plot of Residuals



Figure 4 203. Plot of predicted versus actual



Figure.4.204: Normal plot of residuals for leaching of sphalerite in HCl-NaNO₃ solution

Figure.4.205: Plot of predicted versus actual experimental values for leaching of sphalerite in HCl-NaNO₃ solution

The predicted vs actual plots (Figures 4.201, 4.203 and 4.205) reveal how the models predict over the range of data under investigation. It also shows values not properly predicted by the model. For high level of prediction of the experimental data, it is expected that the plots should scatter around the 45° line. The trend followed by the plots confirms that the actual response values closely aligned with the predicted.

4.4.4: Three dimensional surface plots for sphalerite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants

The interactive effects of contact time and acid concentration for the leaching of sphalerite using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants were displayed in Figures 4.206, 4.207 and 4.208. The simultaneous increase of the independent variables (contact time and acid concentration) within the design space was positive on the dependent variable (yield). Above acid concentration of 3.50M, the significant effect recorded on the dependent variable began to dwindle.

Figures 4.209, 4.210 and 4.211 show the representation of the combined effects of contact time and steering speed on the response for the leaching of sphalerite using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solutions. It is observed in Figure 4.209 that the leaching process was more favourable at lower values of stirring speed. Similar result was also observed in Figure 4.210. On the contrary, increasing stirring speed for sphalerite leaching with HCl-NaNO₃ solution was positive on the solution.



Figure.4.206: 3D Plot of the effect of time and acid conc for sphalerite leaching with HCl-KCl solution



Figure.4.208: 3D Plot of the effect of time and acid conc for sphalerite leaching with



Figure.4.207: 3D Plot of the effect of time and acid conc for sphalerite leaching with HCl-KClO₃ solution



Figure.4.209: 3D Plot of the effect of time and steering speed for sphalerite leaching





Figure.4.210: 3D Plot of the effect of time and stirring speed for sphalerite leaching with HCl- KClO₃ solution

Figure.4.211: 3D Plot of the effect of time and stirring speed for sphalerite leaching with HCl-NaNO₃ solution

3-D surface plots pictured in Figures 4.212, 4.213 and 4.214 followed a similar trend for the interactive effects of time and liquid-to-solid ratio for the leaching of sphalerite on HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ solutions. The yield increased as liquid-to-solid ratio increased over the time of the study. This could be as a result of unsaturation of the lixiviants. Figures 4.215, 4.216 and 4.217 depict the interaction between contact time and solution temperature. It is seen from the plots that upward review of time and solution temperature resulted to increase in yield (%Zn dissolved). Approaching 348K for Figures 4.215 and 4.216, a milder effect on the response was observed. The directly proportional relationship of solution temperature on the response may be as a result of increase in kinetic energy of the system which in-turn increased the rate of collision (molecular interactions) of the reacting molecules.





Figure.4.214: 3D Plot of the effect of time and L/S ratio for sphalerite leaching with HCl- NaNO₃ solution



Figure.4.215: 3D Plot of the effect of time and contact temperature for sphalerite leaching with HCl-KCl solution



Figure.4.216: 3D Plot of the effect of time and contact temperature for sphalerite leaching with HCl- KClO₃ solution



Figure. 4.217: 3D Plot of the effect of time and contact temperature for sphalerite leaching with HCl-NaNO₃ solution

4.4.5 RSM Modeling of the Leaching Process of Ilmenite Using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ Lixiviants

Tables E7 to E9 in appendix E present the interaction of the controllable leaching process variables and the corresponding independent variables for ilmenite ore in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants. The experimental data was fitted to the linear, 2FI, quadratic and cubic models to generate regression models. The adequacy of each type of model under review was evaluated using analysis of variance (ANOVA).

In Tables 4.37, 4.38 and 4.39, standard deviation, mean square error and F-values presented for quadratic model seem comparatively low. This suggests that the quadratic model better fitted the experimental data. Also, the predicted R^2 values of 0.7775 and 0.9284 for the leaching of ilmenite in HCl-KCl and HCl-NaNO₃ for the quadratic model are closest to unity when compared with the values presented for cubic, 2FI and linear models. This corroborates the submission that the quadratic model best correlates the actual and predicted data for the leaching process. The predicted R^2 values consider all effects and adjusted R^2 values consider only square effects and interaction effects between two input variables (Jie *et al.*, 2014). Predicted R^2 values of 0.7775, 0.9442 and 0.9284 are in reasonable agreement with the adjusted R^2 values of 0.9763, 0.9934 and 0.9920 (the difference is <0.2). The coefficient of determination, R^2 , was recorded to be 0.9916, 0.9977 and 0.9971 indicating that only 0.84%, 0.23% and 0.29% of the total variations could not be explained by the models.

As shown in Tables 4.37 to 4.39, the quadratic model has the lowest prediction error sum of squares (PRESS) values (753.36 and 286.88) for the leaching of ilmenite in HCl-KCl and HCl-NaNO₃ lixiviants when compared with the linear (777.41 and 372.38), 2FI (2116.48 and 1298.83) and cubic (2298.76 and 5096.17) models. The smaller the PRESS value, the better the model's predictability. It is observed that the PRESS value for quadratic model (265.90) is higher than the value recorded for cubic model (74.31) for ilmenite in HCl-KClO₃ lixiviant. However, quadratic model was also selected because it is well known that most RSM designs are too small to estimate cubic models therefore some of the cubic terms were aliased. Based on these findings, quadratic model was chosen and further computations on experimental data were done using the quadratic model.

Table 4.37: Model summary for ilmenite in HCl-KCl

Source	Std.	MSE	F-Value	Lack of Fit p-	\mathbb{R}^2	Adjusted	Predicted	PRESS
	Dev.			value		\mathbf{R}^2	\mathbf{R}^2	
Linear	4.47	24.69	5442.93	< 0.0001	0.8469	0.8174	0.7704	777.41
2FI	5.29	40.63	8956.33	< 0.0001	0.8680	0.7442	0.3750	2116.48
Quadratic	1.61	4.73	1043.30	< 0.0001	0.9916	0.9763	0.7775	753.36
Cubic	0.60	2.12	466.83	< 0.0001	0.9994	0.9967	0.3211	2298.76

Table 4.38: Model summary for ilmenite in HCl-KClO₃

Source	Std.	MSE	F-Value	Lack of Fit p-	\mathbf{R}^2	Adjusted	Predicted	PRESS
	Dev.			value		\mathbf{R}^2	\mathbf{R}^2	
Linear	2.65	8.61	34.16	0.0005	0.9618	0.9545	0.9421	275.94
2FI	3.00	13.00	51.55	0.0002	0.9697	0.9414	0.8039	934.90
Quadratic	1.01	1.64	6.52	0.0288	0.9977	0.9934	0.9442	265.90
Cubic	0.47	0.07	0.27	0.6286	0.9997	0.9986	0.9844	74.31

Table 4.39: Model summary for ilmenite in HCl-NaNO₃

Source	Std.	MSE	F-Value	Lack of Fit p-	R^2	Adjusted	Predicted	PRESS
	Dev.			value		\mathbf{R}^2	\mathbf{R}^2	
Linear	3.06	11.57	1374.48	< 0.0001	0.9393	0.9277	0.9070	372.38
2FI	3.77	20.71	2460.41	< 0.0001	0.9431	0.8898	0.6757	1298.83
Quadratic	1.02	1.90	225.49	< 0.0001	0.9971	0.9920	0.9284	286.88
Cubic	0.89	4.70	557.84	< 0.0001	0.9988	0.9939	-0.2726	5096.17

Table 4.40 tabulates ANOVA for ilmenite leaching using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃. The models' F-values 64.98, 235.30 and 192.16 imply that the models are significant. Model F-value is calculated as a ratio of mean square regression and mean square residual (Khataee *et al.*, 2010). Values of P-value less than 0.0500 indicate model terms are significant. In general, it can be considered that higher Fisher's F-test values and lower p-values indicate the relative significance of each term. Based on this consideration, C, AB, AC, AD, BC, BE, CD, CE, DE, B², C², D²; AC, AD, BC, BD, BE, CD, B², C², D² and AB, AC, AD, AE, BC, BD, CD, CE, DE, B², C² are insignificant model terms for ilmenite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media respectively.

Table 4.40ANOVA for response surface quadratic model for ilmenite leaching

		F-value			P-value	
Source	Ilm-HCl- KCl	Ilm-HCl- KClO ₃	Ilm-HCl- NaNO ₃	Ilm-HCl- KCl	Ilm-HCl- KClO ₃	Ilm-HCl- NaNO ₃
Model	64.98	235.30	192.16	< 0.0001	< 0.0001	< 0.0001
A-	902.14	3803.04	3087.35	< 0.0001	< 0.0001	< 0.0001
Temperature						
B-L/S	92.71	86.56	194.65	< 0.0001	< 0.0001	< 0.0001
C-Stirring	4.83	13.30	7.60	0.0504	0.0038	0.0186
Speed						

D-Acid Conc.	27.16	138.40	83.13	0.0003	< 0.0001	< 0.0001
E-Time	83.00	495.59	247.55	< 0.0001	< 0.0001	< 0.0001
AB	2.10	10.68	1.37	0.1751	0.0075	0.2668
AC	1.09	0.23	0.20	0.3197	0.6424	0.6623
AD	0.42	2.14	0.28	0.5309	0.1717	0.6052
AE	7.68	6.51	3.90	0.0182	0.0269	0.0740
BC	3.95	1.41	0.42	0.0723	0.2596	0.5321
BD	5.18	0.08	1.17	0.0438	0.7821	0.3026
BE	2.85	0.99	5.04	0.1193	0.3413	0.0464
CD	3.78	0.10	1.38	0.0779	0.7562	0.2649
CE	0.01	7.79	0.29	0.9370	0.0176	0.5986
DE	0.65	7.56	0.53	0.4375	0.0189	0.4816
A^2	150.94	117.11	174.60	< 0.0001	< 0.0001	< 0.0001
B^2	0.05	0.34	2.18	0.8243	0.5698	0.1676
C^2	0.14	4.50	1.74	0.7149	0.0574	0.2141
D^2	0.13	0.61	6.12	0.7210	0.4512	0.0309
E^2	15.77	15.57	20.55	0.0022	0.0023	0.0009
Adeq Precision						
Ilmenite-HCl-K	Cl -	40.208				
Ilmenite-HCl-K	ClO ₃ -	62.793				
Ilmenite-NaNO ₃	-	61.329				

Adequacy Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Ratios 40.208, 62.793 and 61.329 recorded for HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media respectively indicate an adequate signal thus the models generated can be used to navigate the design space.

From the ANOVA results, variables or interaction of variables whose p-value (probability value) are greater than 0.05 (i.e. 5% level of significance) were eliminated from the model equation generated. The final equations for ilmenite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media in coded values can be expressed as:

$$\begin{split} Y_{\text{HCl-KCl}} &= 78.93 + 9.85\text{A} + 3.16\text{B} + 1.71\text{D} + 2.99\text{E} + 1.11\text{AE} + 0.92\text{BD} - 3.65\text{A}^2 \\ &- 1.18\text{E}^2 \end{split} \\ (4.36) \\ Y_{\text{HCl-KClO3}} &= 75.51 + 12.65\text{A} + 1.91\text{B} + 0.75\text{C} + 2.41\text{D} + 4.57\text{E} + 0.82\text{AB} - 0.64\text{AE} - 2.01\text{A}^2 \\ &- 0.73\text{E}^2 \end{split} \\ Y_{\text{HCl-NaNO3}} &= 73.75 + 11.56\text{A} + 2.90\text{B} + 0.57\text{C} + 1.90\text{D} + 3.27\text{E} + 0.57\text{BE} - 2.49\text{A}^2 \\ &- 0.85\text{E}^2 \end{split}$$

In Equations (4.36), (4.37) and (4.38) all the linear factors (solution temperature (A), liquidto-solid ratio (B), steering speed (C), acid concentration (D) and contact time (E)) were significant except for steering speed (C) in Equation (4.36) (p-values < 0.05). The effect of the linear interactions AB, AC, AD, BC, BE, CD, CE, DE; AC, AD, BC, BD, BE, CD; AB, AC, AD, AE, BC, BD, CD, CE, DE in Equations (4.36), (4.37) and (4.38) respectively are insignificant (p-values > 0.05) therefore are not present in the equation. In the same vein, the quadratic effects of liquid-to-solid ratio, steering speed and acid concentration (B², C² and D²) did not appear in Equations (4.36) and (4.37) respectively while only B² and C² did not present in equation (4.38). The positive sign in front of the terms indicates synergetic effect while the negative sign implies antagonistic effect of the factor on the response. Equations 4.36, 4.37 and 4.38 show that the linear effect of all the factors have synergetic effect on the dependent variable.

The normal probability versus residual plots (Figures 4.218, 4.220 and 4.222) show whether the residuals follow a normal distribution. When the plotted points follow a straight line it implies that there is a good relationship between the experimental and the predicted values of response. In some cases moderate scatter are expected. Tables E7, E8 and E9 in appendix E show the predicted and experimental data for the leaching of ilmenite in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants. The results obtained present that the selected quadratic model was adequate in predicting the response variables for the experimental data.

Dredicted

Predicted



Figure.4.218: Normal plot of residuals for leaching of ilmenite in HCl-KCl solution





Figure.4.219: Plot of predicted versus actual experimental values for leaching of ilmenite in HCl-KCl solution







Th Figure.4.222: Normal plot of residuals for leaching of ilmenite in HCl-NaNO₃ solution **pr**

between the actual and predicted values.

Figure.4.223: Plot of predicted versus actual experimental values for leaching of ilmenite in HCl-NaNO₃ solution

4.4.6: Three dimensional surface plots for ilmenite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants

Figures 4.224, 4.225 and 4.226 illustrate the effects of the interaction of time and acid concentration on leaching process response. From the 3D plots, it is seen that there is a positive effect on the dependent variable, yield (%Fe dissolution), as time and acid concentration increases for HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants. A steady increase in the response was observed as time increased for HCl-KClO₃ and HCl-NaNO₃ lixiviants, above 105 minutes for HCl-KCl lixiviant displayed a mild observable effect on the response. A steady increase on yield was displayed as acid concentrations were reviewed upward for HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants at all interaction points within the design space.

Figures 4.227, 4.228 and 4.229 displays the 3D plots of the interactive effects of contact time and steering speed for ilmenite leaching process using HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions as lixiviants. Figures 4.228 and 4.229 show initial synergetic effect of stirring speed on the response for HCl-KClO₃ and HCl-NaNO₃ lixiviants. Above 300rpm, there was no observable effect on the yield regardless of time increase. In Figure 4.227, there was gradual increment on the response as stirring speed was increased for HCl-KCl lixiviant over the range of values under investigation. Above 105 minutes the interactive effects of steering speed and contact time was insignificant on the response for leaching of ilmenite in HCl-KCl.



Figure.4.224: 3D Plot of the effect of time and acid conc for ilmenite leaching with HCl-KCl solution



Figure.4.226: 3D Plot of the effect of time and acid conc for ilmenite leaching with HCl-NaNO₃ solution



Figure.4.225: 3D Plot of the effect of time and acid conc for ilmenite leaching with HCl-KClO₃ solution



Figure.4.227: 3D Plot of the effect of time and steering speed for ilmenite leaching with HCl-KCl solution





3-D Figure.4.228: 3D Plot of the effect of time and steering speed for ilmenite leaching with HCl- KClO₃ solution

Figure.4.229: 3D Plot of the effect of time and steering speed for ilmenite leaching with HCl-NaNO₃ solution

the study. This could be as a result of unsaturation of the lixiviants. Figures 4.233, 4.234

and 4.235 depict the interaction between contact time and solution temperature. It is seen from the plots that upward review of time and solution temperature resulted to increase in yield (%Fe dissolved). Approaching 340K for Figure 4.233, a milder effect on the response was observed.



Figure.4.230: 3D Plot of the effect of time and L/S ratio for ilmenite leaching with HCl-KCl solution



Figure.4.231: 3D Plot of the effect of time and L/S ratio for ilmenite leaching with HCl-KClO₃ solution



Figure.4.232: 3D Plot of the effect of time and L/S ratio for ilmenite leaching with HCl-NaNO₃ solution



Figure.4.233: 3D Plot of the effect of time and contact temperature for ilmenite leaching with HCl-KCl solution





Figure.4.234: 3D Plot of the effect of time and contact temperature for ilmenite leaching with HCl- KClO₃ solution

Figure.4.235: 3D Plot of the effect of time and contact temperature for ilmenite leaching with HCl-NaNO₃ solution

4.5 RSM numerical optimization for the leaching of chalcopyrite, sphalerite and ilmenite ores in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants

A cardinal objective of designing an experiment is to optimize its process variables. The essense of optimization of a process culminates from the immense need to finding the best (optimum) factor levels where the response is maximized or minimized. The response surface methodology approach was employed to identify the optimum factor level combinations that give the maximum yield for chalcopyrite, sphalerite and ilmenite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants.

A systemic combination of the controllable process variables in Equation (3.4) aided by Design Expert Software was used to generate optimal response solutions presented in Tables F1 to F9. Of interest is deriving a reasonable %yield of copper and zinc from sulfide minerals (Nigerian chalcopyrite and sphalerite, respectively) and iron from ilmenite at a reduced time interval under low solution temperature and acid concentration. A balance of trade-off based on economic consideration was investigated in selecting the best solution. The selection of the optimum solution was to a great extent hinged on residence time and solution temperature. These variables are major contributory factors to the economic cost implication of the leaching process.

Experiments were run at the optimal conditions of the process variables. This is done to ascertain the closeness of the experimental and predicted values at optimal conditions. Design Expert trial version 11 predicted optimal percentage of yield of copper, zinc and iron from

chalcopyrite, sphalerite and ilmenite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ lixiviants as 95.18%, 95.78%, 94.76%; 93.18%, 96.05%, 87.51% and 96.26%, 93.13%, 90.76% respectively (Tables F1 to F9 in appendix F). These values were obtained at 343.19K solution temperature, 19.26 l/g liquid-to-solid ratio, 282.62rpm steering speed, 2.36M acid concentration and contact time of 102.56 minutes; 341.53K solution temperature, 24.13L/g liquid-to-solid ratio, 310.14rpm steering speed, 3.57M acid concentration and contact time of 99.54 minutes; 341.08K solution temperature, 24.90 l/g liquid-to-solid ratio, 211.48rpm steering speed, 3.94M acid concentration and contact time of 105.8 minutes; 338.59K solution temperature, 24.07 l/g liquid-to-solid ratio, 204.30rpm steering speed, 3.94M acid concentration and contact time of 84.88 minutes; 346.53K solution temperature, 23.87 l/g liquid-to-solid ratio, 200.37rpm steering speed, 3.89M acid concentration and contact time of 107.92 minutes; 346.03K solution temperature, 22.86L/g liquid-to-solid ratio, 387.54rpm steering speed, 3.20M acid concentration and contact time of 87.54 minutes; 347.99K solution temperature, 24.40 l/g liquid-to-solid ratio, 399.70rpm steering speed, 3.98M acid concentration and contact time of 119.12 minutes; 347.82K solution temperature, 24.95 l/g liquid-to-solid ratio, 379.91rpm steering speed, 3.98M acid concentration and contact time of 118.62 minutes; 347.86K solution temperature, 24.68 l/g liquid-to-solid ratio, 327.98rpm steering speed, 4.00M acid concentration and contact time of 117.23 minutes respectively. 93.43%, 94.01% and 92.77%; 94.82%, 94.12% and 88.73%; 95.10%, 91.28% and 89.21% obtained experimentally at the same condition of the process variables are in close agreement with the predicted values by the software.

4.6 Adaptive Neuro-Fuzzy Inference System (ANFIS)

ANFIS was also used to predict the behaviour of chalcopyrite, sphalerite, ilmenite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions adopting the method presented in Figure 3.1. The prediction results of the artificial intelligence system were presented in Tables E1 to E9 in appendix E. Plates 4.10 to 4.18 present sample pictorials of the fuzzy logic controller with ruleviewer. The ruleviewer block shows the fuzzy inference process during the simulation. Fuzzy inference is the process of formulating the mapping from a given input to an output using fuzzy logic. Plate 4.10 displays the five inputs of the chalcopyrite in HCl-KCl binary solution leaching matrix (Table E1 in Appendix E): input 1(solution temperature), input2(liquid-to-solid ratio), input 3 (stirring speed), input 4 (acid concentration), input 5 (contact time) and output (% Cu dissolved). For run 1 of the matrix, solution temperature = 333K, liquid-to-solid ratio = 20 l/g, stirring speed = 300rpm, acid concentration = 3M and contact time = 90 mins. At this experimental condition, a predicted response value of 88.4%

was recorded. Plates 4.11 - 4.18 follow the same trend. Their corresponding matrices are presented in Tables E2 – E9 in Appendix E.



Plate 4.10: Fuzzy logic controller with ruleviewer for chalcopyrite in HCl-KCl

Plate 4.11: Fuzzy logic controller with ruleviewer for chalcopyrite in HCl-KClO₃



Plate 4.12: Fuzzy logic controller with ruleviewer for chalcopyrite in HCl-NaNO₃

input1 = 333	input2 = 20	input3 = 300	input4 = 3	input5 = 90	output = 83.4
1					
ž 🔤					
5					
7					
8					
10					
12					
14					
16					
18					
19					
21					
23					
25					
27					
29	A				

Plate 4.13: Fuzzy logic controller with ruleviewer for sphalerite in HCl-KCl

input = 333 1 1 3 1 3 3 4 5 4 5 4 5 4 5 4 5 4 5 4 5 4 5 4 5				input5 = 90	output = 79.1
Input: [333;20;300;	3;90]	Plot points:	101	Nove: left rigt	nt down up
Opened system Until	tled, 243 rules			Help	Close

Plate 4.16: Fuzzy logic controller with ruleviewer for ilmenite in HCl-KCl

input1 = 333 1 2 3 3 4 4 4 5 6 4 4 4 5 6 4 4 4 5 6 4 4 4 5 6 4 4 4 5 6 4 4 4 5 6 4 4 4 5 6 4 4 4 5 6 4 4 4 5 6 4 4 4 5 6 4 4 4 5 6 4 4 4 5 7 7 8 7 8 7 8 7 8 7 8 7 8 7 8 7 8 7 8					output = 75.5
Input: [333;20;30	0;3;90]	Plot points:	101	Move: left rig	ht down up
Opened system U	ntitled, 243 rules			Help	Close

Plate 4.17: Fuzzy logic controller with ruleviewer for ilmenite in HCl- KClO₃

input = 333					output = 73.6
Input: [333;20;30	0;3;90]	Plot points:	101	Move: left rig	ht down up
Opened system Un	ntitled, 243 rules			Help	Close

Plate 4.18: Fuzzy logic controller with ruleviewer for ilmenite in HCl- NaNO₃

4.7 Comparism of RSM and ANFIS Predictions

Figures 4.236 to 4.244 show the correlation of ANFIS and RSM predictions with the experimental data. The coefficient of determination of values presented for ANFIS is closer to unity compared with RSM. Therefore, it can be said that for this study that ANFIS better predicted the leaching system of chalcopyrite, sphalerite, ilmenite in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions.



Figure. 4.236: Parity plot of ANFIS and RSM predicted vs experimental values for chalcopyrite in HCI-KCI



Figure 4.238: Parity plot of ANFIS and RSM





Figure. 4.237: Parity plot of ANFIS and RSM predicted vs experimental values for chalcopyrite in HCI-KCIO₃



Figure 4.239: Parity plot of ANFIS and RSM





Figure 4.242: Parity plot of ANFIS and RSM predicted vs experimental values for Ilmenite in HCI-KCI



Figure 4.243: Parity plot of ANFIS and RSM predicted vs experimental values for Ilmenite in HCl-KClO $_3$



Figure 4.244: Parity plot of ANFIS and RSM predicted vs experimental values for Ilmenite

To further confirm the better performance of ANFIS over RMS in this research, the experimental, RSM and ANFIS data were subjected to error analysis. The error functions considered are listed in Table 4.41

Error function	Equation and number	Reference
Root mean square error,	RMSE = $\sqrt{\frac{1}{n} \sum_{i=1}^{n} (y_{i,exp} - y_{i,pred})^2}$ (4.39)	Pakravan <i>et al.,</i> 2014
Chi square (χ^2)	$\chi^{2} = \sum_{i=1}^{n} \frac{(y_{i,p} - y_{i,e})^{2}}{y_{i,p}} $ (4.40)	Maran <i>et</i> <i>al.</i> , 2013
Model predictive error (%)	$MPE(\%) = \frac{100}{n} \sum_{i=1}^{n} \left \frac{y_{i,exp} - y_{i,pred}}{y_{i,pred}} \right (4.41)$	Maran <i>et</i> <i>al.</i> , 2013

Table 4.41:	Error	functions	and	its	eq	uatio	ns

On Tables 4.42 – 4.44, the values calculated for RMSE (equation 4.39), Chi square (χ^2) (equation 4.40) and MPE (%)(equation 4.41) were compared to examine the prediction capabilities of RSM and ANFIS models. It is observed that ANFIS values were lower for RMSE, Chi square (χ^2) and MPE (%).This indicates the superiority of ANFIS over RSM in predicting the percentage of copper, zinc and iron leached from chalcopyrite, sphalerite and ilmente in HCi-KCl, HCl-KClO₃ and HCl-NaNO₃ media.

	Table 4.42: Com	parison betweer	RSM and ANFIS	error prediction f	for chalcopyrite leaching
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1		1 1.	υ
Lixiviant	Parameters	RSM	ANFIS
HCI-KCI	RMSE	1.8925	0.1773
	Chi square	1.5036	0.0114
	MPE (%)	0.1098	0.0004
HCl-KClO ₃	RMSE	0.6355	0.5403
	Chi square	0.1461	0.1025
	MPE (%)	0.0026	0.0005
HCl-NaNO ₃	RMSE	0.8946	0.2059
	Chi square	0.3315	0.0172
	MPE (%)	0.0183	0.0005

Lixiviant	Parameters	RSM	ANFIS
HCI-KCI	RMSE	1.4362	0.2078
	Chi square	0.8787	0.0166
	MPE (%)	0.0023	0.0005
HCl-KClO ₃	RMSE	1.1872	0.2582
	Chi square	0.5583	0.0250
	MPE (%)	0.0105	0.0005
HCl-NaNO ₃	RMSE	0.9368	0.2540
	Chi square	0.3847	0.0264
	MPE (%)	0.0016	0.0005

Table 4.43: Comparison between RSM and ANFIS error prediction for sphalerite leaching

Table 4.44: Comparison between RSM and ANFIS error prediction for ilmenite leaching

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Lixiviant	Parameters	RSM	ANFIS
HCl-KCl	RMSE	0.9428	0.0266
	Chi square	0.3886	0.0003
	MPE (%)	0.0032	0.0005
HCl-KClO ₃	RMSE	0.5894	0.1985
	Chi square	0.1515	0.0167
	MPE (%)	0.0018	0.0005
HCl-NaNO ₃	RMSE	0.5981	0.0363
	Chi square	0.1542	0.0006
	MPE (%)	0.0066	0.0005

4.8 ANFIS-PSO Numerical Optimization for the Leaching of Chalcopyrite, Sphalerite and Ilmenite Ores in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ Lixiviants

Particle swarm optimization (PSO) technique was applied in optimizing the predictions of ANFIS using Matlab (Version 2010). At the end of PSO algorithm, optimum yields of 96.95%, 97.85% and 95.74% were obtained at chalcopyrite leaching in HCl-KCl, HCl-KClO₃

and HCl-NaNO₃ lixiviants at temperature of 345.16K, liquid-to-solid ratio of 22.58 l/g, steering speed of 303.22rpm, acid concentration of 1.26M and 105.48 minutes contact time; 337.7K solution temperature, 20 l/g liquid-to-solid ratio, steering speed of 200rpm, 1M acid concentration and 90 minutes contact time and 348.33K solution temperature, liquid-to-solid ratio of 26 l/g, 401rpm steering speed, 3.52M acid concentration and 121 minutes contact time. 95.10%, 95.92% and 94.78% obtained experimentally at the same condition of the process variables are in close agreement with the PSO predictions. 95.40%, 97.72% and 90.91%, were predicted by PSO at 346K solution temperature, 24 l/g liquid-to-solid ratio, 400rpm steering speed, 3.5M acid concentration and 120 minutes contact time; 347.59K solution temperature, 24.62 l/g liquid-to-solid ratio, 399.11rpm steering speed, 3.8M acid concentration and 120.6 minutes contact time; 342.39K solution temperature, 23.39 l/g liquid-to-solid ratio, 398.58rpm steering speed, 3.19M acid concentration and 118.58 minutes contact time for sphalerite leaching in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ media. Also, 93.53%, 96.98% and 88.24% obtained experimentally at the same condition of the process variables are in close agreement with the PSO predictions. 98.83%, 95.57% and 92.85% were predicted ilmenite leaching at 346.55K solution temperature, 24.59 l/g liquid-to-solid ratio, 400.32rpm steering speed, 3.77M acid concentration and 120.32 minutes contact time; 344.29K solution temperature, 24.29 l/g liquid-to-solid ratio, 399.94rpm steering speed, 3.64M acid concentration and 119.93 minutes contact time; 341.97K solution temperature, 23.97 l/g liquid-to-solid ratio, 399.45rpm steering speed, 3.48M acid concentration and 119.45 minutes contact time HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions. 96.95%, 96.68% and 90.90% obtained experimentally at the same condition of the process variables are in close agreement with the PSO predictions.

CHAPTER FIVE CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions have been successfully applied to leaching of chalcopyrite, sphalerite and ilmenite of Nigerian origin. Based on the foregoing, the following conclusions were drawn from the results and findings:

- Characterization of chalcopyrite from Ohankwu Ikwo mine, in Ikwo LGA, Ebonyi state, sphalerite from Ihietutu mine, Ivo LGA, Ebonyi state and ilmenite from Egon mine, Egon LGA, Nassarawa state confirmed that copper, zinc and iron respectively are part of the dominant metals in the ores.
- 2. The selected leachants were favourable in the leaching process.
- 3. Dissolution of chalcopyrite, sphalerite and ilmenite ores were dependent on acid concentration, oxide concentration, particle size, solution temperature, stirring speed, contact time and liquid-to-solid ratio.
- 4. Diffusion controlled Kröger and Zigler kinetic model best described the kinetics of the leaching system.
- 5. In the overall performance of the leachants, HCl- KClO₃ marginally outperformed HCl-KCl and HCl-NaNO₃.
- 6. ANFIS and RSM gave excellent predictions of the leaching process for the ores under investigation. However, ANFIS predicted better than RSM.

5.2 Recommendations

- 1. A study on the profitability of recycling the leachants should be considered.
- 2. Batch process was used in this study, further study which will accommodate continuous process is recommended.
- Some other formulations of leachants should be tried for dissolution of ores of Nigerian origin.

5.3 Contribution to knowledge

- Characterization of chalcopyrite from Ohankwu Ikwo mine, in Ikwo LGA, Ebonyi state, sphalerite from Ihietutu mine, Ivo LGA, Ebonyi state and ilmenite from Egon mine, Egon LGA, Nassarawa state.
- 2. Elaborate leaching kinetics of chalcopyrite, sphalerite and ilmenite in HCl-KCl, HCl-KClO₃ and HCl-NaNO₃ binary solutions were effectively elucidated.
- 3. The work presents statistical models establishing relationship between the investigated controllable variables and the response variable.
- 4. The research added to the existing literature reports and optimization data on the leaching of chalcopyrite, sphalerite and ilmenite using a recent predictive tool (ANFIS).
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APPENDIX A CHARACTERIZATION RESULTS



X-RAY DIFFRACTOGRAM

Plate A1: X-ray diffractogram for raw chalcopyrite sample



Plate A2: X-ray diffractogram for raw sphalerite sample



Plate A3: X-ray diffractogram for raw ilmenite sample

SEM



Plate A4: SEM micrograph for Chalcopyrite residue leached with HCI-KCI



Plate A5 : EDX spectrum of Chalcopyrite residue leached with HCI-KCI





Plate A8: SEM micrograph for Sphalerite residue leached with HCI-KCI



Plate A9 : EDX spectrum of Sphalerite residue leached with HCI-KCI



Diato A12: SEM micrograph for Ilmonito residuo

Diata A12, EDV spactrum of Ilmanita residua





Plate A14: SEM micrograph for Ilmenite residue leached with HCl-NaNO $_3$

Plate A15 : EDX spectrum of Ilmenite residue leached with HCl-NaNO $_3$

APPENDIX B DISSOLUTION STUDIES

Table B1: Effect of acid concentration on the dissolution of Chalcopyrite, Sphalerite and Ilmenite

	% Yield			
Acid Conc (M)	Chalcopyrite	Sphalerite	Ilmenite	
1	77.46	80.61	67.22	
2	90.11	82.6	73.08	
3	93.82	86.8	77.23	
4	96.75	88.73	80.11	

Table B2: Effect of oxidants concentrations on the dissolution of Chalcopyrite

Oxidant		%	Cu dissolved	
Conc (M)	HCl	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃
0	77.46			
0.15		86.59	74.33	75.17
0.3		89.17	75.23	77.53
0.45		91.82	84.01	82.49
0.6		93.75	92.16	85.67

Table B3: Effect of oxidants concentrations on the dissolution of Sphalerite

Oxidant		%	Zn dissolved	
Conc (M)	HCl	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃
0	80.61			
0.15		70.57	76.21	66.29
0.3		81.74	83.05	77.41
0.45		85.08	85.66	82.35
0.6		87.95	91.22	86.13

Oxidant		%	Fe dissolved	
Conc (M)	HCl	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃
0	67.22			
0.15		64.05	61.83	59.19
0.3		71.32	71.47	63.18
0.45		77.26	73.57	71.25
0.6		81.83	81.09	76.62

Table B4: Effect of oxidants concentrations on the dissolution of Ilmenite

Table B5: Effect of Particle size on the dissolution of Chalcopyrite

Particle size	<u>%Cu dissolved</u>		
(µm)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃
75	93.75	92.16	85.67
150	89.33	82.25	79.99
300	86.53	78.13	76.85
600	75.34	70.26	69.26

Table B6: Effect of Particle size on the dissolution of Sphalerite

Particle size		%Zn dissolved		
(µm)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃	
75	87.95	91.22	86.13	
150	78.1	79.42	77.03	
300	69.24	72.59	70.01	
600	63.61	70.62	68.05	

Table B7: Effect of Particle size on the dissolution of Ilmenite

Particle size	%Fe dissolved			
(µm)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃	
75	81.83	81.09	76.62	
150	79.26	77.47	70.95	
300	75.93	71.93	70.29	
600	70.54	67.82	62.79	

Table B8: Effect of Temperature on the dissolution of Chalcopyrite

Temperature	%Cu dissolved			
(°C)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃	
30	32.88	58.4	34.54	
45	73.56	80.63	65.37	
60	92.75	92.16	85.67	
75	96.47	91.81	88.21	

Table B9: Effect of Temperature on the dissolution of Sphalerite

Temperature		%Zn dissolved		
(°C)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃	
30	46.05	44.61	50.02	

45	72.84	71.29	73.39
60	87.95	91.22	86.13
75	90.55	95.52	89.67

Table B10: Effect of Temperature on the dissolution of Ilmenite

Temperature	%Fe dissolved			
(°C)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃	
30	49.03	47.81	45.83	
45	67.13	68.53	64.92	
60	81.83	81.09	76.62	
75	88.78	91.35	84.92	

Table B11: Effect of Steering speed on the dissolution of Chalcopyrite

Steering speed	%Cu dissolved		
(rpm)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃
100	86.91	89.92	79.88
200	92.95	90.12	82.17
300	96.47	92.9	88.21
400	96.07	93.26	90.87
500	98.57	93.2	91.76

Table B12: Effect of Steering speed on the dissolution of Sphalerite

Steering speed		%Zn dissolved				
(rpm)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃			
100	80.56	81.74	83.27			
200	86.36	88.97	84.39			
300	90.55	95.52	89.67			
400	91.04	92.36	90.12			
500	88.66	91.56	90.05			

Table B13: Effect of Steering speed on the dissolution of Ilmenite

Steering speed		%Fe dissolved				
(rpm)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃			
100	85.17	88.44	82.25			
200	87.21	90.15	83.11			
300	88.78	91.35	84.92			
400	89.81	90.24	85.91			
500	90.01	90.87	85.74			

%Cu dissolved				
HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃		
79.08	84.91	78.39		
92.85	88.14	82.98		
96.47	92.9	88.21		
98.46	91.77	89.91		
97.76	93.99	91.14		
	HCl-KCl 79.08 92.85 96.47 98.46 97.76	%Cu dissolved HCl-KCl HCl-KClO3 79.08 84.91 92.85 88.14 96.47 92.9 98.46 91.77 97.76 93.99		

Table B14: Effect of Liquid-to-solid ratio on the dissolution of Chalcopyrite

Table B15: Effect of Liquid-to-solid ratio on the dissolution of Sphalerite

Liquid-to-solid	%Zn dissolved				
ratio (L/g)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃		
10	79.47	84.72	73.42		
15	85.74	90.13	80.35		
20	90.55	95.52	89.67		
25	93.17	95.66	91.91		
30	94.85	96.72	93.98		

Table B16: Effect of Liquid-to-solid ratio on the dissolution of Ilmenite

Liquid-to-solid	%Fe dissolved				
ratio (L/g)	HCl-KCl	HCl-KClO ₃	HCl-NaNO ₃		
10	81.17	88.02	79.86		
15	84.92	88.57	82.44		
20	88.78	91.35	84.92		
25	92.89	93.17	89.27		
30	97.03	96.08	92.17		

APPENDIX C DISSOLUTION KINETICS DATA AND ILL-FITTED KINETICS PLOTS

101				
Time		%Cı	u dissolved	
(minutes)	1M	2M	3M	4M
0	0	0	0	0
30	46.06	47.21	50.98	53.59
60	64.58	70.92	74.97	77.25
90	75.45	85.11	89.16	90.98
120	77.86	89.65	92.05	95.77
150	77.46	90.11	93.82	96.75
180	78.66	90.73	94.25	96.87

Table C1: Effect of Time at various acid concentrations on the dissolution of Chalcopyrite in HCl

Table C2: Effect of Time at various oxidant concentrations on the dissolution of Chalcopyrite in HCl-KCl

Time		%Cı	u dissolved	
(minutes)	0.15M	0.30M	0.45M	0.60M
0	0	0	0	0
30	38.94	45.93	50.98	51.22
60	62.19	68.22	71.97	73.99
90	77.43	80.20	84.16	88.24
120	82.95	86.52	90.05	92.08
150	86.59	89.17	91.82	93.75
180	88.29	89.53	91.25	94.91

 Table C3: Effect of Time at various particle sizes on the dissolution of Chalcopyrite in HCl-KCl

Time		%Cu dissolved					
(minutes)	75µm	150µm	300µm	600µm			
0	0	0	0	0			
30	51.22	48.25	43.77	32.36			
60	73.99	65.28	61.20	57.17			
90	88.24	77.19	72.65	66.64			
120	92.08	80.37	76.19	71.53			
150	93.75	89.33	86.53	75.34			
180	94.91	90.82	87.62	80.14			

Table C4: Effect of Time at various solution temperature on the dissolution of Chalcopyrite in HCl-KCl

Time	%Cu dissolved

(minutes)		45°C	60°C	75°C	90°C
0	0	0	0	0	0
30	8.22	22.54	51.22	63.05	56.94
60	13.14	50.02	73.99	86.12	80.87
90	20.94	62.09	88.24	92.51	91.73
120	26.75	69.81	92.08	95.91	94.90
150	32.88	73.56	92.75	96.47	95.77
180	36.24	78.25	94.91	97.53	96.67

Table C5: Effect of Time at various steering speed on the dissolution of Chalcopyrite in HCl-KCl

Time			%Cu d	dissolved	
(minutes)	100rpm	200rpm	300rpm	400rpm	500rpm
0	0	0	0	0	0
30	53.11	58.85	63.05	61.89	60.95
60	73.02	80.51	86.12	82.11	85.73
90	84.93	89.97	92.51	94.01	94.38
120	86.32	92.28	95.91	95.66	97.24
150	86.91	92.95	96.47	96.07	98.57
180	87.23	93.39	97.53	97.36	98.88

Table C6: Effect of Time at various liquid-to-solid ratio on the dissolution of Chalcopyrite in HCl-KCl

Time			%Cu c	dissolved	
(minutes)	10L/g	15L/g	20L/g	25L/g	30L/g
0	0	0	0	0	0
30	24.59	42.34	63.05	74.59	81.87
60	46.02	68.27	86.12	90.56	93.77
90	66.90	86.53	92.51	96.18	94.61
120	77.36	91.73	95.91	96.22	95.96
150	79.08	92.85	96.47	98.46	97.76
180	79.32	93.58	97.53	98.34	98.56

Time		%Ci	u dissolved	
(minutes)	0.15M	0.30M	0.45M	0.60M
0	0	0	0	0
30	48.02	50.67	54.34	72.46
60	55.15	55.23	68.39	84.44
90	60.89	68.21	72.84	91.34
120	63.76	71.95	80.42	91.49
150	74.33	75.23	84.01	92.16
180	76.2	80.11	85.11	92.90

Table C7: Effect of Time at various oxidant concentrations on the dissolution of Chalcopyrite in $HCl-KClO_3$

Table C8: Effect of Time at various particle sizes on the dissolution of Chalcopyrite in HCl-KClO₃

Time		%Cu dissolved					
(minutes)	75µm	150µm	300µm	600µm			
0	0	0	0	0			
30	72.46	70.28	63.13	52.69			
60	84.44	75.32	69.75	60.23			
90	91.34	80.08	75.57	64.96			
120	91.49	81.58	76.29	69.02			
150	92.16	82.25	78.13	70.26			
180	92.90	82.89	78.97	72.81			

Table C9: Effect of Time at various solution temperature on the dissolution of Chalcopyrite in HCl-KClO $_3$

-	miller meneg					
	Time	_		%Cu c	dissolved	
	(minutes)	30°C	45°C	60°C	75°C	90°C
	0	0	0	0	0	0
	30	32.60	58.49	72.46	71.34	70.31
	60	46.17	71.26	84.44	84.12	80.88
	90	54.66	78.96	91.34	90.62	90.37
	120	57.22	79.11	91.49	91.96	89.11
	150	58.4	80.63	92.16	91.81	90.78
	180	58.07	81.57	92.90	94.43	91.95

Table C10: Effect of Time at various steering speed on the dissolution of Chalcopyrite in $HCl-KClO_3$

Time	%Cu dissolved

(minutes)		200rpm	300rpm	400rpm	500rpm
0	0	0	0	0	0
30	60.92	65.40	72.46	73.09	74.30
60	72.54	73.70	84.44	84.75	87.65
90	80.08	85.92	91.34	91.34	90.91
120	88.54	90.06	91.49	92.84	92.10
150	89.92	90.12	92.16	93.26	93.20
180	89.54	91.21	92.90	93.99	93.72

Table C11: Effect of Time at various liquid-to-solid ratio on the dissolution of Chalcopyrite in HCl-KCl

Time			%Cu o	dissolved	
(minutes)	10L/g	15L/g	20L/g	25L/g	30L/g
0	0	0	0	0	0
30	50.20	66.13	72.46	78.35	81.64
60	69.81	75.93	84.44	80.54	79.05
90	76.22	80.95	91.34	82.32	89.05
120	85.02	87.39	91.49	89.37	90.24
150	84.91	88.14	92.16	91.77	93.99
180	85.16	88.69	92.90	93.11	93.85

Table C12: Effect of Time at various oxidant concentrations on the dissolution of Chalcopyrite in HCl-NaNO₃

Time		%Cı	u dissolved	
(minutes)	0.15M	0.30M	0.45M	0.60M
0	0	0	0	0
30	36.75	43.26	47.14	58.95
60	55.84	60.63	66.38	75.12
90	68.76	71.94	78.23	80.07
120	73.08	75.24	79.04	82.04
150	75.17	77.53	82.49	85.67
180	76.49	79.36	83.44	87.25

Table C13: Effect of Time at various particle sizes on the dissolution of Chalcopyrite in HCl-NaNO₃

Time		%Cu dissolved					
(minutes)	75µm	150µm	300µm	600µm			
0	0	0	0	0			
30	58.95	50.39	48.75	42.14			
60	75.12	63.11	60.14	54.37			

90	80.07	75.53	71.98	61.06
120	82.04	80.93	75.61	66.23
150	85.67	79.99	76.85	69.26
180	87.25	80.78	77.06	70.81

Table C14: Effect of Time at various solution temperature on the dissolution of Chalcopyrite in HCl-NaNO₃

Time			%Cu	dissolved	
(minutes)	30°C	45°C	60°C	75°C	90°C
0	0	0	0	0	0
30	10.11	42.09	58.95	63.53	59.64
60	22.20	53.84	75.12	75.18	68.94
90	27.91	60.53	80.07	83.25	77.61
120	32.03	63.18	82.04	86.54	80.57
150	34.54	65.37	85.67	88.21	80.99
180	37.89	67.30	87.25	89.85	83.46

Table C15: Effect of Time at various steering speed on the dissolution of Chalcopyrite in HCl-NaNO₃

Time		%Cu dissolved					
(minutes)	100rpm	200rpm	300rpm	400rpm	500rpm		
0	0	0	0	0	0		
30	57.39	59.44	63.53	68.51	67.29		
60	68.28	71.53	75.18	78.16	79.58		
90	76.53	78.09	83.25	87.05	88.39		
120	79.54	82.52	86.54	88.99	89.09		
150	79.88	82.17	88.21	90.87	91.76		
180	80.05	83.62	89.85	93.23	94.11		

Table C16: Effect of Time at various liquid-to-solid ratio on the dissolution of Chalcopyrite in HCl-NaNO $_3$

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Time			%Cu d	dissolved	
(minutes)	10L/g	15L/g	20L/g	25L/g	30L/g
0	0	0	0	0	0
30	51.23	55.37	63.53	66.48	68.73
60	63.98	67.85	75.18	76.08	78.01
90	72.48	75.86	83.25	86.28	87.92
120	76.13	80.83	86.54	87.15	89.37
150	78.39	82.98	88.21	89.91	91.14
180	79.59	83.97	89.85	90.16	92.67

Time		%Zt	n dissolved	
(minutes)	1 M	2M	3M	4M
0	0	0	0	0
30	48.29	50.73	51.30	52.63
60	65.65	67.75	71.51	76.28
90	72.17	75.82	79.24	83.35
120	78.24	81.50	83.48	85.50
150	80.61	82.60	86.80	88.73
180	81.75	83.54	87.95	90.01

Table C17: Effect of Time at various acid concentrations on the dissolution of Sphalerite in HCl

Table C18: Effect of Time at various oxidant concentrations on the dissolution of Sphalerite in HCl-KCl

Time		%Zı	n dissolved	
(minutes)	0.15M	0.30M	0.45M	0.60M
0	0	0	0	0
30	49.80	51.10	53.85	54.22
60	61.92	63.19	68.67	70.53
90	64.97	74.58	74.74	78.39
120	68.44	76.12	81.64	85.37
150	70.57	81.74	85.08	87.95
180	73.43	82.11	87.71	89.12

Table C19: Effect of Time at various particle sizes on the dissolution of Sphalerite in HCl-KCl

Time		%Zn dissolved					
(minutes)	75µm	150µm	300µm	600µm			
0	0	0	0	0			
30	54.22	46.35	41.31	35.09			
60	70.53	53.23	46.81	41.47			
90	78.39	58.17	53.52	47.45			
120	85.37	76.09	68.15	59.83			
150	87.95	78.10	69.24	63.61			
180	89.12	79.48	70.28	64.96			

IICI KCI						
Tin	ne			%Zn d	dissolved	
(minu	ites)	30°C	45°C	60°C	75°C	90°C
0		0	0	0	0	0
30)	6.67	38.67	54.22	64.99	63.81
60)	25.25	56.45	70.53	77.36	73.35
90)	34.92	65.43	78.39	82.22	75.84
12	0	43.16	72.31	85.37	87.14	86.18
15	0	46.05	72.84	87.95	90.55	90.05
18	0	47.94	73.05	89.12	92.28	91.36

Table C20: Effect of Time at various solution temperature on the dissolution of Sphalerite in HCl-KCl

Table C21: Effect of Time at various steering speed on the dissolution of Sphalerite in HCl-KCl

Time		%Zn dissolved					
(minutes)	100rpm	200rpm	300rpm	400rpm	500rpm		
0	0	0	0	0	0		
30	55.24	61.45	64.99	62.37	63.28		
60	67.11	74.16	77.36	78.12	75.73		
90	75.97	80.69	82.22	85.55	82.41		
120	79.14	83.18	87.14	88.27	87.51		
150	80.56	86.36	90.55	91.04	88.69		
180	85.26	89.05	92.28	93.93	90.38		

Table C22: Effect of Time at various liquid-to-solid ratio on the dissolution of Sphalerite in HCl-KCl

mer mer					
Time			%Zn d	dissolved	
(minutes)	10L/g	15L/g	20L/g	25L/g	30L/g
0	0	0	0	0	0
30	56.48	60.27	64.99	71.71	73.06
60	66.26	72.36	77.36	82.36	85.21
90	73.64	78.02	82.22	87.79	89.19
120	76.07	82.93	87.14	90.81	91.75
150	79.47	85.74	90.55	93.17	94.85
180	80.08	86.94	92.28	94.63	95.92

Table C21: Effect of Time at various oxidant concentrations on the dissolution of Sphalerite in $HCl-KClO_3$

(min	utes)	0.15M	0.30M	0.45M	0.60M
()	0	0	0	0
3	0	44.05	50.17	52.72	56.99
6	0	60.52	65.49	70.25	74.97
9	0	69.06	75.33	79.91	85.77
12	20	73.22	79.95	84.03	89.53
1:	50	76.21	83.05	85.66	91.22
18	30	76.94	83.99	86.29	93.85

Table C22: Effect of Time at various particle sizes on the dissolution of Sphalerite in HCl-KClO₃

Time		%Zı	n dissolved	
(minutes)	75µm	150µm	300µm	600µm
0	0	0	0	0
30	56.99	49.38	42.32	37.48
60	74.97	55.25	49.58	43.55
90	85.77	61.62	54.72	49.16
120	89.53	72.91	66.44	61.71
150	91.22	79.42	72.59	70.62
180	93.85	80.37	74.21	71.84

Table C23: Effect of Time at various solution temperature on the dissolution of Sphalerite in HCl-KClO₃

Time			%Zn d	dissolved	
(minutes)	30°C	45°C	60°C	75°C	90°C
0	0	0	0	0	0
30	25.12	45.82	56.99	57.73	51.72
60	36.73	61.73	74.97	76.93	70.17
90	39.22	67.13	85.77	89.12	84.71
120	43.51	70.65	89.53	94.13	91.58
150	44.61	71.29	91.22	95.52	91.98
180	45.21	72.17	93.85	96.94	92.39

Table C24: Effect of Time at various steering speed on the dissolution of Sphalerite in HCl-KClO₃

Time		%Zn dissolved					
(minutes)	100rpm	200rpm	300rpm	400rpm	500rpm		
0	0	0	0	0	0		
30	53.01	56.45	57.73	61.22	64.09		
60	64.56	72.16	76.93	79.38	77.45		

90	72.18	79.27	89.12	83.16	80.29
120	77.21	84.13	94.13	87.73	88.24
150	81.74	88.97	95.52	92.36	91.56
180	83.45	90.69	96.94	94.05	92.11

Table C25: Effect of Time at various liquid-to-solid ratio on the dissolution of Sphalerite in $HCl-KClO_3$

Time (minutes)			%Zn d	dissolved	
	10L/g	15L/g	20L/g	25L/g	30L/g
0	0	0	0	0	0
30	51.35	54.21	57.73	59.76	65.61
60	68.32	73.96	76.93	77.92	80.15
90	79.64	85.84	89.12	91.49	92.18
120	83.71	89.34	94.13	94.11	95.21
150	84.72	90.13	95.52	95.66	96.72
180	84.95	91.23	96.94	95.97	96.93

Table C26: Effect of Time at various oxidant concentrations on the dissolution of Sphalerite in $HCl-NaNO_3$

Time		%Zn dissolved				
(minutes)	0.15M	0.30M	0.45M	0.60M		
0	0	0	0	0		
30	41.21	53.81	59.95	64.27		
60	53.50	61.09	70.51	75.06		
90	58.58	70.56	78.29	81.45		
120	64.61	76.39	81.54	85.39		
150	66.29	77.41	82.35	86.13		
180	68.75	78.53	85.62	88.69		

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Table C26: Effect of Time at various particle sizes on the dissolution of Sphalerite in HCl-NaNO₃

Time	%Zn dissolved				
(minutes)	75µm	150µm	300µm	600µm	
0	0	0	0	0	
30	64.27	55.67	50.11	47.91	
60	75.06	69.11	55.79	51.83	
90	81.45	73.25	64.31	59.87	
120	85.39	75.62	68.30	65.27	
150	86.13	77.03	70.01	68.05	

180	88.69	78.64	73.32	69.55

HCI-INaINO ₃						
Time	%Zn dissolved					
(minutes)	30°C	45°C	60°C	75°C	90°C	
0	0	0	0	0	0	
30	12.10	41.53	64.27	68.05	65.98	
60	27.73	51.11	75.06	78.98	76.51	
90	37.63	62.36	81.45	83.20	78.41	
120	47.22	68.47	85.39	85.14	81.74	
150	50.02	73.39	86.13	89.67	84.78	
180	51.39	74.26	88.69	90.59	85.89	

Table C27: Effect of Time at various solution temperature on the dissolution of Sphalerite in $HCl-NaNO_3$

Table C28: Effect of Time at various steering speed on the dissolution of Sphalerite in HCl-NaNO₃

Time			%Zn d	dissolved	
(minutes)	100rpm	200rpm	300rpm	400rpm	500rpm
0	0	0	0	0	0
30	59.73	63.64	68.05	72.26	76.76
60	70.81	71.48	78.98	81.38	83.95
90	77.77	80.94	83.20	83.15	85.64
120	80.55	81.36	85.14	86.28	88.42
150	83.27	84.39	89.67	90.12	90.05
180	85.26	88.05	90.59	92.77	93.71

Table C29: Effect of Time at various liquid-to-solid ratio on the dissolution of Sphalerite in $HCl-NaNO_3$

Time			%Cu o	dissolved	
(minutes)	10L/g	15L/g	20L/g	25L/g	30L/g
0	0	0	0	0	0
30	50.13	58.18	68.05	71.57	73.87
60	60.23	69.23	78.98	81.58	86.12
90	64.52	72.27	83.20	87.79	90.73
120	70.17	76.38	85.14	90.72	93.04
150	73.42	80.35	89.67	91.91	93.98
180	74.08	83.22	90.59	92.15	94.67

APPENDIX D ILL-FITTED PLOTS

Ill-fitted Plots for Chalcopyrite dissolution in HCl-KCl, HCl-KClO3 and HCl-NaNO3





Fig D1: DTLF Kinetic Plots for Chalcopyrite in HCl-KCl at different Particle sizes



Fig D3: DTLF Kinetic Plots for Chalcopyrite in HCl-KCl at different Oxidant Concentrations

Fig D2: DTLF Kinetic Plots for Chalcopyrite in HCl-KCl at different Acid Concentrations



Fig D4: DTLF Kinetic Plots for Chalcopyrite in HCl-KCl at different Solution Temperature







Fig D7: DTPL Kinetic Plots for Chalcopyrite in HCl-KCl at different Particle sizes



Fig D8: DTPL Kinetic Plots for Chalcopyrite in HCl-KCl at different Acid Concentrations



Fig D11: DTPL Kinetic Plots for Chalcopyrite in HCl-KCl at different Steering Speed



Fig D12: DTPL Kinetic Plots for Chalcopyrite in HCl-KCl at different pulp densities



Fig D13: SCR Kinetic Plots for Chalcopyrite in HCl-KCl at different Particle sizes



Fig D17: SCR Kinetic Plots for Chalcopyrite in HCl-KCl at different Steering Speed



Fig D14: SCR Kinetic Plots for Chalcopyrite in HCl-KCl at different Acid Concentrations



Fig D18: SCR Kinetic Plots for Chalcopyrite in HCl-KCl at different pulp densities


Fig D19: MKM Kinetic Plots for Chalcopyrite in HCl-KCl at different Particle sizes



Fig D21: MKM Kinetic Plots for Chalconvrite









Fig D20: MKM Kinetic Plots for Chalcopyrite in HCl-KCl at different Acid Concentrations



Fig D22: MKM Kinetic Plots for Chalconvrite









Fig D27: Jander Kinetic Plots for Chalcopyrite



Fig D29: Jander Kinetic Plots for Chalcopyrite in HCl-KCl at different Steering Speed





Fig D28: Jander Plots for Chalcopyrite in HCl-



Fig D30: Jander Kinetic Plots for Chalcopyrite in HCl-KCl at different pulp densities





Fig D35: Ginstling-Brounshtein Kinetic Plots for Chalcopyrite in HCl-KCl at diff. Steering Speed



Fig D36: Ginstling-Brounshtein Kinetic Plots for Chalcopyrite in HCl-KCl at diff. pulp densities

Time (minutes)





Dissolution of Chalcopyrite in HCl-KClO₃



Fig D41: DTPL Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Oxidant



Fig D43: DTPL Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Steering Speed





Fig D42: DTPL Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Solution Temperature



Fig D44: DTPL Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different pulp densities





Fig D47: SCR Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Steering Speed



Fig D49: MKM Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different oxidant concentriion





Fig D48: SCR Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different pulp densities



Fig D50: MKM Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Solution





Fig D53: Jander Kinetic Plots for Chalcopyrite in $HCl-KClO_3$ at different Oxidant



Fig D55: Jander Kinetic Plots for Chalcopyrite in $HCl-KClO_3$ at different Steering Speed



Fig D57: ZLT Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Oxidant Concentration



Fig D54: Jander Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Solution



Fig D56: Jander Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different pulp densities



Fig D58: ZLT Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Solution Temperatures



Fig D59: Kroger Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Oxidant



Fig D61: ZLT Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Steering Speed



Fig D63: Ginstling Kinetic Plots for





Fig D60: Kroger Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Solution



Fig D62: ZLT Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Pulp densities



Fig D64: Ginstling Kinetic Plots for Chalcopyrite in HCl-



Dissolution of Chalcopyrite in HCl-NaNO₃



Fig D67: DTLF Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different Oxidant





Fig D68: DTLF Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different Solution





Fig D73: DTPL Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different Steering Speed



Fig D75: SCR Kinetic Plots for Chalcopyrite in



Fig D77: SCR Kinetic Plots for Chalcopyrite in $HCl-NaNO_3$ at different Steering Speed



Fig D74: DTPL Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different pulp densities



Fig D76: SCR Kinetic Plots for Chalcopyrite in



Fig D78: SCR Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different pulp densities



Fig D79: MKM Kinetic Plots for Chalcopyrite in HCl-NaNO $_3$ at different oxidant



Fig D81: MKM Kinetic Plots for Chalconvrite



Fig D83: Jander Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different Oxidant



Fig D80: MKM Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different Solution



Fig D82: MKM Kinetic Plots for Chalconvrite



Fig D84: Jander Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different Solution



Fig D85: Jander Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different Steering Speed











Fig D86: Jander Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different pulp densities











Fig D93: Ginstling Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different



Fig D94: Ginstling Kinetic Plots for Chalcopyrite in HCl-NaNO₃ at different Pulp













Dissolution of Sphalerite ore in HCl-KClO₃



Fig D101: DTPL Kinetic Plots for Sphalerite in HCl-KClO₃ at different Particle Sizes



Fig D103: DTPL Kinetic Plots for Sphalerite in HCl-KClO₃ at different Oxidant Concentrations



Fig D102: DTPL Kinetic Plots for Sphalerite in HCl-KClO₃ at different Acid Concentrations



Fig D104: DTPL Kinetic Plots for Sphalerite in HCl-KClO₃ at different Solution Temperature



Fig D107: SCR Kinetic Plots for Sphalerite in HCl-KClO₃ at different Particle Sizes



Fig D109: SCR Kinetic Plots for Sphalrite in HCl-KClO₃ at different Oxidant Concentrations





Fig D108: SCR Kinetic Plots for Sphalerite in HCl-KClO₃ at different Acid Concentrations



Fig D110: SCR Kinetic Plots for Sphalerite in HCl-KClO₃ at different Solution Temperature





Fig D113: MKM Kinetic Plots for Sphalerite in HCl-KClO₃ at different Particle Sizes



Fig D115: MKM Kinetic Plots for Sphalerite in $HCl-KClO_3$ at different oxidant concentriion





Fig D114: MKM Kinetic Plots for Sphalerite in HCl-KClO₃ at different Acid Concentrations









Fig D119: Jander Kinetic Plots for Sphalerite in $HCl-KClO_3$ at different Particle Size



Fig D121: Jander Kinetic Plots for Sphalerite in HCl-KClO₃ at different Oxidant concentration



Fig D123: Jander Kinetic Plots for Sphalerite in HCl-KClO₃ at different Steering Speed



Fig D120: Jander Kinetic Plots for Sphalerite in HCl-KClO₃ at different Acid Concentrations



Fig D122: Jander Kinetic Plots for Sphalerite in HCl-KClO₃ at different Solution Temperatures



Fig D124: Jander Kinetic Plots for Sphalerite in HCl-KClO₃ at different pulp densities



Fig D125: ZLT Kinetic Plots for Sphalerite in HCl-KClO₃ at different Particle Sizes







Fig D129: ZLT Kinetic Plots for Sphalerite in HCl-KClO₃ at different Steering Speed





Fig D126: ZLT Kinetic Plots for Sphalerite in HCl-KClO₃ at different Acid Concentrations



Fig D128: ZLT Kinetic Plots for Sphaleyrite in HCl-KClO₃ at different Solution Temperatures



Fig D130: ZLT Kinetic Plots for Sphalerite in HCl-KClO₃ at different Pulp densities





Fig D133: Ginstling Kinetic Plots for Sphalerite in HCl-KClO₃ at different Oxidant



 $\mathbf{I} \qquad \begin{array}{l} \mbox{Fig D135: Ginstling Kinetic Plots for Sphalerite} \\ \mbox{in HCl-KClO}_3 \mbox{ at different Steering Speed} \end{array}$





Fig D134: Ginstling Kinetic Plots for Sphalerite in HCl-KClO₃ at different Solution



Fig D136: Ginstling Kinetic Plots for Sphalerite in HCl-KClO₃ at different Pulp densities





Fig D139: DTLF Kinetic Plots for Sphalerite in HCl-KCl at different Steering Speed



Fig D143: DTPL Kinetic Plots for Sphalerite in HCl-KCl at different Steering Speed



Fig D140: DTLF Kinetic Plots for Sphalerite in HCl-KCl at different pulp densities



Fig D144: DTPL Kinetic Plots for Sphalerite in HCl-KCl at different pulp densities



Fig D145: SCR Kinetic Plots for Sphalerite in HCl-KCl at different Oxidant Concentrations





Fig D149: MKM Kinetic Plots for Sphalerite in HCl-KCl at different oxidant concentrtion



Fig D146: SCR Kinetic Plots for Sphalerite in HCl-KCl at different Solution Temperature



Fig D150: MKM Kinetic Plots for Sphalerite in HCl-KCl at different Solution Temperatures



Fig D151: MKM Kinetic Plots for Sphalerite in HCl-KCl at different Steering Speed







Fig D155: Jander Kinetic Plots for Sphalerite in HCl-KCl at different Steering Speed





Fig D152: MKM Kinetic Plots for Sphalerite in HCl-KCl at different pulp densities



Fig D154. Jander Kinetic Plate for Schalerite in



Fig D156: Jander Kinetic Plots for Sphalerite in HCl-KCl at different pulp densities









Fig D163: Ginstling Kinetic Plots for Sphalerite in HCl-KCl at different Steering Speed



Fig D162: Ginstling Kinetic Plots for Sphalerite in HCl-KCl at different Solution Temperatures



Fig D164: Ginstling Kinetic Plots for Chalcopyrite in HCl-KCl at different Pulp

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Dissolution of Sphalerite ore in HCl – NaNO₃

Fig D167: DTLF Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Steering Speed



Fig D169: DTPL Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Oxidant Concentrations





Fig D`168: DTLF Kinetic Plots for Sphalerite in HCl-NaNO₃ at different pulp densities



Fig D170: DTPL Kinetic Plots for Sphalerite in HCl-NaNO₃at different Solution Temperature





Fig D173: SCR Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Oxidant Concentrations



Fig D175: SCR Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Steering Speed





Fig D174: SCR Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Solution Temperature



Fig D176: SCR Kinetic Plots for Sphalerite in $HCl-NaNO_3$





Fig D179: MKM Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Steering Speed



Fig D181: Jander Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Oxidant concentration



Fig D183: Jander Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Steering Speed



Fig D180: MKM Kinetic Plots for Sphalerite in HCl-NaNO₃ at different pulp densities



Fig D182: Jander Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Solution Temperatures



Fig D184: Jander Kinetic Plots for Sphalerite in HCl-NaNO₃ at different pulp densities



Fig D185: Kroger Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Oxidant Concentration



Fig D187: Kroger Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Steering Speed



Fig D189: Ginstling Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Oxidant



Fig D186: Kroger Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Solution Temperatures



Fig D188: Kroger Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Pulp density



Fig D190: Ginstling Kinetic Plots for Sphalerite in $HCl-NaNO_3$ at different Solution



Fig D191: Ginstling Kinetic Plots for Sphalerite in HCl-NaNO₃ at different Steering Speed



Fig D192: Ginstling Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different Pulp



Fig D193: DTLF Kinetic Plots for Ilmenite in HCl at different acid concentrations



Fig D194: DTLF Kinetic Plots for Ilmenite in HCl-KCl at different oxidant concentrations





Dissolution of Ilmenite in HCl-KCl



Fig D197: DTLF Kinetic Plots for Ilmenite in HCl-KCl at different Stirring speed





Fig D201: DTPL Kinetic Plots for Ilmenite in HCl-KCl at different Oxidant Concentrations



Fig D198: DTLF Kinetic Plots for Ilmenite in HCl-KCl at different Liquid-to-solid ratio





Fig D202: DTPL Kinetic Plots for Ilmenite in HCl-KCl at different Solution Temperatures











Fig D207: SCR Kinetic Plots for Ilmenite in HCl-KCl at different Oxidant Concentrations



Fig D204: DTPL Kinetic Plots for Ilmenite in HCl-KCl at different Liquid-to-solid



Fig D206: SCR Kinetic Plots for Ilmenite in



Fig D208: SCR Kinetic Plots for Ilmenite in HCl-KCl at different Solution Temperatures



Fig D209: SCR Kinetic Plots for Ilmenite in HCl-KCl at different Stirring Speed



Fig D211: MKM Plots for Ilmenite in HCl-KCl



Fig D213: MKM Plots for Ilmenite in HCl-KCl at different Oxidant Concentrations





Fig D210: SCR Kinetic Plots for Ilmenite in HCl-KCl at different Liquid-to-solid ratio



Fig D212: MKM Plots for Ilmenite in HCl-KCl



Fig D214: MKM Plots for Ilmenite in HCl-KCl at different Solution Temperatures





Fig D217: Jander Kinetic Plots for Ilmenite in HCl-KCl at different Acid Concentrations



Fig D219: Jander Kinetic Plots for Ilmenite in HCl-KCl at different Oxidant Concentrations





Fig D218: Jander Kinetic Plots for Ilmenite in HCl-KCl at different Particle sizes



Fig D220: Jander Plots for Ilmenite in HCl-KCl at different Solution Temperatures







Fig D223: ZLT Kinetic Plots for Ilmenite in HCl-KCl at different Acid concentration

Fig D224: ZLT Kinetic Plots for Ilmenite in HCI-KCl at different Particle sizes



Fig D225: ZLT Kinetic Plots for Ilmenite in HCl-KCl at different Oxidant Concentrations



Fig D227: ZLT Kinetic Plots for Ilmenite in HCl-KCl at different Steering Speed



Fig D229: Ginstling-Brounshtein Kinetic Plots for Ilmenite in HCl-KCl at different Acid concentrations



Fig D226: ZLT Plots for Ilmenite in HCl-KCl at different Solution Temperatures



Fig D228: ZLT Kinetic Plots for Ilmenite in HCl-KCl at different Liquid-to-solid ratio



Fig D230: Ginstling-Brounshtein Kinetic Plots for Ilmenite in HCl-KCl at different Particle sizes



Fig D231: Ginstling-Brounshtein Kinetic Plots for Ilmenite in HCI-KCl at different Oxidant Concentrations



Fig D233: Ginstling-Brounshtein Kinetic Plots for Ilmenite in HCl-KCl at different Stirring Speed



Fig D232: Ginstling-Brounshtein Kinetic Plots for Ilmenite in HCl-KCl at different Solution Temperatures



Fig D234: Ginstling-Brounshtein Kinetic Plots for Ilmenite in HCl-KCl at different Liquid-to-solid ratio



Fig D236: DTLF Kinetic Plots for Ilmenite in HCl-KClO₃ at different Particle sizes



Ilmenite in HCl-KClO₃



Fig D235: DTLF Kinetic Plots for Ilmenite in HCl-KClO₃ at different Oxidant Concentrations





Fig D239: DTLF Kinetic Plots for Ilmenite in HCl-KClO₃ at different Liquid-to-solid ratio



Fig D243: DTPL Kinetic Plots for Ilmenite in HCl-KClO₃ at different Steering Speed



Fig D240: DTPL Kinetic Plots for Ilmenite in HCl-KClO₃ at different Oxidant Concentrations



Fig D244: DTPL Kinetic Plots for Ilmenite in HCl-KClO₃ at different Liquid-to-solid ratio



Fig D245: SCR Kinetic Plots for Ilmenite in HCl-KClO₃ at different Oxidant Concentrations



Fig D247: SCR Kinetic Plots for Ilmenite in



Fig D249: SCR Kinetic Plots for Ilmenite in HCl-KClO₃ at different Liquid-to-solid ratio



Fig D246: SCR Kinetic Plots for Ilmenite in HCl-KClO₃ at different Particle sizes



Fig D248: SCR Kinetic Plots for Ilmenite in



Fig D250: MKM Kinetic Plots for Ilmenite in HCl-KClO₃ at Oxidant concentrations


Fig D251: MKM Kinetic Plots for Ilmenite in HCl-KClO₃ at different Particle sizes



Fig D255: Jander Kinetic Plots for Ilmenite in HCl-KClO₃ at different Oxidant concentration





Fig D252: MKM Kinetic Plots for Ilmenite in HCl-KClO₃ at different Solution Temperatures



Fig D256: Jander Kinetic Plots for Ilmenite in HCl-KClO₃ at different Particle sizes





FigD261: Kroger Kinetic Plots for Ilmenite in HCl-KClO₃ at different Particle sizes



Fig D263: Kroger Kinetic Plots for Ilmenite in HCl-KClO₃ at different Steering Speed



Fig D262: Kroger Kinetic Plots for Ilmenite in HCl-KClO₃ at different Solution Temperatures



Fig D264: Kroger Kinetic Plots for Chalcopyrite in HCl-KClO₃ at different liquid-





Fig D265: ZLT Kinetic Plots for Ilmenite in HCl-KClO₃ at different Oxidant Concentration

Fig D266: ZLT Kinetic Plots for Ilmenite in HCl-KClO₃ at different Particle sizes



Fig D267: Kroger Kinetic Plots for Ilmenite in HCl-KClO₃ at different Oxidant Concentration



Fig D269: Ginstling Kinetic Plots for Ilmenite in HCl-KClO₃ at different Particle sizes



I Fig D271: Ginstling Kinetic Plots for Ilmenite in HCl-KClO₂ at different Stirring Speed





Fig D268: Kroger Kinetic Plots for Ilmenite in HCl-KClO₃ at different Solution Temperatures



Fig D270: Ginstling Kinetic Plots for Ilmenite in HCl-KClO₃ at different Solution



Fig D272: Ginstling Kinetic Plots for Ilmenite in HCl-KClO₂ at different Liquid-to-solid ratio





Fig D275: DTLF Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Solution Temperature



Fig D279: DTPL Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Particle sizes



Fig D276: DTLF Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Stirring speed



Fig D280: DTPL Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Solution Temperature



Fig D281: DTPL Kinetic Plots for Ilmenite in $HCl-NaNO_3$ at different Steering Speed



Fig D283: SCR Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Oxidant Concentrations



Fig D285: SCR Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Solution Temperatures



Fig D282: DTPL Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Liquid-to-solid ratio



Fig D284: SCR Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Particle sizes



Fig D286: SCR Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Stirring speed



Fig D287: SCR Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Liquid-to-solid ratio



Fig D289: MKM Kinetic Plots for Ilmenite in HCl-KClO₃ at different Particle sizes



Fig D291: MKM Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Steering Speed





Fig D288: MKM Kinetic Plots for Ilmenite in HCl-NaNO₃ at Oxidant concentrations



Fig D290: MKM Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Solution Temperatures



Fig D292: MKM Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Liquid-to-solid ratio





Fig D295: Jander Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Solution Temperatures



Fig D297: Jander Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Liquid-to-solid ratio





Fig D296: Jander Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Stirring speed



Fig D298: Kroger Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Oxidant Concentration





Fig D303: ZLT Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Liquid-to-solid ratio



Fig D305: Ginstling Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Particle sizes



Fig D304: Ginstling Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Oxidant Concs



Fig D306: Ginstling Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Solution



Fig D307: Ginstling Kinetic Plots for Ilmenite in HCl-NaNO₃ at different Stirring Speed



Fig D308: Ginstling Kinetic Plots for Ilmenite in $HCl-NaNO_3$ at different Liquid-to-solid ratio

S/N	Temp	L/S	Stirring	Acid	Time	Actual	RSM	ANFIS
	1		Speed	Conc			Pred	Pred
1	333	20	300	3	90	88.09	89.19	88.38
2	348	25	200	2	120	92.83	94.57	92.83
3	318	15	200	2	120	55.42	56.13	55.42
4	348	25	200	4	60	89.75	90.67	89.75
5	348	15	200	2	60	59.35	59.45	59.35
6	333	20	500	3	90	86.48	82.51	86.48
7	348	25	400	2	60	85.31	86.75	85.31
8	333	20	300	3	30	51.08	50.82	51.08
9	333	30	300	3	90	89.37	85.83	89.37
10	333	20	300	3	90	88.11	89.19	88.38
11	348	15	400	4	60	65.67	66.81	65.67
12	318	25	400	4	60	48.04	49.28	48.04
13	303	20	300	3	90	19.07	17.58	19.07
14	318	15	400	2	60	33.87	34.29	33.87
15	333	20	100	3	90	75.42	74.57	75.42
16	333	20	300	3	90	88.99	89.19	88.38
17	348	25	400	4	120	93.25	96.03	93.25
18	333	20	300	1	90	80.24	78.35	80.24
19	348	15	200	4	120	88.91	90.34	88.91

 Table E1: Design of experimental matrix for Leaching of Chalcopyrite HCI-KCI

 Lixiviant

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20	333	20	300	3	150	91.48	86.92	91.48
21	363	20	300	3	90	87.02	83.69	87.02
22	333	10	300	3	90	68.66	67.38	68.66
23	333	20	300	5	90	90.08	87.15	90.08
24	348	15	400	2	120	82.06	84.01	82.06
25	318	15	400	4	120	70.86	72.61	70.86
26	318	25	400	2	120	60.47	62.52	60.47
27	333	20	300	3	90	88.07	89.19	88.38
28	318	25	200	2	60	40.89	41.09	40.89
29	333	20	300	3	90	88.1	89.19	88.38
30	333	20	300	3	90	88.93	89.19	88.38
31	318	25	200	4	120	50.87	52.40	50.87
32	318	15	200	4	60	35.98	35.88	35.98

Table E2: Design of experimental matrix for Leaching of Chalcopyrite HCl-K	ClO ₃
Lixiviant	

S/N	Temp	L/S	Stirring	Acid	Time	Actual	RSM	ANFIS
			Speed	Conc			Pred	Pred
1	318	25	400	2	120	81.37	81.50	81.37
2	318	25	400	4	60	81.81	81.66	81.81
3	333	20	300	3	90	90.79	91.16	91.13
4	333	20	300	3	150	90.76	89.95	90.76
5	333	10	300	3	90	85.62	85.21	85.62
6	348	25	400	2	60	86.26	86.26	86.26
7	333	20	300	3	90	89.81	91.16	91.13
8	363	20	300	3	90	80.63	80.08	80.63
9	348	25	400	4	120	93.51	93.95	93.51
10	333	20	300	5	90	93.82	93.56	93.82
11	333	20	300	3	90	89.78	91.16	91.13
12	333	20	300	1	90	87.97	88.04	87.97
13	348	25	200	2	120	91.64	91.72	91.64
14	348	15	200	4	120	93.32	93.64	93.32
15	303	20	300	3	90	53.68	54.04	53.68
16	318	25	200	4	120	82.46	82.40	82.46
17	333	30	300	3	90	93.81	94.04	93.81
18	333	20	300	3	90	90.79	91.16	91.13
19	333	20	300	3	90	92.81	91.16	91.13
20	318	15	400	4	120	80.18	80.55	80.18
21	318	15	200	4	60	67.06	66.80	67.06
22	348	15	200	2	60	85.5	85.38	85.50
23	348	15	400	2	120	88.58	89.10	88.58
24	333	20	300	3	90	92.78	91.16	91.13
25	318	15	400	2	60	65	64.93	65.00
26	333	20	100	3	90	89.67	90.13	89.67

27	318	25	200	2	60	68.54	68.04	68.54
28	333	20	500	3	90	91.6	90.96	91.60
29	333	20	300	3	30	71.88	72.50	71.88
30	348	15	400	4	60	79.66	79.90	79.66
31	348	25	200	4	60	88.52	88.32	88.52
32	318	15	200	2	120	78.21	78.22	78.21

S/N	Temp	L/S	Stirring	Acid	Time	Actual	RSM	ANFIS
	010	1.5	Speed	Conc	100		Pred	Pred
1	318	15	400	4	120	66.79	66.95	66.79
2	333	30	300	3	90	88.97	86.97	88.97
3	333	20	100	3	90	75.63	75.80	75.63
4	318	15	400	2	60	47.94	48.06	47.94
5	318	15	200	2	120	57.21	56.76	57.21
6	333	20	300	3	90	79.14	79.13	78.82
7	348	25	400	2	60	70.32	71.62	70.32
8	348	15	400	2	120	82.01	82.73	82.01
9	348	15	400	4	60	79.73	80.56	79.73
10	333	20	300	3	90	78.15	79.13	78.82
11	348	15	200	2	60	63.28	63.49	63.28
12	318	25	200	2	60	53.22	53.34	53.22
13	318	15	200	4	60	48.19	47.84	48.19
14	333	20	500	3	90	80.46	78.46	80.46
15	333	20	300	3	90	78.48	79.13	78.82
16	333	20	300	3	150	85.67	84.82	85.67
17	303	20	300	3	90	27.23	27.58	27.23
18	318	25	200	4	120	69.93	70.09	69.93
19	318	25	400	4	60	54.01	54.75	54.01
20	333	20	300	3	30	60.71	59.73	60.71
21	333	20	300	3	90	79.55	79.13	78.82
22	333	20	300	3	90	79.09	79.13	78.82
23	318	25	400	2	120	63.21	63.84	63.21
24	348	25	200	2	120	88.63	89.35	88.63
25	333	20	300	5	90	85.49	84.43	85.49
26	348	25	400	4	120	93.69	95.03	93.69
27	333	20	300	1	90	70.7	69.93	70.70
28	333	20	300	3	90	78.53	79.13	78.82
29	363	20	300	3	90	78.05	75.87	78.05
30	333	10	300	3	90	72.71	72.88	72.71
31	348	15	200	4	120	83.37	83.62	83.37
32	348	25	200	4	60	87.54	88.37	87.54

Table E3: Design of experimental matrix for Leaching of Chalcopyrite HCl-NaNO₃ Lixiviant

S/N1	Temp	L/S	Stirring	Acid	Time	Actual	RSM	ANFIS
	1		Speed	Conc			Pred	Pred
1	333	20	300	3	90	83.66	83.74	83.42
2	318	15	400	2	60	45.72	45.88	45.72
3	348	15	200	4	120	89.62	90.60	89.62
4	348	15	200	2	60	60.84	60.55	60.84
5	333	30	300	3	90	86.60	85.97	86.60
6	318	15	200	4	60	55.62	54.42	55.62
7	348	25	200	4	60	88.65	87.74	88.65
8	333	20	300	3	90	83.04	83.74	83.42
9	333	20	300	3	90	82.55	83.74	83.42
10	333	20	300	3	30	57.80	60.26	57.80
11	333	20	300	5	90	90.66	90.56	90.66
12	348	25	400	2	60	69.18	69.63	69.18
13	318	25	200	2	60	62.71	61.78	62.71
14	318	25	200	4	120	79.45	79.79	79.45
15	333	20	300	3	90	83.99	83.74	83.42
16	333	20	300	3	90	83.56	83.74	83.42
17	318	25	400	2	120	67.63	69.34	67.63
18	318	15	200	2	120	45.79	46.75	45.79
19	333	20	500	3	90	78.44	75.62	78.44
20	348	15	400	4	60	88.89	89.08	88.89
21	348	25	200	2	120	84.23	85.47	84.23
22	363	20	300	3	90	82.02	80.12	82.02
23	318	15	400	4	120	71.13	72.57	71.13
24	318	25	400	4	60	42.89	42.45	42.89
25	333	10	300	3	90	72.91	71.59	72.91
26	333	20	100	3	90	77.34	78.22	77.34
27	333	20	300	3	150	89.86	85.46	89.86
28	348	25	400	4	120	92.77	94.50	92.77
29	333	20	300	1	90	67.79	65.94	67.79
30	303	20	300	3	90	35.70	35.65	35.70
31	348	15	400	2	120	70.94	73.28	70.94
32	333	20	300	3	90	83.70	83.74	83.42

Table E4: Design of experimental matrix for Leaching of Sphalerite HCl-KCl Lixiviant

S/N1	Temp	L/S	Stirring	Acid	Time	Actual	RSM	
			Speed	Conc			Pred	
1	333	10	300	3	90	77.23	76.36	77.23
2	348	15	200	4	120	90.44	91.85	90.44
3	348	25	400	4	120	95.93	97.96	95.93
4	348	15	200	2	60	67.57	67.05	67.57
5	333	30	300	3	90	84.18	83.50	84.18
6	333	20	300	3	150	88.18	85.50	88.18
7	318	25	200	2	60	60.97	59.67	60.97
8	333	20	300	3	90	85.83	85.48	85.23
9	363	20	300	3	90	85.34	83.11	85.34
10	333	20	300	5	90	88.56	85.82	88.56
11	333	20	300	3	90	85.34	85.48	85.23
12	348	25	400	2	60	70.49	70.59	70.49
13	318	15	200	4	60	62.8	62.53	62.80
14	348	25	200	2	120	89.17	89.55	89.17
15	333	20	300	3	90	84.74	85.48	85.23
16	333	20	300	3	90	85.99	85.48	85.23
17	333	20	300	3	90	84.26	85.48	85.23
18	318	25	200	4	120	74.18	74.81	74.18
19	348	25	200	4	60	80.05	80.46	80.05
20	318	15	400	4	120	70.29	71.64	70.29
21	318	15	400	2	60	53.25	52.67	53.25
22	318	25	400	2	120	67.07	67.39	67.07
23	318	25	400	4	60	58.96	59.31	58.96
24	348	15	400	2	120	86.25	87.35	86.25
25	333	20	300	1	90	69.28	70.46	69.28
26	333	20	100	3	90	84.33	84.89	84.33
27	333	20	300	3	30	56.59	57.72	56.59
28	348	15	400	4	60	76.49	77.61	76.49
29	318	15	200	2	120	60.77	60.47	60.77
30	333	20	500	3	90	86.53	84.42	86.53
31	333	20	300	3	90	85.19	85.48	85.23
32	303	20	300	3	90	43.94	44.62	43.94

Table E5: Design of experimental matrix for Leaching of Sphalerite HCl-KClO₃ Lixiviant

S/N1	Temp	L/S	Stirring	Acid	Time	Actual	RSM	ANFIS
			Speed	Conc		· -	Pred	Pred
1	333	10	300	3	90	64.47	64.14	64.47
2	318	25	400	4	60	57.93	57.52	57.93
3	303	20	300	3	90	38.34	39.39	38.34
4	318	15	200	2	120	53.36	53.53	53.36
5	333	20	300	3	90	78.63	78.45	78.26
6	348	25	200	2	120	84.29	85.38	84.29
7	333	20	300	3	90	78.74	78.45	78.26
8	348	25	400	2	60	83.15	83.27	83.15
9	318	15	400	4	120	70.71	71.20	70.71
10	318	25	400	2	120	68.31	68.65	68.31
11	333	20	500	3	90	80.29	79.63	80.29
12	348	15	400	4	60	80.58	80.85	80.58
13	333	20	100	3	90	75.65	75.19	75.65
14	333	20	300	3	90	78.08	78.45	78.26
15	333	20	300	3	90	78.63	78.45	78.26
16	348	15	200	4	120	85.11	86.36	85.11
17	318	15	400	2	60	40.74	39.94	40.74
18	333	20	300	3	30	59.70	61.17	59.70
19	318	25	200	4	120	72.06	72.62	72.06
20	348	25	400	4	120	86.43	87.85	86.43
21	318	15	200	4	60	59.12	58.54	59.12
22	348	15	200	2	60	52.72	52.68	52.72
23	333	20	300	3	90	78.46	78.45	78.26
24	333	30	300	3	90	83.59	82.79	83.59
25	333	20	300	3	90	77.04	78.45	78.26
26	348	15	400	2	120	67.84	68.86	67.84
27	363	20	300	3	90	80.08	77.90	80.08
28	333	20	300	5	90	83.88	82.77	83.88
29	333	20	300	1	90	59.42	59.41	59.42
30	348	25	200	4	60	80.70	81.04	80.70
31	333	20	300	3	150	86.37	83.77	86.37
32	318	25	200	2	60	50.96	50.22	50.96

Table E6: Design of experimental matrix for Leaching of Sphalerite HCl-NaNO₃ Lixiviant

S/N1	Temp	L/S	Stirring	Acid	Time	Actual	RSM	ANFIS
			Speed	Conc			Pred	Pred
1	333	20	300	3	30	66.44	68.23	66.44
2	348	15	200	4	120	85.38	84.74	85.38
3	333	20	100	3	90	75.59	77.04	75.59
4	348	15	400	2	120	82.9	82.73	82.90
5	333	20	300	3	90	78.95	78.93	79.05
6	318	15	400	2	60	58.42	57.50	58.42
7	348	25	200	2	120	86.15	86.63	86.15
8	333	20	500	3	90	80.61	79.92	80.61
9	318	15	200	4	60	60.37	58.98	60.37
10	318	15	400	4	120	62.74	62.59	62.74
11	333	10	300	3	90	69.59	72.34	69.59
12	348	25	400	2	60	79.72	80.03	79.72
13	318	25	400	2	120	66.95	67.92	66.95
14	333	30	300	3	90	86.96	84.97	86.96
15	318	25	200	2	60	63.09	62.82	63.09
16	348	15	400	4	60	80.3	79.49	80.30
17	318	25	400	4	60	68.71	69.04	68.71
18	333	20	300	3	90	79.09	78.93	79.05
19	348	15	200	2	60	78.82	77.41	78.82
20	363	20	300	3	90	83.76	84.05	83.76
21	348	25	400	4	120	95.91	96.99	95.91
22	318	25	200	4	120	70.53	71.03	70.53
23	333	20	300	3	90	79.06	78.93	79.05
24	303	20	300	3	90	44.16	44.63	44.16
25	333	20	300	1	90	74.56	75.07	74.56
26	318	15	200	2	120	62.55	61.80	62.55
27	333	20	300	3	90	79.14	78.93	79.05
28	333	20	300	3	90	79	78.93	79.05
29	349	25	200	4	60	81.5	81.34	81.50
30	333	20	300	5	90	81.66	81.91	81.66
31	333	20	300	3	150	81.22	80.19	81.22
32	333	20	300	3	90	79.07	78.93	79.05

 Table E7: Design of experimental matrix for Leaching of Ilmenite HCI-KCI Lixiviant

S/N1	Temp	L/S	Stirring	Acid	Time	Actual	RSM	ANFIS
			Speed	Conc			Pred	Pred
1	348	25	400	4	120	92.64	93.30	92.64
2	318	25	200	4	120	67.76	67.51	67.76
3	348	15	200	4	120	88.5	87.99	88.50
4	333	20	500	3	90	77.09	75.43	77.09
5	333	20	300	3	90	75.68	75.51	75.49
6	318	15	200	4	60	56.13	55.64	56.13
7	333	20	300	3	90	75.93	75.51	75.49
8	318	25	400	4	60	60.31	60.99	60.31
9	333	20	300	5	90	81.19	80.92	81.19
10	348	25	200	2	120	90.04	89.80	90.04
11	318	25	200	2	60	51.15	50.93	51.15
12	348	25	400	2	60	82.55	83.24	82.55
13	318	15	400	2	60	50.41	50.61	50.41
14	333	20	300	3	90	75.8	75.51	75.49
15	348	15	400	4	60	81.9	82.32	81.90
16	333	20	300	3	30	63.77	63.44	63.77
17	333	20	300	3	150	81.52	81.71	81.52
18	333	20	300	3	90	75.81	75.51	75.49
19	333	20	300	3	90	74.83	75.51	75.49
20	348	15	400	2	120	84.69	84.87	84.69
21	318	15	200	2	120	63.14	62.42	63.14
22	348	25	200	4	60	84.84	84.84	84.84
23	363	20	300	3	90	93.07	92.78	93.07
24	333	20	100	3	90	70.91	72.44	70.91
25	318	25	400	2	120	63.48	63.93	63.48
26	348	15	200	2	60	74.64	74.16	74.64
27	333	20	300	1	90	71.12	71.26	71.12
28	333	20	300	3	90	74.86	75.51	75.49
29	318	15	400	4	120	65.82	66.00	65.82
30	333	10	300	3	90	70.57	71.25	70.57
31	303	20	300	3	90	42.01	42.16	42.01
32	333	30	300	3	90	79.71	78.89	79.71

 Table E8: Design of experimental matrix for Leaching of Ilmenite HCl-KClO3 Lixiviant

S/N1	Temp	L/S	Stirring	Acid	Time	Actual	RSM	ANFIS
			Speed	Conc			Pred	Pred
1	333	20	500	3	90	75.45	73.90	75.45
2	318	15	400	4	120	60.39	60.87	60.39
3	333	10	300	3	90	70.23	69.05	70.23
4	333	20	300	3	30	64.73	63.79	64.73
5	348	25	400	4	120	90.75	91.32	90.75
6	318	15	200	2	120	57.41	57.22	57.41
7	333	20	300	3	90	73.5	73.75	73.56
8	348	15	200	2	60	74.74	75.13	74.74
9	348	25	200	4	60	82.89	83.16	82.89
10	348	15	200	4	120	83.53	83.91	83.53
11	348	15	400	2	120	80.11	80.80	80.11
12	333	20	300	3	150	77.07	76.88	77.07
13	318	15	200	4	60	53.92	54.10	53.92
14	333	20	300	3	90	73.61	73.75	73.56
15	303	20	300	3	90	40.46	40.68	40.46
16	318	25	200	4	120	69.24	68.93	69.24
17	333	20	300	3	90	73.72	73.75	73.56
18	348	25	400	2	60	80.32	80.89	80.32
19	318	25	400	2	120	65.46	65.45	65.46
20	318	25	400	4	60	60.14	60.51	60.14
21	348	15	400	4	60	78.53	79.59	78.53
22	318	15	400	2	60	51.88	52.37	51.88
23	333	20	300	5	90	80.34	79.40	80.34
24	348	25	200	2	120	85.01	84.90	85.01
25	333	20	300	3	90	73.5	73.75	73.56
26	333	20	100	3	90	71.19	71.61	71.19
27	363	20	300	3	90	88.27	86.92	88.27
28	333	20	300	1	90	72.01	71.82	72.01
29	333	30	300	3	90	80.62	80.67	80.62
30	318	25	200	2	60	55.59	55.28	55.59
31	333	20	300	3	90	73.54	73.75	73.56
32	333	20	300	3	90	73.48	73.75	73.56

Table E9: Design of experimental matrix for Leaching of Ilmenite HCl-NaNO₃ Lixiviant

APPENDIX F OPTIMAL SOLUTIONS FOR DESIGN OF EXPERIMENTS

Number	Temperature	L/S	Stirring	Acid	Time	Yield	Desirability	
	1		Speed	Conc.			5	
1	343.19	19.26	282.62	2.36	102.56	95.18	1	Selected
2	343.42	17.06	313.85	2.97	110.26	95.49	1	
3	342.75	21.2	337.18	2.22	92.98	95.50	1	
4	343.1	19.36	281.67	2.29	109.86	95.76	1	
5	347.38	24.97	345.72	2.77	104.63	101.14	1	
6	338.95	20.74	305.17	2.37	98.82	95.18	1	
7	345.43	24.97	246.99	2.42	112.05	98.94	1	
8	346.12	20.74	380.4	2.51	92.55	94.97	1	
9	343.86	20.39	220.01	3.01	103.18	96.79	1	
10	342.86	22.36	344.12	2.85	78.43	94.78	1	
11	341.84	24.1	354.48	3.79	71.06	93.32	1	
12	347.91	21.77	243.15	2.26	93.42	96.30	1	
13	347.99	22.04	380.58	2.37	104.51	97.55	1	
14	337.79	23.85	305.17	3.9	81.19	93.78	1	
15	342.85	18.38	281.32	2.29	106.14	93.91	1	
16	343.91	20.46	363.74	2.69	94.76	96.30	1	
17	340.27	24.78	324.76	3.94	118.12	96.72	1	
18	340.27	18.19	264.53	3.87	98.93	95.18	1	
19	347.93	18.87	235.15	3.88	92.86	94.94	1	
20	341.06	18.18	213.88	3.89	119.43	94.93	1	

Table F1: Optimal solutions for the leaching of Chalcopyrite using HCl-KCl

Number	Temperature	L/S	Stirring Speed	Acid Conc	Time	Yield	Desirability	
1	344.41	24.58	221.50	3.73	109.53	95.07	1	Selected
2	343.68	18.52	203.18	2.27	106.15	94.92	1	
3	342.11	21.72	225.62	3.72	103.02	95.16	1	
4	342.49	18.31	206.47	2.29	118.54	95.28	1	
5	341.53	24.13	310.14	3.57	99.54	95.78	1	
6	342.71	19.76	225.12	2.56	114.21	94.84	1	
7	341.15	21.80	375.57	3.95	92.52	95.00	1	
8	337.92	23.58	322.41	3.18	99.27	95.08	1	
9	344.96	16.06	214.20	2.03	105.25	94.95	1	
10	347.44	15.34	201.73	2.52	107.98	94.91	1	
11	344.54	19.39	212.79	3.01	113.71	94.96	1	
12	340.83	20.36	255.79	3.73	115.64	95.25	1	
13	340.41	24.97	399.65	2.76	93.87	94.85	1	
14	339.52	22.38	333.45	3.08	116.59	94.86	1	
15	341.94	17.93	239.01	3.24	118.61	94.89	1	
16	341.64	20.08	205.78	2.56	109.49	94.86	1	
17	337.16	24.97	397.99	2.7	109.54	95.10	1	
18	334.71	21.18	274.44	3.88	113.91	94.93	1	
19	343.59	20.25	218.43	3.58	105.28	94.91	1	
20	336.16	24.95	399.99	2.88	91.24	94.87	1	

Table F2: Optimal solutions for the leaching of Chalcopyrite using HCl-KClO₃

Number	Temperature	L/S	Stirring Speed	Acid Conc.	Time	Yield	Desirability	
1	345.04	24.84	364.11	3.62	119.01	94.02	1	Selected
2	347.71	24.78	319.95	3.61	119.36	94.90	1	
3	345.47	23.13	293.79	3.94	117.07	94.58	1	
4	343.15	24.23	362	3.85	117.13	93.96	1	
5	346.79	24.22	249.02	3.92	101.67	94.59	1	
6	341.08	24.90	211.48	3.94	105.8	94.76	1	
7	347.88	23.13	390.74	4	111.96	93.70	1	
8	346.15	24.78	245.46	3.53	111.53	94.83	1	
9	346.18	23.54	208.05	3.88	104.57	93.96	1	
10	346.62	23.00	260.72	3.97	115.85	94.62	1	
11	344.83	23.83	200.15	3.98	113.2	95.25	1	
12	346.66	22.73	315.7	3.94	117.56	94.31	1	
13	342.1	24.67	370.67	3.95	115.02	93.85	1	
14	347.43	24.02	348.06	3.89	119.36	95.00	1	
15	346.33	24.43	279.72	3.72	103.68	93.98	1	
16	341.09	24.92	357.02	3.98	114.96	93.93	1	
17	346.86	24.86	309.16	3.76	100.29	93.74	1	
18	347.73	24.46	357.6	3.98	109.44	94.63	1	
19	345.98	24.18	250.15	3.9	97.54	93.82	1	
20	342.35	24.58	332.92	3.8	113.52	93.91	1	

Table F3: Optimal solutions for the leaching of Chalcopyrite using HCl-NaNO₃

Number	Temperature	L/S	Stirring	Acid	Time	Yield	Desirability	
			Speed	Conc.				
1	338.59	24.07	204.3	3.94	84.88	93.18	1	Selected
2	338.8	24.15	263.49	2.87	117.97	93.35	1	
3	347.9	20.91	293.15	3.62	86.94	93.03	1	
4	341.54	19.47	361.6	3.55	114.16	94.81	1	
5	337.91	15.56	364.67	3.9	119.41	95.58	1	
6	347.92	20.89	336.54	3.23	119.18	93.51	1	
7	347.06	17.88	315.34	3.51	98.18	93.34	1	
8	346.34	24.05	202.96	3.36	84.44	92.82	1	
9	343.16	15.11	306.19	3.98	80.56	92.82	1	
10	347.88	15.19	382.71	3.41	119.62	93.26	1	
11	347.69	20.96	265.36	3.24	118.81	93.15	1	
12	340.41	24.97	316.19	3.29	102.62	92.88	1	
13	340.56	20.9	319.1	3.45	110.9	94.24	1	
14	343.45	24.82	306.94	2.74	119.69	92.83	1	
15	339.19	18.04	213.99	3.93	102.9	92.87	1	
16	345.48	15.11	366.88	3.52	113.8	94.04	1	
17	347.8	20.15	213.04	3.53	104.39	93.38	1	
18	345.36	22.21	250.59	3.42	118.5	96.03	1	
19	345.54	22.33	249.13	3.73	86.96	94.20	1	
20	341.43	24.91	300.75	2.75	116.27	92.90	1	

Table F4: Optimal solutions for the leaching of sphalerite using HCl-KCl

Number	Temperature	L/S	Stirring Speed	Acid Conc.	Time	Yield	Desirability	
1	344.04	22.13	385.02	3.46	111.52	96.28	1	Selected
2	342.91	23.7	360.56	3.82	113.56	96.47	1	
3	346.33	20.89	366.65	3.11	115.17	96.07	1	
4	346.99	24.77	216.3	3.37	113.31	96.02	1	
5	347.64	24.7	387.23	2.97	118.13	96.16	1	
6	346.53	20.07	239.62	3.93	112.87	96.01	1	
7	345.7	19.99	218.65	3.98	118.45	96.00	1	
8	342.62	23.46	388.38	3.18	118.91	96.00	1	
9	344.92	16.3	381.46	3.89	118.88	96.39	1	
10	343.51	24.59	268.89	3.46	119.59	96.47	1	
11	345.69	24.41	259.79	3.62	118.99	97.11	1	
12	346.94	24.25	382.52	3.06	115.34	96.09	1	
13	347	22.52	259.29	3.62	110.57	96.30	1	
14	347.69	22.65	330.2	3.62	110.39	96.75	1	
15	346.53	23.87	200.37	3.89	107.92	96.05	1	
16	347.19	19.41	290.01	3.61	118.21	96.43	1	
17	346.17	19.67	339.9	3.32	114.95	96.10	1	
18	343.77	23.75	217.74	3.5	116.27	96.06	1	
19	341.6	23.72	212.05	4	119.73	96.12	1	
20	347.05	19.85	373.37	3.64	117.33	97.65	1	

Table F5: Optimal solutions for the leaching of sphalerite using HCl-KClO₃

Number	Temperature	L/S	Stirring	Acid	Time	Yield	Desirability	
			Speed	Conc.				
1	347.63	20.96	238.68	3.19	114.14	86.65	1	Selected
2	339.06	19.95	333.53	3.75	107.85	86.83	1	
3	347.92	24.82	328.58	3.14	89.73	88.44	1	
4	346.03	22.86	387.54	3.2	87.54	87.51	1	
5	345.11	24.99	202.43	2.52	107.12	86.62	1	
6	342.87	24.35	381.06	2.96	114.44	89.19	1	
7	344.96	24.56	347.66	2.35	96.46	87.17	1	
8	346.64	22.6	301.52	3.96	89.31	87.44	1	
9	347.65	22.42	394.77	2.86	114.88	88.05	1	
10	336.82	22.76	353.59	3.8	118.14	86.82	1	
11	340.39	24.15	345.7	2.72	109.93	87.64	1	
12	340.63	22.67	297.55	3.87	98.78	87.23	1	
13	332.73	18.39	209.5	3.99	117.71	86.48	1	
14	345.61	22.86	390.36	3.95	84.68	87.25	1	
15	340.36	23.15	261.94	3.79	112.56	88.45	1	
16	341.04	18.74	385.5	3.91	107.4	86.95	1	
17	339.7	21.01	254.98	3.29	117.53	86.98	1	
18	341.77	15.65	211.75	3.97	112.51	86.87	1	
19	336.67	23.57	204.28	3.78	116.28	87.77	1	
20	343.67	16.85	207.2	3.92	109.03	86.90	1	

Table F6: Optimal solutions for the leaching of sphalerite using HCl-NaNO₃

Number	Temp	L/S	Stirring	Acid	Time	Yield	Desirabilit	
			Speed	Conc			У	
1	74.99	24.40	399.70	3.98	119.12	96.26	1	Selecte
								d
2	74.96	24.96	399.05	3.78	118.63	95.95	1	
3	74.00	24.72	399.40	4.00	119.51	96.38	1	
4	73.98	24.95	395.23	4.00	114.25	95.98	1	
5	74.92	24.99	393.99	3.94	114.15	96.02	1	
6	74.50	24.68	396.87	3.93	119.23	96.15	1	
7	73.12	24.99	395.28	4.00	115.61	95.91	1	
8	74.83	24.74	390.27	3.91	119.11	96.03	1	
9	74.83	24.37	399.85	3.98	119.94	96.27	1	
10	74.97	24.46	398.66	3.89	119.04	95.95	1	
11	75.00	25.00	400.00	4.00	109.70	95.88	1	
12	74.10	24.08	400.00	3.99	120.00	95.82	1	
13	74.95	25.00	400.00	3.77	116.43	95.75	1	
14	74.95	25.00	352.55	4.00	117.59	95.52	1	
15	75.00	24.61	351.56	4.00	120.00	95.38	1	
16	73.16	25.00	392.55	3.67	120.00	95.07	1	
17	75.00	25.00	400.00	4.00	102.98	95.03	1	
18	75.00	24.99	336.70	4.00	116.67	95.02	1	
19	75.00	23.12	400.00	4.00	116.42	94.84	1	
20	75.00	25.00	390.43	3.39	119.83	94.43	1	
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 Table F7: Optimal solutions for the leaching of ilmenite using HCl-KCl

Numbe	Temp	L/S	Stirring	Acid	Time	Yield	Desirabilit	
r	1		Speed	conc			У	
1	74.82	24.95	379.91	3.98	118.62	93.13	1	Selecte
								d
2	74.90	24.96	391.69	3.98	117.34	93.11	1	
3	74.99	24.97	391.67	3.92	119.54	93.14	1	
4	74.98	24.97	395.40	3.95	117.26	93.12	1	
5	75.00	24.99	330.34	3.88	119.95	93.08	1	
6	75.00	25.00	370.07	4.00	112.35	93.03	1	
7	75.00	25.00	364.82	3.78	120.00	92.98	1	
8	75.00	25.00	384.60	3.99	106.24	92.73	1	
9	75.00	23.70	300.55	4.00	120.00	92.57	1	
10	75.00	25.00	200.01	3.73	119.44	91.78	1	
11	75.00	25.00	200.00	3.59	120.00	91.62	1	
12	75.00	25.00	204.65	4.00	111.77	91.61	1	
13	74.25	24.21	200.00	4.00	119.99	91.49	1	
14	75.00	23.17	400.00	4.00	97.78	91.30	1	
15	74.92	25.00	318.08	2.52	120.00	91.16	1	
16	75.00	25.00	399.99	3.98	82.35	91.06	1	
17	75.00	25.00	293.65	2.35	119.86	90.90	1	
18	75.00	20.68	203.60	4.00	120.00	90.53	1	
19	75.00	25.00	218.99	2.05	119.93	90.05	1	
20	75.00	25.00	399.27	4.00	63.75	89.18	1	

Table F8: Optimal solutions for the leaching of ilmenite using HCl-KClO₃

Number	Temp	L/S	Stirring	Acid	Time	Yield	Desirabilit	
			Speed	Conc			У	
1	74.86	24.68	327.98	4.00	117.23	90.76	1	Selecte
								d
2	74.98	24.90	398.13	3.98	113.38	90.77	1	
3	74.75	24.96	310.21	3.93	119.58	90.80	1	
4	74.87	24.92	320.51	3.97	115.96	90.75	1	
5	74.96	25.00	399.63	3.89	116.92	90.78	1	
6	74.47	24.91	327.65	3.96	119.08	90.76	1	
7	74.90	24.41	356.96	4.00	119.60	90.76	1	
8	75.00	24.50	400.00	4.00	116.27	90.69	1	
9	75.00	24.97	219.95	4.00	118.96	90.57	1	
10	74.97	25.00	400.00	3.72	119.99	90.46	1	
11	74.82	24.04	399.50	4.00	120.00	90.45	1	
12	75.00	25.00	328.85	3.65	120.00	90.13	1	
13	73.85	24.98	306.76	3.71	119.99	89.75	1	
14	74.23	25.00	200.00	3.99	110.90	89.48	1	
15	75.00	25.00	293.92	4.00	99.12	89.44	1	
16	74.96	25.00	390.90	3.21	119.94	89.10	1	
17	75.00	25.00	286.51	4.00	94.05	88.86	1	
18	75.00	24.65	200.02	3.52	120.00	88.54	1	
19	75.00	25.00	200.25	3.60	104.73	87.91	1	
20	75.00	24.90	200.00	2.90	120.00	86.88	1	

Table F9: Optimal solutions for the leaching of ilmenite using HCl-NaNO₃

APPENDIX G GEOGRAPHICAL LOCATIONS OF EBONYI MINES

