



UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

Towards the development and determination of trace impurities in battery grade nickel sulphate

By

Mothepane Happy Mabowa

1387468

A thesis submitted to the Faculty of Science, University of the
Witwatersrand, Johannesburg in fulfilment of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

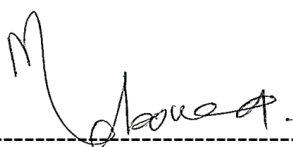
Supervisor: Professor Luke Chimuka

Co-supervisor: Dr. James Tshilongo

October 2024

DECLARATION

I declare that this thesis is my own, unaided work and that it is my work undertaken under the guidance of my supervisors. It is being submitted for the Degree of Doctor of Philosophy in the University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University. The overall research was conceptualised and performed at the Analytical Chemistry Division at Mintek.



(Signature of candidate)

-17----- Day of-----October-----2024

Supervisor: Professor Luke Chimuka

Co-supervisor: Dr. James Tshilongo

DEDICATION

In Memory of My Father (My Captain)in Heaven:

Mr Serurubele Kaizer Chiloane

1958-2020.

ACKNOWLEDGEMENTS

I would like to begin by expressing my profound appreciation to the Almighty God for granting me the strength, patience, knowledge, and ability to undertake this research journey. Without His guidance and blessings, none of this would have been possible.

I extend my sincere appreciation to Professor Luke Chimuka for his exceptional supervision, valuable lessons, unwavering motivation, and constant support throughout this research endeavour.

I am profoundly grateful to Dr. James Tshilongo, my esteemed co-supervisor from the Analytical Chemistry Division at Mintek, for his invaluable expertise and constructive criticism that greatly enriched this study.

Special thanks are extended to Dr. Andile Mkhohlakali and Mr. Sam Mokoena for their positive attitude, encouragement, and willingness to provide technical discussion.

I am grateful to Mintek for their financial support, which enabled the execution of this research. Special thanks to the Analytical Chemistry Division (ACD) for providing the necessary resources and facilities for conducting experiments.

I would like to express my heartfelt appreciation to my parents, Mr. Chiloane (late) and Mrs. Chiloane, for their unwavering love, kindness, support, and encouragement throughout my academic journey. Even though, Mr. Chiloane, is no longer with us, his legacy of perseverance and leadership continues to inspire me. May his soul rest in peace.

My deepest appreciation goes to my beloved husband, Mr. Setsopo Robert Mabowa, and my wonderful children, Tshagofatso Charmaine and Lehlake Moloko Mabowa, for their unwavering support, understanding, and sacrifices throughout

this journey. Their love, prayers, and patience were my pillars of strength, and I am forever grateful for their presence in my life.

ABSTRACT

This study introduces innovative research focused on developing and optimizing advanced extraction techniques for refining nickel hydroxide from secondary material solutions. This precursor to nickel sulfate is effectively purified through impurity removal and precise determination, enhancing the final product to battery-grade standards. The research addresses the extraction of metal hydroxide from secondary sources such as spent batteries and industrial waste, promoting recycling and reducing environmental impact. By refining analytical methodologies and improving impurity control, this study advances the sustainable production of high-quality nickel sulfate essential for advanced rechargeable batteries.

The key challenge addressed in this study is the presence of impurities in secondary material solutions, which complicates the process of refining nickel hydroxide and hinders the production of high-purity nickel sulfate suitable for battery applications. Existing methods for recovering nickel from secondary materials are often inefficient, leading to high impurity levels, low recovery rates, and significant environmental impacts. Current methods such as solvent extraction and precipitation often fail to achieve the desired purity levels for nickel sulfate, necessary for use in high-performance battery manufacturing. Furthermore, these methods can be costly, resource-intensive, and environmentally damaging. Analytical methods used to measure impurities also have limitations. The complex and saturated matrix of battery-grade solutions challenges accurate impurity determination, often necessitating indirect methods such as difference analysis from nickel sulfate, which may not fully capture all impurity types or their concentrations.

To resolve these issues the study focuses on optimizing advanced extraction techniques from these secondary sources. The research includes: (1) investigating the effectiveness of S-Curve precipitation by varying parameters such as pH levels, nickel concentration, precipitate dosage, temperature, impurity concentration, and solubility products; (2) evaluating solvent extraction for copper removal prior to

nickel precipitation; (3) validating various analytical techniques (FAAS, EDXRF, ICP-OES) for trace element analysis; (4) examining lime precipitation for the removal of iron, manganese, and copper; and (5) characterizing β -nickel hydroxide ($\text{Ni}(\text{OH})_2$) using scanning electron microscopy (SEM), X-ray diffraction (XRD) patterns, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS).

The research employed a combination of precipitation methods, solvent extraction, and advanced analytical techniques. The S-curve precipitation of nickel hydroxide was optimised by varying pH levels, nickel concentration, and temperature. The study also examined lime precipitation as a method for impurity removal and used solvent extraction for copper removal before nickel recovery. Various solvents with different ratios were utilized at room temperature for copper extraction, and the 1:5 ratio of 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63-70) proved to be effective. Analytical tools like FAAS, EDXRF, and ICP-OES were employed to validate the concentration of trace impurities, and techniques such as SEM, FTIR, XRD, and XPS were used to characterize the crystalline structure and purity of β - $\text{Ni}(\text{OH})_2$.

The first part of the work entailed devising a technique to extract base metals, specifically nickel, from the waste stream resulting from the nickel sulphide-fire assay waste. This study explores the recovery of nickel (Ni) through a combination of solvent extraction and precipitation techniques. The main objective is to develop an efficient process for separating Ni from copper (Cu) and iron (Fe) impurities, thereby optimising metal recovery at varying pH, concentration with addition of calcium hydroxide at 60°C and contributing to the circular economy. The approach involves using LIX 63-70 for solvent extraction, which effectively loads Cu into the organic phase and allows for Ni liberation into the aqueous phase. Characterization of the S-curve precipitation process was carried out using various analytical techniques. The precipitation of $\text{Ni}(\text{OH})_2$ was optimised at pH 6.5, as evidenced by X-ray diffraction (XRD) patterns, Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The results show that $\text{Ni}(\text{OH})_2$ precipitates in a crystalline β -phase, with XPS confirming the

successful precipitation and minimal presence of Cu and Fe impurities at pH of 6.5 at 60°C. Notably, the study also identifies the presence of Fe and Ca impurities at pH 2.5, as indicated by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and XRD analyses.

The study addresses a critical research gap by providing a detailed assessment of the separation process for Ni from complex waste streams. It demonstrates the efficacy of 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63-70) in selectively extracting Cu and reveals the influence of pH on the purity of Ni(OH)₂ precipitates. The process also involves significant lime consumption for neutralising the feed solution, with about 71% used to adjust the solution to pH 2.0, highlighting the importance of optimising reagent usage. The research presents a successful method for recovering Ni from fire assay waste in separating value-added metals from impurities. The findings contribute to advancements in metal recycling and repurposing, supporting the development of sustainable waste management practices and the promotion of a circular economy.

Paper II evaluates the accuracy and reliability of elemental analysis in synthetic cathode liquor using Energy Dispersive X-ray Fluorescence (EDXRF) and Flame Atomic Absorption Spectroscopy (FAAS) with both factory default settings and after internal calibration and compares these results with those obtained from Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The research aims to test the performance of EDXRF and FAAS for identifying and quantifying elements such as calcium (Ca), sodium (Na), cobalt (Co), iron (Fe), nickel (Ni), copper (Cu), arsenic (As), selenium (Se), antimony (Sb), and bismuth (Bi). The investigations into the impact of these parameters on the variations in absorbance for the targeted impurities guarantee satisfactory linearity and recovery. The recovery was quantified by comparing the concentration of elements in spiking samples and certified reference materials (CRMs) to known quantities, while the sensitivity of each method was assessed by the limits of detection (LOD). Linearity was assessed by constructing calibration curves at a variety of concentrations and calculating the coefficient of determination (R^2) to guarantee precise results at

varying concentration levels. Initial EDXRF results using default settings showed substantial inconsistencies, particularly with Ca, where measured values invariably showed 0 mg/L despite actual concentrations ranging from 0 to 0.15 mg/L, and Ni, where measured concentrations varied between 493,327 and 529,280 mg/L compared to the true value of 120,000 mg/L. After calibration, EDXRF displayed better accuracy for Co, Fe, and Cu but experienced limits with light elements like Se and Sb due to high LOD. FAAS demonstrated effective results for Co, Cu, Fe, and Mg but encountered limits, particularly in detecting low amounts of metals like Na. FAAS readings for Na demonstrated high variability with a standard deviation (SD) of 505.24 mg/L and a relative standard deviation (RSD) of 23.39%. Furthermore, differences in FAAS measurements for Ca, Fe, and Ni were seen, with fluctuations in standard deviation (SD) and relative standard deviation (RSD) suggesting a certain level of inconsistency. The ICP-OES results confirm the accuracy of FAAS by closely aligning with its measurements for elements such as Co and Ni. The precision of FAAS is further demonstrated by the low standard deviations (8.08 mg/L for Co and 4 mg/L for Ni) of ICP-OES results (e.g., Co: 990 mg/L, Ni: 126 mg/L). This validation underscores the dependability of FAAS to these components due to selection of FAAS for its cost-effectiveness and broad applicability in industrial analysis. Evaluation of numerous methods is crucial for a thorough evaluation of elemental analysis accuracy, as evidenced by the comparison with ICP-OES. In addition, it is crucial to distinguish between the discourse on analytical methods and recovery metrics, as recovery rates are more closely associated with preconcentration techniques than with the analytical methods themselves. This work aims to fill a significant research need by emphasising the need for internal calibration for EDXRF and the necessity of using several analytical methods in conjunction to obtain dependable results. It stresses the strengths and limits of each method, providing a complete approach to enhancing analytical accuracy in industrial applications.

The study in Paper III investigates the characterisation and retrieval of β -Ni(OH)₂ from fire assay waste using chemical precipitation. Various analytical methods are used to confirm the successful synthesis and purity of the molecule. Nickel

hydroxide ($\text{Ni}(\text{OH})_2$) is a functionally diverse chemical with a broad spectrum of uses. A hexagonal crystalline structure of $\beta\text{-Ni}(\text{OH})_2$ is confirmed by X-ray diffraction (XRD) analysis, therefore validating the successful precipitation procedure. Fourier-transform infrared spectroscopy (FTIR) spectra provide additional evidence for the presence of nickel hydroxide by displaying distinct peaks associated with $\nu(\text{OH})$ and $\nu(\text{NiO})$ bonds. The X-ray photoelectron spectroscopy (XPS) analysis reveals the significant Ni^{2+} oxidation peak, which confirms the successful precipitation at a pH of 6.5. Additionally, XPS analysis detects the presence of contaminants such as chlorine and calcium in the waste matrix. Scanning electron microscopy (SEM) shows layered granules with a predominantly transparent brucite analogue crystalline phase, typical of $\beta\text{-Ni}(\text{OH})_2$. It also exposes rough textures and uneven aggregation, indicating increased oxide concentrations on the Ni surface. The presence of nickel (Ni) and oxygen (O), as well as calcium (Ca) impurities arising from the chemical precipitation process, is confirmed by energy-dispersive X-ray spectroscopy (EDX). An investigation of particle size distribution indicates an average particle size of 2.0 μm . The results of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) indicate a reduction in Ni concentrations, with recorded values of 62.7 g/L in the pregnant leach solution, 0.8 g/L in the precursor solution, and 0.501 g/L in the solid precipitate (cake). The copper loading efficiency is measured to be 79%, accompanied by a nickel loss of 9.73% and a nickel recovery rate of around 90.27%. This effective separation process demonstrates a cost-efficient and environmentally responsible method for recycling nickel from acidic chloride media, underlining the broader potential for nickel reuse in industrial processes.

This study conducts a comparative analysis of nickel oxide (NiO) that is derived from fire assay nickel sulphide (FA-NiS) and produced through chemical precipitation and sol-gel methods. The focus is on the structural, morphological, and sensing properties of the NiO. This research is significant in that it is the first to report on the application of NiO synthesised from waste materials for volatile organic compound (VOC) sensing. The primary goal is to clarify the distinctions in properties between NiO obtained through these methods and evaluate their

suitability for environmental sensing applications. Nickel was initially extracted from the raffinate using 5,8-diethyl-7-hydroxydodecan-6-oxime. Subsequently, nickel hydroxide ($\text{Ni}(\text{OH})_2$) was precipitated with lime ($\text{Ca}(\text{OH})_2$) at pH levels of 2.5 and 6.5. The hydroxide was subsequently transformed into NiO through a thermal treatment process. The presence of nickel and oxygen at pH 6.5, as well as iron, nickel, and oxygen at pH 2.5, was verified through the use of scanning electron microscopy (SEM)-energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). In both the sol-gel and chemical precipitation procedures, the X-ray diffraction (XRD) analysis demonstrated a cubic crystal structure with high average crystal sizes of 39-41 nm. The sol-gel process resulted in homogenous spherical particles, as evidenced by SEM imaging, whereas chemical precipitation resulted in aggregated layered grains. It is important to note that NiO precipitated at pH 2.5 exhibited coalesced hexagonal particles with a substantial amount of nickel and iron. The transition from nickel hydroxide to nickel oxide is essential because NiO is highly effective for VOC sensing due to its semiconductor properties. The study highlights the importance of utilising NiO in the detection of volatile organic compounds (VOCs) and the impact of each synthesis method on the material's sensory capabilities.

Using certified reference materials, analytical methodologies, such as inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray fluorescence (XRF), demonstrated high-purity NiO (approximately 75%) with a low relative standard deviation (RSD <0.05%) and 90% recovery. The CRM AMIS 56 and SARM 33 were analysed alongside the samples to ensure reliable results were reproducible. Even at the lowest concentration of 1.5 ppm, NiO derived from fire assay waste demonstrated unambiguous sensing responses at 25°C and 150°C, with recovery times of 80 and 120 seconds, respectively. The potential of NiO from fire assay waste as an intriguing candidate for VOC sensing applications under ambient conditions was indicated by the highest response ($R_g/R_a = 1.198$ for 45 ppm ethanol) observed at 150°C. The findings in paper IV highlight the suitability of nickel oxide synthesized from different methods for environmental sensing applications, particularly in volatile organic compounds detection.

In Paper V, the focus is on the removal and characterization of impurities from pregnant nickel solutions at various pH levels, with an emphasis on enhancing nickel recovery and sustainable resource management. Lime is used as a precipitation agent to target impurities such as iron, lead, tin, manganese, and copper. The study employs inductively coupled plasma optical emission spectrometry (ICP-OES) to quantify and characterize these impurities. The objectives include improving analytical approaches for detecting trace contaminants, evaluating ICP-OES reliability for quality control, and assessing precipitation efficiency across different pH levels.

Results reveal successful Fe^{3+} precipitation within the pH range of 2.0-3, alongside efficient manganese and copper precipitation at pH 5.5-6 and 4-6, respectively, aligning with established behaviours. The findings emphasise the significance of pH control for optimizing impurity removal from pregnant nickel solution, offering insights for enhancing nickel recovery processes in industrial settings. ICP-OES, supported by standard solutions and certified reference materials (CRMs), demonstrated exceptional linearity with correlation coefficients above 0.9995. The method showed high sensitivity, with detection limits and recoveries of CRM samples consistently within 10%. The study found that precipitation efficiency varies significantly with pH. Nickel (Ni) exhibited reduced precipitation at pH 2.02, with substantial precipitation occurring only at pH 6.5. Manganese (Mn) began precipitating at pH 2, achieving a peak removal efficiency of 98% at pH 6. Copper (Cu) precipitation started at pH 4, with a maximum efficiency of 99.3% between pH 4 and 6. Iron (Fe^{3+}) was efficiently removed at pH 2.0-3.0.

Significant variations in contaminant concentrations were observed, influenced by pH and precipitation agents. Fe^{3+} was removed with 100% efficiency at pH 2.5, while Cu precipitation was highly effective (99.3%) between pH 4 and 6. The decrease in Ni concentration at pH 2.02 was attributed to interactions with other metals rather than direct Ni precipitation. SEM revealed the morphology of the precipitates, showing a cauliflower-like structure for $\text{Ni}(\text{OH})_2$ at pH 6.5 and the EDX confirmed the elemental composition of the precipitates, including Fe, Cu, Ni,

Sn, Si, Al, Cl, Ca, and hydroxyl groups (OH), highlighting the presence of impurities precipitated at pH 2.5. This research highlights the effectiveness of ICP-OES and EDX in trace impurity analysis and provides insights into optimizing precipitation processes, contributing to better recycling strategies and quality control in nickel processing and battery-grade materials. The study found that β -Ni(OH)₂ precipitated optimally at pH 6.5, with a recovery rate of approximately 90.27% and minimal copper (79% loading efficiency) and iron impurities. Lime precipitation effectively removed Fe³⁺ at pH 2.5 and Cu between pH 4 and 6, with high removal efficiencies. Analytical methods such as EDXRF and FAAS, when calibrated, provided accurate results for trace elements, though discrepancies were noted for certain elements. The advancements in extraction and purification techniques, coupled with improved analytical methods and the novel application of NiO in VOC sensing, contribute significantly to the field of nickel recovery and processing. This research supports sustainable recycling practices and enhances the practical utility of recovered nickel, advancing both industrial applications and waste management strategies. Overall, this thesis contributes to advancing the understanding of impurity removal processes in nickel recovery and underscores the importance of precise control and characterization techniques in industrial applications.

PUBLICATIONS AND MANUSCRIPTS

The candidate author's contribution to the listed manuscripts spearheaded all aspects of the research process, from proposal, objectives, planning and executing experiments to interpreting data and manuscript writing and revisions. This included chemical precipitation, extraction, chemical analysis, and interpretation. Co-authors contributed by providing feedback and suggestions for manuscript improvements, while the principal author implemented these suggestions.

PUBLICATIONS

1. **Happy Mothepane Mabowa**, Andile Mkhohlakali, Sam Mokoena, James Tshilongo, and Luke Chimuka (2024). *Removal of Nickel from Nickel Sulfite-Fire Assay Dissolution Filtrate Through Precipitation*. ACS Omega, 9 (5), 5592-5600 <https://doi.org/10.1021/acsomega.3c07623>., **Published**.
2. **Happy Mothepane Mabowa**; Luke Chimuka; James Tshilongo (2024). *Elemental Analysis for Synthetic Battery-Grade Cathode Liquor*. NCSLI Measure, The Journal of Measurement Science. **Manuscript Accepted for publication**.
3. **Happy Mothepane Mabowa**; Andile Mkhohlakali; Luke Chimuka; James Tshilongo (2024). *A comparative study of sol-gel process and chemical precipitation of NiO from fire assay waste: Structural characterization and insights into VOCs sensing application*. Journal of Environmental Chemical Engineering. 16, 100531, doi.org/10.1016/j.envadv.2024.100531 **Published**.
4. **Happy Mothepane Mabowa**; Andile Mkhohlakali; James Tshilongo; Luke Chimuka (2024). *Separation and Characterisation of Nickel Hydroxide from Waste Solution using Ca(OH)₂ Precipitation In Chloride Media*. Separations, 11(4), 96; <https://doi.org/10.3390/separations11040096>., **Published**.

5. **Happy Mothepane Mabowa**; Andile Mkhohlakali; Sam Mokoena; James Tshilongo; Luke Chimuka. *Optimization of Impurity Removal from Pregnant Nickel Solution Using Lime Precipitation: pH Control and Analytical Characterization.*, 2024. **Manuscript Submitted, under review**

6. **Mabowa, M.H**; Mkhohlakali, A; Tshilongo, T; Chimuka, L (2024). *Separation and Characterisation of Nickel Hydroxide from Waste Solution using $\text{Ca}(\text{OH})_2$ Precipitation In Chloride Media*. Prime Archives in Chemistry: 3rd Edition. **Published.**

CANDIDATE CONTRIBUTION TO ARTICLES

1. Andile Mkhohlakali, Tien-Chien Jen, Kabelo Ledwaba, Sivuyisiwe Mapukata, **Mothepane Happy Mabowa**, Mokgehle R Letsoalo, Napo Ntsasa and James Tshilongo (2024). *Influence of surfactant on sol-gel-prepared TiO_2 : characterization and photocatalytic dye degradation in water*. *Journal: Frontiers in Chemical Engineering, section Environmental Chemical Engineering*. Candidate contribution: involved in conceptualizing the idea, did experiments, analysed the data, and wrote the review. Sec. Environmental Chemical Engineering, 6, <https://doi.org/10.3389/fceng.2024.1352283>.

2. Rerani, Vhonani and **Mabowa, Mothepane Happy** and Wagner Nicola (2024). Characterisation of Rare Earth Element-Bearing Mineral Phases Present in South African Coal Ash Using Mineral Liberation Analysis. Candidate contribution: conceptualised the design of experiments, wrote the manuscript, analysis of results, supervised, and revision of the manuscript. *Fuel*, 368(4):131661, <https://doi.org/10.1016/j.fuel.2024.131661>.

3. Nehemiah Mukwevho, Napo Ntsasa, Andile Mkhohlakali, **Happy Mothepane Mabowa**, Luke Chimuka, Mokgehle Refiloe Letsoalo (2024). The Impact of Induced Industrial and Urban Toxic Elements on Sediment Quality. *Water*. 16(17), 2485, DOI:10.3390/w16172485.

CONFERENCE OUTPUTS

1. **Mabowa, M.H;** Tshilongo, J; Chimuka, L (2021). Elemental analysis for battery-grade cathode liquor. Test and Measurements. 25-26 October, Virtual, South Africa.
2. **Happy Mothepane Mabowa;** James Tshilongo; Luke Chimuka (2024). The separation of valuable metals from PGE waste filtrate extracted using a hydrometallurgical technique, 10-14 March, Drakensburg, South Africa.
3. **Happy Mothepane Mabowa,** Andile Mkhohlakali, James Tshilongo, Luke Chimuka (2024). From Fire Assay Nickel Sulfite Collection Waste to Nickel Hydroxide, ALTA2024, Perth Australia.
4. **Happy Mothepane Mabowa,** Andile Mkhohlakali, James Tshilongo, Luke Chimuka (2024). From Fire Assay Nickel Sulfite Collection Waste to Nickel Hydroxide, SAIMM 2nd Battery Materials, 2024, Mpumalanga South Africa.

OTHER RESEARCH OUTPUTS

1. Wagner, N.J, Rerani, V.P., Biswas, S., **Mabowa, M.H,** Baiyenguni, C. The occurrence of rare earth elements in South African coal ash: identification and characterisation. WOCA 2024, Grand Rapids, Michigan. Candidate contribution: Design experiments and wrote the manuscript. Co-authors helped with the analysis of results and revision of the manuscript.

TABLE OF CONTENTS

DECLARATION	I
DEDICATION	II
ACKNOWLEDGEMENTS	III
ABSTRACT	V
PUBLICATIONS AND MANUSCRIPTS	XIII
TABLE OF CONTENTS	XVI
LIST OF FIGURES	XVIII
LIST OF TABLES	XIX
LIST OF ABBREVIATIONS	XX
CHAPTER ONE: INTRODUCTION	1
1.1 BACKGROUND AND MOTIVATION	2
1.2 NICKEL HYDROXIDE RE-DISSOLUTION IN H ₂ SO ₄	5
1.3 STATEMENT OF PROBLEM	6
1.4 THESIS OUTLINE AND FRAMEWORK	7
CHAPTER TWO: LITERATURE REVIEW	11
2.1 THE ROLE OF NICKEL IN RESOURCE RECOVERY AND ITS TRANSITION TO BATTERY-GRADE NICKEL SULFATE	12
2.1.1 <i>Nickel as a Vital Contribution for the Revolution of an Electric Vehicle Lithium-Ion Batteries (LIB)</i>	14
2.1.2 <i>Purifying the Power: Revealing the Science Behind High-Purity Nickel Sulphate for State-of-the-Art Batteries</i>	Error! Bookmark not defined.
2.1.3 <i>The Quest for Purity: Overcoming Challenges in High-Purity Nickel Sulphate Production</i>	21
2.1.4 <i>Unveiling the Role of Nickel Sulphate in Cathode Development for Lithium-ion Batteries</i>	Error! Bookmark not defined.
2.2 IGNITING THE FORGE: FIRE ASSAY TECHNIQUES UNRAVELLING THE MYSTERIES OF PLATINUM GROUP METALS	21
2.2.1 <i>The Analytical Techniques for Pre-Concentration of Platinum Group Elements in Ores</i>	21

2.2.2	<i>Forging the Future: Harnessing the Ancient Art of Fire Assaying for Precious Metal Extraction</i>	Error! Bookmark not defined.
2.2.3	<i>Re-forging the Future: Recycling Resources for Sustainable Battery Manufacturing</i>	23
2.3	TRANSFORMING COPPER MINING: THE EVOLUTION OF SOLVENT EXTRACTION TECHNIQUES	23
2.4	CHEMICAL PRECIPITATION: HARNESSING CRYSTALLIZATION FOR METAL RECOVERY	25
2.4.1	<i>Unlocking Nickel's Potential: The Power of Hydroxide Precipitation</i>	26
2.4.2	<i>Conquering Iron: Strategies for Effective Precipitation</i>	28
2.4.3	<i>The oxidation of iron results in the precipitation</i>	29
2.5	AN OVERVIEW PROCESS AND APPLICATION OF SOL-GEL METHODS	29
2.6	THE ROLE OF METAL OXIDE SEMICONDUCTORS IN DETECTING VOLATILE ORGANIC COMPOUNDS (VOCs)	30
CHAPTER THREE: RESEARCH OBJECTIVES AND APPROACH		43
3.1	INTRODUCTION - JUSTIFICATION OF THE STUDY	44
3.2	AIM OF THE STUDY	44
3.3	HYPOTHESIS	45
3.4	RATIONALE OF THE STUDY	45
3.5	RESEARCH OBJECTIVES	46
3.6	RESEARCH APPROACH	47
3.7	INTERPRETATION OF DATA AND QUALITY CONTROL	48
CHAPTER FOUR: PUBLICATION AND MANUSCRIPTS		51
4.1 PAPER I		52
4.2 PAPER II		82
4.3 PAPER III		122
4.3 PAPER IV		144
4.5 PAPER V		170
CHAPTER FIVE: CONCLUSION AND RECOMEDATIONS		187
5.1	CONCLUSION	188
5.2	RECOMMENDATIONS	190
APPENDIX : SUPPORTING INFORMATION FOR PAPER I-V		192

LIST OF FIGURES

Figure 2.1: Solid nickel (II) sulphate hexahydrate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ crystals (Mabowa et al., 2024)	12
Figure 2.2: Schematic map of the Bushveld Complex in South Africa (Ikaneng, 1997-2006)	13
Figure 2.3: Schematic diagram of the electrolyte solution used for electroless nickel plating on super duplex stainless steel SAF2507 (Byung-Hyun, 2024)	17
Figure 2.4: a) Chemical structure for 5,8-diethyl-6-hydroxy-7-oximinododecane; b) 2-hydroxy-3-chloro-5-tert-nonylbenzophenone	25

LIST OF TABLES

Table 2.1: Nickel specifications for battery-grade sulphate.....	16
---	----

LIST OF ABBREVIATIONS

AAS	Atomic absorption Spectroscopy
BES	Battery energy storage
BEV	Battery-powered electric vehicle
BMR	Base metal refinery
CRM	Certified reference material
EDXRF	Energy Dispersive X-ray –fluorescence
EtoH	Ethanol
EV	Electric vehicle
FA	Fire assay
FAAS	Flame atomic absorption Spectroscopy
FTIR	Fourier-transform infrared spectroscopy
ICE	International combustion engine
ICP-OES	Inductively coupled plasma optical emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
IX	Ion exchange
LIB	Lithium-ion battery
LME	London metal exchange
LOD	Limit of detection
LOQ	Limit of quantification
NiCd	Nickel cadmium
NiMn	Nickel manganese
NiS-FA	Nickel sulphate fire assay
NPI	Nickel pig ion
PGE	Precious group element
PGM	Precious group metal
PLS	Pregnant leach solution
PWS	Pregnant waste solution

SEM	Scanning electron microscopy
SX	Solvent extraction
TEM	Transmission electron microscopy
VOC	Volatile organic compound
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffractometer
XRF	X-ray fluorescence

CHAPTER ONE: INTRODUCTION

This chapter introduces the technological advancements aimed at enhancing the purity of battery-grade nickel sulfate. It also gives background and motivation for the research. A brief introduction to nickel sulphate categories is given addressing limitations, related with impurities. The concise synopsis of the concerns that require explanation is provided.

1.1 Background and Motivation

Nickel (Ni) is an essential metal widely used in the production of stainless steel, generation of renewable energy technologies, and especially in the fabrication of batteries. Nickel's anti-corrosion properties are crucial in various industries. It prevents oxidation in stainless steel, making it essential for kitchenware and medical tools. Ni-copper (Cu) alloys are used in marine applications to protect against saltwater corrosion. Additionally, Ni's corrosion resistance benefits energy sectors, particularly in nuclear reactors and renewable energy storage systems, ensuring reliability and longevity. The growing need for high-purity nickel sulphate (NiSO_4) is fuelled by its crucial function in manufacturing ultra-efficient lithium-ion batteries for electric vehicles (EVs) and energy storage systems (Berckmans et al., 2017; ADB, 2018; EEA, 2016). The aforementioned request emphasises the necessity of resolving possible deficiencies of essential minerals such as Ni, which are expected as a result of imbalances between supply and demand (EEA, 2016).

In response to these challenges, stricter environmental regulations and a focus on resource conservation highlight the need for advanced refining technologies capable of economically processing Ni-containing waste streams. Effective recovery of Ni from these sources demands innovative extraction and refining techniques. Additionally, the development of advanced analytical methods is crucial for accurately assessing purity and ensuring compliance with industry standards. Techniques such as Flame Atomic Absorption Spectroscopy (FAAS) and Energy Dispersive X-ray Fluorescence (EDXRF) are utilised for online monitoring due to their low maintenance costs, affordability, and rapid performance. However, FAAS has limitations in sensitivity and can suffer from burner clogging with saturated samples, while EDXRF may face challenges with complex matrices. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), though offering exceptional sensitivity, can be hindered by intense chemical interferences that can switch off the torch, block the tubing, and contaminate the RF coil. This study aims to explore the feasibility and effectiveness of innovative approaches to extract Ni from unconventional sources within industrial waste streams and to

evaluate novel refining techniques and analytical methodologies. By integrating these advancements, the study seeks to establish a streamlined and sustainable process for producing high-purity battery-grade NiSO_4 , addressing both the increasing demand and environmental stewardship. In addition to recovery methods, purification processes such as solvent extraction (SX) and ion exchange (IX) are crucial for separating Ni from other metal ions, ensuring the high purity needed for battery applications (Berckmans et al., 2017).

In the worldwide Ni industry, South Africa holds a prominent position as a primary producer of high-purity NiSO_4 . The recent establishment of a new \$20 million NiSO_4 refinery in South Africa's Northwest Province marks a significant milestone in the quest for high-purity battery-grade materials (Creamer, 2021). Employing the improved domestic refining capabilities of the country has significantly strengthened its capacity to fulfil the demands of the electric car industry (Creamer, 2021; Friedland, 2017). Nevertheless, obstacles persist in the process of refining Ni from industrial by-products and waste streams. In ore deposits, Ni frequently coexists with platinum group metals (PGMs) and Cu, adding complexity to separation procedures.

The Sherrit® atmospheric matte leach technique produces a basic NiSO_4 solution from the matte of a PGM converter. This solution contains iron (Fe) and cobalt sulphates (CoSO_4), with Fe being an unwanted impurity and cobalt (Co) being a potentially useful by-product if properly isolated (Van Schalkwyk et al., 2011; Thyse et al., 2011). Base Metals Refineries (BMRs) at Western Platinum Limited, Northam Platinum, Zimplats, and Impala Platinum Limited use a modified version of the Sherrit® industrial process. In this approach, the matte undergoes partial dissolution, during which Cu precipitates via cementation and metathesis processes. The procedure results in the formation of a solid residue and a concentrated NiSO_4 solution that contains significant quantities of Ni, Co, Fe, and a small amount of sulphur (Dorfling et al., 2011). The objective of this study is to assess the efficacy of solvent extraction and precipitation methods to purify impurities and analytical methods for the determination of elements such as Cu, Fe, manganese (Mn), lead

(Pb), chlorine (Cl), and magnesium (Mg) in order to improve the purity of the NiSO_4 product derived from fire assay.

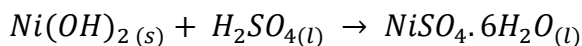
FAAS, EDXRF and ICP-OES are essential analytical techniques for evaluating these pollutants. Despite its cost-effectiveness, FAAS has limitations in sensitivity for identifying minute contaminants in matrices with large concentrations as well as burner clogging with saturated samples. For instance, FAAS might struggle to accurately measure trace levels of impurities like lead (Pb) or manganese (Mn) if their concentrations are close to the saturation point of the sample, leading to potential inaccuracies in result. In contrast, ICP-OES offers exceptional sensitivity and the capacity to analysis several elements concurrently, rendering it more appropriate for demanding purity criteria (Yahorava et al., 2016). The significance of accurate analytical methods in guaranteeing the utmost purity of NiSO_4 is emphasised by this comparison. Effective impurity management remains a challenge, requiring precise preconcentration to meet industry standards (Mabowa et al., 2024). Metal impurities, such as Cu, Fe, Mn, Pb, chlorine (Cl), and Mg, must be removed at distinct stages of the purification process. The detection and quantification of these low-level metal impurities, often present in concentrations of less than 5 mg/L in high-purity solutions above 20%, demand reliable analytical methods to ensure product quality and market compliance (Yahorava et al., 2016; Kgarira et al., 2016).

In addition to battery production, Ni's adaptability also applies to technologies such as catalysts and ethanol sensors. Nickel hydroxide (Ni(OH)_2), an essential constituent in lithium-ion batteries with advanced performance, also exhibits promise in various additional uses (Chen et al., 1999). Advancements in hydroxide-based precipitation techniques for extracting Ni from waste streams emphasise their environmental advantages and economic viability (Asokbunyararat et al., 2017). Yet, attaining a high level of purity in the manufacturing of NiSO_4 , especially in eliminating contaminants such as magnesium (Mg) and calcium (Ca), continues to be challenging (Mabowa et al., 2024).

It is imperative to tackle these issues not just to satisfy the growing need but also to promote environmental sustainability. Incorporating analytical techniques and novel refining methods can help develop environmentally friendly methods for producing high-purity NiSO_4 (Institute, 2016). These advancements are in line with the overarching objective of promoting a circular economy, in which Ni is recycled and repurposed, therefore minimising environmental burden and maximising resource utilisation.

1.2 Nickel hydroxide re-dissolution in H_2SO_4

In the pursuit of developing high-purity battery-grade nickel sulfate, a critical step is the efficient re-dissolution of nickel hydroxide (Ni(OH)_2) in sulfuric acid (H_2SO_4) at controlled conditions. This process not only ensures the production of nickel sulfate (NiSO_4) with desired concentration but also facilitates the accurate determination and minimization of trace impurities. An experiment was performed at a temperature of 70°C to establish the ideal amount of sulfuric acid required to dissolve Ni(OH)_2 and create a solution containing approximately 62.7 g/L of NiSO_4 with a pH range of 5.2-5.5. At first, 60% of the required amount of sulfuric acid, calculated based on the nickel content of the wet cake, was added. However, only a partial dissolution occurred, thus more increments of sulfuric acid were needed. Full dissolving was accomplished at around 100% of the stoichiometric demand, and throughout this procedure, the pH decreased significantly from 6.2 to 2.3. To achieve the desired pH range, a tiny quantity of Ni(OH)_2 was reintroduced into the solution while keeping the temperature at 70°C and assuring vigorous stirring. The implementation of this optimised re-dissolution process is crucial in order to achieve the production of NiSO_4 with a high level of purity. This is critical for minimising the presence of any trace contaminants in the battery-grade material. Exacting management of these procedures guarantees the creation of a NiSO_4 solution that satisfies the rigorous quality criteria necessary for sophisticated battery uses, where even slight contaminants can have a substantial effect on performance and longevity. Equation 1 was used to calculate amount of acid required:



1

1.3 Statement of Problem

The production of high-purity $NiSO_4$ faces several challenges, primarily related to maintaining stringent purity standards crucial for optimal battery performance. Key issues include managing impurities from various sources, ensuring analytical sensitivity for trace contaminants, and establishing rigorous quality control procedures (Bourcier et al., 2016; Sangwal, 2007). Battery-grade $NiSO_4$ must meet strict purity as tabulated in Table 2.1, the criteria to avoid compromising battery efficiency, necessitating thorough control over impurities during synthesis, processing, and raw material acquisition, particularly targeting heavy and alkali metals.

Conventional analytical methods such as FAAS, EDXRF, and ICP-OES may lack the precision needed to detect trace impurities at required levels. ICP-OES offers high sensitivity and a broad detection range, making it suitable for complex matrices and trace analysis. FAAS is effective but has lower detection thresholds and can face interference issues (Mullin, 2001; Davey et al., 1997). FAAS is limited by its sensitivity and can encounter issues with burner clogging in saturated samples, which hinders its ability to detect trace contaminants at the low levels required for high-purity $NiSO_4$. Similarly, while EDXRF is efficient for real-time analysis, it may not offer the precision needed for detecting very low concentrations of certain impurities. Selecting the appropriate technique depends on the required sensitivity and accuracy for $NiSO_4$ production. Effective quality control involves standardized testing and continuous monitoring to balance high purity with cost-efficiency and scalability. These limitations in detection sensitivity and analytical performance underscore the need for advanced methods capable of reliably identifying and quantifying trace impurities at levels below 5 mg/L.

Addressing these challenges requires a multidisciplinary approach integrating advancements in separation, analytics, quality assurance, and manufacturing.

Sustainability goals necessitate reducing waste, energy consumption, and environmental impact during NiSO_4 production (Institute, 2016). Purification of Ni(OH)_2 is essential for ensuring the high quality of the final NiSO_4 product.

Crystallization, the final stage in hydrometallurgical processing, forms solid crystals from a supersaturated solution. Impurities such as Na, Cl, and Mg can affect solubility and crystal properties, influencing the transition from metastable to stable phases (Sangwal, 2007). Understanding the effects of impurities on crystallization is vital for improving product purity and quality. For instance, L-glutamic acid can hinder phase stability, highlighting the importance of kinetic factors in the crystallization process (Davey et al., 1997).

1.4 Thesis Outline and Framework

The thesis is divided into various chapters:

Chapter One

The general introduction, problem statement and project justification are briefly discussed.

Chapter Two

This chapter provides a comprehensive exploration of nickel sulphate and nickel hydroxide covering their origin, applications, extraction methods, and determination challenges. The insights into the sources of these compounds, their diverse industrial uses, and the various techniques employed to extract them. Additionally, the chapter delves into the analytical challenges associated with determining the elemental composition of nickel sulphate and nickel hydroxide, including discussions on sample preparation issues and the impact of matrix effects on accurate analysis. Through a structured approach and detailed examination of the relevant literature on these important compounds, their production processes, and the analytical considerations involved.

Chapter Three

The research objectives and approach are presented in this section.

Chapter Four

This chapter includes a collection of five manuscripts that have been produced from this work.

Paper I

In this paper, the Removal of Nickel from Nickel Sulfite-Fire Assay (NIS-FA) Dissolution Filtrate through Precipitation is reported.

Paper II

In this paper, the applicability of atomic absorption spectroscopy for trace analysis elements in high nickel purity is investigated.

Paper III

In this paper, the synthesis and characterization of nickel hydroxide from waste solution using Ca(OH)_2 precipitation from chloride media is described.

Paper IV

In this paper, a comparative study of sol-gel prepared, and solvent extracted NiO from fire assay waste: Structural characterization and insights into VOCs sensing application is reported

Paper V

The optimization of impurity removal from pregnant nickel solution: pH-controlled lime precipitation and analytical characterization is reported in this paper.

Chapter Five

The overall conclusion is given, and recommendations are presented in this chapter

REFERENCES

- ADB. (2018, December). *Handbook on Battery Energy Storage System*. Mandaluyong: Asian Development Bank. doi: <http://dx.doi.org/10.22617/TCS189791-2>
- Asokbunyarat, V., Lens, P., & Annachhatre, A. (2017). *Permeable Reactive Barriers for Heavy Metal Removal* (Vol. 1).
- Berckmans, G., Messagie, M., Smekens, J., Omar, N., Vanhaverbeke, & Van Mierlo, J. (2017). Cost projection of state of the art Lithium-ion batteries for electric vehicles up to 2030. *Energies*, 10(9), 1314.
- Bourcier, D., Féraud, J., Colson, D., Mandrick, K., Ode, D., Brackx, E., & Puel, F. (2016). Influence of particle size and shape properties on cake resistance and compressibility during pressure filtration. *Chemical Engineering Science*(144), 176-187.
- Chen, J., Bradhurst, D., Dou, S., & Liu, H. (1999). Nickel hydroxide as an active material for the positive electrode in rechargeable alkaline batteries. *Journal of the Electrochemical Society*, 146(10), 3606–3612.
- Choi, K., & Azimi, G. (2023, September 27). Crystallization of nickel sulfate and its purification process: towards efficient production of nickel-rich cathode materials for lithium-ion batteries. *RCS Advances*, 13(41), 28501–28512.
- Creamer, M. (2021). Thakadu commissions nickel sulphate refinery. North West, South Africa.
- Darnley, A. (1995). *A Global Geochemical Database for Environmental and Resource Management: Recommendations for International Geochemical Mapping*. UNESCO, IGCP Project 259. Paris: Earth Sciences .
- Davey, R., Blagden, N., Potts, A., & Docherty, R. (1997). Polymorphism in Molecular Crystals: Stabilization of a Metastable Form by Conformational Mimicry. *Journal of the American Chemical Society*(119), 1767-1772.
- EEA. (2016). *Electric Vehicles in Europe*. Copenhagen: European Environment Agency.
- Friedland, R. (2017). Clean TeQ investor presentation . *Mining Indaba: Investing in african mining conference* (pp. 18-21). Cape town: Clean TeQ investor.

- Institute, N. (2016). The life of Ni Nickel Institute, [Online]. Retrieved from <https://nickelinstitute.org/media/1190/thelifeofni>.
- Kgaria, M., Yahorava, O., & Sehlola, C. (2016). *Thakadu Flowsheet Development*. Randburg: Mintek.
- Mabowa, M., Mkhohlakali, A., Mokoena, S., Tshilongo, J., & Chimuka, L. (2024). Removal of Nickel from Nickel Sulfite-Fire Assay Dissolution Filtrate Through Precipitation. *ACS Omega*, 9 (5), 5592-5600. doi:10.1021/acsomega.3c07623
- Mullin, J. (2001). Crystallization. (Elsevier, Ed.) *Science*, 280-284.
- Sangwal, K. (2007). *Additives and Crystallization Processes: From Fundamentals to Applications*. Hoboken, New Jersey: John Wiley & Sons.
- Yahorava, O., Bazkho, O., Kgaria, M., Mottay, R., & Sehlolo, C. (2016). *Evaluate removal of impurities from LONMIN nickel sulphate solution*. Randburg: Mintek.

CHAPTER TWO: LITERATURE REVIEW

This chapter provides a literature review, starting with the pivotal role of $(\text{NiSO})_4$ in enhancing cathode performance for lithium-ion batteries, which is essential for the competitiveness of battery electric vehicles. It focuses on the importance of nickel recovery from industrial waste streams, particularly through innovative refining techniques aimed at producing battery-grade $(\text{NiSO})_4$. The discussion highlights the significance of preconcentration methods in optimizing nickel extraction from waste sources, which is essential for supporting the growing demand for sustainable battery production. Techniques such as solvent extraction and chemical precipitation are reviewed as efficient preconcentration steps for improving the purity and yield of nickel during the recovery process. Lastly, the chapter explores the role of hydroxide precipitation in the synthesis of $\text{Ni}(\text{OH})_2$, a vital precursor in the production of rechargeable batteries. In addition, it addresses the importance of managing impurities such as iron through controlled precipitation to ensure the purity and quality of nickel compounds during recovery. This focus on refining processes aligns with the overarching objective of sustainable resource management in battery manufacturing.

2.1 The Role of Nickel in Resource Recovery and its Transition to Battery-Grade Nickel Sulfate

Nickel (Ni), the fifth most abundant element (AE) in Earth's crust, finds application in over 300,000 products (Stopic & Friedrich, 2016). Incorporating cathode materials like lithium nickel manganese cobalt oxide (Li-NMC), which is commonly used in lithium-ion batteries (LIB) for mobile devices and electric vehicles (EVs), serves as the positively charged component of the cathode. Nickel (II) sulphate usually refers to the inorganic compound with the formula $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (nickel sulphate hexahydrate) whose typical appearance is depicted in Figure 2.1. This highly soluble blue-coloured salt is a common source of the nickel ion (Ni^{2+}) for electroplating.



Figure 2.1: Solid nickel (II) sulphate hexahydrate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ crystals (Mabowa et al., 2024)

Geologically, nickel is found in two primary forms: sulphides and laterite minerals. Sulphide deposits, primarily located in Australia, Canada, Russia, and South Africa, are typically accessed through underground mining. In contrast, laterite deposits, distributed across regions such as Western Australia, Indonesia, Cuba, Colombia, New Caledonia, Venezuela, Brazil, and the Dominican Republic, are found closer

to the surface. These laterite deposits consist mainly of nickeliferous limonite, $(\text{Fe,Ni})\text{O}(\text{OH}) \cdot n\text{H}_2\text{O}$, and garnierite, $(\text{Ni,Mg})_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$, which together account for 60% of the global nickel reserve base. Magmatic sulphide deposits, which occur in magmatic settings, contain pentlandite $(\text{Ni,Fe})_9\text{S}_8$, a highly sought-after ore due to its higher nickel content and easier extractability (Butt & Cluzel, 2013; Dalvi et al., 2004). Most of these resources are extracted by open pit mining methods (Ikaneng, 1997-2006). These differences affect the global Ni supply chain, highlighting the importance of sourcing strategies, cost considerations, and sustainability challenges in meeting growing demand for Ni in industries like electric vehicle batteries and renewable energy. The geographic location of the Bushveld Complex in South Africa, a significant source of sulphide deposits, is depicted in the map inset in Figure 2.2.

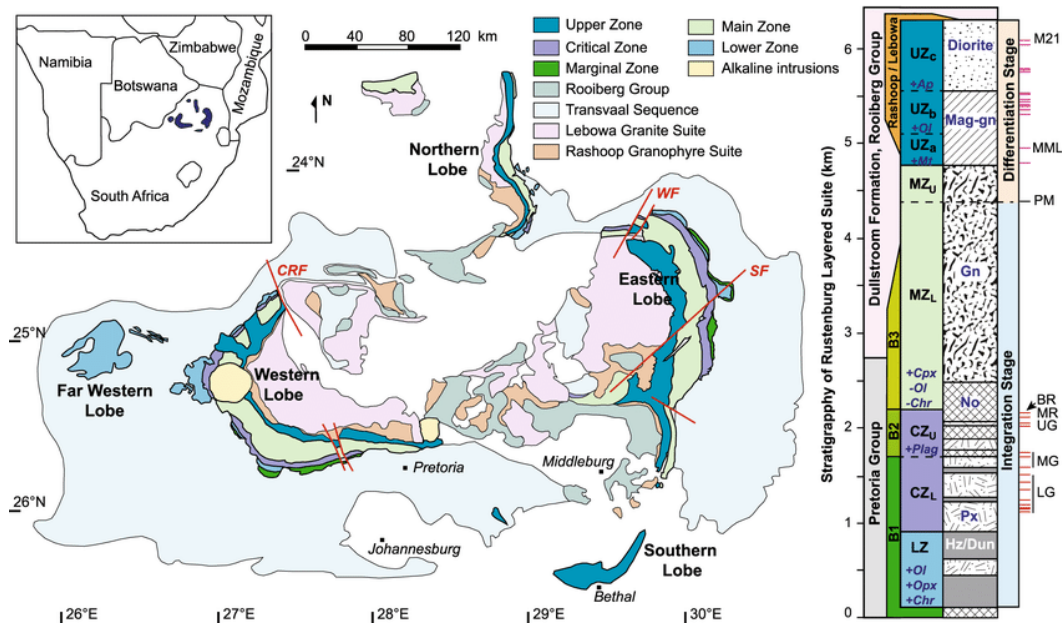


Figure 2.2: Schematic map of the Bushveld Complex in South Africa (Ikaneng, 1997-2006)

It is imperative to concentrate on the particular types of Ni utilised in advanced applications due to the uneven distribution of Ni resources throughout the world and the differences in their extraction techniques. To meet the criteria for battery-grade Ni, which is necessary for producing NMC cathode materials, nickel sulphate hexahydrate $(\text{NiSO}_4 \cdot 6\text{H}_2\text{O})$ is commonly used (Ma et al., 2020; Jung et al., 2021;

Agatzini et al., 2009). Following that, the refined product is subjected to a series of chemical treatments, one of which is the utilisation of sulphuric acid (H_2SO_4). Battery performance, safety, and longevity can be negatively impacted by trace impurities, which must be removed by the chemical treatment procedure. Also, it improves the battery's electrochemical characteristics, which means it will always be reliable and of high quality. Chemical treatments are also required to achieve the required purity levels to comply with strict regulatory criteria. In line with the issue description and general research objectives, the research seeks to establish a sustainable and efficient process for generating battery-grade nickel sulphate by attending to these aspects. This delves into the degrees of each step in the extraction and refining process, shedding light on the complexities involved in obtaining NiSO_4 for use in cutting-edge battery technologies. The solution containing NiSO_4 is further processed through crystallization, separation, washing, and drying steps to obtain the final product. Throughout this production journey, stringent quality control measures are implemented to ensure the end product meets the demanding standards required for its use in high-performance batteries. The general concept revolves around transforming raw Ni resources into a purified form suitable for advanced technologies, with a focus on achieving the utmost quality for optimal battery performance.

2.1.1 Nickel as a Vital Contribution for the Revolution of an Electric Vehicle Lithium-Ion Batteries (LIB)

In the evolution of LIBs, particularly for EVs, Ni plays a pivotal role (Institute Nickel, 2021). As a crucial component in the cathode of LIBs, Ni significantly enhances the performance, energy density, and overall efficiency of EV batteries. The shift towards nickel-rich cathode formulations, such as Nickel Cobalt Manganese (NCM) and Nickel Cobalt Aluminum (NCA), highlights Ni's importance in optimizing battery chemistry (Institute Nickel, 2021). This transition enables higher energy storage capacity, allowing EVs to achieve longer ranges on a single charge. Additionally, the relative abundance and lower cost of Ni compared to Co make it an economically viable choice, contributing to the scalability and

affordability of EVs. Moreover, the versatility of Ni in various cathode compositions supports efforts to reduce reliance on Co, addressing environmental and ethical concerns associated with Co mining. Ongoing research and development underscore Ni's crucial role in advancing sustainable and high-performance battery technologies, which are essential for the widespread adoption of electric mobility.

The rapid growth of EVs and energy storage systems has led to a significant increase in the demand for nickel sulfate (NiSO_4). As battery manufacturers enhance the energy density of their products by increasing the Ni ratio in cathodes, the demand for NiSO_4 is expected to grow by 25% annually over the next nine years (Fraser et al., 2021). However, the specifications for the purity of battery precursor materials, such as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, are stringent and vary globally, affecting capital and operating costs for pre-treatment and crystallization plants (Fraser et al., 2021).

According to Ma et al. (2020), the hydrometallurgical process for producing high-purity NiSO_4 involves several key stages: pretreatment, acid leaching, separation/purification, and crystallization. This intricate process begins with the extraction of nickel from various ores, including sulfide and laterite types. The extracted nickel then undergoes refining to remove impurities, followed by a series of chemical treatments with sulfuric acid (H_2SO_4). Each of these steps requires precise control and optimization to ensure the production of high-purity NiSO_4 . The detailed procedures involved in each stage ranging from the initial ore processing to the final crystallization highlight the complexity of obtaining NiSO_4 for advanced battery technologies. This thorough approach ensures that the final product meets the stringent quality standards necessary for high-performance lithium-ion batteries (ADB, 2018).

The production of batteries necessitates the use of exceptionally pure raw materials, leading suppliers to develop specialized treatment methods to meet strict purity requirements as indicated in Table 2.1. Standards for contaminants are consistently rigorous, and deviations are not acceptable (VanDeventer & McDevitt, 2019).

Table 2.1 illustrates the anticipated impurity levels in battery-grade NiSO_4 solutions, with specifications agreed upon between suppliers and end-users, resulting in some variability.

Table 1.1: Nickel specifications for battery-grade sulphate

Element	Specification mg/L
Nickel, as Ni	> 223000
Cobalt, as Co	≤ 100
Manganese, as Mn	≤ 2
Iron, as Fe	≤ 3
Copper, as Cu	≤ 1
Sodium, as Na	≤ 15
Calcium, as Ca	≤ 4
Magnesium, as Mg	≤ 10
Zinc, as Zn	≤ 3
Lead, as Pb	≤ 5
Chromium, as Cr	≤ 5
Cadmium, as Cd	≤ 1
Aluminium, as Al	≤ 5
Silicon, as Si	≤ 10
Potassium, as K	≤ 10
Chloride, as Cl	≤ 10
Insoluble	≤ 50

Battery-grade NiSO_4 must meet stringent specifications to ensure its efficacy in LIBs. Chemical purity exceeding 99.9% is essential, with strict limits on impurity levels such as Co, Fe, Cu, and Zn, as depicted in Table 2.1. Fine particle size and low moisture content are critical for uniform electrode fabrication and to avoid water-induced reactions. The material should be colorless or light-colored, indicating clarity and the absence of visible impurities. Nickel and sulfate content, expressed as percentages, are key specifications influencing LIB performance. Additionally, the dissolution rate in H_2SO_4 , trace element analysis, and compliance with industry standards ensure the material's suitability for high-performance LIBs, supporting the reliability, safety, and efficiency of electric vehicles and other battery applications.

The composition of LIBs features a stainless steel or Ni-plated casing that encloses the cathode and anode, separated by a separator and immersed in organic

electrolytes. Electroless Ni plating is applied to heat-treated super duplex stainless steel (SDSS) SAF2507, with its behavior over time studied by Byung-Hyun (2024), as illustrated in Figure 2.3. The cathode typically comprises an active material mixed with carbon and a polymeric binder, coated onto an aluminum current collector. The choice of active materials is based on their specific potential and capacity, tailored to the application's needs. In LIBs, NiSO_4 serves as a key precursor, particularly in Ni-rich cathode formulations like NCM and NCA. These formulations enhance LIB energy density, contributing to higher battery capacity and runtime, which are crucial for electric vehicles and portable electronics (Pillot, 2014; Friedland, 2017).

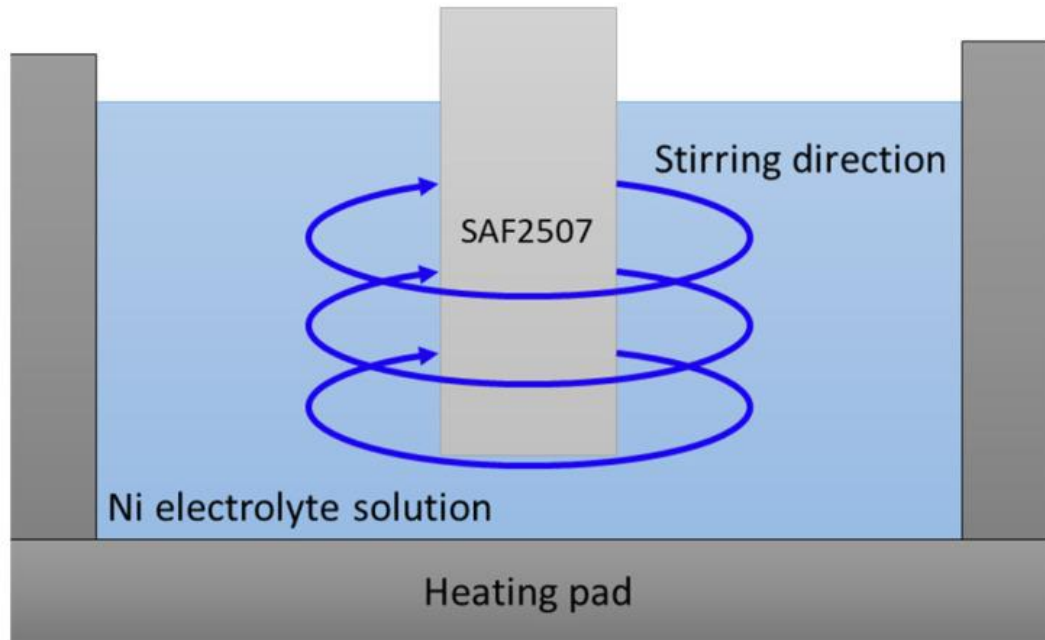


Figure 2.3: Schematic diagram of the electrolyte solution used for electroless nickel plating on super duplex stainless steel SAF2507 (Byung-Hyun, 2024)

In addition to economic benefits, Ni-rich cathodes derived from NiSO_4 offer improved thermal stability, enhancing LIB safety and reliability. They also help reduce dependence on Co, aligning with sustainability goals and addressing ethical concerns related to Co mining (Institute, 2016). Ongoing research continues to refine cathode compositions using NiSO_4 , driving advancements in energy density,

lifespan, and charging capabilities and positioning NiSO_4 as a critical component in the development of sustainable, high-performance LIB technologies.

2.1.2 Precision in Purity with Analytical Approaches to Trace Element Control in High-Quality Nickel Sulfate for Batteries

Numerous elements occur in different matrices at low levels of content, and several of these elements were not detectable by analytical methods for a long time (Bulska & Ruszczyńska). The knowledge about their presence appeared with the development of analytical technology and caused the origin of the term “trace elements.” A new scientific term, "ultra-trace elements," emerged in the second half of the twentieth century as a result of advances in analytical techniques. "Trace elements" are defined by the International Union of Pure and Applied Chemistry (IUPAC) (McNaught & Wilkinson, 1997). Generally, Ultra-trace elements are typically defined as elements present in low concentrations, less than 1 part per billion (ppb) or 0.001 mg/L. These elements are so sparse that they require highly sensitive analytical techniques to detect and measure them accurately. Unlike trace elements, which are present in concentrations ranging from 1 mg/L to 100 mg/L, ultra-trace elements are found in concentrations below 0.001 mg/L, making their accurate analysis crucial for various scientific and industrial applications. This implies that they are present in extremely low quantities and require highly sensitive analytical techniques to detect and measure them accurately.

Understanding trace and ultra-trace elements is crucial across scientific, industrial, and technical fields. These elements, despite their low concentrations, can significantly impact the properties and performance of materials and devices. Accurate measurement of these low-concentration elements is essential, as even small amounts can alter the functionality and safety of products. Therefore, implementing stringent contamination control procedures and ensuring the accuracy of measurements are critical, particularly when using highly sensitive analytical instruments.

The increasing sensitivity of analytical techniques has highlighted concerns about contamination and the challenges in accurately measuring elements present in concentrations as low as parts per billion or less. Errors in trace and ultra-trace elemental analysis often stem from issues in sample collection, storage, preparation, and analysis. To ensure the purity of NiSO_4 , it is vital to consistently verify the precision of analytical results. Kgaria et al. (2016) emphasized the need for thorough monitoring of impurities introduced during the leaching process. Adhering to strict product specifications highlights the importance of accurately determining trace impurities to meet the high standards required for NiSO_4 products used in advanced applications.

The process of purifying and quantifying minute contaminants in high-purity NiSO_4 is a complex and comprehensive procedure that is necessary to maintain the strict quality requirements required for LIB applications. This procedure is essential to guarantee that the NiSO_4 attains the requisite levels of purity necessary for maximum battery performance, safety, and lifetime. Efficient purification methods are essential for eliminating even the tiniest amounts of contaminants that may impact the electrochemical characteristics of LIBs, guaranteeing compliance with industry rules and standards for the final product.. Even at low concentration levels, the impurities, particularly Fe and Mg, shorten the shelf life of the battery considerably due to corrosion. Currently, there is a diverse range of analytical methodologies available that enable the quantification of elemental composition at both trace and ultra-trace concentrations.

Effective sample preparation is crucial for accurate determination of trace elements and contaminants in complex matrices. Prior to instrumental analysis, thorough preparation, including extraction and mineralization, is often required. This is especially important for analyzing LIB, where impurities such as Co, Fe and Cu can significantly impact performance. These contaminants can reduce battery capacity, cycle life, and energy density, and increase self-discharge rates, which in turn affects efficiency and safety (Institute, 2016). The presence of impurities can lead to structural issues and thermal runaway, emphasizing the need for stringent

purification and quality control measures to ensure battery-grade NiSO₄ meets high purity standards.

Researchers employ advanced analytical techniques to measure trace impurities with high sensitivity and precision. Techniques such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), ICP-OES, and Atomic Absorption Spectrometry (AAS) are frequently used (Badocco et al., 2015; Butler et al., 2013). Calibration with standard solutions and quality control samples are critical for maintaining accuracy. Despite their effectiveness, these techniques face challenges due to the complex nature of environmental samples, which may contain significant amounts of soluble solids and inorganic molecules like Ca, K, Na and Mg. This complexity can introduce non-spectral and spectrum interferences, complicating direct analysis.

To address these challenges, sample preparation techniques, such as mineralization and dilution, are employed to minimize interference and prepare samples for analysis. For instance, Butler et al. (2013) highlight the importance of removing organic matter through mineralization or dilution to reduce contamination from concurrent chemicals. Thangavel et al. (2015) also emphasize the necessity of meticulous sample preparation to avoid issues arising from sample matrices, which can affect the accuracy of trace element analysis. This step is crucial for achieving accurate measurements, as sample matrices can significantly impact analytical outcomes.

Moreover, methods such as precipitation and chromatographic separation are used to purify samples by removing impurities. Continuous method validation, routine monitoring, and ongoing improvements are essential for ensuring the reliability and repeatability of the analysis. Data detailing impurity concentrations are meticulously analyzed and documented to confirm that the high-purity NiSO₄ consistently meets the stringent specifications required for advanced LIBs.

2.1.3 The Quest for Purity: Overcoming Challenges in High-Purity Nickel Sulphate Production

The production of high-purity nickel sulfate (NiSO_4) for advanced LIB involves overcoming significant challenges to meet stringent quality standards. Achieving exceptionally low levels of impurities, such as Co, Fe and Cu, is crucial as even trace contaminants can impair battery performance by altering electrochemical properties and reducing cycle life. The variability in Ni feedstocks from different ores adds complexity to producing consistently high-purity NiSO_4 . Advanced purification techniques, including SX, precipitation, and chromatographic separation, are employed to target specific impurities while managing production costs and minimizing environmental impact. Maintaining quality consistency across batches involves rigorous quality control, continuous process monitoring, and adapting to evolving industry standards. Additionally, handling fine particles is essential for effective electrode fabrication. Analytical challenges include accurately measuring trace impurities at parts per million or billion levels using sensitive techniques like ICP-MS and ICP-OES. Addressing matrix interference, limited availability of certified reference materials, and instrumental variability requires method optimization, matrix-matched calibration, and standardized protocols. Continuous innovation and improvements in both purification and analytical methods are vital for advancing the reliability and performance of high-purity NiSO_4 in LIB.

2.2 Igniting the Forge: Fire Assay Techniques Unravelling the Mysteries of Platinum Group Metals

2.2.1 The Analytical Techniques for Pre-Concentration of Platinum Group Elements in Ores

Precious metals, such as PGEs, are often present in ores at very low levels. To overcome these challenges, a pre-concentration step is essential to enable their accurate quantification. The lead fire assay and the nickel sulphide (NiS) method

are two analytical procedures that are well recognised in the platinum sector for the purpose of collecting and pre-concentrating PGEs (Mabowa et al., 2024). These methods play a crucial role in enhancing the sensitivity and precision of subsequent analytical measurements, allowing for the reliable determination of precious metal concentrations in complex ore samples.

The waste generated during the fire assay process, often overlooked as mere by-product, harbours a wealth of untapped resources, particularly in the form of Ni. As the demand continues to surge, driven by the rapid growth of EVs and renewable energy storage systems, the need to efficiently recover and recycle this valuable metal becomes increasingly paramount. Within this context, the waste filtrate from NiS collection methods emerges as a new frontier in resource recovery (Mabowa et al., 2024). This waste stream contains residual Ni and other precious metals, representing an untapped reservoir that can be harnessed to meet the rising demand for battery applications. By implementing optimized extraction and recovery processes, mining companies can extract additional value from their waste streams, contributing to both environmental sustainability and economic viability.

The recycled waste aligns perfectly with the principles of resource conservation and responsible stewardship. It lessens the reliance on the extraction of virgin Ni, which in turn lessens the impact on the environment that is linked with conventional mining methods. Moreover, integrating recycled Ni into battery manufacturing not only addresses the growing demand for sustainable energy storage solutions but also enhances the economic resilience of production processes. In essence, treating the waste from fire assay methods to recover Ni not only unlocks a new source of valuable metal but also embodies a proactive step towards building a more sustainable and circular economy. By repurposing waste streams and maximizing resource utilization, the mining industry can play a pivotal role in advancing towards a cleaner and more resource-efficient future.

2.2.2 Advancing Sustainability Through Efficient Resource Recovery from Waste Streams

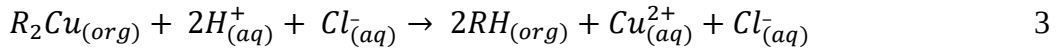
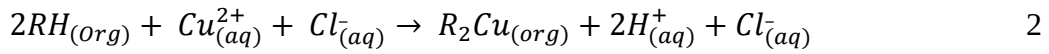
Traditional extraction methods often result in significant waste, including valuable resources contained in filtrate from sulphide collection. Addressing this waste through efficient recovery processes presents a promising solution for meeting the rising demand for battery materials while minimizing environmental impacts. By optimizing waste processing, mining companies can extract additional value from these by-products, promoting a circular economy and enhancing sustainable resource management.

Recycling from waste not only aligns with principles of conservation and responsible stewardship but also reduces reliance on untouched resources and lessens the environmental footprint associated with conventional mining. Incorporating recycled materials into battery production helps meet the growing need for sustainable energy solutions and improves economic viability by providing a steady supply of raw materials. This approach mitigates the risks associated with fluctuating resource prices and encourages innovation in clean energy technologies (Mabowa et al., 2024). As resource demand intensifies, recovering valuable materials from waste becomes crucial for the mining industry, fostering both environmental sustainability and economic growth.

2.3 Transforming Copper Mining: The Evolution of Solvent Extraction Techniques

Copper (Cu), often present as an impurity in pregnant Ni waste, is a valuable commodity that warrants attention due to its economic significance. Efficiently extracting Cu from Ni waste not only helps in purifying the Ni but also recovers a valuable resource, contributing to resource efficiency and sustainability. The commonly favoured approach for refining pregnant leach solutions (PLS) and boosting Cu concentration is the application of the SX method. This method relies on the disparate solubility of compounds or metal complexes in two non-mixable

liquids specifically, an aqueous phase and an organic solvent phase. By selectively extracting Cu^{2+} ions, which tend to migrate from the aqueous solution to the organic solvent, the leach solution is purified, resulting in an increased Cu concentration. In the extraction process, the organic solvent includes an extractant that selectively reacts with Cu, distinguishing it from other metal cations present in the PLS. The observed phenomenon of selective reaction results in the preferred migration of copper ions from the aqueous phase to the organic phase as indicated in Equation 1 (Schlesinger et al., 2011). The interaction of the extractant with the Cu^{2+} ion involves chelation. All other constituents in the PLS remain in the aqueous phase, often referred to as the raffinate or barren aqueous solution. The recovery of Cu from the loaded organic phase involves its contact with a strong acid, causing the Cu to be stripped into the advanced electrolyte for subsequent electrowinning as indicated in Equation 2 (Schlesinger et al., 2011). The stripped organic solvent is then returned for recycling to the extraction step, while the resulting enriched solution becomes an electrolyte suitable for the electrowinning of Cu.



Originally designed to recover Cu from low-grade dump-leach solutions, Cu SX took an unexpected turn. The initial reagent introduced in 1963, 5, 8- diethyl-6-hydroxy-7-oximinododecane (LIX 63) illustrated in Figure 2.4, lacked the required extraction power for typical dump-leach solutions (Swanson, 1964). Subsequent reagents, namely 2-hydroxy-5-tert-nonylbenzophenone oxime (LIX 65) and 5-dodecyl-2-hydroxybenzophenone (LIX 64), were introduced to address this limitation. In March 1968, a pivotal development, the first operational commercial copper SX plant, Ranchers Bluebird, commenced operations (Power, 1970).

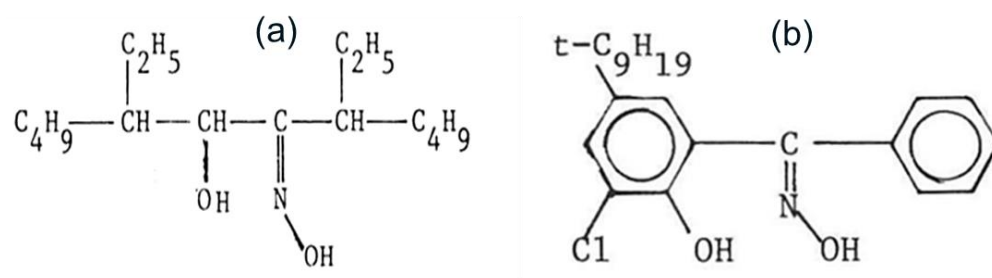


Figure 2.4: a) Chemical structure for 5,8-diethyl-6-hydroxy-7-oximinododecane; b) 2-hydroxy-3-chloro-5-tert-nonylbenzophenone

This marked a significant milestone, expanding the application of the extraction beyond its initial purpose and establishing its effectiveness in recovering copper from diverse solutions. The extraction of metals, either in the form of ions or salts, from an aqueous phase into an organic phase through liquid/liquid extraction has been documented for quite some time. The identification of SX has been a crucial method for separating metals in solutions. The utilisation of this technique is progressively being employed in the field of hydrometallurgy for the purpose of segregating, refining, and enhancing the concentration of various metals, including Ni, Co, Zn, uranium, and rare earths (U, and REs).

2.4 Chemical Precipitation: Harnessing Crystallization for Metal Recovery

To produce high-purity Ni, effectively separating impurities such as Fe is critical. In many Ni recovery processes, Fe is a common contaminant that can affect the overall purity and quality of the final nickel product. Understanding the behavior of Fe during precipitation and its removal is essential to ensure the success of the Ni purification process.

Precipitation is a fundamental chemical process characterized by reactive crystallization, which involves nucleation and growth stages (Karpinski & Wey, 2002). This method is particularly effective for metals like Fe, which has a tendency to precipitate from solution, forming various compounds such as oxides,

hydroxides, and complex minerals including jarosite, goethite, and hematite. In industrial applications, numerous precipitation methodologies have been developed to tailor the process for specific types of precipitates based on conditions, influencing their filterability, stability, and potential for reuse or disposal.

In the context of sustainable resource management, chemical precipitation is crucial for recovering and recycling valuable metals from complex matrices like spent LIBs. For instance, a significant study by Contestabile et al. (1999) detailed a laboratory-based procedure for LIB treatment and recycling. This procedure involved multiple stages: classification, trituration, sieving, selective separation of active elements, dissolving lithium cobalt, and precipitating cobalt hydroxide.

A key aspect of this process is the recovery of Ni, a valuable component of LIBs. Ni can be efficiently recovered as $\text{Ni}(\text{OH})_2$ by adding a lime solution, typically a 4 M calcium hydroxide ($\text{Ca}(\text{OH})_2$) solution. The precipitation of $\text{Ni}(\text{OH})_2$ requires careful control, starting at pH 6 and considered complete at pH 6.5 (Mabowa et al., 2024). Proper selection of chemical precipitation agents is crucial for this process, as noted by Ou et al. (2005). Despite the effectiveness of lime solutions, the formation of stable complexes between lime and cobalt can impede quantitative recovery, highlighting the need for further optimization.

2.4.1 Unlocking Nickel's Potential: The Power of Hydroxide Precipitation

Much like its role in our daily lives, Ni assumes a prominent role as one of the fundamental metallic elements. Various industries, such as construction, road infrastructure, and metallurgical sectors, depend on both main and supporting raw materials for their functioning (Michele, 2020; Cempel & Nikel, 2006; Larco, 2014; Wanta et al., 2018; Nieto et al., 2013; Institute, 2016). These basic materials are essential for maintaining the strength and effectiveness of infrastructure and industrial processes. The remarkable physical and chemical properties it possesses contribute to its widespread utilization in multiple sectors. The material possesses notable characteristics such as strong resistance to corrosion and chemical

reactions, exceptional ability to be stretched without breaking, ease of combining with other metals, ability to exhibit magnetism at room temperature, capability to be used for electroplating, possession of catalytic properties, and the ability to be completely recycled (Institute, 2016; Wanta et al., 2016; Bidault et al., 2009; Zhu et al., 2013; Wanta et al., 2020). The material's chemical inertness guarantees its stability and durability in different settings, preventing any deterioration that could potentially affect its function. The resilience of this material, along with its remarkable ductility, increases its adaptability and practicality in industrial applications. Ductility is the property of a material that enables it to be easily moulded and moulded without breaking, which is essential for the manufacturing and production of components. Chemical resistance safeguards the material from negative reactions, while ductility allows for its versatile use and adaption in many applications, demonstrating a harmonious equilibrium between durability and functional flexibility. There are several techniques available to obtain or recycle Ni. Following this, the procedure of purifying or completing is crucial to acquire a pure Ni commodity.

The Ni(OH)_2 chemical is a commonly utilised derivative product. The molecule in question can be classified as an intermediate product due to its derivative nature. The molecule needs to be further processed to be utilised to its full potential. According to Liu et al. (2011), the most common use of Ni(OH)_2 composites is as an active component in the anode for various electrochemical energy storage and conversion devices. The compound, when included in electrode materials for rechargeable batteries, can help the battery function well and provide favourable electrochemical characteristics, such as high specific energy, cyclability, and power density (Chen et al., 1999). The significance of Ni(OH)_2 structure and electrochemical characteristics extends beyond its use in rechargeable battery production. There are several methods for synthesising it, including hydrolysis in polyol medium, *Chimie douce*, electrochemical technique, and precipitation (Ramesh & Kamath, 2006). The hydroxide precipitation process is the most often utilised of these synthesis techniques. The advantages of this technology are its low cost, ease of use, and controllability (Asokbunyarat et al., 2017). The idea behind

the hydroxide precipitation technique is to use an alkaline chemical as a precipitating agent to change water-soluble ions into water-insoluble molecules. In the hydroxide precipitation process, precipitating agents such as sodium hydroxide (NaOH), magnesium oxide (MgO), calcium oxide (CaO), and Ca(OH)_2 are typically utilised. By adding these alkaline substances, the pH of the solution will rise, which will lead to the formation of conditions where a metal ion is less soluble in the liquid phase. Wang et al. (2005) state that the hydroxide precipitation process often entails the interaction between metal cations and hydroxide ions, resulting in the formation of a precipitate. This technique is frequently used to cleanse and isolate metal ions from solutions. By adding a calculated amount of H_2SO_4 (98%) gradually to the wet NiSO_4 cake, the Ni(OH)_2 can be re-dissolved in H_2SO_4 to create a liquor containing NiSO_4 as indicated in section 1.2.

2.4.2 Conquering Iron: Strategies for Effective Precipitation

Iron content assumes vital significance due to its potential to disrupt processes and incur undesirable consequences, such as the inadvertent co-precipitation of valuable metals and escalated operational expenses. Notably, ferrous (Fe^{2+}) can undergo precipitation at pH levels approximately at or above 7, while ferric (Fe^{3+}) precipitation is feasible at a pH exceeding 0, with a preference towards the latter to circumvent the necessity for higher pH operation, which is correlated with augmented co-precipitation tendencies. Ordinarily, the conversion of Fe^{2+} to Fe^{3+} precedes precipitation, a process that can transpire either during the leaching phase or downstream operations (Crundwell et al., 2011; Schlesinger et al., 2011).

According to Loan et al. (2006), traditional removal methods often include the formation of iron oxides or hydroxides, which generally involve the simultaneous precipitation of various divalent and trivalent elements. Noteworthy advancements have been made in iron removal methodologies, especially within the sulphate systems prevalent in industry. These methodologies have demonstrated potential applicability to analogous processes in the purification of Cu and Ni in sulphate environments. However, the direct transference of Fe removal principles from

sulphate to chloride systems necessitates further inquiry and validation (Wang et al., 2011). Effective Fe control mandates thorough regulation of precipitation parameters and perpetual adaptation of established protocols to suit the distinctive requisites of specific processes, accentuating the continuous imperative for pioneering research and developmental endeavours in this domain.

2.4.3 The oxidation of iron results in the precipitation

A sample of the solution waste impurities containing Ni-rich waste solution that was contaminated with impurities of copper (3.87 g/L), in addition to other significant amounts of zinc, sodium, potassium, lead, cobalt, aluminium, manganese, silicon, chromium, and manganese, was used for the iron removal optimisation tests. These tests were carried out on a sample of the waste solution. Both the elimination of tiny contaminants that were present in the feedwaste solution and the determination of the ideal conditions for iron rejection were the motivations for the tests that were carried out.

The solution contained a significant amount of iron (Fe) in the form of ferric (Fe^{3+}), which was almost entirely present. The extent of the oxidation of iron was monitored through the observation of precipitate formation, and the evaluation was based on the decrease in the concentration of iron in the solution that was being analysed. Because the Eh measurements were affected by a background of roughly 62.7g/L Ni, they couldn't serve as an indicator for the amount of the precipitation. The results ranged from 260 to 340 mV, which indicates that the Eh measurements were influenced by the background.

2.5 An Overview Process and Application of Sol-Gel Methods

The sol-gel process is a commonly used wet-chemical method in materials science and ceramic engineering. It is utilised to create metal oxides and other materials by converting a chemical solution into a gel-like network. This procedure commonly employs metal alkoxides and metal chlorides, which undergo hydrolysis and

polycondensation to produce metal-oxo (M–O–M) or metal-hydroxo (M–OH–M) polymers. These polymers undergo a transformation into a gel-like system that has both liquid and solid phases. This leads to the formation of structures that can range from individual particles to interconnected polymer networks.

Colloids, which have a low particle density, require the removal of a substantial amount of fluid to attain gel-like characteristics. This can be accomplished through sedimentation or expedited by centrifugation. The elimination of the solvent phase through desiccation is accompanied by contraction and compaction, resulting in a final microstructure that is affected by the arrangement of pores in the gel. Additional thermal treatment, known as firing, is necessary to improve mechanical characteristics and stability by promoting polycondensation and densification.

The sol-gel process provides numerous benefits, such as cost-efficiency and meticulous regulation of the chemical composition and microstructure of the end product. The process enables the production of materials in several formats, including films (via dip coating or spin coating), shaped objects (such as monolithic ceramics and fibres), and powders (such as microspheres and nanospheres). This approach is employed in various disciplines, such as optics, electronics, energy, and medicine. Sol-gel technology has undergone tremendous advancements since its inception in the mid-1800s, with companies like Schott Glass playing a major role in its development (Suchea, Christoulakis, & Androulidaki, 2008). Sol-gel processing offers several intrinsic benefits, such as improved homogeneity and purity of raw materials, reduced preparation temperatures, precise control over particle size and shape, and the capability to produce innovative non-crystalline solids (Suchea, Christoulakis, & Androulidaki, 2008).

2.6 The Role of Metal Oxide Semiconductors in Detecting Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are frequently encountered in everyday life, presenting themselves through the scent of petrol, paint and nail polish. Volatile

organic compounds (VOCs) have adverse impacts on air quality, leading to ozone layer depletion and posing risks to human health (Singh et al., 2022), (Huang, Zeng, & Li, 2022). MOS gas sensors detect gases by measuring changes in resistance. When oxygen molecules come into contact with the MOS surface, they stick to it and take away electrons. This process forms an electron depletion layer (EDL) in n-type semiconductors or a hole accumulation layer (HAL) in p-type semiconductors. Nickel oxide (NiO), a semiconductor with positive charge carriers, has attracted attention because of its strong oxidising properties, outstanding catalytic activity, and elevated electrical conductivity in gas sensors (Liu, et al., 2022). More than 1,000 studies focussing on gas sensors based on NiO have been published, with a particular emphasis on the past five years. Li et al., 2022 produced ultrathin Ni(OH)_2 nanosheets without additional surfactants. This led to the formation of porous NiO nanosheets that facilitated gas diffusion and acetone detection.

These sensors showed a notable sensitivity to 100 parts per billion (ppb) of acetone gas and a minimum detection limit of 0.8 ppb. Nevertheless, the performance of pure NiO in reacting with ethanol is frequently unsatisfactory, leading scientists to enhance its effectiveness by implementing diverse alterations including morphological manipulation, doping, integration of noble metal particles, and the formation of composites with n-type semiconductors.

References

- ADB. (2018, December). *Handbook on Battery Energy Storage System*. Mandaluyong: Asian Development Bank. doi: <http://dx.doi.org/10.22617/TCS189791-2>
- Agatzini-Leonardou, S., Tsakiridis, P., Oustadakis, P., Karidakis, T., & Katsiapi, A. (2009). Hydrometallurgical process for the separation and recovery of nickel from sulphate heap leach liquor of nickeliferous laterite ores. *Mining engineering*, 22, 1181–1192.
- Albrecht, T., Addai-Mensah, J., & Fornasiero, D. (2011). Effect of pH, Concentration and Temperature on Copper and Zinc Hydroxide Formation/Precipitation in Solution., (pp. 1-10).
- Asokbunyarat, V., Lens, P., & Annachhatre, A. (2017). *Permeable Reactive Barriers for Heavy Metal Removal*.
- Asokbunyarat, V., Lens, P., & Annachhatre, A. (2017). *Permeable Reactive Barriers for Heavy Metal Removal* (Vol. 1).
- Avena, M., Vazquez, M., Carbonio, R., De Pauli, C., & Macagno, V. (1994). Journal of Applied Electrochem. A simple novel method for preparing $Ni(OH)_2$ Part I: Structural studies and voltam-metric response, 24, 256.
- Badocco, D., Lavagnini, I., Mondin, A., Tapparo, A., & Pastore, P. (2015). Limit of detection in the presence of instrumental and non-instrumental errors: study of the possible sources of error and application to the analysis of 41 elements at trace levels by ICP-MS technique. *Elsevier*, 107, 178-184.
- Balintova, M., & Petrilakova, A. (2011). Study of pH Influence on Selective Precipitation of Heavy Metals from Acid Mine Drainage. *14th International Conference on Process Integration, Modelling and Environmental Engineering*. 25, pp. 345-350. Slovakia: Technical University of Kosice, Civil Engineering Faculty, Institute of Building and. doi:DOI:10.3303/CET1125058
- Basturkcü, H., & Acarkan, N. (2017). Selective nickel-iron separation from atmospheric leach liquor of a lateritic nickel ore using the para-goethite method. *Physicochemical Problems of Mineral Processing*, 53(1), 212-226.

- Berckmans, G., Messagie, M., Smekens, J., Omar, N., Vanhaverbeke, & and Van Mierlo, J. (2017). Cost projection of state of the art Lithium-ion batteries for electric vehicles up to 2030. *Energies*, 10(9), 1314.
- Bernard, M., Cortes, R., Keddam, M., Takenouti, H., Bernard, P., & Senyarrich, S. (1996). Structural defects and electrochemical reactivity of β -Ni(OH)₂. *Journal of Power Sources*, 63(2), 247-254.
- Bidault, F., Brett, D., Middleton, P., Abson, N., & Brandon, N. P. (2009). A new application for nickel foam in alkaline fuel cells. *International Journal of Hydrogen Energy*, 34(16), 6799–6808.
- Bings, N., Bogaerts, A., & Broekaert, J. (2008). Atomic Spectroscopy. *Analytical Chemistry*, 80(12), 4317-4347.
- Bourcier, D., Féraud, J., Colson, D., Mandrick, K., Ode, D., Brackx, E., & Puel, F. (2016). Influence of particle size and shape properties on cake resistance and compressibility during pressure filtration. *Chemical Engineering Science*(144), 176-187.
- Bulska, E., & Ruszczyńska, A. (2017, May). Analytical Techniques for Trace Element Determination. *Physical Sciences Reviews*, 2(5), 2017-8002. doi:10.1515/psr-2017-8002
- Bulska, E., & Ruszczyńska, A. (2017). Analytical Techniques for Trace Element Determination. *Physical Sciences Reviews*, 2(5), 20178002. Retrieved from <https://doi.org/10.1515/psr-2017-8002>
- Butler, O., Cairns, W., Cook, J., & Davidson, C. (2013). Atomic spectrometry update. Environmental analysis. *Journal of Analytical Atomic Spectrometry*, 28, 177-216.
- Butt, C., & Cluzel, D. (2013). Nickel laterite ore deposits: weathered serpentinites. *Elements*, 9(2), 123-128.
- Byung-Hyun, S. K. (2024). Effect of Secondary Phase on Electroless Ni Plating Behaviour of Super Duplex Stainless Steel SAF2507 for Advanced Li-Ion Battery Case. *Materials*, 17(6), 1441. doi:doi: 10.3390/ma17061441
- Cabanas-Polo, S., Suslick, K., & Sanchez-Herencia, A. (2011). Effect of reaction conditions on size and morphology of ultrasonically prepared Ni(OH)₂

- powders. *Ultrasonics Sonochemistry*, 18(4), 901-906.
doi:<https://doi.org/10.1016/j.ultsonch.2010.11.017>
- Cempel, M., & Nikel, G. (2006). Nickel: A review of its sources and environmental toxicology. *Polish Journal of Environmental Studies*, 15(3), 375-382.
- Chen, J., Bradhurst, D., Dou, S., & Liu, H. (1999). Nickel hydroxide as an active material for the positive electrode in rechargeable alkaline batteries. *Journal of the Electrochemical Society*, 146(10), 3606–3612.
- Cheng, Y. (2008). Determination of trace elements in high-purity nickel by inductively coupled plasma mass spectrometry with microwave digestion. *Metallurgical Analysis*, 28(3), 9-13.
- Cheng, Y. (2008). Determination of trace elements in high-purity nickel by inductively coupled plasma mass spectrometry with microwave digestion. *Metallurgical Analysis*, 28(3), 9-13.
- Choi, K., & Azimi, G. (2023, September 27). Crystallization of nickel sulfate and its purification process: towards efficient production of nickel-rich cathode materials for lithium-ion batteries. *RCS Advances*, 13(41), 28501–28512.
- Chung, D. S., & Lee, H. K. (2013). Extraction and sample preparation. *Journal of Chromatography*, 1300, 1-235.
- Civici, N. (1999). Analytical parameters obtained during the application of EDXRF spectrometry in geochemical mapping of Albania. *Albanian Journal of Natural and Tech. Sciences*, 29(3).
- Claassen, J., & Sandenbergh, R. (2007). Influence of mixing on the quality of iron precipitates in zinc - rich solutions. *Hydrometallurgy*, 87, 112-123.
- Contestabile, M., Panero, S., & Scrosati, B. (1999). A laboratory-scale lithium battery recycling process. *Journal of Power Sources*, 75(8), 1-2.
- Creamer, M. (2021). Thakadu commissions nickel sulphate refinery. North West, South Africa.
- Crundwell, F., Moats, M., Ramachandran, V., Robinson, T., & Davenport, W. (2011). Separation of Nickel and Cobalt by Solvent Extraction. In: *Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals. Elsevier*, 315-326.

- Dalvi, A., Bacon, W., & Osborne, R. (2004). The Past and the Future of Nickel Laterites. *PDAC 2004 International Convention* (pp. 23-50). Ontario, L5K 1Z9 Canada : Trade Show & Investors Exchange.
- Darnley, A. (1995). *A Global Geochemical Database for Environmental and Resource Management: Recommendations for International Geochemical Mapping*:. UNESCO, IGCP Project 259. Paris: Earth Sciences .
- Davey, R., Blagden, N., Potts, A., & Docherty, R. (1997). Polymorphism in Molecular Crystals: Stabilization of a Metastable Form by Conformational Mimicry. *Journal of the American Chemical Society*(119), 1767-1772.
- Du, H., Wang, Y., Yuan, H., & Jiao, L. (2016). Facile synthesis and high capacitive performance of 3D hierarchical Ni(OH)₂ microspheres. *Electrochimica Acta*, 84-91. doi:10.1016/j.electacta.2016.02.190
- EEA. (2016). *Electric Vehicles in Europe*. Copenhagen: European Environment Agency.
- Elci, L., Soylak, M., Uzun, A., Buyukpatir, E., & Dogan, M. (2000). Determination of trace impurities in some nickel compounds by flame atomic absorption spectrometry after solid phase extraction using Amberlite XAD-16 resin . *Fresenius' Journal of Analytical Chemistry*, 368(4), 358-361.
- Exchange, T. L. (2023). Special Contract Rules for Primary Nickel. London, England.
- Feng, W., & Yingping, N. (2020). *Determination of Elements in Ternary Material Nickel-Cobalt-Manganese Hydride by ICP-OES*. China: Agilent Technologies .
- Fierro, C., Zallen, A., Koch, J., & Fetcenko, M. A. (2006). The Influence of Nickel-Hydroxide Composition and Microstructure on the High-Temperature Performance of Nickel Metal Hydride Batteries. *J. Electrochem. Soc*, 156, AA492-A496.
- Fraser, J., Anderson, J., Lazuen, J., Lu, Y., Heathman, O., Brewster, N., & Bedder, J. (2021). *Study on future demand and supply security of nickel for electric vehicle batteries*. Roskill. Luxembourg: European Union. doi:doi:10.2760/212807

- Friedland, R. (2017). Clean TeQ investor presentation . *Mining Indaba: Investing in african mining conference* (pp. 18-21). Cape town: Clean TeQ investor.
- Hall, D., Lockwood, D., Bock, C., & MacDougall, B. (2015). Nickel hydroxides and related materials: A review of their structures, synthesis and properties. 4471(2174). doi:<https://doi.org/10.1098/rspa.2014.0792>
- Harris, G., & White, C. (2008). Recent developments in the high-strength chloride leaching of base metal sulphide ores. *ALTA Nickel/Cobalt*. Perth.
- Hart, T. (2015). *The use of nickel based particles in the electronics industry*. Wombourne: Hart Materials Limited.
- Hineman, A., & Neubauer, K. (2020). *Analysis of Impurities in Nickel by with the Avio 500 ICP-OES*.
- Huang, B., Zeng, W., & Li, Y. (2022). Synthesis of ZnO@ZIF-8 nanorods with enhanced response to VOCs. *Journal of the Electrochemical Society*, 169(4). Retrieved from <https://doi.org/10.1149/1945-7111/ac61be>
- Ikaneng, M. (1997-2006). *Overview of the Nickel Industry in South Africa*. Department of Mineral Resource. Pretoria: Department of Mineral Resource. Retrieved from <http://www.dme.gov.za>
- Ingram, A. (2014). *Toyota gasoline engine achieves thermal efficiency of 38 percent*. El Segundo: Green car reports.
- Institute Nickel. (2021). Retrieved from <http://batteryuniversity.com/>
- Institute, N. (2016). The life of Ni Nickel Institute, [Online]. Retrieved from <https://nickelinstitute.org/media/1190/thelifeofni>.
- Johnson, R. (1984). Trace element analysis of silicates by means of energy-dispersive Xray spectrometry. *X-Ray Spectrometry*, 13(6), 15.
- Jung, J.-Y., Sui, P.-C., & Zhang, J. (2021). A review of recycling spent lithium-ion battery cathode materials using hydrometallurgical treatments. *Journal of Energy Storage*, 35, 102217.
- Karpinski, P., & Wey, J. (2002). Precipitation processes. In A. Myerson, *Handbook of Industrial Crystallization* (pp. 141-160). Butterworth-Heinemann: Elsevier. doi:<https://doi.org/10.1016/B978-075067012-8/50008-2>
- Kettaf, S., Guellatri, O., Harat, A. K., Momodu, D., Dangbegnon, J., Manyala, N., & Guer7ioune, M. (2019). Electrochemical measurements of synthesized

nanostructured β -Ni(OH)₂ using hydrothermal process and activated carbon based nanoelectroactive materials. *SN Applied Sciences*. doi:DOI:10.1007/s42452-018-0038-3

- Kgaria, M., Yahorava, O., & Sehlola, C. (2016). *Thakadu Flowsheet Development*. Randburg: Mintek.
- Kiani, M., Mousavi, M., & Ghasemi, S. (2010). Size effect investigation on battery performance: comparison between micro- and nano-particles of β -Ni(OH)₂ as nickel battery cathode material. *Journal of Power Sources*, 17(1), 5794-5800.
- Kujirai, O., & Yamada, K. (1994). Simultaneous determination of seven trace impurities (Al, As, Cr, Fe, Ti, V and Zr) in high-purity nickel metal and nickel oxide by coprecipitation and inductively coupled plasma-atomic emission spectrometry. *Fresenius' Journal of Analytical Chemistry*, 11, 719-723.
- Kyle, J. (2010). Nickel laterite processing technologies – where to next? *ALTA Nickel/Cobalt/Copper Conference*, (pp. 1–36). Perth.
- Larco, G. (2014). Nickel, world production and demand nickel, world production and demand. *Balk. Min. Congr*, 28-34.
- Li, C., Choi, P., Kim, K., & Masuda, Y. (2022, 367). High performance acetone gas sensor based on ultrathin porous NiO nanosheet. *Sensors and Actuators B: Chemical*, 367, 132143. doi:<https://doi.org/10.1016/j.snb.2022.132143>
- Liu, H. W., Cao, G., Pan, G., Yang, X., Qiu, M., Sun, C., . . . and Zhang, H. (2022). Construction of hollow NiO/ZnO p-n heterostructure for ultrahigh performance toluene gas sensor. *Materials Science in Semiconductor Processing*, 48(4), 4787-4794. doi:<https://doi.org/10.1016/j.ceramint.2021.11.015>
- Liu, Y., Bai, J., Li, Y., Yang, L., Wang, Y., Li, Y., . . . and Lu, G. (2022). Preparation of PdO-decorated NiO porous film on ceramic substrate for highly selective and sensitive H₂S detection. *Ceramics International*, 48(4), 4787-4794. doi:<https://doi.org/10.1016/j.ceramint.2021.11.015>

- Liu, Z., Tay, S., & Li, X. (2011). Rechargeable battery using a novel iron oxide nanorods anode and a nickel hydroxide cathode in an aqueous electrolyte. *ChemComm*, 47(46), 12473–12475.
- Loan, M., Newman, O., Cooper, R., Farrow, J., & Parkinson, G. (2006). Defining the Paragoethite process for iron removal in zinc hydrometallurgy. *Hydrometallurgy*, 81, 104-129.
- Ma, Y., Svärd, M., Xiao, X., Gardner, J., Olsson, R., & Forsberg, K. (2020). Precipitation and crystallization used in the production of metal salts for Li-ion battery materials : A review. *10*(12), 1609.
- Mabowa, H., Mkhohlakali, A., Mokoena, S., Tshilongo, J., & Chimuka, L. (2024). Removal of Nickel from Nickel Sulfite-Fire Assay Dissolution Filtrate Through Precipitation. *ACS Omega*, 9, 5592-5600. doi:<https://doi.org/10.1021/acsomega.3c07623>
- Mabowa, M., Mkhohlakali, A., Mokoena, S., Tshilongo, J., & Chimuka, L. (2024). Removal of Nickel from Nickel Sulfite-Fire Assay Dissolution Filtrate Through Precipitation. *ACS Omega*, 9 (5), 5592-5600. doi:10.1021/acsomega.3c07623
- Magnusson, B., & Örnemark, U. (2014). *Eurachem Guide: The Fitness for Purpose of Analytical Methods—A Laboratory Guide to Method Validation and Related Topics* (2 ed.). United Kingdom: Eurachem: Teddington.
- McNaught, A., & Wilkinson, A. (1997). *IUPAC. Compendium of Chemical Terminology (the “Gold Book”)* (2 ed.). Oxford: Blackwell Scientific Publications. doi:10.1351/goldbook
- Michele, M. S. (2020). *Nickel Statistic and information*.
- Mullin, J. (2001). Crystallization. (Elsevier, Ed.) *Science*, 280-284.
- Narayan, R. (2015). Effect of Crystallinity of β - and β bc -Nickel Hydroxide Samples on Chemical Cycling. *Indian Journal of Materials Science*, 2015(II), 1-7. doi:doi: 10.1155/2015/820193
- Nieto, A., Montaruli, V., & Cardu, M. (2013). The strategic importance of nickel: scenarios and perspectives aimed at global supply. *Trans. Soc. Min., Met. Explor*, 334, 510–518.

- Nozari, I., & Aziz, A. (2020). An investigation into the Extraction Behavior of Copper from Sulfate Leach Liquor Using Acorga M5640 Extractant: Mechanism, Equilibrium, and Thermodynamics. *Mining Metallurgy Exploration*, 37(5), 1673-1680. doi:doi: 10.1007/s42461-020-00280-z.
- Ou, X., Sun, X., Zhao, Q., & Fan, F. (2005). Progress in recovery technology of waste lithium-ion battery. *Journal of Inorganic Chemistry*, 37(9), 11.
- Pillot, C. (2014). Battery Market Development for Consumer Electronics, Automotive, and Industrial. *Battery Market* (pp. 26-24). Nice, France: Avicenne Energy Analysis.
- Potts, P., Webb, P., & Slvonen, S. (1984). Energy-dispersive X-ray fluorescence analysis of silicate rocks for major and trace elements. *X-Ray Spectrometry*, 13(2), 1.
- Power, K. (1970). Operation of the First Commercial Copper Liquid Ion Exchange and Electrowinning Plant. *AIME Annual Meeting*. New York.
- Qin, Z., Wang, Y., Huang, X., Shen, W., Yu, J., & Li, J. (2020). A Facile Synthesis of Three Dimensional β -Ni(OH)₂ Composed of Ultrathin Nanosheets for High Performance Pseudocapacitor. *Journal of Inorganic and Organometallic Polymers and Materials*, 30(6), 2089-2097.
- Ramesh, T., & Kamath, P. (2006). Synthesis of nickel hydroxide: Effect of precipitation conditions on phase selectivity and structural disorder. *Journal of Power Sources*, 156(2), 655-661.
- Rudusuela, K. (2020). *Nickel in batteries*. Nickel Institute. Canada: Nickel Magazine. Retrieved from <https://nickelinstitute.org/about-nickel-in-batteries/>
- Sangwal, K. (2007). *Additives and Crystallization Processes: From Fundamentals to Applications*. Hoboken, New Jersey: John Wiley & Sons.
- Schlesinger, M., King, M., Sole, K., & Davenport, W. (2011). In M. K. Schlesinger, *Extractive metallurgy of copper* (5th ed., pp. 252-256). Oxford: Elsevier.
- Singh, S., Deb, J., Kumar, S., Sarkar, U., & Sharma, S. (2022). Selective N,N-dimethylformamide vapor sensing using MoSe₂/multiwalled carbon nanotube composites at room temperature. *ACS Applied Nano Materials*, 5(3), 391303924. Retrieved from <https://doi.org/10.1021/acs>

- Song, Q., Tang, Z., Guo, H., & Chan, S. (2002). Structural characteristics of nickel hydroxide synthesized by a chemical precipitation route under different pH values. *Journal of Power Sources*, 112(2), 428-434.
- Stopic, S., & Friedrich, B. (2016). Hydrometallurgical processing of nickel lateritic ores. 64(4), 1033–1047.
- Suchea, M., Christoulakis, S., & Androulidaki, M. a. (2008). CaS:Eu,Sm and CaS:Ce,Sm films grown by embedding active powder into an inert matrix. *Mater. Materials Science and Engineering: B — Advanced Functional Solid-State Materials*, 150(2), 130-134.
- Swanson, R. A. (1964). A New Reagent for the Extraction of Copper. *1964 AIIME Annual Meeting*. New York.
- Thangavel, S., Dash, K., Dhavile, S., & Sahayam, A. (2015). Determination of traces of As, B, Bi, Ga, Ge, P, Pb, Sb, Se, Si and Te in high-purity nickel using inductively coupled plasma-optical emission spectrometry (ICP-OES). *Elsevier*, 131, 505-509.
- Thompson, M., Ellison, S., & Wood, R. (2002). Harmonized guidelines for single-laboratory validation of methods of analysis. *Pure and Applied Chemistry*, 74, 835-855. doi:DOI: <https://dx.doi.org/10.1351/pac200274050835>
- Thyse, E., Akdogan, G., Taskine, P., Vilojoen, K., & Eksteen, J. (2013). Towards understanding nickel converter matte solidification. *Minerals Engineering*, 54, 39-51. doi:<https://doi.org/10.1016/j.mineng.2013.03.023>
- Van Schalkwyk, R. (2011). . *Leaching of Ni-Cu-Fe-S Peirce Smith converter matte: Effects of the Fe-endpoint and leaching conditions on the kinetics and mineralog*. Stellenbosch: University of Stellenbosch.
- VanDeventer, J., & McDevitt, W. (2019). Application of Solvent-Impregnated Resins for Production of High-Purity Nickel and Cobalt Liquors. *ALTA* (pp. 1-2). Peth, Australia: Presented at the Alta Metallurgical Conference.
- Wang, K., Li, J., McDonald, R., & Browner, R. (2011). The effect of iron precipitation upon nickel losses from synthetic atmospheric nickel laterite leach solutions: Statistical analysis and modelling. *Hydrometallurgy*, 109, 140-152.

- Wang, L., Vaccari, D., Li, Y., & Shammass, N. (2005). *Chemical Precipitation* (Vol. 3). Physicochemical Treatment Processes.
- Wang, L., Vaccari, D., Li, Y., & Shammass, N. (2005). *Chemical precipitation, Physicochem. Treat. Process* (Vol. 3).
- Wanta, K., Gunawan, W., Susanti, R., Gemilar, G., Petrus, H., & Astuti, W. (2020). Subcritical water as a solvent for extraction of nickel and aluminum ions from reforming spent catalysts., 742.
- Wanta, K., Perdana, C., & Petrus, H. (2016). Evaluation of shrinking core model in leaching process of Pomalaa nickel laterite using citric acid as leachant at atmospheric conditions. *IOP Conference Series: Materials Science and Engineering*, 162.
- Wanta, K., Putra, F., Susanti, R., Gemilar, G., Astuti, W., Virdhian, S., & Petrus, H. (2019). Pengaruh derajat keasaman (pH) dalam proses presipitasi hidroksida selektif nikel logam dari larutan ekstrak spent catalyst. *Jurnal Rekayasa Proses*, 13(2), 94-105.
- Wanta, K., Tanujaya, F., Susanti, R., Petrus, H., Perdana, I., & Astuti, W. (2018). Studi kinetika proses atmospheric pressure acid leaching bijih laterit limonit menggunakan larutan asam nitrat konsentrasi rendah. *Jurnal Rekayasa Proses*, 12(2), 19.
- Wanta, K., Tanujayaa, F., Putraa, F., Susantia, R., Gemilarb, G., Astutic, W., & Bayu, P. H. (2020). Synthesis and Characterization Of Nickel Hydroxide From Extraction Solution Of Spent Catalyst. *Metalurgi*, 3, 111-118.
- Wanta, K., Tanujayaa, F., Putraa, F., Susantia, R., Gemilarb, G., Astutic, W., & Bayu, P. H. (2020). Synthesis and Characterization of Nickel Hydroxide from Extraction Solution of Spent Catalyst. *Metalurgi*, 3, 111-118.
- Watanabe, K., Kikuoka, T., & Kumagai, N. (1995). J. Appl. Electrochem. *Physical and electrochemical characteristics of nickel hydroxide as positive material for rechargeable alkaline batteries*, 25, 219.
- Weiller, C., & Sioshanshi, R. (2014). The role of plug-in electric vehicles with renewable resources in electricity systems. *Claire Weiller & Ramteen Sioshansi, 2014. "The Role of Plug-In Electric Vehicles with Renewable Revue d'économie industrielle, De Boeck Université, 0(4), 291-316.*

- Xinchao, W., Roger, C., Viadero, J., & Karen, M. (2005). Recovery of Iron and Aluminum from Acid Mine Drainage by Selective Precipitation. *Environmental Engineering Science*, 22(6), 745-755.
- Yahorava, O., Bazkho, O., Kgaria, M., Mottay, R., & Sehlolo, C. (2016). *Evaluate removal of impurities from LONMIN nickel sulphate solution*. Randburg: Mintek.
- Younas, M., Druon-Bocquet, S., Romero, J., & Sanchez, J. (2015). Experimental and Theoretical Investigation of Distribution Equilibria and Kinetics of Copper(II) Extraction with LIX 841 and TFA. *Separation Science and Technology*, 50(10), 1523-1531.
- Zhu, D., Zhang, X., & Ding, H. (2013). Tool wear characteristics in machining of nickel-based superalloys. *International Journal of Machine Tools and Manufacture*, 64, 60–77.

CHAPTER THREE: RESEARCH OBJECTIVES AND APPROACH

The focus of this chapter is on the explanation of the purpose, goals, and research approach employed in the study, outlining both the overall and objectives. Moreover, it offers a deeper understanding of the underlying motive behind the study and delivers the hypothesis that forms the basis of the research endeavour. In a nutshell, this chapter provides an overview of the study's aim, objectives, and research approach, aligned with the accomplishments of this thesis.

3.1 Introduction - Justification of the Study

This study is crucial for research due to its innovative approach to extracting Ni from unconventional or overlooked sources within industrial waste streams. Unlike traditional methods that primarily target known sources, this study seeks to explore and exploit previously unexplored avenues for Ni recovery, thus broadening the resource base for extraction. By developing and implementing new refining techniques and analytical methodologies, this approach not only expands the available sources of Ni but also demonstrates a significant step forward in advancing sustainable resource utilization practices within the metal refining industry.

The research underscores the importance of sustainable and efficient methods for extracting Ni from unconventional sources within industrial waste streams. Conventional methods often overlook these sources, leading to limited reservoirs and resource depletion. By exploring and harnessing previously untapped avenues for Ni recovery, this research aims to expand the pool of available nickel sources, contributing to resource conservation and sustainability. Additionally, the development of novel refining techniques and analytical methodologies is poised to enhance recovery while promoting environmentally friendly practices within the metal refining sector. Ultimately, this study aims to address the increasing demand for Ni while mitigating environmental impact, offering significant societal and environmental benefits.

3.2 Aim of the Study

The aim this study is to develop an efficient and sustainable process for producing battery-grade nickel sulphate. This involves exploring innovative approaches to extract Ni from unconventional or overlooked sources within industrial waste streams, implementing novel refining techniques, and improving analytical

methodologies to ensure the production of high-quality nickel sulphate suitable for battery manufacturing.

3.3 Hypothesis

battery-grade purity NiSO_4 can be produced from non-traditional sources, such as industrial waste streams, using an innovative and environmentally friendly method and reliable analytical techniques that will enable the precise detection and control of trace impurities to meet quality standards.

3.4 Rationale of the Study

The rationale behind this study is multifaceted challenges within the Ni industry, including resource scarcity, environmental impact, and the burgeoning demand for battery materials. Furthermore, a significant analytical challenge exists in accurately determining impurities within high-grade NiSO_4 . Analytical methods typically focus on analysing high concentrations above 20%, necessitating the calculation of impurities by difference due to the complex matrix of battery-grade material and chemical interference in the analytical instrumentation. Thangavel et al. (2015) has reported an industrialized analysis of multi-trace elements in the Ni medium which he overcame by developing a new sample digestion and matrix separation approach for the determination of the elements. Furthermore, Feng, W., and Yingping from Agilent Technologies in China has determined the elements in the ternary material Nickel-Cobalt-Manganese Hydride using ICP-OES. Feng and Yingping (2020) employed the standard addition method to overcome matrix interferences in the analysis of Nickel-Cobalt-Manganese Hydride using ICP-OES.

The research from Hineman and Neubauer (2020) reported the Analysis of Impurities in 1% Ni by with the Avio 500 ICP-OES Following London Metal Exchange Guidelines. These challenges emphasize the critical need for innovative approaches in both extraction methodologies and analytical techniques to ensure that production meets stringent quality standards. Hineman and Neubauer (2020)

addressed high matrix interferences in nickel analysis using PerkinElmer's Avio 550 Max ICP-OES. Their method incorporated Multi-Component Spectral Fitting (MSF), which allowed for accurate detection of impurities specified by the London Metal Exchange (LME), overcoming spectral interferences caused by the high nickel matrix. This demonstrates the effectiveness of MSF in ensuring precise impurity measurements at the defined LME concentrations.

The study conducted by Cheng (2008) employed inductively coupled plasma mass spectrometry with microwave digestion to identify trace components in high-purity Ni. It was found that the matrix effect could be eliminated by matching matrix or selecting Sc, Rh as an internal standard element and the spectral interference could be calibrated by selecting different isotope or correction equation of interference elements. While the report by Yahorava et al. (2016) emphasized the analytical challenges faced in impurity analysis during the evaluation of removal of impurities from NiSO₄ solution. By addressing these challenges, this study aims to not only expand the available Ni resources through unconventional extraction methods but also improve the accuracy and reliability of impurity analysis, thereby contributing to the advancement of sustainable practices within the metal refining industry. To the best knowledge and after an extensive review of the existing literature, there has been no prior publication or study that specifically addresses the comprehensive investigation outlined in this study.

3.5 Research Objectives

The primary focus of this research was to explore novel avenues for extracting Ni from unconventional or overlooked sources within industrial waste streams, with a specific aim of developing a process to remove impurities by using solvent extraction and chemical precipitation and method development for impurity analysis using FAAS, ICP-OES and EDXRF for the manufacturing of nickel sulphate battery-grade quality.

1. To investigate the effectiveness of S-Curve precipitation, under detailed parameters at different pH levels, for recovering nickel (Ni) by considering the following parameters: pH levels, Ni concentration, precipitate dosage, Temperature, impurity concentration, precipitation kinetics and solubility products.
2. To evaluate the efficiency of traditional solvent extraction, particularly focusing on copper (Cu) extraction, before S-Curve precipitation.
3. Evaluate an alternative method such as FAAS, EDXRF and ICP-OES for analysing trace elements during the purification process of high-purity nickel sulphate, crucial for battery manufacturing.
4. To investigate the effectiveness of lime precipitation for removing impurities from pregnant nickel solution (PNS) across various pH levels.
5. Characterization of β -Nickel hydroxide ($\text{Ni}(\text{OH})_2$) synthesized through a precipitation process using various analytical techniques such as SEM, XPS, FTIR, and XRD.

3.6 Research Approach

The research approach varied across the papers, each focusing on different aspects of nickel recovery and purification. In Paper I, experimental studies were conducted to assess the effectiveness of S-Curve precipitation for nickel recovery under varying pH conditions, aiming to optimize the process parameters for maximum extraction efficiency. Paper II, on the other hand, centred on evaluating alternative analytical techniques, such as FAAS, ICP-OES and portable handheld EDXRF, for trace element analysis during the purification of high-purity nickel sulphate, involving experimental comparisons to enhance method accuracy and precision. Meanwhile, Paper III delved into the experimental synthesis of β -Nickel hydroxide ($\text{Ni}(\text{OH})_2$) via a precipitation process, conducting thorough characterization to gain insights into its structural and chemical properties. Paper IV embarked on experimental synthesis of nickel oxide (NiO) using different methods like chemical precipitation and sol-gel process, followed by detailed characterization to

understand NiO properties and its potential for environmental sensing applications. Similarly,

Lastly, Paper V involved conducting experimental investigations to evaluate the effectiveness of lime precipitation in removing impurities from pregnant waste solution (PWS) across varying pH levels. Experimental designs were formulated to conduct precipitation experiments at different pH levels, with data collection involving measurements of impurity concentrations before and after precipitation using techniques like titration and ICP-OES. Data analysis focused on assessing changes in impurity concentrations relative to pH levels to determine the efficiency of impurity removal. Furthermore, the characterization of precipitates was conducted through EDX analysis to understand the elemental composition of the resulting precipitates. Method validation was carried out to ensure the reliability and accuracy of impurity determination methods. The study's interpretation centred on drawing conclusions regarding the optimization of lime precipitation for impurity removal from PWS, emphasizing the importance of pH control in industrial applications. Moreover, morphological investigations through scanning electron microscopy (SEM) provide insights into the structure and morphology of the precipitates. Overall, the research approach integrates experimental observations with analytical characterization to comprehensively understand the precipitation process and its implications for nickel recovery processes.

3.7 Interpretation of Data and Quality control

The manuscripts utilized data treatment techniques to analyse the results comprehensively. Quality control involved the careful monitoring of factors such as reproducibility and precision. Data was recorded in triplicate, and average values were given along with standard deviations. The Horwitz, ANOVA and Variance function tools were employed for data interpretation, aiding in the assessment of method performance and validation. Additionally, the limit of detection and limit of quantification (LOD & LOQ) for the analytes investigated in the study was rigorously determined using the analytical instruments employed. This stringent

approach ensured the reliability and accuracy of the findings, contributing to the scientific rigour of the research outcomes.

REFERENCES

- Cheng, Y. (2008). Determination of trace elements in high-purity nickel by inductively coupled plasma mass spectrometry with microwave digestion. *Metallurgical Analysis*, 28(3), 9-13.
- Feng, W., & Yingping, N. (2020). *Determination of Elements in Ternary Material Nickel-Cobalt-Manganese Hydride by ICP-OES*. China: Agilent Technologies .
- Hineman, A., & Neubauer, K. (2020). *Analysis of Impurities in Nickel by with the Avio 500 ICP-OES*.
- Thangavel, S., Dash, K., Dhavile, S., & Sahayam, A. (2015). Determination of traces of As, B, Bi, Ga, Ge, P, Pb, Sb, Se, Si and Te in high-purity nickel using inductively coupled plasma-optical emission spectrometry (ICP-OES). *Elsevier*, 131, 505-509.
- Yahorava, O., Bazkho, O., Kgaria, M., Mottay, R., & Sehlolo, C. (2016). *Evaluate removal of impurities from LONMIN nickel sulphate solution*. Randburg: Mintek.

CHAPTER FOUR: PUBLICATION AND MANUSCRIPTS

This chapter presents the published articles, submitted manuscripts and manuscripts for consideration for the examination of the thesis. The subheadings in each paper are referenced and numbered following the specific guidelines of the journal to which they were published or submitted for review. Consequently, the design of all five papers, including topics, subtopics, and referencing styles, differs. However, all the published articles have been formatted to suit the requirements of this thesis submission with the Digital Object Identifier. For manuscripts submitted for review, line numbers have been removed and the page numbers formatted to cater for the thesis submission requirements. The Figures and Tables have been inserted in appropriate positions close to where they are mentioned in the body of the text. Cover letters submitted to each journal are not included in this thesis. Page numbers for published manuscripts have been removed to cater for the page format requirements for the thesis. It should be noted that Papers I, III, IV has been published while Paper II has been accepted for publication and Paper V has been submitted to different journals and they are under review.

4.1 PAPER I

This paper is entitled “The Removal of Nickel from Nickel Sulfite-Fire Assay (NIS-FA) Dissolution Filtrate through Precipitation. **Published ACS Omega, 2024, <https://doi.org/10.1021/acsomega.3c07623>**

Highlights

- ◇ Response to environmental regulations and resource conservation.
 - ◇ Exploration of economically viable recycling for filtrate disposal costs.
 - ◇ Emphasis on recovering valuable constituents, especially Ni and Cu.
 - ◇ Investigation of S-Curve precipitation for metal recovery.
 - ◇ High concentrations of Ni and Cu in NiS-FA waste.
 - ◇ Selective Cu removal via solvent extraction.
 - ◇ Efficiency of S-Curve precipitation in separating Ni from Fe.
-

Authors Contributions

Happy Mothepane Mabowa - The main author played a central role in the research process, leading the design of the methodology, supervising data collection and analysis, ensuring compliance with ethical standards, securing funding, and maintaining communication with collaborators and funding agencies.

Andile Mkhohlakali - Contributed to data collection, interpretation, and manuscript revision.

Sam Mokoena - Contributed to experimental design and manuscript revision.

James Tshilongo - Contributed to data collection, interpretation, supervision, and manuscript revision.

Luke Chimuka - Contributed to data collection, interpretation, supervision, and manuscript revision.

The Removal of Nickel from Nickel Sulphite-Fire Assay Dissolution Filtrate through Precipitation

Happy Mothepane Mabowa^{1,3*}, Andile Mkhohlakali¹, Sam Mokoena², James Tshilongo^{1,3}, Luke Chimuka³

*Corresponding author's email: happyc@mintek.co.za

¹Analytical Chemistry Division, MINTEK, 200 Malibongwe Drive, 2155, South Africa

²Hydrometallurgy Division, MINTEK, 200 Malibongwe Drive, 2155, South Africa

³School of Chemistry, University of the Witwatersrand, Private Bag 3, PO WITS, 2050, South Africa

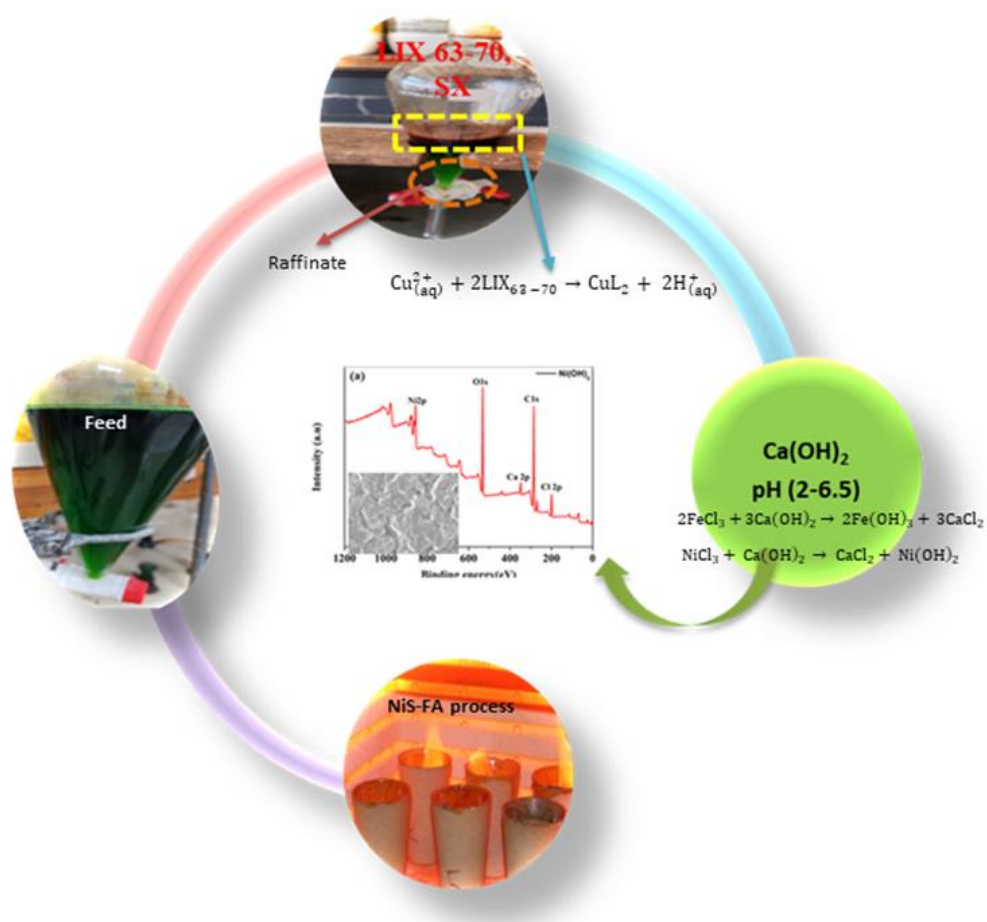
Abstract

This study responds to stringent environmental regulations and the increasing focus on resource conservation by exploring economically viable refining technologies through recycling. With the rising costs of filtrate disposal, there is a significant emphasis on removing and recycling valuable constituents, particularly nickel and copper (Ni and Cu). Herein, we employ analytical techniques with the aim of investigating an alternative method for recovering Ni and other valuable metals from nickel sulphide-fire assay (NiS-FA) filtrate using S-Curve precipitation under optimal conditions. The waste from fire assay procedure contains substantial amounts of Ni and other critical metals, such as concentrations of (62.7 g/L) of Ni and (3.87 g/L) of Cu. Prior to precipitation of Ni, traditional solvent extraction methods were applied, specifically targeting the removal of copper (Cu). However, iron (Fe) and other primary impurities require further selective separation processes. A pivotal aspect of this research involves applying S-Curve precipitation with precise parameters at different pH levels. Analytical techniques reveal a minor depletion occurs as Ni is separated from Fe at a pH of 2.5, resulting in the formation of a refined Ni stream that is then refined into a mixed hydroxide Ni(OH)₂ product. The efficiency of 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63-70) in extracting

value-added metals from fire assay waste is exceptionally high, integrating recycling and repurposing of value-added base metals to promote a circular economy.

Keywords: S-Curve, Precipitation, $\text{Ni}(\text{OH})_2$ Recovery, Nickel Sulphide-Fire Assay

Graphical Abstract



1. INTRODUCTION

Nickel (Ni) is a vital metallic element widely utilised in numerous industries due to its outstanding corrosion resistance. Estimated to be present in the Earth's crust in a concentration of 80 ppm, Ni is a silver-white, hard, and ductile metal that ranks 24th in abundance¹. In addition to Ni being economically valuable, the Ni price fluctuating is similar to other metals and the price is relatively high. Ni by-products, like those from spent batteries, present health and environmental risks through air, water, and soil pathways. Mitigation requires strict regulations, advanced recycling, and comprehensive treatment. Ongoing research and public awareness are vital for addressing challenges posed by Ni pollutants^{2,3}. Exposure to surroundings with high levels of Ni pollution can cause a range of pathological effects in people, including contact dermatitis, lung fibrosis, kidney and cardiovascular disorders. There are various techniques reported in previous studies for the removal of Ni from different types of waste. Two different approaches can be applied to solid wastes: (i) Hydrometallurgy, a method that involves solvent extraction, leaching waste metal into a solution and recovering the target metal; (ii) Pyrometallurgy, this method involves treating waste metal with heat to recover the target metal^{4,5}. Herein, we address the environmental and economic challenges associated with the removal of Ni from nickel sulphide (NiS), which is a by-product of the fire assay fusion process used for the dissolution of precious group elements (PGEs). While NiS fire assay is widely used for concentrating trace elements and precious metals from samples, and the residues from this process contain valuable PGEs, the waste generated from this process poses significant environmental concerns and presents opportunities for economic recovery⁶. This method is well-established in the mining and metallurgical industries for the efficient extraction of these valuable metals. The method involves fusing Ni, sulphur (S), sodium carbonate (Na_2CO_3), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), and a PGE-containing sample in a clay crucible at 1000°C - 1300°C. The resulting NiS button is crushed, dissolved in hydrochloric acid (HCl), and filtered to obtain a precious metal residue. This process is commonly used in analytical chemistry for isolating and concentrating trace elements and precious metals from samples. The filtrate, which contains high concentrations of Ni and

other valuable metals, is disposed of as process waste and includes a variety of metal contaminants such as copper, iron, zinc, sodium, potassium, lead, cobalt, aluminum, manganese, silica, and chromium and magnesium (Cu, Fe, Zn, Na, K, Pb, Co, Al, Mn, Si, Cr and Mg). Cu and Ni in the waste are valuable elements that can be further processed and purified.

Methods like chemical precipitation, electrolytic membranes, and ion exchange are utilised to eliminate impurity metal ions and refine Ni aqueous solutions^{7,8}. Despite their effectiveness, they are often limited by high costs, impracticality for small-scale applications, and difficulties with material regeneration⁹. In contrast, precipitation is widely employed for waste treatment due to its cost-effectiveness and practicality for large-scale applications. However, traditional precipitation methods, which involve lime, sulphides, or hydroxides, generate a voluminous sludge that cannot be reused and requires disposal in landfills. This not only poses environmental hazards but also results in the loss of valuable minerals. Additionally, subsequent treatment incurs significant operational costs, especially in terms of energy consumption¹⁰. Several treatment processes have been reported in the literature for the Ni ions removal from liquid waste, including adsorption¹¹, ion exchange¹², chemical precipitation¹³ and electrochemical methods: electrode ionisation¹⁴. Hydroxide precipitation, a conventional method for metal plating waste treatment, relies on the low solubility of metal hydroxides under alkaline conditions. This process involves forming metal hydroxide solid phases, which are then separated from wastewater through sedimentation, flotation, and filtration. Sulphide precipitation is another procedure that results in minimal solubility of metal sulphides, making it efficient for both free and complex metals.¹⁵ The metal sulphide waste has a strong acid generation potential which makes it undesirable for disposal. Metal sulphide waste generates strong acids during the leaching of PGEs, as the acids used dissolve the metal sulphides and result in acidic by-products in the filtrate. This acidity complicates disposal. Coagulants, including ferric chloride (FeCl_3), alum, and various polyelectrolytes, are commonly used in hydroxide precipitation applications to address solid formation and separation issues and enhance the clarity of the supernatant.

Concentrated nickel hydroxide $\text{Ni}(\text{OH})_2$ or sulphides in precipitated sludge are extremely hazardous and life-threatening wastes that must be disposed of at a high cost to the industry using specialised facilities³. It is essential for environmental preservation and resource conservation that Ni-containing wastewater is effectively recovered and re-used. The development of closed-recycle systems or effluent-free technology is critical. Ni recycling has attracted considerable interest to provide options for re-use and repurposing the value-added metal at the same time circumventing the environmental pollution risk¹. Analysing trace elements in wastewater that contain Ni involves employing diverse inorganic techniques^{16,17,18}. Effective precipitation techniques are fundamental in the recovery and purification of nickel from various sources. Among these techniques, the use of lime ($\text{Ca}(\text{OH})_2$) plays a pivotal role in the precipitation of nickel hydroxide ($\text{Ni}(\text{OH})_2$), which is a critical step in the process. Lime (calcium hydroxide) is introduced to adjust the pH and facilitate the formation of nickel hydroxide, a crucial reagent for achieving high-purity nickel. This study also utilised 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63-70) to address impurities such as copper in the nickel recovery. To the best of our knowledge, there is no $\text{Ni}(\text{OH})_2/\text{NiSO}_4$ recovered from fire assay waste reported in the literature. Herein, we aim to remove and recover nickel from nickel sulphide fire assay dissolution filtrate through precipitation from the precious group elements filtration solution (waste).

2. MATERIAL AND REAGENTS

The Ni filtrate used in this study was collected from NiS Laboratory within the Analytical Chemistry Division in Randburg South Africa, 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63-70) supplied by BASF South Africa (Pty) Ltd. All reagents were analytical grade and used without further modification, ACS, ISO grade, sodium hydroxide A.R, 65% (w/w) of nitric acid, calcium hydroxide from ACE chemicals and sodium peroxide from Merck Group (Pty) Ltd. Throughout the studies, Milli-Q system Type 1 water (Millipore Milli-Q® Direct 16 Water

Purification System) from Merck was used to prepare ultrapure water (18.2 MΩ cm).

2.1 Characterisation and Analytical Analysis

In this study, an Agilent 5110 Vertical Dual View (VDV) inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to determine the metal concentration following extraction. The pH of the solutions was measured using an OPR pH meter from Mettler-Toledo Ltd. (Australia). The precipitated samples were subjected to X-ray diffraction (XRD) patterns recording Ultima IV X-Ray DI powder diffractometer using Cu K α radiation operating at 40 kV (diffraction wavelength $\lambda = 0.15406$ nm), with a scanning rate of 4°/min throughout the 15° to 90° range to determine the structure of the Ni(OH)₂ precipitate. SEM-EDS: Morphology imaging was performed using a Zeiss Cross Beam 540 with an InLens detector at 2 kV, 79 pA, and a working distance of 5 mm. Cross-section imaging was conducted at 20 kV and 5 nA using a Backscattered Electron detector. EDS analysis was carried out at 20 kV and 5 nA with an Oxford Xmax EDS detector and Aztec analysis software. PerkinElmer PinAAcle 900T series AA Spectrometers controlled by Syngistix™. The X-ray photoelectron spectroscopy (XPS) analysis was performed using a Shimadzu XPS instrument with a monochromatic Al K α X-ray source at 1486.6 eV which operates with a 400 μ m spot size, constant pass energies of 20 eV for high-resolution and 100 eV for survey scans and The Fourier-transform infrared spectroscopy (FTIR) analysis was conducted using a Shimadzu IRTracer-100 spectrometer. The instrument operated with a resolution of 4 cm⁻¹ and covered a wavenumber range from 4000 to 400 cm⁻¹.

2.2 Solvent Extraction of Cu²⁺

The extraction of Cu was carried out utilizing LIX 63-70, an oxime reagent, with LIX 63-70 serving as an accelerator. The extraction experiments were conducted in 125 mL separator funnels at room temperature, utilizing an organic-to-aqueous (O/A) ratio of 1:5. The aqueous phase comprised a filtrate containing Cu, Ni, Fe,

and other impurities within a chloride matrix. This approach highlights the detailed methodology employed for the efficient extraction of Cu, focusing on the key components and procedural steps critical for achieving optimal results under the specified conditions.

2.3 Precipitation of Fe^{3+} , Cu^{2+} and Ni^{2+}

A 2 L jacketed batch reactor equipped with an overhead stirrer at 333 rpm was used to ensure effective suspension of the seeding material in the solution as displayed in Figure 1. 1L of sample was used to conduct the test work and 25 mL of sample was taken at each pH variation. Temperature measurements were conducted using a thermometer, while the pH during the reduction process was monitored using a pH meter. The tests were operated at 60°C and heating was provided by circulating hot water through the jacket of the reactor (Kgaria et al., 2016). The pH of the solution was increased in small increments using 20% (m/m) $\text{Ca}(\text{OH})_2$. The targeted pH points were 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0 and 7.5. After reaching equilibrium at each pH increment, the reactor content was stirred for an additional 15 minutes before a sample was taken and filtered, and pH was recorded. At the end of the test, the slurry was filtered using the Whatman ashless 125 mm filter paper grade 44. The volume of filtrate and the mass of residue were recorded. The filter cake was dried at 50°C overnight for 12 hours in an oven supplied by Labotec EcoTherm Economy. Solution samples from each pH increment and a sample from the filter cake were analysed for base metals, HCl, Na and K.

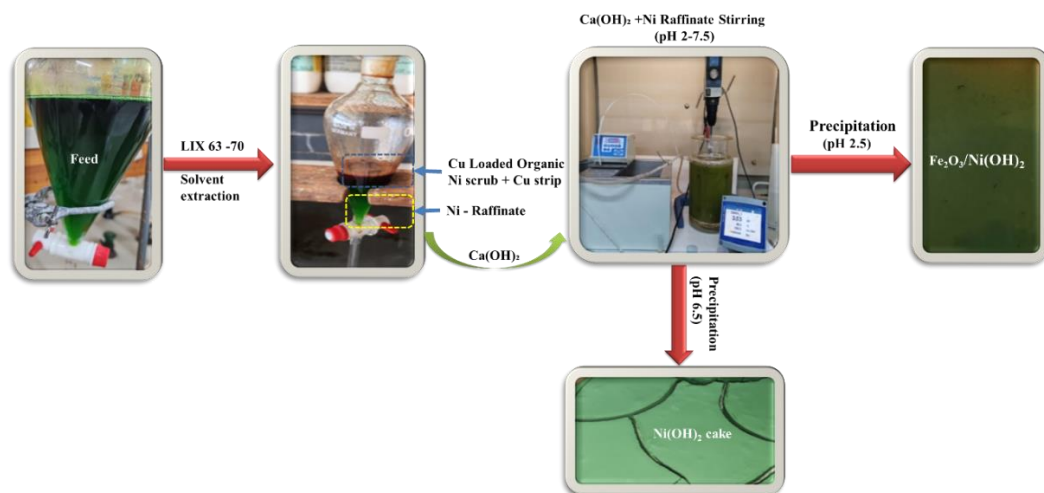


Figure 1. Schematic diagram showing solvent extraction and precipitation Ni-case (powder).

2.4 Sample Preparation

The elemental concentration in the solutions was analysed using ICP-OES. The concentration of Na and K was analysed by atomic absorption spectroscopy (AAS). Titration of acid was done by wet chemistry method for HCl. The acid titration of HCl was done using standardised 1M of NaOH in an auto-titration system with a pH probe and a 1:1 ratio. The titration for HCl in the sample is critical to calculate the amount of lime needed to neutralise HCl in the reaction. The dissolutions in this study utilized concentrated HNO_3 and both dissolutions and dilutions were carried out using ultrapure water. Calibration solutions for aqueous ICP-OES in 5% HNO_3 were prepared with materials from high purity standards. ICP-OES measurements were conducted using argon supplied by Afrox, South Africa with a purity grade of 99.996%. Sample preparation for ICP-OES analysis involved pipetting a 5 mL sample into a 25 mL volumetric flask, adding 4% nitric acid (HNO_3), 1.25 mL of 0.2 g/L scandium (Sc) internal standard, and filling to the mark with ultrapure water. The preparation of samples for AAS analysis was diluted ten times by pipetting 2.5 mL sample into a 25 mL volumetric flask with 4% (HNO_3). For solids, the sample mass was weighed in a crucible with the addition of fluxes such as NaOH and Na_2CO_3 , the mixture was fused and digested in concentrated HNO_3 to ensure complete dissolution of the sample and fluxes. To cover the entire range of trace and matrix elements in the waste filtrate solution, calibration solutions were made in the following concentration range: from 0.1 to 10,000 ppm. For quality check verifications sample number 1, 5, and 11 run was done in duplicate with results within 5% of each other being averaged. The precision of an analytical method is directly influenced by the concentration of the analyte, regardless of the characteristics of the analyte, matrix, or the method employed. This relationship can be determined using the statistical data analysis.

3. RESULTS AND DISCUSSION

3.1 Head Sample Filtrate Solution Waste

There were also notable concentrations of Zn, Na, K, Pb, Co, Al, Mn, Si, Cr and Mn. Although the solution was predominantly chloride media, there was a notable concentration of sulphur, which is a notable impurity that is introduced during the process of fire assay in the form of the flux that is added. The findings suggest that there are no viable processes reported to recover Cu and Ni from filtrate solution from PGE's preparation. Based on the concentration of the major elements, Ni and Cu are commonly regarded as valuable metals while Fe is classified as impurity elements. Furthermore, the concentration levels of both Ni and Cu are sufficiently high and would justify any effort for recovery. Contrary, the concentration of all the elements listed under minor elements is too low to be considered for recovery.

Table 1 presents the chemical analyses of the feed sample. The results show that the feed solution contained 280 g/L of hydrochloric acid (HCl) and a chlorine (Cl) concentration of 80 g/L. This confirms that the solution was prepared by dissolving the solid material in concentrated HCl (32%) and that the solution is in a chloride matrix. The presence of HCl and varying Ni concentrations affects ion peak intensities in the analysis of high-purity Ni samples using ICP-OES. Existing literature suggests that the influence of chlorine (Cl) on the matrix is insignificant. Nevertheless, when dealing with Ni samples with high content, the matrix effects were observed to inhibit the signals of the analyte isotopes. The major metals in the filtrate solution were Ni (62.7 g/L), Fe (4.72 g/L) and Cu (3.87 g/L). From the literature survey, it has been observed that no viable processes are reported to recover Cu and Ni from filtrate solution from PGE's preparation.

Table 1. Chemical Composition of the Feed Solution

Element & Compounds	Feed Concentration (g/L)	Raffinate	Major elements
Ni	62.7	62.7	

Fe	4.72	2.6
Cu	3.87	0.8
Cl	274	274
	Concentration (ppm)	Minor elements
Zn	73.9	71.6
K	22.5	22.5
Na	210	22.5
Pb	10.2	10.2
Co	9.8	9.8
Al	7.3	7.3
Mn	6.7	0.48
Ca	4.53	-
Si	4.11	-
Cr	3.51	3.51
Mg	2.69	-
As	0.26	0.26
Ag	0.25	-
Cd	0.23	0.23
S	162	144

Based on the concentration of the major elements, Ni and Cu are commonly regarded as valuable metals while Fe is classified as impurity elements. Furthermore, the concentration levels of both Ni and Cu are sufficiently high at above 100 ppm and would justify any effort for recovery. Contrary, the concentration of all the elements listed under minor elements are too low, at 100 ppm or below to be considered for recovery.

3.2 Solvent Extraction of Copper (Cu)

The pre-extraction stage of copper (Cu) before precipitation using 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63-70) typically involves the formation of a complex between the oxime groups in the reagent and the Cu ions¹⁹⁻²¹. The utilisation of solvent extraction (SX) as a pre-extraction method is a strategic

measure to prevent Cu loss during precipitation in the presence of iron (Fe). SX extraction of Cu precipitation processes coexistence of Fe leads to co-precipitation, causing Cu loss in the form of Cu-Fe hydroxide precipitates, as illustrated in Figure S1 and Table S1 in supporting information.v The detection of Cu in the energy-dispersive X-ray spectroscopy (EDX) analysis during the precipitation of Fe₂O₃ in Figure S1 highlights the need to prevent Cu loss. To address this, a pre-treatment step employing SX is applied, selectively extracting Cu and enhancing the overall efficiency of copper extraction.

The specific reaction can be represented as indicated:



Where $\text{Cu}_{(\text{aq})}^{2+}$ (3.87 g/L) represents Cu ions in the aqueous phase, CuL_2 represents the formed complex of Cu with LIX 63-70. Two molecules (denoted by 2LIX_{63-70}) of the oxime reagent LIX 63-70 and $2\text{H}_{(\text{aq})}^{+}$ indicates protons that may be involved in the complex formation process.

In this study, the extraction of Cu using LIX 63-70 was applied, focusing on the initial complex formation between the oxime groups of the reagent and Cu ions. This intricate process led to the efficient transfer of Cu from the pregnant leach solution (PLS)/aqueous phase to the organic phase, accomplished at ambient temperature and low pH values (~0-0.2) within a concise fifteen-minute contact time. The oxime functional groups exhibited a notable affinity for metal ions, particularly Cu, contributing to the high extraction efficiency of 79% as described and compared in the literature^{19,20}. The resulting aqueous phase termed the raffinate, revealed a Cu concentration of 800 ppm as determined by ICP-OES. A comparative analysis with Acorga M5640 and Mextral 5640H underscored LIX 63-70's efficacy demonstrating notably faster equilibrium conditions²¹. With an O/A ratio of 1:5, LIX 63-70 achieves faster equilibrium at 25°C, reducing extractant use and operational time. While Mextral 5640H extracts over 93% copper at pH 1, its optimal performance in highly acidic conditions and a higher O/A ratio (1:1) limit

its versatility. Acorga M5640's 40% efficiency further underscores LIX 63-70's advantage in balancing speed, efficiency, and cost in industrial applications. Furthermore, the previous study highlighted the pH dependency of Cu extraction, emphasizing the influence performance of both Acorga M5640 and Mextral 5640H²⁰. This research, which reported the extraction of 79% Cu using LIX 63-70 at room temperatures for a contact time of fifteen minutes, provides valuable insights into the effectiveness of the solvent as an extractant for Cu under specific conditions, contributing to the broader understanding of solvent extraction processes²².

3.3 Precipitation S-Curve for Major Elements

The precipitation experiments conducted have elucidated the profound impact of solution pH and metal concentration on the precipitation kinetics of dissolved ions, particularly in the initial phase of the precipitation process. Figure 2 encapsulates the precipitation S-curves delineating the precipitation behaviours of major metals within the raffinate solution. Analysis of the S-curve plots reveals a distinctive pH-dependent precipitation hierarchy among Fe, Cu, and Ni.

Notably, the initial pH of the feed sample is ~0-0.1 and the results indicate that Fe precipitates at a lower pH as opposed to Cu and Ni. Achieving complete precipitation of Fe was realized at a pH of 2.5 as illustrated in Figure 2 with the reaction shown in equation 2, underscoring its heightened proclivity for precipitation under mildly acidic conditions. The raffinate was reacted with lime to produce iron (III) hydroxide $\text{Fe}(\text{OH})_3$ precipitate at pH 2.5 as shown in equation 2 was analysed by ICP-OES and the results are shown in Table 2. The precipitate cake was dried and characterised by XRD and SEM. In contrast, Cu demonstrated full precipitation at a marginally higher pH of 4.5, signifying a differential pH sensitivity in its precipitation dynamics. Ni exhibited distinct behaviour, with complete removal from the solution occurring at a pH of 6.5 as denoted in Figure 2 with the reaction shown in equation 3, further accentuating its unique precipitation profile compared to both Fe and Cu. These findings contribute a nuanced understanding of the pH-mediated precipitation characteristics of major metals in

the raffinate solution, presenting valuable insights for the optimisation of the precipitation process in the selective separation and recovery of Fe, Cu, and Ni.



The precipitate cake of was subjected to drying in an oven at a temperature of 50°C overnight for 12 hours in an oven. This drying process is employed to remove any remaining moisture content from the precipitate, leading to the formation of a dry and stable product. The temperature is indicative of a relatively mild drying condition, often chosen to prevent excessive heat-induced transformations while efficiently evaporating moisture. This step is crucial in many chemical processes to obtain a solid and dry form of the $\text{Fe}(\text{OH})_3$ precipitate for further analysis or use in subsequent stages of experimentation.

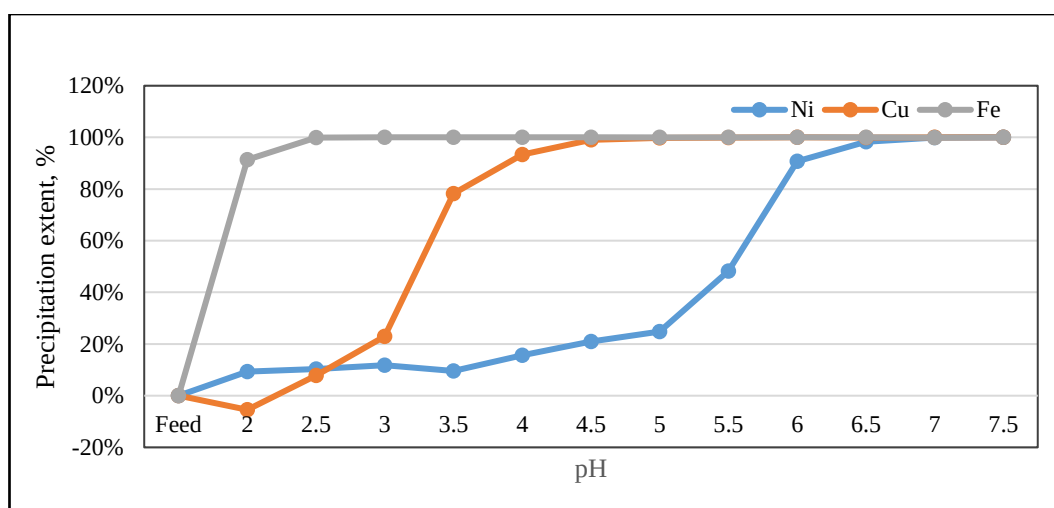
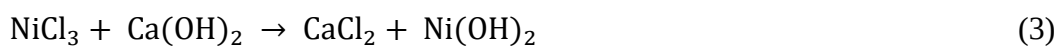


Figure 2. Precipitation S-Curve Plots of Major Elements (Cu, Fe and Ni)

Although both Cu and Ni were removed at relatively higher pH values compared to Fe, the precipitation of these metals initiated at pH 2 for Ni and pH 2.5 for Cu. This observation suggests that while there is a potential for selectively separating Ni from Cu and Fe through precipitation, the process inherently leads to the loss of both metals. This would result in losses of 10% for Ni and 8% for Cu. Consequently, the pre-extraction of Cu emerges as a strategically suitable stage to prevent the loss of 8% of Cu during subsequent precipitation processes. The metal concentration

profiles in Figure 3 show that there was a significant drop in the concentrations of Ni, Cu, and Fe after neutralisation to pH 2.0 the Fe concentration is 0.238 g/L. The decrease in Cu and Ni concentrations was primarily due to precipitation caused by the increase in pH from the addition of the 20% lime slurry, while the drop in Fe concentration resulted from both precipitation and the dilution effect of the lime slurry. The concentration of Fe at pH 2.5 was <2 ppm (parts per million) which correlates with the precipitation S-curves which reported complete precipitation of Fe and the precipitation of rust-coloured Fe(OH)₃. The Cu concentration dropped slightly between pH 2.0 and 3.5, and a significant drop below 2 ppm was achieved at pH 5.5.



The concentration of Cu ions, as well as the surface electrical properties of materials and their interaction with ions, are significantly influenced by the pH of the solution³⁰. These observations were based on contact times ranging from 10 to 120 minutes. At pH 5.5, Cu adsorption efficiency varied between 50.7% and 93.0%, depending on the contact period. The increase in adsorption efficiency at higher pH levels can be attributed to the enhanced interaction between Cu ions and the adsorbent surface. Although the adsorption efficiency fluctuated, the difference in efficiency remained relatively consistent for the same contact times. However, contact times for other analytes were not reported, nor were they outlined in the methodology, limiting a comprehensive comparison. The research reported that the concentration of Ni was stable between pH 2.0 and 5.0 followed by a sharp decline between pH 5.0 and 7.5. While Fe can be separated from Cu and Ni at pH 2.5, there are still losses of 10% for Ni and 8% for Cu. This highlights the potential for selective separation, but further optimization is required to minimize metal losses during the process. The precipitation of Ni (II) decreases as the solution pH rises. Initially, the time-growth plots show a curved pattern due to rapid removal, eventually flattening as the removal process slows down near saturation of 100% at pH 2.5, 4.5 and 6.5 for Fe, Cu and Ni respectively. However, the highest precipitation of Ni (II) occurs under alkaline conditions. Figure 3 indicates that Ni

(II) uptake by lime in the chemical precipitation is more pronounced at alkaline pH levels up to 5.0, with minimal removal, and it increases progressively with a further rise in pH, reaching its peak at pH 6.5.

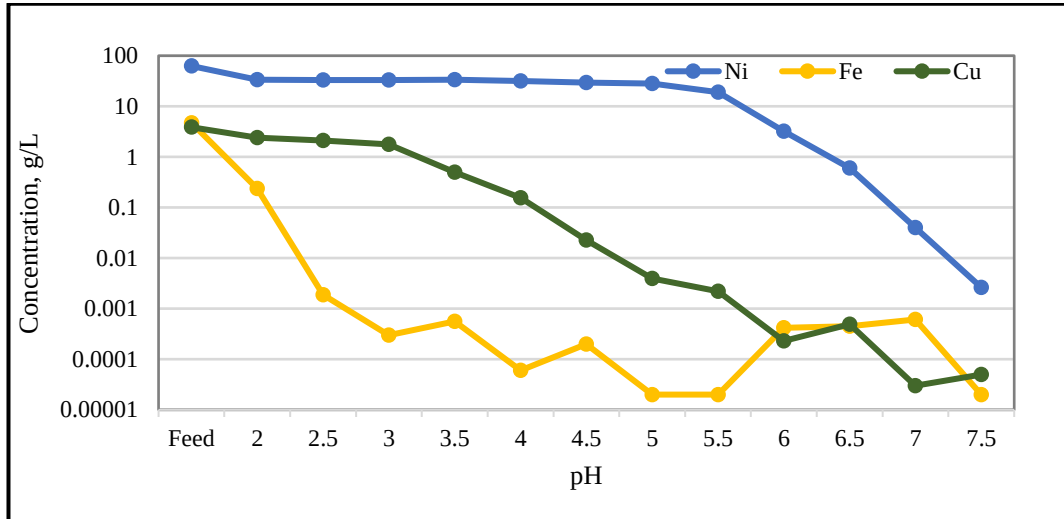


Figure 3. Metal Concentration vs pH for Major Elements (Ni, Cu and Fe)

The summarised analyses of lime consumption for the S-curve test are provided in Table 2 and were analysed by ICP-OES. At pH 2, 71% of the lime needed for the process has been utilized, initiating the pH adjustment and starting metal precipitation. By pH 2.5, lime consumption slightly increases, but cumulative utilization remains stable at 71%, indicating that most of the lime required for initial precipitation is already used. At pH 3, lime utilization rises to 72% as additional lime is used to further adjust the pH and precipitate more metal ions. At pH 4.5, lime consumption increases significantly, with cumulative utilization reaching 76%, indicating more effective pH adjustment and metal removal. By pH 6.5, lime utilization nears completion at 98%, showing that nearly all the lime has been consumed to facilitate metal precipitation. Finally, at pH 7.5, lime utilization reaches 100%, signifying that all added lime has been used up, and the precipitation process is complete, with minimal remaining metals in the solution. The total lime consumption for the S-curve precipitation was 3.96 kg/kg of available Ni.

Table 2. Lime Consumption Analyses

pH	Lime consumption, Ni (kg/kg)	Cumulative lime utilisation, %
2	2.8	71
2.5	2.83	71
3	2.85	72
3.5	2.9	73
4	2.94	74
4.5	3.02	76
5	3.08	78
5.5	3.33	84
6	3.75	95
6.5	3.87	98
7	3.92	99
7.5	3.96	100

3.3.1 Structural and Morphological Properties

SEM image in Figure 4 (a) depict the layered granule with nearly spherical particles which is typical $\text{Ni}(\text{OH})_2$ and this corroborates with previous literature²³. The rough surface may correspond to high oxides from the precipitation with lime on the Ni surface, and rough agglomeration also corresponds to typical features formed during the precipitation process. In addition, the aggregation may attributed to non-post treatment^{14,24,27}. EDX confirms the existence of Ni and O (in the form of hydroxide) rather than oxides. Interestingly, the EDS spectra show no Cu traces which indicates that Cu was loaded to the organic phase reaction process shown Equation 1, before the precipitation process and the remaining Cu in raffinate was precipitated at pH 4.5. The Ca impurities observed are likely due to the addition of lime, which forms $\text{Ca}(\text{OH})_2$. This compound then reacts with dissolved metal chlorides to produce CaCl_2 , as outlined in the reaction process shown in Equation 3. Furthermore, the element map in Figure 4 (c) displays the Ni distribution and other elements corresponding to EDX spectra. Figure 4 (d), depicts the XRD pattern

which represents the β -Ni(OH)₂ formed during the precipitation process. Since all diffraction peaks indicate the β -Ni(OH)₂ hexagonal phase and the peaks indexed 2 θ values 24°, 29°, 30°, 45°, 50°, and 60° corresponding (001), (100), (101), (102), (103), (110) respectively^{24,25}, and matches with the joint committee on powder diffraction standards(JCPDS):73-1520 standard.

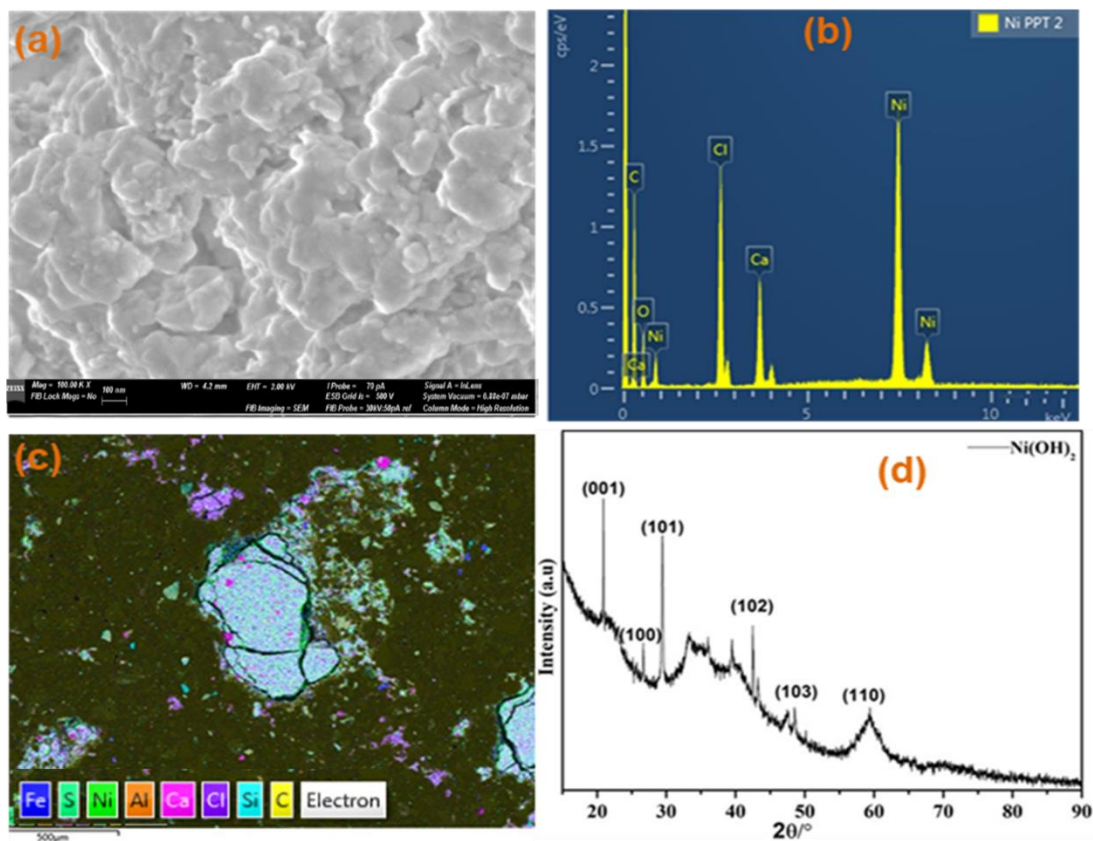


Figure 4. SEM micrograph (a); EDX Spectra (b); SEM-EDX overall Element Distribution Map (c); and XRD Pattern of Ni(OH)₂ (d).

The states of the chemical composition and electronic structure of the Ni(OH)₂ surface are characterised by X-ray photoelectron spectroscopy (XPS) as displayed in Figure 5. The survey spectrum of Ni(OH)₂ was recorded from 0 to 1300 eV to capture a comprehensive range of binding energies and identify the elemental composition and chemical states present. The peaks allocated around 860 eV, 510 eV, and 300 eV, are assigned to Ni 2p, O1s²⁶, and C1s which indicates that Ni(OH)₂ was precipitated successfully at pH 6.5 as supported by Table S1. The results collaborate with the previous studies²⁷.

The photoelectron peaks around 200 and 350 eV are due to Cl and Ca from the HCl (from the waste matrix) impurities and lime respectively. Figure 5 (b) shows the spectrum of Ni2p, the peaks located around 873 eV and 855.87 eV are ascribed to Ni ($2p_{1/2}$) and Ni ($2p_{3/2}$) respectively. The O1s photoelectron peak could be deconvoluted into three peaks, as shown in Figure 5 (c). The hydroxyl species in Ni(OH)₂ surface is confirmed by the O1s of the metal oxide located around 531 eV. Other O1s peaks indicate the carbon dioxide (CO₂) impurities observed with FTIR in Figure 6.

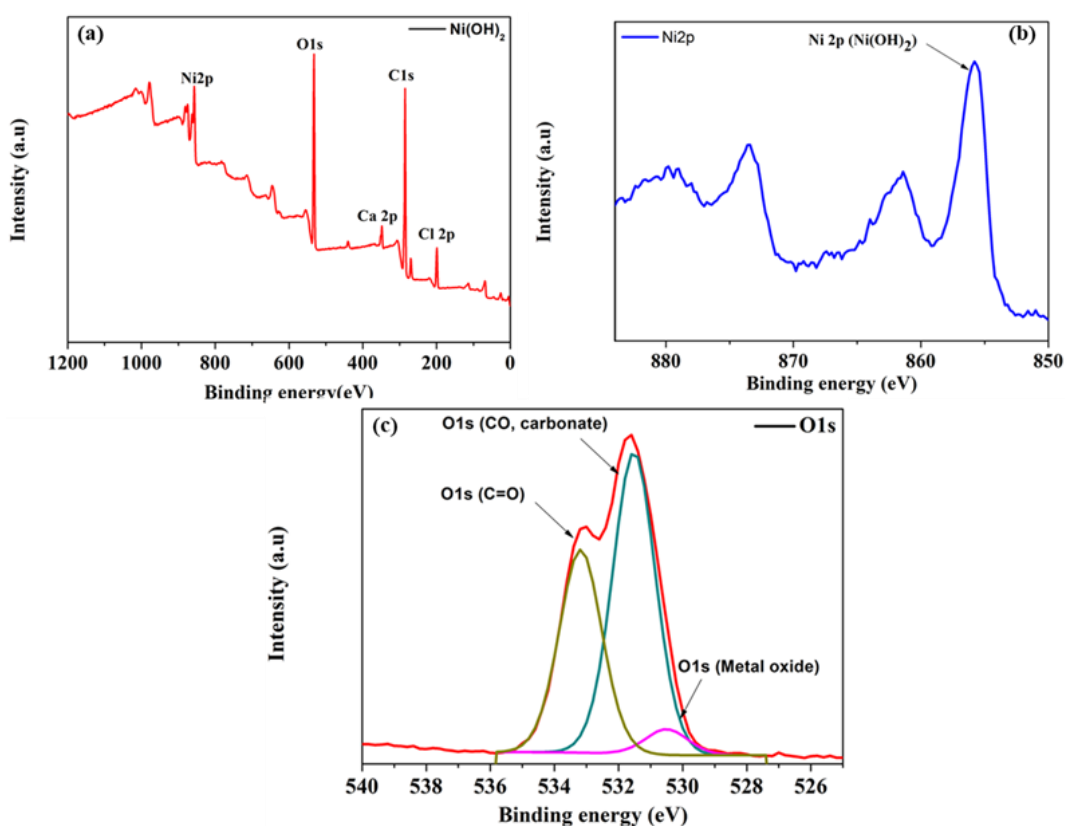


Figure 5. XPS Spectra Survey of Ni(OH)₂ (a); Ni2p Spectra (b); and O1s Spectra of β -Ni(OH)₂ (c).

In Figure 6, the Fourier transform infrared (FTIR) spectra of Ni(OH)₂ are presented, revealing distinctive peaks at 450-600 cm⁻¹ and 1100 cm⁻¹, corresponding to the ν (Ni-O) stretching vibrations in the β -phase of Ni(OH)₂ and ν (O-Ni-O), respectively. Another stretching vibration band around 1000 cm⁻¹ is associated with ν (Ni-O-Ni). These observations are consistent with the literature²⁴. Noteworthy, the

strong bending vibration band that can be seen around 1600 cm^{-1} is attributed to a hydroxyl group of Ni(OH)_2 . The broad stretching vibration peak at 3450 cm^{-1} is ascribed asymmetric $\nu(\text{OH})$ stretching mode from water/ metal hydroxyl in α -phase $\nu(\text{Ni-OH})$. These observations are consistent with the literature²⁸. The sharp peak around 1620 cm^{-1} is ascribed to $\delta(\text{OH})$ bending vibration²⁸ on the Ni surface. The aforementioned results confirm that Ni(OH)_2 was precipitated successfully. The other vibration bands around 2200 cm^{-1} , and 1330 cm^{-1} are attributed to $\nu(\text{C-O})$ stretching, and $\nu(\text{C-H})$ from the minor impurities. The later results collaborate with the XPS results in Figure 5, which indicate that Cu was completely loaded in the organic phase as illustrated in equation 1 and only Ni(OH)_2 was precipitated at pH 6.5. All functional groups are summarised in Table 3, they are consistent with Figure 4. These are also consistent with Table S2 and Table S3 which illustrate the XPS and EDX results which is Ni(OH)_2 .

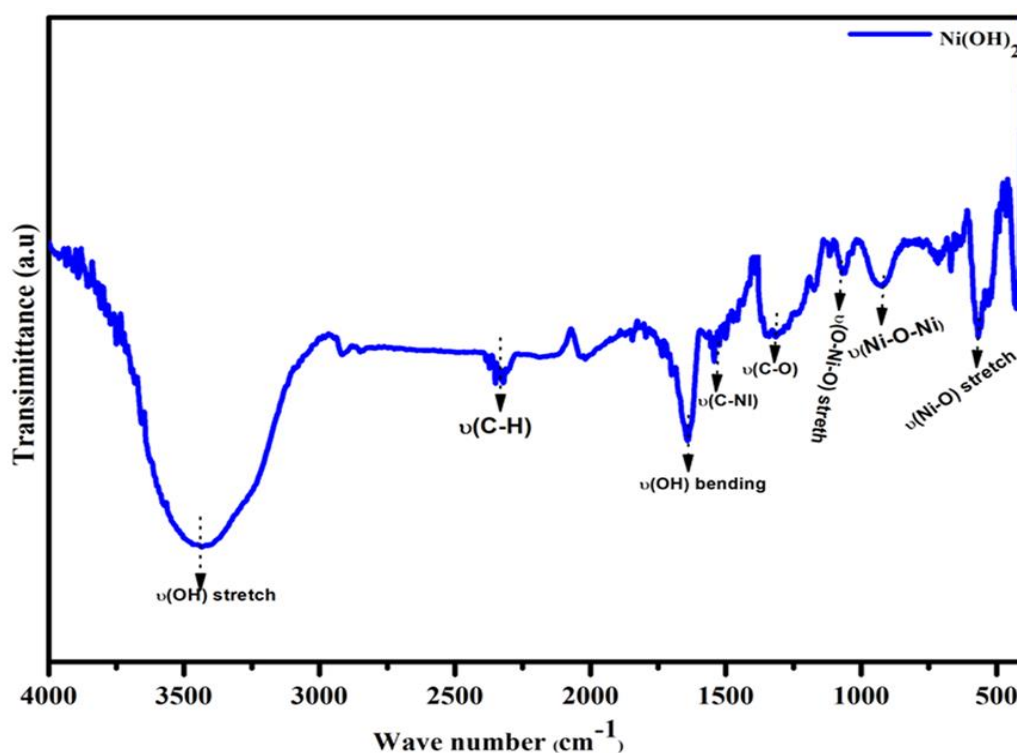


Figure 6. FTIR Spectra of Ni(OH)_2 .

Table 3. Summary of FTIR Results Showing the Ni(OH)₂ Functional Groups

Functional groups	Wave number (cm ⁻¹)	Assignment
V(SiO), ν (O-Ni-O)	470-800	NiO and Ni-OH
ν (OH)	3400	stretch vibration of OH of H ₂ O and β -Ni(OH) ₂ phase
δ (OH)	1650	Bending vibration of OH of H ₂ O
ν (C-H)	2300	C-H stretching due to C impurities
ν (C-O)	1460	CO stretching vibration, due to carbon/ carbonate impurities

The decline in Cu content within the precipitates under elevated acid concentrations, illustrated in Figure 7 (b), is ascribed to the rise in the equilibrium ferric (Fe³⁺) concentration in the solution is also depicted in Figure S1 and Table S1. This escalation leads to a slower nucleation rate, resulting in larger particles, as evidenced in Figure 7 (b), and a comparatively reduced precipitation of divalent ions or solution occlusion. This phenomenon aligns with the findings of Ruiz et al.,¹⁸ who also noted an enlargement in particle size under higher acid concentrations showing a flower-like indicate a typical Fe(OH)₃ hierarchical nanostructures as a result of controlled nucleation.

Figure 7 (a, b) shows the SEM, EDX of Ni(OH)₂ with high Fe impurity at pH 2.5, the surface morphology is similar to SEM micrographs of Ni(OH)₂ illustrated in Figure 4(a), rough surface with layered granules and nearly spherical particles, however, the EDX indicates the presence of Fe in Ni(OH)₂. These results confirm the expected experimental results according to the S-curve where Fe remained in Ni-rafinate at pH 2.5. Noteworthy, the Fe impurity is very high and the XRD indicates the Fe peaks with the slight 2 θ shift around 50° and the results confirm with XPS (Figure 5). The 2 θ shift may be attributed to the substitution of Ni atoms in the crystal structure by Fe atoms. The EDX spectra also indicates the high Ca content as impurity which is attributed to lime (Ca(OH)₂) used during the

precipitation. The later results are consistent with XPS results in Table S3 and S4 of the supporting information.

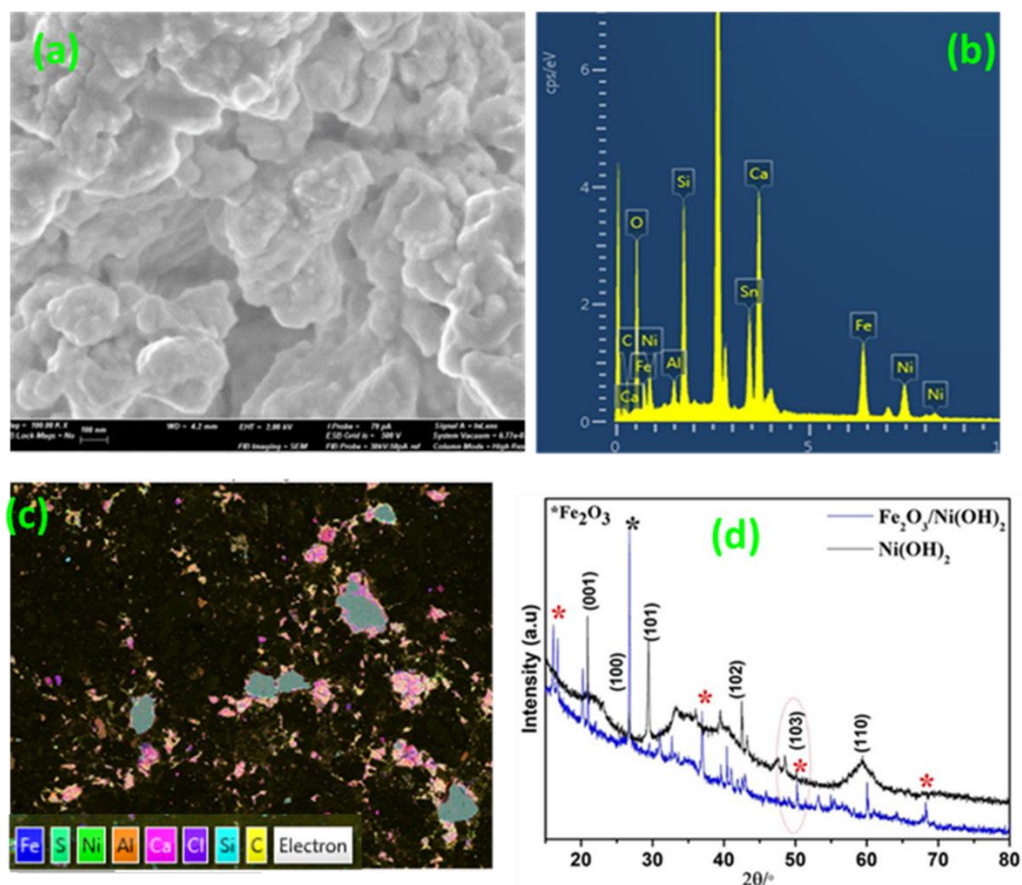


Figure 7. SEM micrograph (a); EDX spectra (b); SEM-EDX overall element map (c); and XRD pattern (d) of $\text{Fe}_2\text{O}_3/\text{Ni(OH)}_2$.

In Figure 8, Fe, Ni, and O were consistently detected in the survey spectra of the $\text{Fe}_2\text{O}_3/\text{Ni(OH)}_2$ from 0 to 1000, as displayed in Figure 8 (a). The photoelectron peaks around 880 and 720 eV and 520 eV are assigned to Ni2p and Fe2p, respectively. The results are consistent with EDX results, which indicate that at pH 2.5, both Fe and Ni precipitated. The peaks allocated around 855 eV and 875 eV are ascribed to Ni2p ($3/2$), and Ni2p ($1/2$), respectively. The peaks show the XPS characteristic peaks of Ni. Around 712 and 726 correspond to Fe2p ($2/3$) and Fe2p ($1/2$), and this method could be attributed to Fe^{3+} . The results show strong agreement with EDX, which shows the existence of Fe and Ni and $(\text{OH})_2$ species. The

existence of Fe and Ni at pH 2.5 is also displayed in the EDX results in Table S1 and XPS results in Table S4.

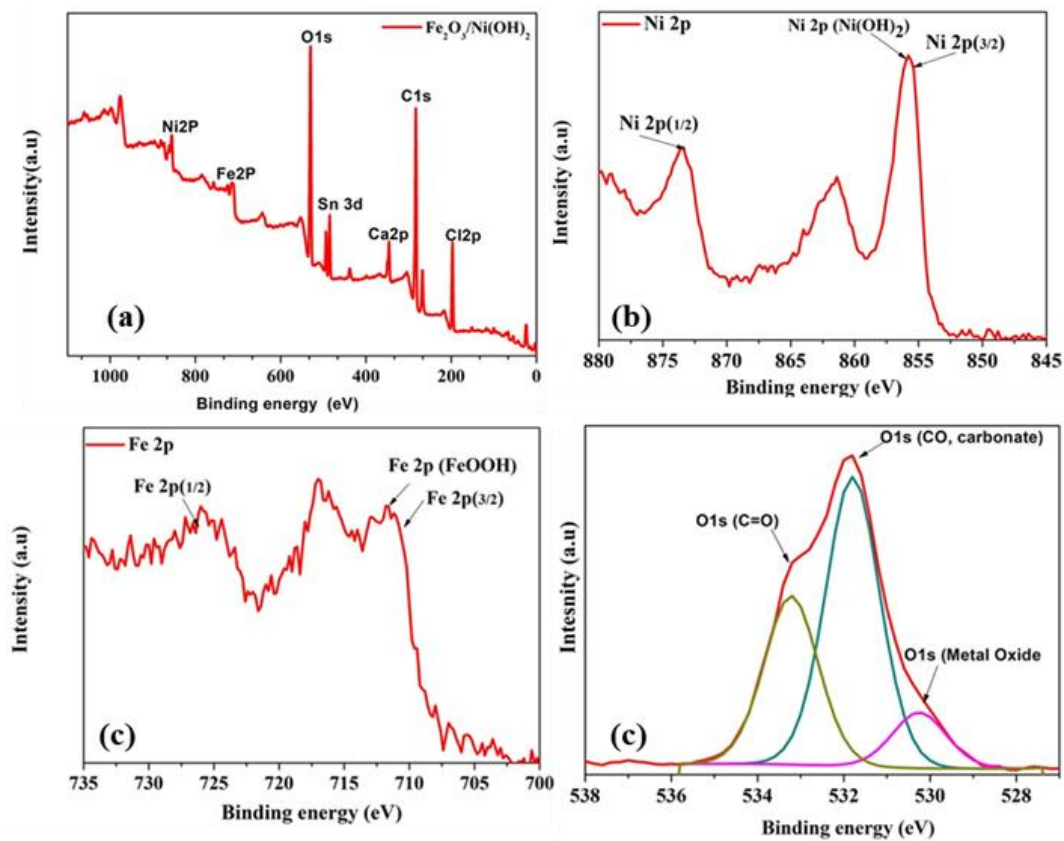


Figure8. XPS spectra survey of $\text{F}_2\text{O}_3/\text{Ni}(\text{OH})_2$ (a); Fe2p (b); Fe, Ni2p (c); and O1s (d).

4. CONCLUSION

Separation of Ni(OH)_2 by solvent extraction from the fire assay waste was successful, LIX 63-70 exhibit the high efficiency to load Cu in the organic layer and liberate Ni in the aqueous phase. In addition, chemical analyses of the head sample showed that the solution was very acidic with an HCl concentration of 280 g/L and contained high Ni and Cu, with concentrations of 62.7 g/L and 3.87 g/L, respectively. Fe was the only notable impurity element with a concentration of 4.72 g/L. The results for the precipitation S-curve showed that Ni and Cu can be separated from Fe at pH 2.5 with minimum losses and produce a Ni-Cu stream that could be processed further to produce a mixed hydroxide product.

The total lime consumption for neutralising the feed solution to pH 7.5 was 3.96 kg/kg of Ni. About 71% (i.e. 2.80 kg Ca(OH)_2 /kg Ni) of the total lime consumption was used to neutralise the acid in the solution and obtain pH 2.0. In general, the filtrate solution produced during PGE analyses contains relatively high concentrations of valuable metals. Physico-chemical characterization of the precipitate aligns closely with the S-shaped precipitation curve observed due to the process described in the section. XRD revealed the formation of a crystalline β - Ni(OH)_2 phase, while FTIR confirmed the presence of relevant functional groups, both indicating the successful precipitation at pH 6.5. In addition, the non-detected Cu and Fe at pH 6.5, as confirmed by EDX and XPS indicates that LIX 63-70 loaded the Cu in the organic phase and only Ni(OH)_2 precipitated at pH 6.5. Interestingly, EDX and XRD showed the composite of $\text{Fe}_2\text{O}_3/\text{Ni(OH)}_2$ at pH 2.5 which corroborates the precipitation S-curve, indicating that traces Ni precipitated with Fe as impurity. The classical solvent separation using LIX 63-70 exhibits high efficiency for separating value-added metal from fire assay waste. The aforementioned approach provides with recycling and repurposing of value-added base metal for the circular economy.

ACKNOWLEDGEMENTS

The authors would like to express sincere gratitude to Mintek for financial support through Science Vote grant number: ASR-00002313 and for permission to publish this work.

SUPPORTING INFORMATION

The utilisation of the analytical instruments is essential for evaluating the effectiveness of the solvent extraction pre-treatment in mitigating Cu loss during precipitation in the presence of Fe. The supporting information provided in Figure S1, Table S1, S2, S3 and S4 in support of the comprehensive analysis of the surface morphology and elemental composition of the sample by EDX and XPS analysis.

REFERENCES

- [1] V. Coman, B. Robotin, and P. Ilea, "Nickel recovery/removal from industrial wastes: A review," *Resour. Conserv. Recycl.*, vol. 73, pp. 229–238, 2013, doi: 10.1016/j.resconrec.2013.01.019.
- [2] A. El-Naggar *et al.*, "Nickel in soil and water: Sources, biogeochemistry, and remediation using biochar," *J. Hazard. Mater.*, vol. 419, no. May, p. 126421, 2021, doi: 10.1016/j.jhazmat.2021.126421.
- [3] K. I. Dermentzis, D. I. Marmanis, A. K. Christoforidis, N. C. Kokkinos, and D. K. Stergiopoulos, "Recovery of metallic nickel from waste sludge produced by electrocoagulation of nickel bearing electroplating effluents," *4th Int. Conf. Sustain. solid waste Manag.*, pp. 23–25, 2016.
- [4] S. Krishnan *et al.*, "Current technologies for recovery of metals from industrial wastes: An overview," *Environ. Technol. Innov.*, vol. 22, p. 101525, 2021, doi: 10.1016/j.eti.2021.101525.
- [5] K. Binnemans and P. T. Jones, "The Twelve Principles of Circular Hydrometallurgy," *J. Sustain. Metall.*, vol. 9, no. 1, pp. 1–25, 2023, doi: 10.1007/s40831-022-00636-3.
- [6] R. Juvonen, T. Lakomaa, and L. Soikkeli, "Determination of gold and the platinum group elements in geological samples by ICP-MS after nickel sulphide fire assay: Difficulties encountered with different types of geological samples," *Talanta*, vol. 58, no. 3, pp. 595–603, 2002, doi: 10.1016/S0039-9140(02)00330-2.
- [7] M. L. Strauss, L. A. Diaz, J. McNally, J. Klaehn, and T. E. Lister, "Separation of cobalt, nickel, and manganese in leach solutions of waste lithium-ion batteries using Dowex M4195 ion exchange resin," *Hydrometallurgy*, vol. 206, no. September, p. 105757, 2021, doi: 10.1016/j.hydromet.2021.105757.
- [8] Y. Ren, Y. Ran, J. Yang, and Y. Wei, "High Value Conversion Technology of Nickel in Waste Electrolytes of Nitrogen Trifluoride by Electrolysis," *Separations*, vol. 10, no. 9, 2023, doi: 10.3390/separations10090477.
- [9] Y. Bulut and Z. Tez, "Adsorption studies on ground shells of hazelnut and

- almond,” *J. Hazard. Mater.*, vol. 149, no. 1, pp. 35–41, 2007, doi: 10.1016/j.jhazmat.2007.03.044.
- [10] T. P. Phetla, F. Ntuli, and E. Muzenda, “Reduction crystallization of Ni, Cu, Fe and Co from a mixed metal effluent,” *J. Ind. Eng. Chem.*, vol. 18, no. 3, pp. 1171–1177, 2012, doi: 10.1016/j.jiec.2012.01.008.
- [11] M. Taseidifar, F. Makavipour, R. M. Pashley, and A. F. M. M. Rahman, “Removal of heavy metal ions from water using ion flotation,” *Environ. Technol. Innov.*, vol. 8, pp. 182–190, 2017, doi: 10.1016/j.eti.2017.07.002.
- [12] M. A. Keane, “The removal of copper and nickel from aqueous solution using Y zeolite ion exchangers,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 138, no. 1, pp. 11–20, 1998, doi: 10.1016/S0927-7757(97)00078-2.
- [13] O. Tünay and N. I. Kabdaşlı, “Hydroxide precipitation of complexed metals,” *Water Res.*, vol. 28, no. 10, pp. 2117–2124, 1994, doi: 10.1016/0043-1354(94)90022-1.
- [14] H. Lu, J. Wang, B. Yan, and S. Bu, “Recovery of nickel ions from simulated electroplating rinse water by electrodeionization process,” *Water Sci. Technol.*, vol. 61, no. 3, pp. 729–735, 2010, doi: 10.2166/wst.2010.894.
- [15] X. Zhang *et al.*, “Selective separation of metals from wastewater using sulfide precipitation: A critical review in agents, operational factors and particle aggregation,” *J. Environ. Manage.*, vol. 344, no. June, p. 118462, 2023, doi: 10.1016/j.jenvman.2023.118462.
- [16] N. Bader, “Sample preparation for flame atomic absorption spectroscopy : An overview sample preparation for flame atomic absorption spectroscopy : an overview Nabil Ramadan Bader,” no. January 2011, 2017.
- [17] M. E. Mahmoud, I. M. M. Kenawy, M. A. H. Hafez, and R. R. Lashein, “Removal, preconcentration and determination of trace heavy metal ions in water samples by AAS via chemically modified silica gel N-(1-carboxy-6-hydroxy) benzylidenepropylamine ion exchanger,” *Desalination*, vol. 250, no. 1, pp. 62–70, 2010, doi: 10.1016/j.desal.2009.09.009.
- [18] A. N. Pham, A. L. Rose, A. J. Feitz, and T. D. Waite, “Kinetics of Fe(III) precipitation in aqueous solutions at pH 6.0-9.5 and 25°C,” *Geochim.*

- Cosmochim. Acta*, vol. 70, no. 3, pp. 640–650, 2006, doi: 10.1016/j.gca.2005.10.018.
- [19] M. Younas, S. Druon-Bocquet, J. Romero, and J. Sanchez, “Experimental and Theoretical Investigation of Distribution Equilibria and Kinetics of Copper(II) Extraction with LIX 84 I and TFA,” *Sep. Sci. Technol.*, vol. 50, no. 10, pp. 1523–1531, 2015, doi: 10.1080/01496395.2014.978943.
- [20] I. Nozari and A. Azizi, “An Investigation into the Extraction Behavior of Copper from Sulfate Leach Liquor Using Acorga M5640 Extractant: Mechanism, Equilibrium, and Thermodynamics,” *Mining, Metall. Explor.*, vol. 37, no. 5, pp. 1673–1680, 2020, doi: 10.1007/s42461-020-00280-z.
- [21] M. Hosseinzadeh, J. Petersen, and A. Azizi, “Solvent Extraction Studies of Copper from a Heap Leach Liquor Using Mextral 5640H,” *Minerals*, vol. 12, no. 10, pp. 1–14, 2022, doi: 10.3390/min12101322.
- [22] S. Panigrahi, P. K. Parhi, K. Sarangi, and K. C. Nathsarma, “A study on extraction of copper using LIX 84-I and LIX 622N,” *Sep. Purif. Technol.*, vol. 70, no. 1, pp. 58–62, 2009, doi: 10.1016/j.seppur.2009.08.013.
- [23] H. W. Park, J. S. Chae, S. Park, K. Kim, and K. C. Roh, “Nickel-based layered double hydroxide from guest vanadium oxide anions Nickel-Based Layered Double Hydroxide From Guest Vanadium Oxide Anions,” *Met. Mater. Int.*, no. February, 2017, doi: 10.1007/s12540-013-4034-2.
- [24] Z. Qin, Y. Wang, X. Huang, W. Shen, J. Yu, and J. Li, “A Facile Synthesis of Three Dimensional β -Ni(OH)₂ Composed of Ultrathin Nanosheets for High Performance Pseudocapacitor,” *J. Inorg. Organomet. Polym. Mater.*, vol. 30, no. 6, pp. 2089–2097, 2020, doi: 10.1007/s10904-019-01360-4.
- [25] R. Thimmasandra Narayan, “Effect of Crystallinity of β - and β bc -Nickel Hydroxide Samples on Chemical Cycling ,” *Indian J. Mater. Sci.*, vol. 2015, no. ii, pp. 1–7, 2015, doi: 10.1155/2015/820193.
- [26] A. C. Mkhohlakali, X. Fuku, R. M. Modibedi, L. E. Khotseng, S. C. Ray, and M. K. Mathe, “Electrosynthesis and characterization of PdIr using electrochemical atomic layer deposition for ethanol oxidation in alkaline electrolyte,” *Appl. Surf. Sci.*, vol. 502, no. October 2019, pp. 144–158, 2020, doi: 10.1016/j.apsusc.2019.144158.

- [27] X. Yu, J. Zhao, Y. Tong, and M. Zhang, “Hydrogen Evolution Reaction in Alkaline Media: Alpha- or Beta-Nickel Hydroxide on the Surface of Platinum?,” *ACS Energy Lett.*, vol. 3, no. March 2021, pp. 237–244, 2018, doi: 10.1021/acsenenergylett.7b01103.
- [28] J. Huotari, V. Kekkonen, J. Puustinen, J. Liimatainen, and J. Lappalainen, “Pulsed Laser Deposition for Improved Metal-oxide Gas Sensing Layers,” *Procedia Eng.*, vol. 168, pp. 1066–1069, 2016, doi: 10.1016/j.proeng.2016.11.341.
- [29] M. Kgaria, O. Yahorava, ,and C. Sehlola,. *Thakadu Flowsheet Development*. Randburg: Mintek. 2016.
- [30] G. Ahmed, M. Zaki, A. Atta, S. Samaha, H. Nasr, and F. Nour , Electroremoval of copper ions from aqueous solutions using chemically synthesized polypyrrole on polyester fabrics. *Journal of Water Process Engineering*, 43, 102287, 2021, Retrieved from <https://doi.org/10.1016/j.jwpe.2021.102287>

4.2 PAPER II

This paper entitled “Elemental Analysis for Battery-Grade Synthetic Cathode Liquor” has been accepted for publication.

Highlights

- ◇ Evaluation of an alternative method for analysing trace elements during nickel sulphate purification.
 - ◇ Use of Flame Atomic Absorption Spectroscopy (FAAS) and portable Energy Dispersive X-ray Fluorescence (EDXRF).
 - ◇ Objective to assess accuracy, precision, and repeatability while optimizing the purification process.
 - ◇ Promising results including excellent linearity, high recovery rates, minimal bias, and precise measurements.
 - ◇ Validation of the method's effectiveness in analysing trace impurities in battery-grade nickel sulphate.
-

Authors Contributions

Happy Mothepane Mabowa - The main author played a central role in the research process, leading the design of the methodology, overseeing data collection and analysis, ensuring compliance with ethical standards, securing funding, and maintaining communication with collaborators.

James Tshilongo - Contributed to data collection, interpretation, supervision, and manuscript revision.

Luke Chimuka - Contributed to data collection, interpretation, supervision, and manuscript revision.

Elemental Analysis for Battery-Grade Synthetic Cathode Liquor

M. H. Mabowa^{1,2*}, J. Tshilongo¹, L. Chimuka²

* Corresponding author's email: happyc@mintek.co.za;

¹ Mintek, Analytical Chemistry Division, 200 Malibongwe Drive, 2155, South Africa

² School of Chemistry, University of the Witwatersrand, Private Bag 3, PO WITS, 2050, South Africa

Abstract

This study evaluates the accuracy and reliability of elemental analysis in synthetic cathode liquor using Energy Dispersive X-ray Fluorescence (EDXRF) with factory default settings and post-calibration, and compares results with Flame Atomic Absorption Spectroscopy (FAAS) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The objective was to assess EDXRF's effectiveness in detecting elements such as calcium (Ca), cobalt (Co), iron (Fe), nickel (Ni), and others. Initial EDXRF data showed significant discrepancies: Ca was consistently reported as 0 mg/L despite actual values up to 0.15 mg/L, and Ni was overestimated, ranging from 493,327 to 529,280 mg/L compared to an actual value of 120,000 mg/L. Post-calibration, EDXRF showed improved accuracy for Co, Fe, and Cu but struggled with light elements like selenium (Se) and antimony (Sb) due to high Limits of Detection (LOD). FAAS effectively analyzed Co, Cu, and Fe but had limitations for elements like Na, showing high variability (SD = 505.24 mg/L, RSD = 23.39%). ICP-OES confirmed the accuracy of the results. This study underscores the need for calibration and the use of multiple analytical techniques to ensure reliable measurements in industrial applications.

Keywords: Cathode, High-purity, Battery, Nickel Sulphate, FAAS, EDXRF

1. Introduction

The projected growth of the electric vehicle (EV) market for the next two decades predicts a simultaneous increase in the demand for the major metals used in the batteries to power these vehicles, namely lithium, manganese, nickel, and cobalt. Battery producers require feedstock of very high purity nickel. The lithium-ion battery (LIB) has seen significant advancement in recent years, owing largely to the chemistry of the cathode, which continues to trend toward higher quantities of nickel. Nickel (Ni) lends several benefits to EV batteries, improving the overall economics of the battery, as well as its market appeal [1]. Nickel sulphate is a key material used to produce cathode materials for LIB. However, Mg, Co, As, Fe, Ca, Cu, and Na (magnesium, cobalt, arsenic, iron, calcium, copper, and sodium) in the cathode liquor are some of the elements that deposit quantitatively at the cathode during leaching or are found in the stream and thereby contaminate the nickel-metal product. These impurities are carried over from the leach solution after dissolving the ore or concentrated in an industrial acid and thus deteriorate the quality of the product before it is generated by crystallization or electrowinning. This specific battery industry requires most of these impurities to be only present at 5 mg/L and less. Thus, suppliers are required to devise innovative treatment methods to meet strict demands.

Several analytical techniques, including spectrophotometry [2], neutron activation analysis [3], atomic absorption spectrometry (AAS) [4], inductively coupled plasma optical- emission spectrometry (ICP-OES) [5] and inductively coupled plasma mass spectrometry (ICP-MS) [6] have been applied for trace impurities determination in high purity nickel. However, most authors have indicated that AAS is not appropriate for multi-element routine analysis because AAS instrumentation is typically constructed as a mono-element method and the applicability of this technique is often limited by inadequate detection limits [7]. The applicability of the AAS was challenged by this research and it was found to be applicable for multi-element routine analysis. Time consumption turned out to be the drawback when working with cathode liquor with a complex sample matrix. Handheld energy

dispersive x-ray fluorescent (EDXRF) generated user interest over the last few years due to the availability of user-friendly equipment at a reasonable price, portability, and reliable and rapid data. There is no sample pretreatment required. One of the EDXRF drawbacks is insufficient sensitivity at trace levels; the detection limits (around 1 mg/L for most elements) are considerably higher than those achieved with AAS and ICP-MS-based methods. Flame atomic absorption spectrometry (FAAS) and EDXRF are equipment that is used for elemental analysis and monitoring of the purification process as the methods are convenient and cost-effective, have a fast turnaround time, and require no or few sample preparations for evaluating and monitoring the purification process. FAAS suffers challenges such as burner logging due to high viscosity in high concentrations of the cathode liquor, which results in contamination in the mixing chamber and burner compartment and causes a delay of data while thoroughly cleaning and recalibrating the instrument. The current study aimed at evaluating the feasibility of using FAAS and EDXRF techniques for direct quantification of the most common impurities in cathode liquor. The contents of Co, Na, Ca, Mg, Cu, and Fe in high purity Ni were directly determined by FAAS and EDXRF.

2. Experimental

2.1 Equipment

A fast sequential FAAS (make: Varian spectrAA 220FS spectrometer with introduction pump system software) was the instrument equipped with a fully integrated atomizer was used for the analysis. The operating parameters for FAAS are tabulated in Table 1. Selecting a wavelength for the element of interest is important for providing the desired working concentration range. For quantifying low concentration levels of the element in a complex matrix, the key performance attributes will probably be detection versatility and accuracy. Therefore, the most sensitive wavelength was chosen for each element and all potential interferences were identified and carefully corrected by using nitrous oxide-acetylene fuel.

Table 1 provides a comprehensive overview of the analytical parameters for several elements using FAAS, with a focus on the precise conditions necessary for obtaining accurate measurements. Each individual element is examined using a specific wavelength, and the resolution and sensitivity of the detection are determined by the matching spectral bandpasses. The optimal working range refers to the concentration range within which accurate measurements can be reliably obtained. The current values of the lamp are adjusted to achieve an adequate level of signal strength while also maintaining a balance between sensitivity and the lifespan of the lamp. The selection of fuel and support gases, such as acetylene combined with air or nitrous oxide, has an impact on the stoichiometry of the flame, which in turn impacts the analytical outcomes and interferences. Reducing flames are utilised in calcium analysis to prevent interference, whilst oxidising flames are employed for enhancing sensitivity and accuracy in the analysis of other elements such as Co, Cu, and Ni. The particular characteristics of each element emphasise the necessity for a customised method in FAAS to provide precise and accurate analysis of elements at varying sample concentrations and analytical demands.

A handheld EDXRF (make: Hitachi X-MET8000 Expert Geo 50 kV) X-MET8000 Geo handheld XRF (X-ray fluorescence) analyser was used. The X-MET8000 Geo uses novel BOOST™ technology, with a system that has detection limits that are low enough for fast and accurate measurement of critical elements in Table 2. According to the information from the supplier, the EDXRF provides accurate analysis for light elements such as (Mg, Al, Si, P, S, Cl), with relatively low detection limits of 50 mg/L to 1500 mg/L for some solution samples, and outstanding precision for results. The advantage of EDXRF is the functionality to test a wide range of elements with its versatile standardless fundamental parameters (FP) methods or to use its empirical calibrations when results traceability and high accuracy are important.

Table 1. Operating conditions for FAAS.

Elements	wavelength λ (nm)	Spectral band pass (nm)	Optimum working range (mg/L)	Lamp Current (mA)	Burner	Support	Flame stoichiometry
Ca	422.7	0.5	1.0 to 4.0	3.5	Acetylene	Nitrous Oxide	Reducing
Co	240.7	0.2	3.0 to 12.0	7	Acetylene	Air	Oxidising
Co	347.4	0.2	200 to 1000	7	Acetylene	Air	Oxidising
Cu	324.7	0.5	2.0 to 8.0	3.5	Acetylene	Air	Oxidising
Cu	249.2	0.5	200 to 800	3.5	Acetylene	Air	Oxidising
Fe	248.3	0.2	2.5 to 10	5	Acetylene	Air	Oxidising
Mg	202.6	1	5.0 to 20	3.5	Acetylene	Air	Oxidising
Na	330.2	0.5	100 to 400	5	Acetylene	Air	Oxidising
Ni	351.5	0.5	35 to 140	3.5	Acetylene	Air	Oxidising

Table 2. Specification of EDXRF

Working conditions of X-MET8000 Expert Geo	
Description	Ultimate performance for measuring a variety of geochemical samples including REEs, light elements, and pathfinders
X-Ray Tubes	50 kV
X-Ray Tube Filters	6-position filter wheel
Detector	25 mm ² large area SDD with BOOST™ technology
Element Range	Mg - U
IP54 and MIL-STD-810G	Yes
Weight (with Battery)	1.5 kg
Battery Life	10 h - 12 h
Protection Against Detector Window Damage	Prolene window
Calibrations	Standardless with light elements and REEs (rare earth elements)

2.2 Standards and Reagents

All reagents used were prepared from analytical-grade (AR). Ultrapure water, specific resistance above 18.0 M Ω ·cm from a Milli-Q de-ionization unit (Millipore, USA.), was used throughout the experiment. Commercially available standard stock solutions each containing 1000 mg/L single elements of Na, Ca, Cd, Mg, Mn, Zn, Cu, Co, Ni, Al, and Cr in HNO₃ from Anacon CC were used to prepare synthetic standard calibration solutions from the single-element stock solutions and diluted with 5 % H₂SO₄ in 1 % NS to matrix-match the samples.

A similar procedure was followed to prepare the spike sample solution by using certified reference material (CRM) containing multi-element 1000 mg/L of Cu, Co, Fe, Zn, Ni, Mn, and Mg in HNO₃ purchased from DeBryun Spectroscopic Solution as a control sample. Chemical salts from ACE chemicals were used for the preparation of synthetic samples: CoSO₄·7H₂O, ZnSO₄·7H₂O, NaSO₄·6H₂O, NiSO₄·6H₂O, MnSO₄·H₂O, CaSO₄·2H₂O, MgSO₄, CuSO₄·5H₂O, Fe₂(SO₄)₃·XH₂O, Al₂(SO₄)₃·18H₂O, NaCl. Standard solutions of Cd, Cr, As, Se, Te, Bu, Bi, and Sb in HNO₃ were used for the preparation of synthetic samples due to the unavailability of sulfate salts. Standards for calibration of the instrument were multi-element standard solutions:

- FAAS: 140 mg/L Ni in 5 % H₂SO₄ (standard) containing 6 impurities
- EDXRF: Standards that range from 5 mg/L to 1000 mg/L of multi-element standard solutions were used for calibration verification prepared from 1000 mg/L stock solutions from Anacon CC standards and diluted with a 5 % H₂SO₄ matrix.

2.3 Analytical Procedure

The provided information outlines the preparation of twelve multi-element samples in a solution containing 5% sulfuric acid (H₂SO₄), prepared using Milli-Q water. Each sample contains 12 impurities typically found in approximately 12.5 % Ni cathode liquor, as listed in Table 3. Notably, chromium (Cr), tellurium (Te), bismuth (Bi), selenium (Se), arsenic (As), antimony (Sb), and cadmium (Cd) were

introduced using a standard solution, while chlorine (Cl) was introduced as sodium chloride (NaCl). The samples are categorized as feed samples, representing a synthetic feed, and samples labeled TDK1-5. The utilisation of a 5% concentration of sulfuric acid in the formulation of these samples likely serves various purposes, such as maintaining a stable pH, facilitating dissolution of sample components, and preventing precipitation of metal ions. Milli-Q water, known for its high purity, ensures minimal contamination and interference during sample preparation. The inclusion of standard solutions containing specific elements ensures the reproducibility and accuracy of the analytical measurements, allowing for the quantification of impurities present in the cathode liquor. Additionally, the synthetic feed samples provide insights into the composition of the starting material used in the production process.

Overall, the preparation of these multi-element samples serves as a crucial step in the analytical workflow, enabling the subsequent determination of impurity concentrations and facilitating process optimization and quality control in nickel production. The systematic approach to sample preparation and the inclusion of standard solutions underscore the rigor and reliability of the analytical methodology employed in this study.

Table 3 presents the changes in concentration of several reagents in a 250 mL experimental setup under five distinct test circumstances (TDK 1 to TDK 5). The concentration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ stays consistent at 134.31 g/L, demonstrating its predominant function in the solution. Additional substances such as $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NaSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ exhibit a consistent decline in concentration from TDK 1 to TDK 5, indicating a methodical reduction in gradient. Elements such as arsenic (As), selenium (Se), tellurium (Te), bismuth (Bi), and antimony (Sb) likewise exhibit a declining pattern, ranging from 0.5 mL in TDK 1 to 0 mL in TDK 5. The compounds $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and MgSO_4 are continuously omitted from the experiment, with a concentration of 0 g/L. Chlorine exhibits a comparable decrease pattern, declining from 0.06 g/L to 0 g/L. The deliberate modification in concentrations of the reagents is likely intended to investigate their

individual and combined impacts on the experimental results, thereby gaining understanding of their functions and interactions.

Table 3 Anticipated preparation of samples from cathode liquor. Samples such as As, Se, Te, Bi, and Sb were used as standard solutions due to the unavailability of sulfate salts.

Reagent used	Feed req (g/L)	TDK 1 (g/L)	TDK 2 (g/L)	TDK 3 (g/L)	TDK 4 (g/L)	TDK 5 (g/L)	V (250 mL)
NiSO₄.6H₂O	134.3	134.3	134.31	134.31	134.31	134.31	
CoSO₄.7H₂O	1.19	0.6	0.3	0.12	0.01	0	
Na₂SO₄.6H₂O	4.63	2.32	1.16	0.23	0.01	0	
CaSO₄.2H₂O	0	0	0	0	0	0	
MgSO₄	0	0	0	0	0	0	
CuSO₄.5H₂O	2.95	1.47	0.74	0.2	0.01	0	
Fe₂(SO₄)₃.XH₂O	2.69	1.79	0.9	0.18	0.01	0	
As (mL)	1	0.5	0.25	0.1	0.05	0	
Se (mL)	1	0.5	0.25	0.1	0.05	0	
Te (mL)	1	0.5	0.25	0.1	0.05	0	
Bi (mL)	1	0.5	0.25	0.1	0.05	0	
Sb (mL)	1	0.5	0.25	0.1	0.05	0	
Cl	0.12	0.06	0.03	0.02	0	0	

The analytical performance of the FAAS and EDXRF methods for trace elemental analysis of Co, Mg, As, Fe, Cu, Se, Te, Bi, Pb, Ca, Cl, Sb, and Na were evaluated by preparing a cathode liquor containing ~12.5 % Ni as nickel sulfate (NS) with a laboratory scale as per the anticipated values from the stream. The risk of losing the analyte elements was avoided by storing the samples in a tightly sealed container to avoid crystallization, which would require heating at temperatures ranging from approximately 55 °C to 60 °C to re-dissolve. The effect of the Ni (~22.3 %) matrix on the FAAS and EDXRF will be discussed in this work. The correction for a matrix was made using 5 % H₂SO₄ in 1 % NS solution as a diluent and additional Sr for

Mg standard preparation. The Sr is often employed to mitigate interference effects that may compromise the precise quantification of Mg.

3. Results and Discussion

3.1 Calibration Linearity

Linear calibrations were obtained for six elemental impurities in ~22.3 % Ni with correlation coefficients greater than 0.99 by FAAS. All calibration lines (for six elements) were linear with a slope close to ~0.99 and $R^2 \sim 1$ indicating the feasibility for direct analysis of trace impurities in the cathode liquor. The calculated values for elemental concentrations with the selected wavelength are within the concentration range in Ni standard are presented in Table 4. Linear calibrations were obtained for all six (6) elements examined, with R^2 closer to 1. in Figure 1.

Standard error (SE), correlation coefficients (R^2), limits of detection and quantification (LOD and LOQ), particular wavelengths (λ), calibration standards, and other critical analytical performance parameters are displayed in the Table 4. for elements evaluated using FAAS. Elements such as Co, Fe, Ca, Mg, Na, Ni and Cu exhibit high R^2 values (mostly above 0.999), which suggests exceptional linearity in their calibration curves. The LOD and LOQ exhibit substantial variation between the elements, indicating variations in sensitivity. Among them, Fe demonstrates the lowest LOD (0.1147 mg/L), while sodium exhibits the greatest (5.3323 mg/L). The readings are accompanied with standard errors, which indicate the precision of the measurements. Among the measures, calcium has the lowest standard error of 0.0068. The precise wavelength of each element is carefully chosen to achieve the best possible detection. The calibration standards are designed to cover a wide range, customised to match the expected concentration levels of each element. This extensive dataset highlights the exactness and correctness of FAAS in examining diverse elements, showcasing its efficacy in quantitative analysis across a wide range of concentrations.

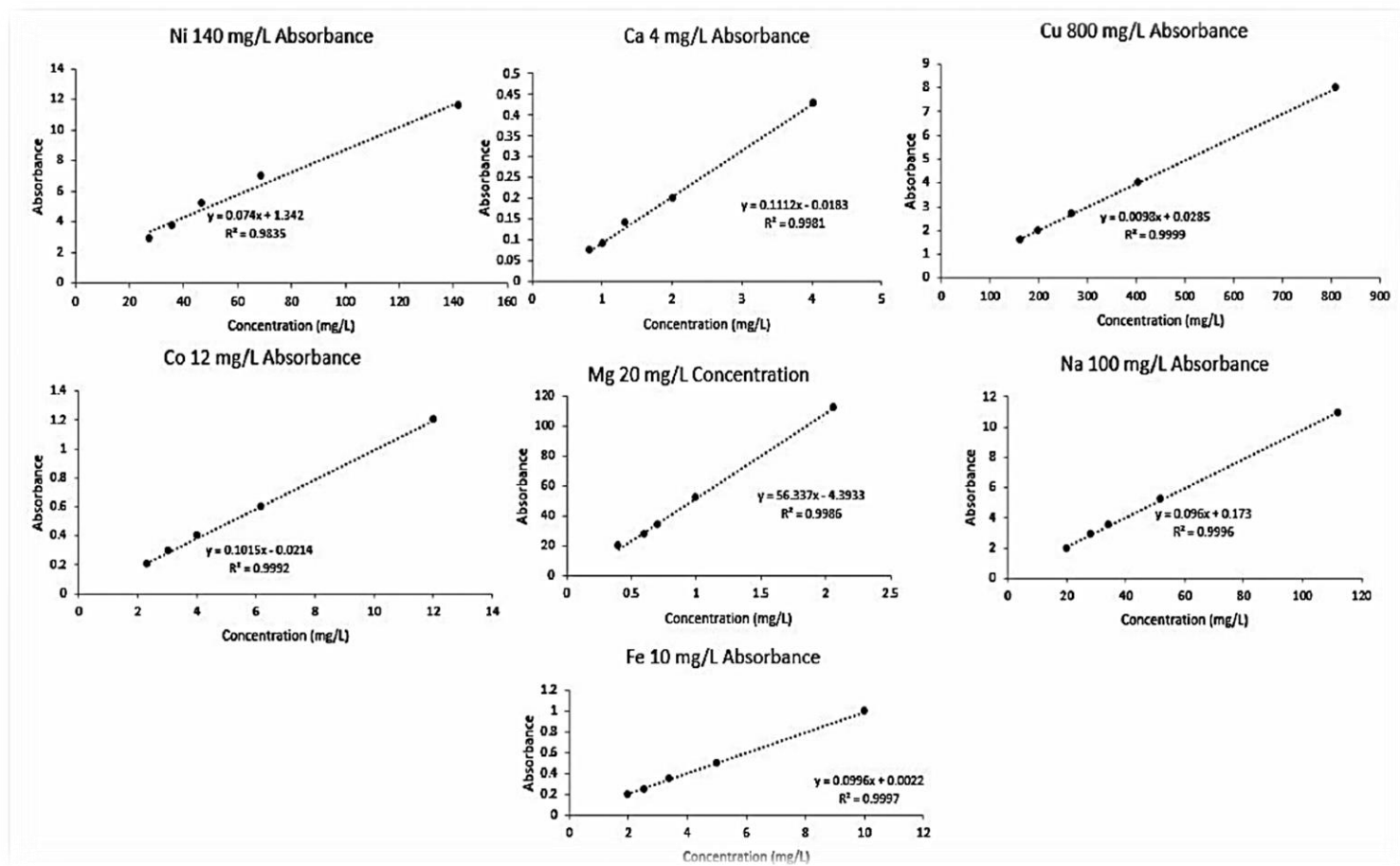


Figure 1 Calibration curves for ~ 22.3 % Ni solutions by FAAS.

Table 4. Multi-element calibration standards.

Element	R^2	LOD	LOQ	SE	λ (nm)	STD 1 (mg/ L)	STD 2 mg/ L	STD 3 mg/ L	STD 4 mg/ L	STD 5 mg/ L
Co	0.999 2	0.324 1	0.98 22	0.09 72	240. 7	2.4	3	4	6	12
Fe	0.999 7	0.114 7	0.34 76	0.03 48	248. 3	2	2.3	3.33	5	10
Ca	0.999 1	0.224 1	0.06 79	0.00 68	422. 7	0.8	1	1.33	2	4
Mg	0.995 9	0.082 1	0.24 87	0.02 47	202. 6	4	5	6.67	10	20
Na	0.999 6	5.332 3	16.1 59	1.41 56	330. 2	20	25	33.3	50	100
Ni	0.983 5	3.018 5	9.14 69	0.90 017	351. 5	28	35	46.6 7	70	140
Cu	0.999 9	3.989 7	12.0 90	1.19 11	249. 2	160	200	266. 87	400	800

3.2 Calibration and verification EDXRF

Standards that range from 5 mg/L to 1000 mg/L of multi-element standard solutions were used for calibration verification of EDXRF prepared from 1000 mg/L stock solutions from Anacon CC standards and diluted with a 5 % H₂SO₄ matrix. The EDXRF was calibrated by scanning actual standards using the factory default settings mode and the gradient R^2 for the standards scanned was closer to 1. The linearity of the factory default mode gave a good indication that the instrument was calibrated. The data algorithms of the R^2 and slope were plotted on the EDXRF and a new method was saved. The data in Table 5 illustrate the closeness to the true actual value of the samples when the instrument was calibrated.

The validation results, as presented in Table 5, serve as the ultimate confirmation of the calibration's efficacy. The measured values closely align with the true actual values of the samples, affirming the accuracy and reliability of the EDXRF analysis. This validation underscores the importance of rigorous calibration protocols in analytical instrumentation, particularly in ensuring the precision and fidelity of

results in diverse applications. The results of this study validate the calibration integrity of the EDXRF instrument, showcasing its ability to accurately analyze samples across a wide concentration range. These findings not only enhance the confidence in the instrument's performance which highlight the significance of meticulous calibration procedures in analytical methodologies.

The results in Table 5 evaluate the exactness and consistency of observed concentrations for Cu, Co, Ca, Fe and Ni compared to known standard amounts that vary from 1000 mg/L to 0 mg/L. Table 5 illustrates that the observations for all elements exhibit a high level of precision at higher concentrations, with an RSD of less than 5%. Nevertheless, there are minor variations at lower concentrations, with RSD values exceeding 10% for Cu in STDs 9 and 10, Co in STD 9, Ca in STD 10, Fe in STDs 9 and 10, and Ni in STDs 9 and 10. The concentrations of Cu are generally accurate, but they tend to be slightly overestimated at lower levels. For example, the concentration was measured at 15 mg/L at STD 9, which is marginally higher than the actual concentration of 10 mg/L. The measurements of Co and Ca demonstrate exceptional accuracy, with Co slightly overestimating at the lowest values and Ca maintaining a high level of consistency throughout. The Fe measurements have great accuracy when the concentration is higher, but tend to yield higher values when the concentration is lower. The Ni measurements exhibit remarkable precision and uniformity across all levels of concentration. The findings demonstrate the dependability of the analytical method employed, emphasising the significance of meticulous calibration, especially at lower concentration levels, to guarantee exact and accurate measurement of these elements.

Table 5. Standard measured for EDXRF vs actual standards. A linear correlation (R^2) between actual values and indications was observed for all elements.

Standard (STD)	1	2	3	4	5	6	7	8	9	10
STD concentration mg/L	1000	800	600	400	200	100	50	25	10	0
Cu mg/L measured	1000	780	589	401	218	98	48	25	15	0
Cu mg/L Actual	1000	800	600	400	200	100	50	20	10	5
Median	1000	790	594.5	400.5	209	99	49	22.5	12.5	2.5
N	2	2	2	2	2	2	2	2	2	2
SD	0.00	14.14	7.78	0.71	12.73	1.41	1.41	3.54	3.54	3.54
RSD	0.00	1.79	1.31	0.18	6.09	1.43	2.89	15.71	28.28	141.42
Co mg/L measured	1006	810	615	409	212	99	54	18	11	0
Co mg/L Actual	1000	800	600	400	200	100	50	20	10	5
Median	1003	805	607.5	404.5	206	99.5	52	19	10.5	2.5
N	2	2	2	2	2	2	2	2	2	2
SD	4.24	7.07	10.61	6.36	8.49	0.71	2.83	1.41	0.71	3.54
RSD	0.42	0.88	1.75	1.57	4.12	0.71	5.44	7.44	6.73	141.42
Ca mg/L measured	999	809	613	402	198	97	55	18	9	0
Ca mg/L Actual	1000	800	600	400	200	100	50	20	10	5
Median	999.5	804.5	606.5	401	199	98.5	52.5	19	9.5	2.5
N	2	2	2	2	2	2	2	2	2	2
SD	0.71	6.36	9.19	1.41	1.41	2.12	3.54	1.41	0.71	3.54

RSD	0.07	0.79	1.52	0.35	0.71	2.15	6.73	7.44	7.44	141.42
Fe mg/L measured	998	798	599	413	189	98	47	18	15	0
Fe mg/L Actual	1000	800	600	400	200	100	50	20	10	5
Average	999	799	599.5	406.5	194.5	99	48.5	19	12.5	2.5
N	2	2	2	2	2	2	2	2	2	2
SD	1.41	1.41	0.71	9.19	7.78	1.41	2.12	1.41	3.54	3.54
RSD	0.14	0.18	0.12	2.26	4.00	1.43	4.37	7.44	28.28	141.42
Ni mg/L measured	1004	801	603	403	203	103	52	22	12	0
Ni mg/L Actual	1000	800	600	400	200	100	50	20	10	5
Median	1002	800.5	601.5	401.5	201.5	101.5	51	21	11	2.5
N	2	2	2	2	2	2	2	2	2	2
SD	2.83	0.71	2.12	2.12	2.12	2.12	1.41	1.41	1.41	3.54
RSD	0.28	0.09	0.35	0.53	1.05	2.09	2.77	6.73	12.86	141.42

The linear calibrations obtained for eight elements demonstrate the effectiveness of the calibration process, with correlation coefficients exceeding 0.95 for Cr and Cd, and reaching 1 for the remaining elements. A correlation coefficient of 1 indicates a perfect linear relationship between the measured and known concentrations, reflecting the accuracy and precision of the calibration method employed. However, it is noteworthy that Mg, bismuth (Bi), selenium (Se), arsenic (As), tellurium (Te), and antimony (Sb) were not calibrated using Energy Dispersive X-ray Fluorescence (EDXRF) due to their low concentrations, falling below the instrument's limit of detection (LOD) for these respective elements. This limitation indicates that the concentrations of these elements in the samples were below the detection threshold of the EDXRF instrument, rendering calibration impractical.

Furthermore, Na was identified as undetectable by EDXRF, implying that its concentration could not be accurately quantified using this analytical technique. This underscores the importance of employing complementary methods, such as FAAS or Inductively Coupled Plasma Mass Spectrometry (ICP-MS), for the determination of elements that are not amenable to analysis by EDXRF. The linear calibrations for most elements exhibit excellent correlation coefficients, the inability to calibrate Mg, Bi, Se, As, Te, Sb, and the undetectability of Na by EDXRF highlight the need for alternative analytical approaches for accurate quantification of these elements in the samples. This acknowledgement underscores the importance of selecting appropriate analytical techniques tailored to the specific elemental compositions and concentrations of the samples under investigation.

In the newly developed method, M (gradient) and C (y-intercept) coefficients were determined for each element and utilized for internal calibration of the EDXRF analysis. This calibration approach ensures accurate quantification of the elemental concentrations within the samples. To validate the calibration, the same standards were analyzed using a previously calibrated method, resulting in a change in slope from 3 to 1, as depicted in Figure 2.

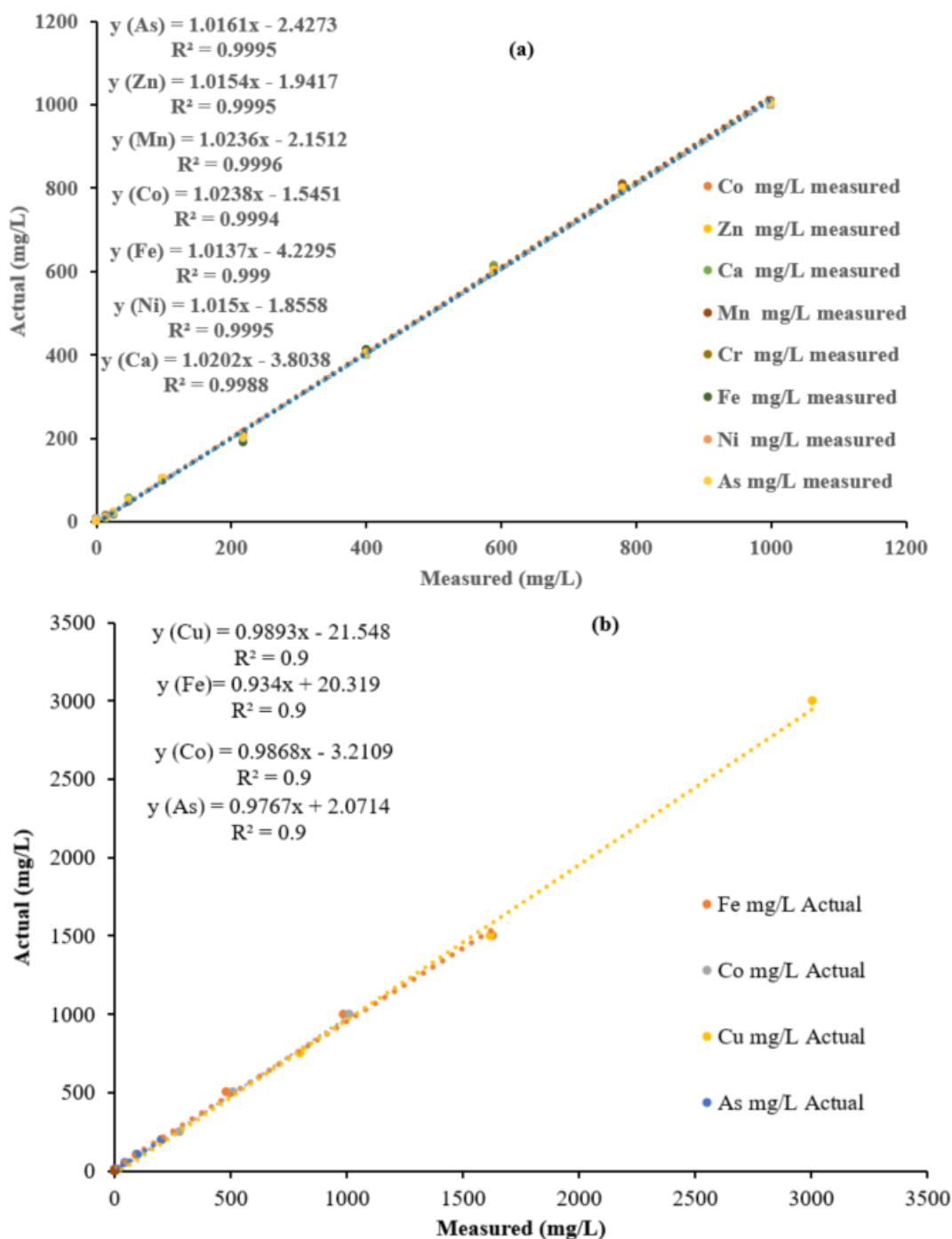


Figure 2 EDXRF standard solution data. (a) Factory default scanned data. (b) Calibrated method data.

This alteration signifies the effectiveness of the updated calibration procedure in enhancing the precision and reliability of the EDXRF analysis. Concurrently, the concentrations of trace impurities, including Na, Co, Ca, Mg, Cu, and Fe, within the cathode liquor were determined using FAAS. This analytical technique offers

high sensitivity and accuracy in quantifying trace elements within complex matrices. Additionally, the concentration of nickel sulfate in the cathode liquor, approximately 12.5% (120 g/L), was analysed using FAAS to ensure consistency throughout the assay and purification process. This quality control measure ensures the reliability of the obtained results and verifies the stability of the nickel sulfate concentration, a crucial parameter in the production process. Overall, the combination of internal calibration using EDXRF and FAAS analysis provides a robust framework for accurately determining elemental concentrations within the cathode liquor. The meticulous calibration procedure and quality control measures underscore the commitment to obtaining precise and reliable analytical data, essential for optimizing process efficiency and product quality in industrial applications.

The analysis reveals notable discrepancies in the recovery of Na, Ca, and Mg concentrations within the samples under scrutiny. Notably, sample TDK 5 exhibited an over-recovery of sodium, leading to a false-positive result. This discrepancy suggests that the actual sodium concentration in the samples may be lower than initially calculated, given the observed deviation from the limit of detection (LOD) of 5.3323 mg/L. Similarly, calcium samples derived from the feed to TDK 5 consistently exhibited over-recovery, despite their concentrations falling below the LOD of 0.2241 mg/L. This overestimation, indicated by false positives ranging between approximately 2.1 mg/L and 5.2 mg/L, raises concerns regarding the accuracy of the analytical procedure employed. Moreover, magnesium samples also displayed over-recovery, with a calculated LOD of 0.0821 mg/L. These findings collectively suggest a systematic issue with the recovery of these elements, possibly influenced by factors such as sample preparation, instrumentation, or method sensitivity.

However, the majority of trace impurities in the cathode liquor demonstrated a satisfactory correlation between actual and measured data, as indicated in Table 6. Despite this, both magnesium and calcium samples falling below the LOD exhibited poor recovery rates, primarily due to false-positive readings. This

highlights the critical need for a more robust analytical approach to accurately quantify trace elements in samples with concentrations near or below the LOD. The analysis for Ni demonstrates high precision and accuracy, with recovery percentages close to 100%, low standard deviations (SD), and relative standard deviations (RSD) ranging from 0.59% to 1.17%, indicating reliable measurements. Co exhibits acceptable precision, with recovery percentages ranging from 89.3% to 137.2%. However, the RSD reaches 22.18% at the lowest concentration, indicating an increase in variability. Na exhibits high RSD values, particularly at lower concentrations, and a range of recovery percentages from 0% to 122.65%, which underscores the challenges associated with precision. Ca and Mg exhibit extremely high RSD values and extremely low recovery percentages (0% to 2.88% for Ca and 0% to 1.02% for Mg). This suggests that there are significant issues with accuracy and precision, potentially due to method sensitivity or matrix effects. RSD values increase as concentrations decrease, indicating moderate recovery percentages with significant variability in Cu measurements. Recovery percentages exceeding 100% are observed at higher concentrations in Fe data, which may indicate overestimation or contamination issues. Significant variability is observed at lower concentrations, which negatively impacts measurement reliability.

To address these challenges and enhance the accuracy of measurements, spiking the samples with known concentrations of magnesium and calcium above the LOD is proposed. By introducing spiked samples into the analysis, it becomes possible to evaluate the recovery rates more accurately and mitigate the occurrence of false positives. The inclusion of spiked samples, as detailed in Table 7, provides valuable insights into the performance of the analytical method under controlled conditions. The demonstrates a variety of precision and accuracy levels for distinct sample IDs. The recovery percentages for Co are generally high, ranging from 79% to 99.8%. However, the range of RSD values is significant, with the lowest concentration reaching 94.22%, indicating a higher degree of variability. Na measurements exhibit a wide recovery range of 88.5% to 102.5%, with RSD values ranging from 0.24% to 141.42%. These values are notably high at lower concentrations, which indicates that precision challenges may exist. The low recovery percentages and

extremely high RSD values (137.18% to 141.42%) of Ca suggest that there are issues with accuracy and consistency, particularly at low concentrations. Magnesium (Mg) exhibits high RSD values (140.98% to 141.42%) and low recovery percentages, which indicate substantial precision issues. Variability and potential sensitivity issues are indicated by the recovery percentages of Cu measurements, which range from 79% to 109%, and RSD values that range from 0.26% to 141.42%. Iron (Fe) exhibits high recovery percentages (up to 109.9%) but also high RSD values (0.51% to 141.42%), particularly at lower concentrations, which impacts measurement reliability. In general, the data indicates that the analytical results may be susceptible to reliability issues, particularly at lower concentrations, due to variability and accuracy issues. This approach facilitates a more comprehensive understanding of recovery efficiencies and aids in refining the analytical protocol to achieve more reliable results. In conclusion, while the analysis highlights certain discrepancies in the recovery of Na, Ca, and Mg concentrations, the proposed strategy of spiking samples offers a promising avenue for improving accuracy and reliability in elemental analysis. Further investigation and refinement of analytical techniques are warranted to address these challenges effectively and ensure the integrity of the analytical data obtained.

Table 6. Elemental analysis of synthetic cathode liquor by FAAS.

Sample ID	Feed mg/L	TDK 1 mg/L	TDK 2 mg/L	TDK 3 mg/L	TDK 4 mg/L	TDK5 mg/L
Ni FAAS (g/L)	122	121	119	119	122	119
Ni actual (g/L)	120	120	120	120	120	120
Recovery %	98.361	99.1736	100.84	100.84	98.3607	100.84
Median	121	120.5	119.5	119.5	121	119.5
N	2	2	2	2	2	2
SD	1.41	0.71	0.71	0.71	1.41	0.71
RSD	1.17	0.59	0.59	0.59	1.17	0.59
Co FAAS	1000	500	250	100	10	2.5
Co actual	1000	544.8	230.35	89.25	9.54	3.43
Recovery %	100	108.96	92.1	89.3	95.4	137.2
Median	1000	522.4	240.2	94.6	9.8	3.0
N	2	2	2	2	2	2
SD	0	31.68	13.89	7.60	0.33	0.66
RSD	0	6.06	5.79	8.03	3.33	22.18
Na FAAS	3003	1540	705	122.3	5.63	3.44
Na actual	3000	1500	750	150	5	0
Recovery %	99.90	97.40	106.38	122.65	88.81	0.00
Median	3001.50	1520.00	727.50	136.15	5.32	1.72
N	2	2	2	2	2	2
SD	2.12	28.28	31.82	19.59	0.45	2.43
RSD	0.07	1.86	4.37	14.39	8.38	141.42
Ca FAAS	5.2	4.49	3.92	3.76	2.88	2.135
Ca actual	0.15	0.1	0.05	0.025	0	0
Recovery %	2.88	2.23	1.28	0.66	0.00	0.00
Median	2.68	2.30	1.99	1.89	1.44	1.07
N	2	2	2	2	2	2
SD	3.57	3.10	2.74	2.64	2.04	1.51
RSD	133.49	135.26	137.86	139.55	141.42	141.42
Mg FAAS	1.47	1.3	1.17	1.18	1.05	1.24
Mg actual	0.015	0.008	0.004	0	0	0
Recovery %	1.02	0.62	0.34	0.00	0.00	0.00
Median	0.74	0.65	0.59	0.59	0.53	0.62
N	2	2	2	2	2	2
SD	1.03	0.91	0.82	0.83	0.74	0.88
RSD	138.56	139.69	140.46	141.42	141.42	141.42
Cu FAAS	3220	1685	920	231	11.6	1.8
Cu actual	3000	1500	750	200	10	0
Recovery %	93.17	89.02	81.52	86.58	86.21	0.00
Median	3110.00	1592.50	835.00	215.50	10.80	0.90

N	2	2	2	2	2	2
SD	155.56	130.81	120.21	21.92	1.13	1.27
RSD	5.00	8.21	14.40	10.17	10.48	141.42
Fe FAAS	1277.7	817.1	406	87	13	0.75
Fe actual	1500	1000	500	100	5	0
Recovery %	117.40	122.38	123.15	114.94	38.46	0.00
Median	1388.85	908.55	453.00	93.50	9.00	0.38
N	2	2	2	2	2	2
SD	157.19	129.33	66.47	9.19	5.66	0.53
RSD	11.32	14.23	14.67	9.83	62.85	141.42

Table 7. Elemental analysis of spiked synthetic cathode liquor by FAAS.

Elements	Feed (mg/L)	TDK 1 (mg/L)	TDK 2 (mg/L)	TDK3 (mg/L)	TDK4 (mg/L)	TDK5 (mg/L)
Co (AAS) Spiked with 10 mg/L	1008.98	507.9	259.55	108.78	19.98	12.48
Co Actual	1000	500	250	100	10	2.5
Co Recovered %	89.8	79	95.5	87.8	99.8	99.8
Median	1004.49	503.95	254.775	104.39	14.99	7.49
N	2	2	2	2	2	2
SD	6.35	5.59	6.75	6.21	7.06	7.06
RSD	0.63	1.11	2.65	5.95	47.08	94.22
Na (AAS) Spiked with 10 mg/L	3010.25	1509.9	759.5	158.85	15	9.65
Na Actual	3000	1500	750	150	5	0
Na Recovered %	102.5	99	95	88.5	100	96.5
Median	3005.13	1504.95	754.75	154.425	10	4.825
N	2	2	2	2	2	2
SD	7.25	7.00	6.72	6.26	7.07	6.82
RSD	0.24	0.47	0.89	4.05	70.71	141.42
Ca (AAS) Spiked with 10 mg/L	9.85	9.9	10	9.8	8.99	9.75
Ca Actual	0.15	0.1	0.05	0.025	0	0
Ca Recovered %	97	98	99.5	97.75	89.9	97.5
Median	5	5	5.03	4.91	4.50	4.88
N	2	2	2	2	2	2
SD	6.86	6.93	7.04	6.91	6.36	6.89
RSD	137.18	138.59	140.01	140.70	141.42	141.42

Mg (AAS) Spiked with 10 mg/L	9.59	10	9.86	9.83	10	9.89
Mg Actual	0.015	0.008	0.004	0	0	0
Mg Recovered %	95.75	99.92	98.56	98.3	100	98.9
Median	4.8025	5.004	4.932	4.915	5	4.945
N	2	2	2	2	2	2
SD	6.77	7.07	6.97	6.95	7.07	6.99
RSD	140.98	141.20	141.31	141.42	141.42	141.42
Cu (AAS) Spiked with 10 mg/L	3010.9	1508.9	758.9	207.9	20.8	10.25
Cu Actual	3000	1500	750	200	10	0
Cu Recovered %	109	89	89	79	108	102.5
Median	3005.45	1504.45	754.45	203.95	15.4	5.125
N	2	2	2	2	2	2
SD	7.71	6.29	6.29	5.59	7.64	7.25
RSD	0.26	0.42	0.83	2.74	49.59	141.42
Fe (AAS) Spiked with 10 mg/L	1510.86	1010.99	508.9	108.99	15.65	9.74
Fe Actual	1500	1000	500	100	5	0
Fe Recovered %	108.6	109.9	89	89.9	106.5	97.4
Median	1505.43	1005.5	504.45	104.495	10.325	4.87
N	2	2	2	2	2	2
SD	7.68	7.77	6.29	6.36	7.53	6.89
RSD	0.51	0.77	1.25	6.08	72.94	141.42

The utilization of spiking samples with known concentrations has proven instrumental in rectifying over-recovery issues, particularly observed with Mg and Ca in the synthetic cathode liquor analysis. Employing an auto-dilution method, where 1 mL of the sample was diluted with 9 mL of a 10 mg/L prepared solution, resulted in significant enhancements in recovery rates. These improvements were particularly striking for Mg and Ca, with recoveries ranging from approximately 90% to 100%. This precision in recovery rates ensures more accurate determinations of the true concentrations of these elements in the cathode liquor when using Flame Atomic Absorption Spectroscopy (FAAS).

Furthermore, the examination of solution samples using EDXRF without prior calibration revealed varying the R^2 with the roughly scanned samples. Notably, elements like Fe, Cu and Co exhibited strong linear relationships with R^2 values approaching 1, indicating a robust correspondence between measured signals and element concentrations. However, for elements such as Ca, Bi, Sb, As, and Cl the R^2 values were not linear, suggesting potential limitations in the detection or quantification of these elements via EDXRF. Additionally, Mg remained undetected due to a high limit of detection (LOD) on the EDXRF, while Na was non-detectable. The tabulated data provided in Table 8 underlines the significance of calibration and optimization in EDXRF analysis to ensure accurate quantification of elemental concentrations. The statistical analysis of components recorded in different samples indicates significant precision and accuracy variance. The Ca values in the samples range from 4025 to 4239 mg/L, despite being significantly lower (0 to 0.15 mg/L). The high RSD values (70.71% to 141.41%) reflect measurement errors. Fe levels vary widely, from 0 mg/L to 6195 mg/L, significantly above actual values. Fe RSD ranges from 54.59% to 141.42%, especially at low concentrations. Co measurements indicate large RSD values of 141.42% from concentrations (0 to 1000 mg/L), indicating significant variability. Ni assays are much higher than actual values (120000 mg/L), with RSD values of 54.16% to 86.08%, indicating moderate variability. Cu has high RSD values (94.41% to 141.42%), especially at lower concentrations, indicating measurement discrepancies. As and Se measurements are highly variable, with RSD values often

surpassing 100%, suggesting poor precision. Sb has high RSD values of 72.60% to 141.42%, suggesting measurement difficulties. Finally, Bi has significant RSD values, particularly at lower concentrations, indicating analytical process discrepancies. These findings show that elemental measurements are inaccurate and imprecise, especially at low concentrations. This holistic approach, combining spiking of samples for enhanced recovery and meticulous calibration of analytical instruments, significantly bolsters the reliability and accuracy of elemental analysis, particularly within complex matrices like the synthetic cathode liquor. Such stringent methodologies are vital for maintaining the integrity of analytical results, thereby facilitating informed decision-making processes in industrial applications.

Table 8. Elemental analysis of synthetic cathode liquor by Factory default EDXRF.

Name	TDK Feed	TDK1	TDK 2	TDK 3	TDK 4	TDK 5
Ca mg/L measured	4164	4150	4060	4110	4239	4025
Ca mg/L Actual	0.15	0.1	0.05	0.025	0	0
Median	2082	4150	4060	4110	4239	4025
N	2	2	2	2	2	2
SD	2944.29	2934.42	2870.82	2906.19	2997.43	2846.10
RSD	141.41	70.71	70.71	70.71	70.71	70.71
Fe mg/L measured	6195	4386	2434	1010	0	0
Fe mg/L Actual	1500	1000	500	100	5	0
Median	3847.5	4386	2434	1010	2.5	0
N	2	2	2	2	2	2
SD	3319.87	2394.26	1367.54	643.47	3.54	0.00
RSD	86.29	54.59	56.19	63.71	141.42	
Co mg/L measured	4220	2295	1131	495	0	0
Co mg/L Actual	1000	500	250	100	10	2.5
Median	2610	1397.5	690.5	297.5	5	1.25
N	2	2	2	2	2	2
SD	2276.88	1269.26	622.96	279.31	7.07	1.77
RSD	87.24	90.82	90.22	93.88	141.42	141.42
Ni mg/L measured	493327	512761	521423	526525	527069	529280
Ni mg/L Actual	120000	120000	120000	120000	120000	120000
Median	306663.5	512761	521423	526525	527069	529280
N	2	2	2	2	2	2
SD	263982.05	277723.97	283848.93	287456.58	287841.25	289404.66

RSD	86.08	54.16	54.44	54.60	54.61	54.68
Cu mg/L measured	15050	8201	4305	1478	422	431
Cu mg/L Actual	3000	1500	750	200	10	0
Median	9025	4850.5	2527.5	839	216	215.5
N	2	2	2	2	2	2
SD	8520.64	4738.32	2513.76	903.68	291.33	304.76
RSD	94.41	97.69	99.46	107.71	134.87	141.42
As measured mg/L	39	51	0	0	25	0
As mg/L Actual	4	2	1	0.4	0.2	0
Median	21.5	26.5	0.5	0.2	12.6	0
N	2	2	2	2	2	2
SD	24.75	34.65	0.71	0.28	17.54	0
RSD	115.11	130.75	141.42	141.42	139.18	0
Se mg/L measured mg/L	28	36	19	0	0	0
Se mg/L Actual	4	2	1	0.4	0.2	0
Median	16	19	10	0.2	0.1	0
N	2	2	2	2	2	2
SD	16.97	24.04	12.73	0.28	0.14	0.00
RSD	106.07	126.53	127.28	141.42	141.42	0.00
Sb mg/L measured	274	275	308	150	272	173
Sb mg/L Actual	4	2	1	0.4	0.2	0
Median	139	200.8	217.6	145.7	206.7	86.5
N	2	2	2	2	2	2
SD	190.92	193.04	217.08	105.78	192.19	122.33
RSD	137.35	96.15	99.74	72.60	92.98	141.42
Bi mg/L measured	37	37	0	0	0	0

Bi mg/L Actual	4	2	1	0.4	0.2	0
Median	20.5	19.5	0.5	0.2	0.1	0
N	2	2	2	2	2	2
SD	23.33	24.75	0.71	0.28	0.14	0.00
RSD	113.83	126.92	141.42	141.42	141.42	0.00

The elemental analysis of cathode liquor using factory default data from the EDXRF yielded inconclusive results, as highlighted in the tabulated data. This underscores the critical importance of calibrating the instrument before obtaining semi-quantitative data. The inconsistency observed, especially with elements like Ni, emphasized the necessity for internal calibration to ensure data comparability and accuracy. Subsequent scanning of the samples using a calibrated EDXRF method revealed improved linearity for the majority of impurities. This outcome underscored the significance of instrument calibration in generating reliable, indicative, and rapid semi-quantitative data for testing purposes. The importance of this calibration process is illustrated in the tabulated results provided in Table 9. The actual concentrations of Ca ranged from 0 to 0.15 mg/L, the measured values consistently returned 0 mg/L for all samples. The median values, which are also 0 mg/L, also reflect this discrepancy. The high SD and RSD of these measurements, particularly for low concentrations, suggest a significant degree of uncertainty.

The measured concentrations of Fe were in close agreement with the actual values of 0 to 1500 mg/L, ranging from 0 mg/L to 1630 mg/L. The median values are in agreement with the measured data, indicating that the Fe measurements are more precise than the Ca measurements. Nevertheless, the standard deviation and relative standard deviation values suggest that the precision continues to fluctuate. This implies that the measurements are generally precise; however, the variability increases at lesser concentrations. The analysis of Co, Ni, Cu, As, Se, Sb, and Bi demonstrates significant trends in both precision and accuracy. Close alignments of Co measurements with the actual values, with median values indicating reasonable accuracy. However, precision decreases at lower concentrations, as evidenced by a substantial increase in RSD. Though internal consistency is preserved, Ni consistently demonstrates overestimation in measured concentrations in comparison to actual values. This is due to the fact that median values are in agreement with the measured data. Nevertheless, the precision of the measurement decreases as the concentration increases, as evidenced by an increase in the SD and RSD. In general, Cu measurements are consistent with the actual values, with a low RSD at higher concentrations. However, precision decreases at lower levels. As

measurements are precise at elevated concentrations; however, they exhibit enhanced RSD at lower concentrations, suggesting diminished precision. Measurements for Se, Sb, and Bi are consistently negative across all samples, resulting in high RSD values. This suggests that detecting these elements at low concentrations may be difficult.

By calibrating the instrument, variations in data were minimized, leading to more consistent and reliable measurements. This calibration not only enhances the accuracy of elemental analysis but also ensures that the obtained data can be effectively used for decision-making processes and quality control in industrial applications.

Table 9. Elemental analysis of synthetic cathode liquor after internal calibration and validation method by EDXRF.

Name	TDK Feed	TDK1	TDK 2	TDK 3	TDK 4	TDK 5
Ca mg/L Measured	0	0	0	0	0	0
Ca mg/L Actual	0.15	0.1	0.05	0.025	0	0
Median	0.075	0.05	0.025	0.0125	0	0
N	2	2	2	2	2	2
SD	0.11	0.07	0.04	0.02	0	0
RSD	141.42	0	0	0	0	0
Fe mg/L Measured	1630	989	480	95	0	0
Fe mg/L Actual	1500	1000	500	100	5	0
Median	1565	994.5	490	97.5	2.5	0
N	2	2	2	2	2	2
SD	91.92	7.78	14.14	3.54	3.54	0
RSD	5.87	0.78	2.89	3.63	0	0
Co mg/L Measured	1010	512	280	96	9	0
Co mg/L Actual	1000	500	250	100	10	2.5
Median	1005	506	265	98	9.5	1.25
N	2	2	2	2	2	2
SD	7.07	8.49	21.21	2.83	0.71	1.77
RSD	0.70	1.68	8.00	2.89	7.44	141.42
Ni mg/L Measured	123331.8	128190	130356	131631.25	131767	132320
Ni mg/L Actual	120000	120000	120000	120000	120000	120000
Median	121666	124095	125178	125816	125884	126160
N	2	2	2	2	2	2

SD	2355.94	5791.38	7322.66	8224.54	8320.74	8711.56
RSD	1.94	4.67	5.85	6.54	6.61	6.91
Cu mg/L Measured	3006	1620	800	209	15	0
Cu mg/L Actual	3000	1500	750	200	10	0
Median	3003	1560	775	204.5	12.5	0
N	2	2	2	2	2	2
SD	4.24	84.85	35.36	6.36	3.54	0
RSD	0.14	5.44	4.56	3.11	28.28	0
As mg/L Measured	204	98	47	12	0	0
As mg/L Actual	200	100	50	10	5	0
Median	202	99	48.5	11	2.5	0
N	2	2	2	2	2	2
SD	2.83	1.41	2.12	1.41	3.54	0
RSD	1.40	1.43	4.37	12.86	141.42	0
Se mg/L Measured	0	0	0	0	0	0
Se mg/L Actual	1	0.5	0.25	0	0	0
Median	0.5	0.25	0.125	0	0	0
N	2	2	2	2	2	2
SD	0.71	0.35	0.18	0	0	0
RSD	141.42	141.42	141.42	0	0	0
Sb mg/L Measured	0	0	0	0	0	0
Sb mg/L Actual	1	0.5	0.25	0	0	0
Median	0.5	0.25	0.125	0	0	0
N	2	2	2	2	2	2
SD	0.71	0.35	0.18	0	0	0
RSD	141.42	141.42	141.42	0	0	0

Bi mg/L Measured	0	0	0	0	0	0
Bi mg/L Actual	1	0.5	0.25	0	0	0
Median	0.5	0	0	0	0	0
N	2	2	2	2	2	2
SD	0.71	0.35	0.18	0	0	0
RSD	141.42	0	0	0	0	0

The semi-quantitative data for Ca, Se, Sn, Bi, Mg, Te fell below the LOD of the EDXRF equipment. This limitation highlights a drawback of the equipment, particularly its high LOD for light elements, which hinders the accurate quantification and monitoring of impurities in samples. However, despite these limitations, a linear relationship was observed between the actual and measured values for Co, Cu, Fe, and As, with R^2 values close to 0.99, indicating a strong correlation. This suggests that the EDXRF method remains effective for analyzing these elements, despite the limitations with light elements. To overcome the shortcomings of EDXRF, FAAS was employed, with actual samples analyzed using emission spectroscopy for elemental analysis of Co, Cu, Fe, Ca, Mg, and Na. The comparison revealed comparable results between the two methods. Furthermore, a spiked method was utilized for obtaining Mg and Fe concentrations in the actual samples for FAAS analysis.

The plotted data, tabulated in Table 10 and illustrated in Figure 3, indicate that FAAS is suitable for the analysis of Co, Mg, Fe, Cu, Ca, and Na, providing accurate and reliable results for these elements. The accuracy and precision of the elements Ca, Co, Fe, Mg, Ni, Cu, and Na are subject to variation when analysed using various measurement techniques (ICP-OES, AAS). The Ca measurements exhibit some variability, with a SD of 29.51 mg/L and a RSD of 16.86%, suggesting moderate consistency between methodologies. The precision of Co measurements is exceptional, as evidenced by a low standard deviation of 8.08 mg/L and an RSD of 0.82%, which is consistent across all methodologies. Iron (Fe) exhibits a slightly higher variability, with an SD of 2 mg/L and an RSD of 6.45%. This suggests that the measurement is reasonably accurate, but the precision is slightly lower. The magnesium (Mg) measurements exhibit moderate variability, with an SD of 1.53 mg/L and an RSD of 10.18%, suggesting that there is some fluctuation between testing methodologies. Nickel (Ni) demonstrates a high level of precision, with an SD of 4 mg/L and an RSD of 3.17%, indicating a close alignment between the methodologies. The accuracy of the Cu measurements is high, as evidenced by an SD of 147.86 mg/L and an RSD of 4.98%. Nevertheless, Na exhibits the highest degree of variability among the elements analysed, with an SD of 505.24 mg/L and

an RSD of 23.39%. This data suggests that there are substantial discrepancies between the measurement methodologies.

The EDXRF equipment may have limitations in detecting light elements, FAAS proves to be a viable alternative for the analysis of certain elements in the cathode liquor. By employing a combination of analytical techniques, including calibration and spiking methods, it is possible to overcome these limitations and obtain accurate elemental analysis results essential for quality control and process optimization in industrial applications.

Table 10. Elemental analysis of the actual sample by FAAS and ICP-OES.

Actual Sample	Ca	Co	Fe	Mg	Ni	Cu	Na
Sample Name	mg/L	mg/L	mg/L	mg/L	g/L	mg/L	mg/L
Feed (ICP-OES) received	175	990	31	15	126	2960	2160
Feed (ICP-OES)	179	984	33	16	130	2968	2099
Feed (AAS)	126	1000	29	13	122	3220	3003
Median	175	990	31	15	126	2968	2160
Standard deviation (SD)	29.51	8.08	2	1.53	4	147.86	505.24
Relative standard deviation (RSD)	16.86	0.82	6.45	10.18	3.17	4.98	23.39

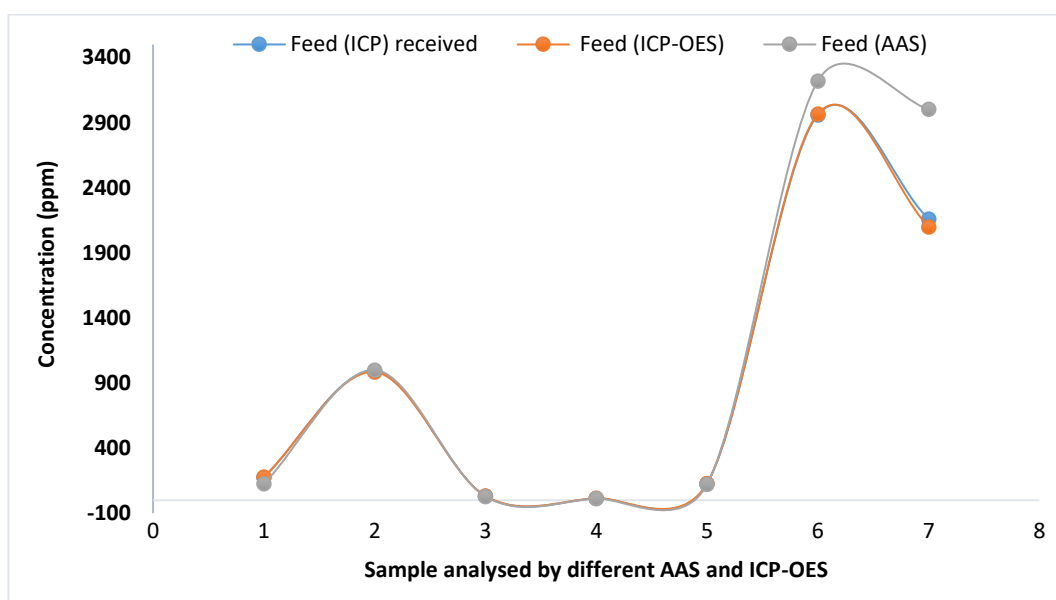


Figure 3. Comparative results for ICP-OES and FAAS on the actual sample.

4. Conclusion

Developing a quick elemental analysis method for monitoring and evaluating the purification process of synthetic cathode liquid in the production of highly purified nickel was the objective of this work. The study focused on optimizing matrix-matching standards and spiking elements as pretreatment for Flame Atomic Absorption Spectroscopy (FAAS) and compared these results with those obtained

from Energy Dispersive X-ray Fluorescence (EDXRF) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

Calibration with reference solutions matched to actual samples was needed for reliable results. The results indicated that FAAS and EDXRF attained satisfactory recovery rates ranging from around 80% to 92%. Spiking samples with 10 mg/L of analytes greatly enhanced the accuracy of low-concentration measurements, with Co, Na, Ca, Mg, Cu, and Fe showing recovery percentages close to or above 90%. Specifically, Na (95%–102.5%) and Ca (97%–99.5%) recovery rates were remarkably high, while Fe (89%–109.9%) and Cu (79%–109%) performance was consistent. By minimising losses and interferences, spiking also improved the comparability of actual and measured values.

ICP-OES results provided a complementary analysis, showing good precision and accuracy for Co, Mg, Fe, Cu, Ca, and Na. Despite advancements, FAAS encountered limitations such as time-consuming calibration, frequent equipment cleaning, and issues with high background Ni concentrations. EDXRF was disadvantaged by high LODs for Al, Mg, Sb, Te, Se, Cd, Cr, and Na, while ICP-OES effectively addressed these constraints. Overall, this study highlights the necessity of calibration and technique modification for reliable elemental analysis in industrial applications.

Acknowledgements

The authors would like to express sincere gratitude to Mintek for financial support through Science Vote grant number: ASR-00002313 and for permission to publish this work.

References

- [1] A. Carlson, "Meeting Nickel Demand for Lithium-Ion Batteries Will Be a Challenge," Feeco international, 2021.
- [2] K. A. Sukhenko, and K. A. Moiseeva, "Determination of lead, bismuth, tin, antimony, and arsenic impurities in nickel alloys and steels," *J Applied Spectroscopy*, 1968, 8(5): 470–473.
- [3] M. Franek, and V. Krivan, "Trace characterization of high-purity nickel by instrumental and radiochemical neutron activation analysis," *Fresenius J Anal Chem*, 1990, 338(1): 28–33.
- [4] L. Elci, M. Soylak, et al., "Determination of trace impurities in some nickel compounds by flame atomic absorption spectrometry after solid-phase extraction using Amberlite XAD-16 resin," *Fresenius J Anal Chem*, 2000, 368(4): 358–361.
- [5] O. Kujirai, K. Yamada, "Simultaneous determination of seven trace impurities (Al, As, Cr, Fe, Ti, V, and Zr) in high-purity nickel metal and nickel oxide by coprecipitation and inductively coupled plasma-atomic emission spectrometry," *Fresenius J Anal Chem*, 1994, 348(11): 719–723.
- [6] Y. Cheng, "Determination of trace elements in high-purity nickel by inductively coupled plasma mass spectrometry with microwave digestion," *Metallurgical Analysis*, 2008, 28(3): 9–13.
- [7] H. L. Xie et al, "Determination of trace elements in high purity gold by high resolution inductively coupled plasma mass spectrometry," *J Wuhan Univ Technol*, 2009, 24(4):608–612.

4.3 PAPER III

This paper entitled “Separation and Characterisation of Nickel Hydroxide from Waste Solution using $\text{Ca}(\text{OH})_2$ Precipitation In Chloride Media” **Published Separations 2024, 11(4), 96; <https://doi.org/10.3390/separations11040096>.**

Highlights

- ◇ Successful validation of the precipitation process for $\beta\text{-Ni}(\text{OH})_2$ using XRD analysis.
- ◇ XPS analysis, confirmed presence of Ni^{2+} of precipitated $\text{Ni}(\text{OH})_2$ oxidation at pH 6.5 and other impurities.
- ◇ $\text{Ni}(\text{OH})_2$ exhibited granules with a typical brucite crystalline phase in SEM imaging.
- ◇ ICP-OES corroborate with EDX indicated the consistence for elemental quantification
- ◇ $\beta\text{-Ni}(\text{OH})_2$ illustrated an intriguing properties for various application.

Authors Contributions

Happy Mothepane Mabowa - The main author conceptualized the methodology, validation, writing the original draft, led the design of the methodology, supervising data collection and analysis, ensured compliance with ethical standards, securing funding, and maintaining communication with collaborators and funding agencies.

Andile Mkhohlakali - Contributed to Formal analysis, Investigation, Data curation, Writing original draft.

James Tshilongo – Contributed to data collection, Supervision, editing, visualization, and acquire funding.

Luke Chimuka - Supervision, data curation, and statistic validation.

Separation and Characterisation of Nickel Hydroxide from Waste Solution using $\text{Ca}(\text{OH})_2$ Precipitation In Chloride Media

Happy Mothepane Mabowa ^{1,2*}, Andile Mkhohlakali ^{1*}, Luke Chimuka ² and James Tshilongo ^{1,2}

¹Analytical Chemistry Division, MINTEK, 200 Malibongwe Drive, 2155, South Africa

²School of Chemistry, University of the Witwatersrand, Private Bag 3, PO WITS, 2050, South Africa

*Correspondence: author's email: happyc@mintek.co.za,

*Co-correspondence: author's email: andilem@mintek.co.za

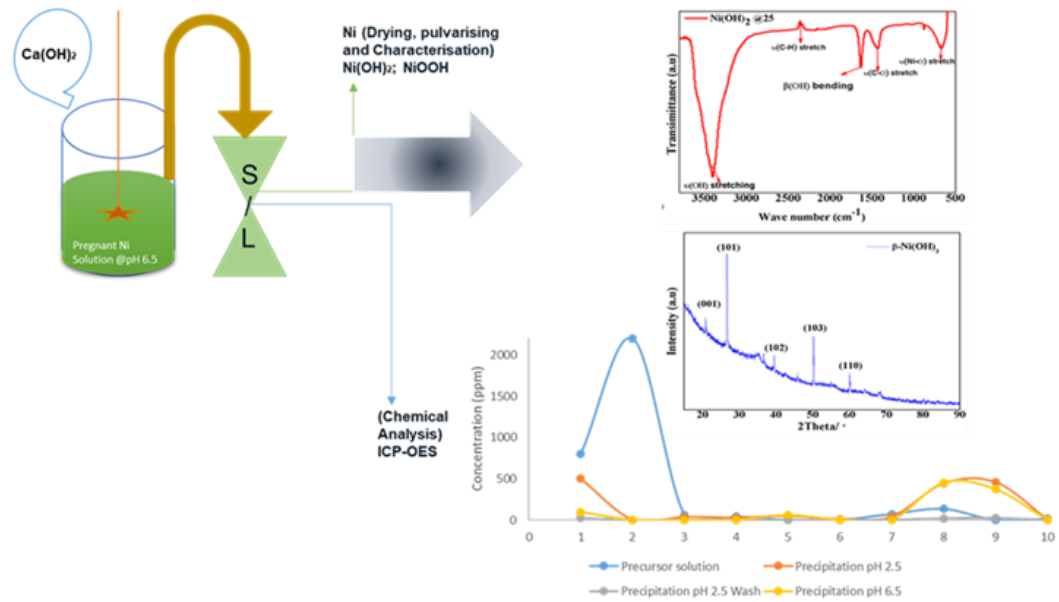
Abstract

Nickel hydroxide ($\text{Ni}(\text{OH})_2$) is a valuable compound derived from nickel, widely utilized across various field because of its versatile properties. This study aims to characterise the as-prepared $\beta\text{-Ni}(\text{OH})_2$ via a chemical precipitation using various analytical techniques. X-ray diffraction (XRD) analysis confirmed the formation of the $\beta\text{-Ni}(\text{OH})_2$ hexagonal crystalline structure, validating the successful precipitation. Fourier-transform infrared spectroscopy (FTIR) spectra exhibited main characteristic peaks of $\nu(\text{OH})$, and $\nu(\text{NiO})$, corresponding to formation of nickel hydroxide ($\text{Ni}(\text{OH})_2$). Subsequent, X-ray photoelectron spectroscopy (XPS) reveals the prominent peak for Ni^{2+} oxidation, confirming successful precipitation of nickel hydroxide at pH 6.5 which identifies the existence of impurities such as chlorine and calcium from the waste matrix. Scanning electron microscopy (SEM) micrographs demonstrated stratified granules with a nearly pure brucite crystalline phase, typical of $\beta\text{-Ni}(\text{OH})_2$. Furthermore, the surface morphology reveal the coarse texture and uneven clustering suggest possible elevated oxide levels on the Ni surface. Energy-dispersive X-ray spectroscopy (EDX) confirmed the presence of nickel (Ni) and oxygen (O), with Ca impurities, attributed to the chemical precipitation process. Particle size distribution analysis estimated an average

particle size of 2.0 μm . Additionally, the precipitation of Nickel was investigated using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The Ni was observed in the decreasing order, 62.7 g/L, 0.8 g/L, and 0.501 g/L in the pregnant leach, precursor solution, and in solid precipitate (cake), respectively. The separation of $\text{Ni}(\text{OH})_2$ through precipitation process from the waste (acidic chloride media) enables efficient recycling and re-use on Nickel, which provide with the cost-effective and environmentally friendly for high efficient utilization of waste (acidic chloride media).

Keywords: Nickel hydroxide; precipitation; elemental composition; acidic chloride media

Graphic Abstract



1. Introduction

Nickel (Ni) can be acquired or recycled through various methods, with the conventional approaches typically involving smelting or leaching techniques [1]. Following these initial steps, a refining or finishing process is employed to yield a pure nickel product or derivatives. The demand for Ni sources, especially for nickel-based battery applications, has surged in recent years. At the same time, due to its exceptional performance, Ni also referred to as the “vitamin of the steel industry”- is widely utilised in a variety of industries as a national strategic resource. In addition, mostly, Nickel is utilized in the manufacturing of non-ferrous alloys, stainless steel and superalloys that has high resistance in corrosion and high temperature. However, traditional methods of nickel extraction often entail environmental consequences and significant costs. As a result, there is growing interest in alternative approaches to Ni recovery, particularly from waste streams. These waste streams, often produced from pyrometallurgy processes from fluxes (Nickel sulphide) for platinum group element (PGE) collection, represent both an attractive secondary source and an environmental contaminant. Despite containing valuable resources, they also harbor harmful contaminants. Harnessing waste to produce nickel hydroxide (Ni(OH)_2) presents a compelling solution. Not only does it hold significant worth as a material with various applications, but it also presents an eco-friendly approach to recovering Ni. However, accessing Ni(OH)_2 from these unconventional sources poses challenges, such as impurities like sodium (Na) or calcium (Ca), which are commonly introduced from the choice of precipitating agent. These impurities can affect the purity and properties of the synthesized Ni(OH)_2 , necessitating careful optimization of the precipitation process. The waste if discarded from these unconventional sources poses challenges, such as strict regulations on effluent Ni concentrations in the effluent, which can constitute up to 10% of the municipal waste stream. This work underpins the optimal conditions to precipitate Ni compounds from the pyrometallurgy process (fire assay) waste which is generated daily in large volumes.

Among the derivatives, nickel hydroxide holds particular significance due to its widespread applications. The focus on studying the precipitation of nickel hydroxide (Ni(OH)_2) primarily stems from its crucial role as a positive electrode material in alkaline rechargeable batteries [2]. Currently, the entire demand for Ni(OH)_2 is met through the chemical precipitation technique [2],[3], [4]. Consequently, this method of preparation has garnered significant attention and has been extensively researched. Several investigations have been conducted to explore the characteristics of Ni(OH)_2 , ranging from its structural and morphological properties to its electrochemical behavior and to understand its properties for application particularly in the realm of rechargeable battery technology [3],[4],[2] [5],[6],[7].

The latter ($\beta\text{-Ni(OH)}_2$) holds significant importance in various fields due to its versatile properties, including catalysis, energy storage, and environmental remediation [8]. Its application in electrochemical devices, such as rechargeable batteries and supercapacitors, has drawn considerable attention owing to its high theoretical capacity and excellent electrochemical performance. In recent years, the synthesis and characterization of $\beta\text{-Ni(OH)}_2$, the most stable phase of the latter, have been extensively studied due to its superior electrochemical properties compared to other phases. This method involves the precipitation of nickel ions (Ni^{2+}) from an aqueous solution, typically using a precipitation agent, such as sodium hydroxide (NaOH) or calcium hydroxide (Ca(OH)_2), followed by subsequent washing and drying steps.

The precipitation method stands out as a prominent technique for synthesizing $\beta\text{-Ni(OH)}_2$ due to its simplicity, scalability, and cost-effectiveness. However, achieving precise control over the synthesis parameters, encompassing pH, temperature, and choice of precipitation agent, is crucial to obtain $\beta\text{-Ni(OH)}_2$ with desired properties. Comprehensive characterization of the synthesized material is essential to understand its structural, functional groups, surface properties, and chemical composition, which directly influence its performance in various applications.

The introduction of alkaline compounds raises the pH of the solution, creating an environment where metal ions exhibit low solubility in the aqueous phase. Typically, during the hydroxide precipitation process, particularly Ni(OH)_2 . The chemical reaction that takes place is indicated in equation 1 [8], [9].



Every metal ion possesses an optimal pH level to achieve the maximum precipitation of metal hydroxides. The pH condition significantly influences the concentration of dissolved metal ions within the solution during the precipitation process[10] [11]. To the best of our knowledge, there is a lack or no optimal conditions investigated for precipitation of Nickel hydroxide in different stages from high acid media such as Nickel sulphide collection processed waste was reported literature.

In this context, this study aims to characterize $\beta\text{-Ni(OH)}_2$ synthesized through a precipitation process. Various analytical instruments including inductively coupled plasma optical emission spectroscopy (ICP-OES), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and X-ray diffraction (XRD) will be employed to elucidate the structural, functional groups, surface properties, and chemical composition of the synthesized Ni(OH)_2 . This work underpins the significance of Ni(OH)_2 , its synthesis methods, and the importance of comprehensive characterization. Additionally, the present work holds significant practical implications for enhancing the chemical precipitation method's treatment efficiency, decreasing its operating expenses, and lowering the generation of secondary pollutants throughout the Ni recycling procedure.

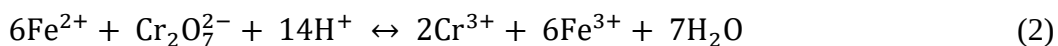
2. Materials and Method

2.1. Reagents and material

The main raw material utilised for this experiment is the waste solution from Analytical Chemistry Division, NiS Laboratory, Mintek, Randburg. This waste solution contains various metal elements as quantifies using ICP-OES, the data is presented in in **Table 1**. 5,8-diethyl-7-hydroxydodecan-6-oxime solvent was used as an extractant for Cu during the extraction of metal ions from the pregnant waste solution. All other chemicals are of analytical grade, and have been used without further purification. Diphenylamine (Sigma Aldrich, St. Louis, MO, USA), Phosphoric acid (H₃PO₄) (Merck (Pty) Ltd., Modderfontein, South Africa), Potassium dichromate (K₂Cr₂O₇) (Sigma Aldrich), sulphuric acid (H₂SO₄, 98% v/v) (Sigma Aldrich), and calcium hydroxide (Ca(OH)₂) (Merck (Pty) Ltd., Modderfontein, South Africa).

2.2. Determination of ferric (Fe³⁺) and ferrous (Fe²⁺) ions

The determination of Fe³⁺ and Fe²⁺ was executed as described in [22]. The precursor solution underwent titration to quantify the presence of ferric and ferrous ions. The concentration of ferrous (Fe²⁺) ions was determined using the dichromatometric method, relying on the reaction described by equation 2.



This is an oxidation-reduction process in which an oxidizing agent, potassium dichromate (K₂Cr₂O₇) reacts with a reducing agent Fe²⁺ ions. Diphenylamine serves as a reversible oxidation-reduction indicator in various chemical reactions and analytical methods. The Fe³⁺ was determined by the iodometric method which is based on equations 3 and 4.





This is an indirect oxidation-reduction process in which an oxidizing agent ferric ions (Fe^{3+}) reacts with a reducing agent (iodide ions). The observed results from the above titration method indicates the Fe^{3+} bearing waste which gives an insight to precipitate the Fe ion at lower pH around 2 to 2.5.

2.3. Synthesis/Preparation process of $Ni(OH)_2$

The synthesis of $Ni(OH)_2$ involved two distinct steps: (1) preparation of the precursor solution, (2) and synthesis of $Ni(OH)_2$. As outlined in the referenced literature [14], with minor adjustments, the pregnant waste solution (PWS) harbored valuable copper (Cu) that could be extracted using solvent extraction (SX). In this method, PWS was introduced into a 1000 mL separating flask at an organic/aqueous ratio of 1:5. Utilizing 5,8-diethyl-7-hydroxydodecan-6-oxime as the organic solvent facilitated the extraction of Cu into the organic phase before the precipitation step. This process is illustrated in **Figure 1**.

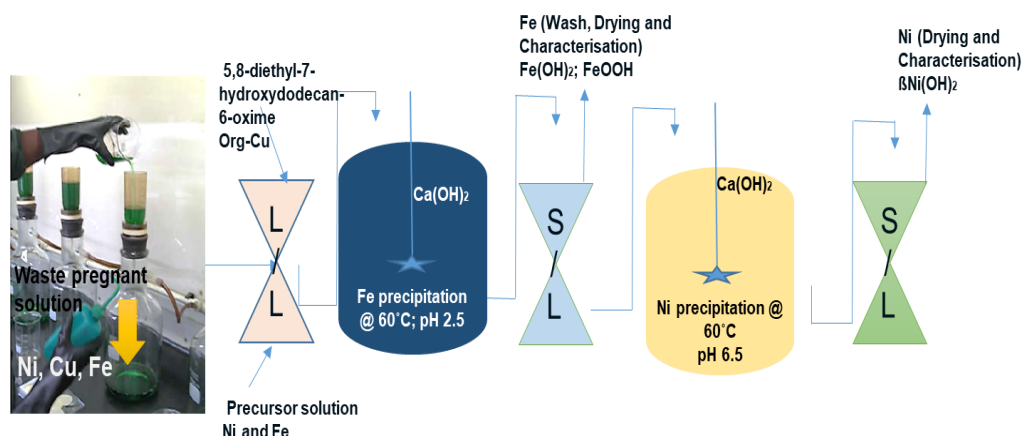


Figure 1. The workflow of $Ni(OH)_2$ synthesis from the waste pregnant solution.

Following the SX process, the raffinate was obtained and the aqueous phase was identified as the precursor solution of the PWS. The precursor solution measured approximately 5000 mL and underwent a chemical precipitation reaction involving the metal ions of the PWS, particularly the Ni^{2+} ions. To prepare for the reaction, a

25% Ca(OH)_2 solution was separately created based on the approximate concentration of the chloride media in the PWS. The precipitation reaction occurred at a temperature of 60°C and pH levels of 2.5 and 6.5, where the precursor solution was blended with the 25% Ca(OH)_2 .

A glass reactor with an overhead stirrer was utilised during the extraction process to ensure that the seeding material was effectively suspended in the solution. During the process, the temperature was continually monitored utilizing a thermometer, while pH levels were measured using a pH meter. The operation maintained a temperature of 60°C , with heating supplied by passing hot water through the reactor's jacket.

Once level of pH reached the target range of 6.5 to 7, the stirring was stopped, and the fluid was filtered using a Buchner funnel. The cake was subsequently dehydrated for 24 hours at a temperature of 55°C . Throughout this phase of evaporation, the phenomenon of precipitation persisted under its fundamental mechanism. Subsequently, the liquid phase was examined to ascertain the residual concentration of Ni^{2+} ions by employing the analytical techniques to yield vital insights into the efficacy and efficiency of the precipitation process.

2.4. The Effect of Precipitation

This experimental study was conducted under conditions designed at pH 6.5, which represents the optimal pH for precipitating Ni^{2+} ions [14] from PWS. After precipitation the solution was characterized by ICP-OES. Previous studies have reported that the optimum pH for precipitating Ni^{2+} ions is pH 10 [12]. Similarly studies in literature [13] observed that an alteration in the stability of metal ions might arise at increased operational temperatures, notably at 60°C , throughout the hydroxide precipitation procedure. This occurrence was substantiated by formation of metal oxides and hydroxide deposits at reduced pH levels. The precipitation reaction involved in synthesizing Ni(OH)_2 is reversible due to the formation of complex compounds that are insoluble in liquids. Typically, this reaction is

exothermic, meaning it releases heat. At higher temperatures, the precipitation reaction occurs, and the equilibrium tends to shift toward the reactants, as explained in the literature [13]. Consequently, this inhibits the formation of precipitates, resulting in a smaller amount being produced. Thus, controlling the temperature during the precipitation process was crucial to ensure optimal yield and efficiency in the synthesis of Ni(OH)_2 .

2.5. Characterization

The characterization of Ni(OH)_2 involved the utilization of several analytical techniques to elucidate its structural, vibrational, surface properties, and chemical composition. The analytical techniques employed includes, XRD analysis, PANalytical Empyrean Diffractometer, Cu anode $k\alpha = 1.5406 \text{ \AA}$, Data acquired at 45 kV: 40 mA, 2θ scan range of 5 to 100 degrees, step size 0.01 degrees was performed to ascertain the crystalline structure of the synthesized Ni(OH)_2 and validate its phase purity. FTIR (SHIMADZU) spectroscopy was employed to analyse the vibrational modes of Ni(OH)_2 and identify functional groups present in the compound. XPS analysis provided insights into the surface chemistry of Ni(OH)_2 , allowing for the identification of surface species and elemental composition. SEM imaging, Zeiss Cross Beam 540 Morphology Utilising an InLens detector, imaging was conducted at 2 kV, 79 pA, and a 5 mm working distance. Utilising a backscatter electron detector, cross-section imaging was obtained at 20 kV and 5 nA. to visualize the morphology and microstructure of the synthesized Ni(OH)_2 , providing information on shape, and surface morphology. ICP-OES, Agilent 5110 Vertical dual view (VDV) USA was utilized to quantitatively analyze the chemical composition of Ni(OH)_2 , providing data on the elemental composition and concentration of impurities.

3. Results and Discussion

3.1. The elemental composition of waste pregnant leach

The elemental composition of waste pregnant leach is displayed in **Table 1**, indicating the major and minor elements. It can be seen that the waste pregnant leach contains higher Ni (62700 ppm), followed by Cl (80000 ppm), Fe (4720 ppm) and Cu (3900 ppm). The highest concentration of Nickel and Cl is attributed to Nickel sulphide (NiS) flux present in the waste (acidic chloride) and Hydrochloric acid (HCl) leaching acid, respectively.

Table 1. The composition of the pregnant waste solution.

Element Composition	Ca	Mn	Pb	Zn	Cu	Fe	Cl	Ni
Concentration (ppm)	4.53	6.7	10	73.9	3900	4720	80000	62700

3.2. The Effect of Pre-Loading of Copper Concentration

The copper (Cu) loading was applied onto the organic material, demonstrating the effectiveness of the oxime utilised, as stated by the report [14]. The organic solvent had a significant attraction towards metal cations, specifically Copper, which resulted in a high extraction efficiency as documented in the literature [15],[16]. In the precursor solution, the aqueous phase, exhibited a Cu concentration of 801 ppm at pH 2.5 and 501 ppm at pH 6.5, as evaluated by ICP-OES. Additionally, the Cu concentration at pH 6.5 was found to be 95.7 ppm in **Figure 2**. As indicated in Table S1 (supplementary information), copper was trapped (loaded) in the organic phase exhibiting high concentration (3097.96 ppm), indicating the high efficiency of the solvent. Furthermore, after the precipitation at pH 6.5 the filtrate during wash showed lowest concentration of 7.43 ppm, as illustrated in table S1 (supplementary information).

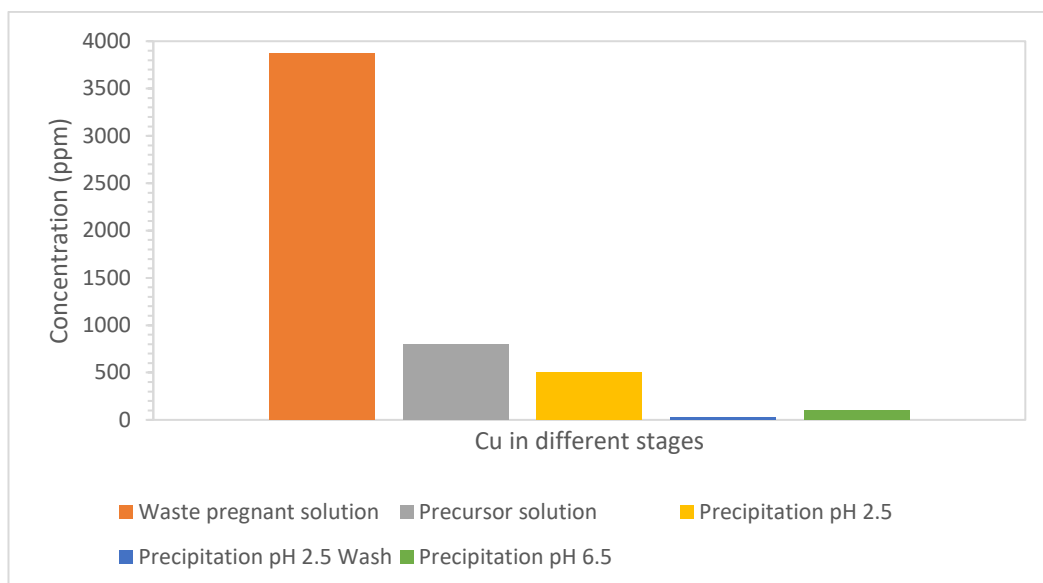
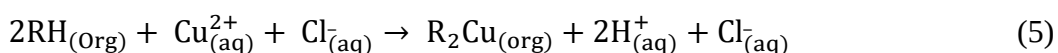


Figure 2. The copper concentration in subsequent stages, higher (concentrated) on waste solution (pregnant solution), followed by (precursor solution), and filtrate after precipitation at different pH (2.5 and 6.5)

Figure 2 represent the copper concentration in different steps (stages) as depicted in **Figure 1**. After the pre-loading stage of Cu removal, the solution was analysed and the precursor solutions contained 50130 ppm of Ni^{2+} ions and 20197 ppm of Fe^{3+} and 801 ppm of Cu^{2+} ions and other impurities shown in **Table 2**. It can be seen that there is a significant drop of Cu concentration from 3870 ppm to 801 ppm, to 501 ppm in the waste pregnant solution and precursor solution, respectively. This could be ascribed to Cu being trapped in the organic phase by oxime functional groups as expressed in equation 5.



The % loading of Cu is approximately 79.3% which the observed trend in this study aligns with the findings in literature [17]. The aforementioned study demonstrated the optimal conditions for investigating the precipitation process of other metal ions, such as Fe in the mixture with nickel (Ni), is achieved at higher temperatures. Specifically, the utilisation of elevated temperatures has an impact on decreasing

the amount of Ni precipitated (Ni loss) during the Fe precipitation procedure at pH 2.5 as illustrated by this groups in literature [14]. Thus, this study confirms the precipitation process of Ni^{2+} ions operates at a temperature of 60°C and pH of 6.5 as indicated in **Table 2** which results that 600 ppm Ni is solution from 62700 ppm Ni in the PWS (**Table 1**) with a recovery of 90.27 % and loss of 9.73 % with Fe at pH 2.5. The decrease in Ni concentration from 3700 ppm to 600 ppm is as expected, it means at pH 6.5, only 600 ppm left in the solution. High concentration of Ni is in the precipitate (cake). This is the key part of this study, at pH 2.5, there is a Ni loss and co-existed with Fe precipitation. Indeed at pH 2.5 Ni co-exist with Fe as explained by this group in literature [14]. In addition, the EDX in the added Figure S3 which verifies the presence of Ni and Fe in the precipitate. Moreover, lower concentration of Ni (600 ppm) in the solution and higher concentration in the solid cake indicates the effectiveness of the precipitation process using $\text{Ca}(\text{OH})_2$.

Table 2. Solution after precipitation at pH 2.5 and 6.5 at 60°C .

		Solutions Samples			
Element		Precursor solution	pH 2.5	Wash	pH 6.5
Cu	ppm	801	501	23.3	95.7
Fe		2197.5	2.3	1.3	0
Ni		50130	3700	1800	600
Co		43	26.4	1.5	0.7
Ca		0	47400	2300	57200
Al		1	10.8	1.2	1.1
Zn		72.7	40.2	2.2	0
S		134.1	446	19.7	456.3
Mg		0	461.9	23.9	375
Pb		14	8	0.2	0

3.3. The Effect of precipitating agent on decreasing Ni^{2+} Ions concentration

The precipitating agent such as $\text{Ca}(\text{OH})_2$ was used and it shows the high efficiency for precipitation of $\text{Ni}(\text{OH})_2$ as displayed in **Table 2**. The results are consistent with the reported literature [12]. Wanta and co-workers identified the alkaline media (KOH) as most effective precipitating agent. Calcium shows an exponential increase from 0.0 ppm to 47400 ppm and 50130 ppm in precursor solution, precipitate at pH 2.5 and in precipitate pH 6.5 respectively [12]. The Ca increase is due to addition of lime in the precipitate. Since Fe precipitates at pH 2.5, its concentration at higher pH levels, such as pH 6.5, is expected to be minimal. However, at pH 2.5, both Ni and Fe co-precipitate, reflecting the presence of Fe as an impurity alongside Ni in the initial stages of the process.

3.4. Structure-morphology characterization of $\text{Ni}(\text{OH})_2$ precipitates

Figure 3(a) illustrates the SEM imaging that is stratified granule composed of approximately pure brucite analog crystalline phase in spherical morphology particles, which is characteristic of $\beta\text{-Ni}(\text{OH})_2$. This finding supports the findings of prior research [14]. The coarse texture may be indicative of elevated levels of oxides on the surface of the Ni, while the uneven clustering is also characteristic of the typical formations. Furthermore, the accumulation could be ascribed to factors other than post-treatment. EDX in **Figure 3(b)** verifies the presence of nickel (Ni) and oxygen (O) derived from the oxides, namely hydroxides. The presence of Ca impurities can be ascribed to the lime originating from the chemical precipitating process with $\text{Ca}(\text{OH})_2$. The estimated mean results from the PSD plot was 2.0 μm in supplementary information.

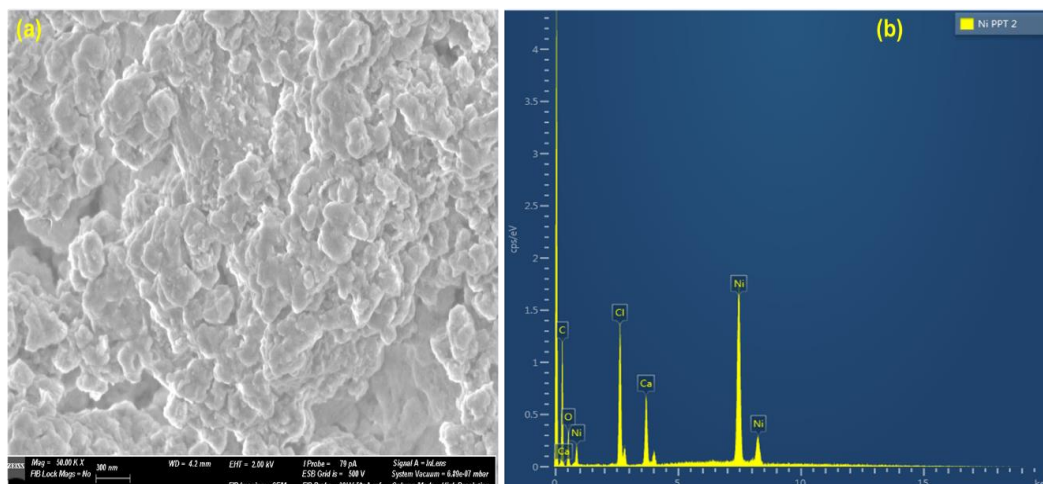


Figure 3. (a) SEM image and (b) EDX of Ni(OH)_2 .

The X-ray diffraction (XRD) pattern depicted in **Figure 4(a)** corresponds to the formation of $\beta\text{-Ni(OH)}_2$. All diffractogram peaks of Ni(OH)_2 indicate the presence of the hexagonal phase of $\beta\text{-Ni(OH)}_2$ at 24° , 29° , 30° , 45° , 50° , and 60° correspond to the crystal planes (001), (100), (101), (102), (103), and (110) respectively [19], [20].

The FTIR spectra **Figure 4(b)** of Ni(OH)_2 exhibit prominent functional group between 450 and 600 cm^{-1} and 1100 cm^{-1} , which correspond to $\nu(\text{Ni-O})$ stretching vibrations of $\beta\text{-Ni(OH)}_2$ and $\nu(\text{O-Ni-O})$, correspondingly. The presence of $\nu(\text{Ni-O-Ni})$ is indicated by a stretching vibration peak at around 1000 cm^{-1} . These observations align with the findings in the literature [19]. The prominent bending vibration band seen at approximately 1600 cm^{-1} is ascribed to the presence of a OH moiety in Ni(OH)_2 . Peak at 3450 cm^{-1} corresponds to the asymmetric stretching mode of the $\nu(\text{OH})$ vibration, which is attributed to the presence of water or metal hydroxide in the α -phase $\nu(\text{Ni-OH})$. The peak observed at 1620 cm^{-1} is attributed to the $\delta(\text{OH})$ bending on surface of Ni. The above mentioned findings validate the successful precipitation of Ni(OH)_2 . The additional vibration bands at approximately 3300 cm^{-1} and 2500 cm^{-1} are ascribed to the stretching of $\nu(\text{C-O})$ and $\nu(\text{C-H})$ caused by the presence of small contaminants which are attributed from carbon species in waste stream.

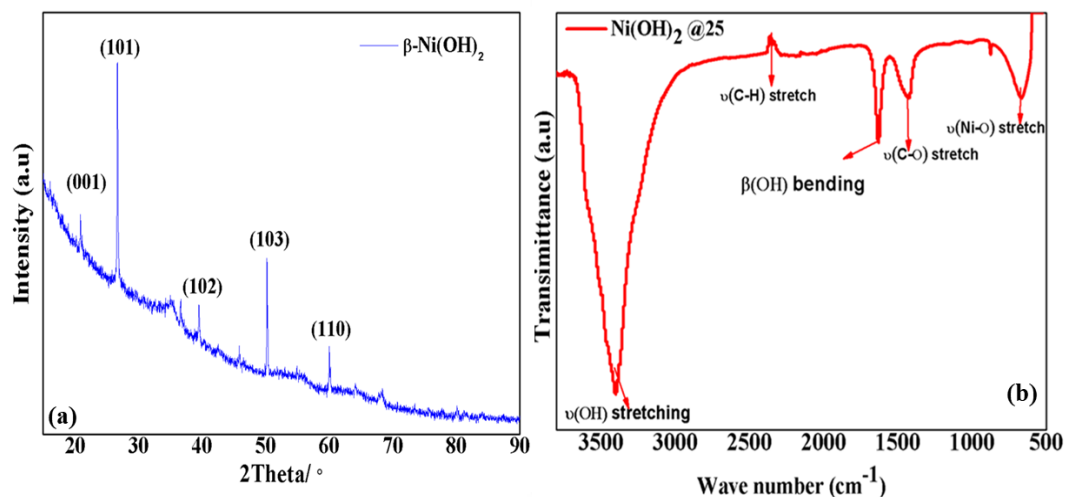


Figure 4. (a) XRD pattern of Ni(OH)₂ and (b) FTIR of Ni(OH)₂.

The electronic structure and oxidation state of nickel hydroxide were determined using XPS, as shown in **Figure 5(a)**. The spectroscopic analysis of Ni(OH)₂ ranging between 0 and 1300 electro volts . Photoelectron line seen at 861 eV, 510 eV, and 300 eV correspond to the Ni2p, O1s, and C1s orbitals, respectively. This suggests that the successful precipitation of Ni(OH)₂ occurred at a pH of 6.5. The photoelectron peaks observed at around 200 eV and 350 eV can be attributed to the presence of chlorine (Cl) and calcium (Ca) impurities originating from the waste matrix of hydrogen chloride (HCl) and lime, respectively. The photoelectron line of oxygen peak (O 1s) can be identified distinct peaks, as illustrated in **Figure 5(d)**. The presence of hydroxyl species on the surface of Ni(OH)₂ is verified by the oxygen photoelectron line (O 1s) peak of MeO (metal-oxide peak), which appears at around 533 eV. The presence of CO₂ impurities found with FTIR in **Figure 5** is indicated by the other O 1s peaks. **Table 3** summarized the elemental composition of β -Ni(OH)₂, the high chloride (metal chloride) (22.4 wt%) can be observed at 199.3 eV binding energy, which can be due to acidic chloride metal and CaCl₂ formed during the precipitation steps. In addition, the XPS spectra line for CaCl₂ is situated at 388.1 eV. The oxygen of the hydroxyl species is located at 531 eV and 533 eV binding energy, which is ascribed to metal-hydroxyl formation, particularly β -Ni(OH)₂. The results are in strong agreement with EDX (**Figure 3**), ICP-OES (**Table 2**) and FTIR (**Figure 4(b)**).

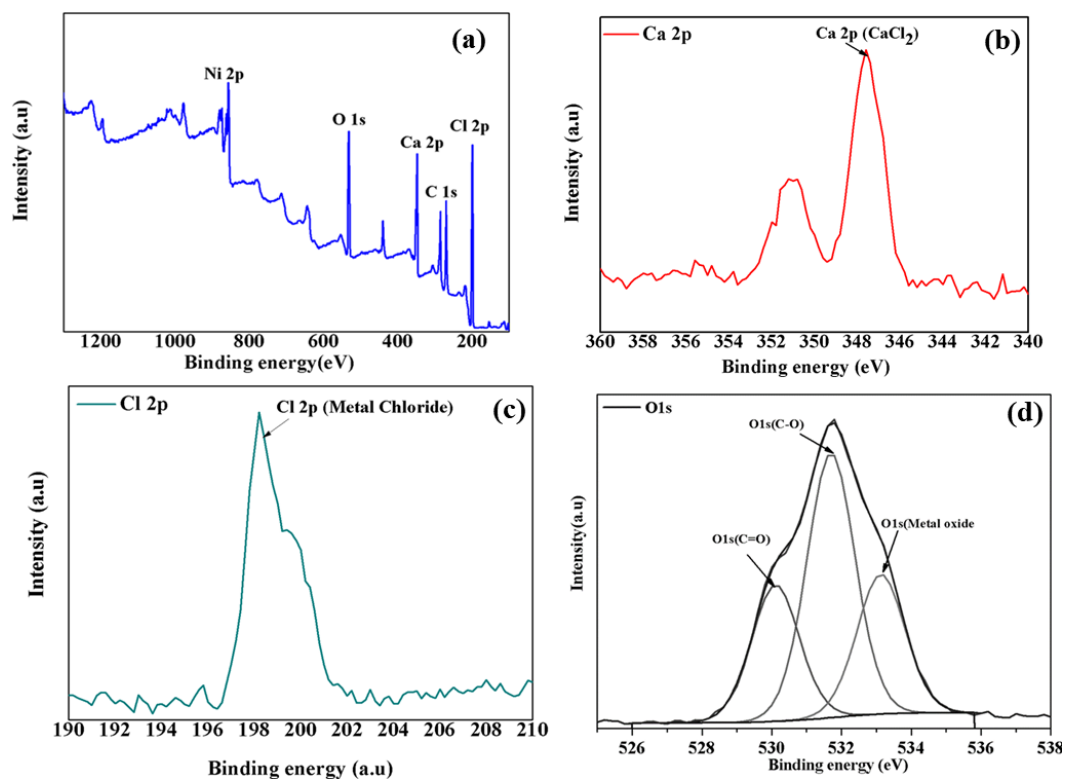


Figure 5. (a) XPS Spectra Survey, (b) Ca 2p spectra, (c) Cl 2p spectra and O1s Spectra of β -Ni(OH)₂.

Table 3. Elemental composition of β -Ni(OH)₂ at pH 6.5.

Element	Peak BE (eV)	Atomic %
C 1s	285.2	36.1
O 1s	531.7	23.5
Cl 2p	199.3	22.4
Ni 2p	856.2	11.8
Ca 2p	348.1	5.2

5. Conclusion

In this study, the preparation and comprehensively characterization of β -Ni(OH)₂ from waste (chloride media) synthesized via a precipitation process and advanced analytical techniques was done successfully. XRD exhibited the while FTIR provided an existence of a -OH moiety which is the attributes of Ni(OH)₂ at 3450 cm⁻¹, 450 and 600 cm⁻¹ and ν (Ni-O) stretching vibrations of β -Ni(OH)₂. XPS analysis confirmed the formation of Ni²⁺ oxidation state which corresponds to the presence of Ni(OH)₂. Furthermore, SEM imaging revealed granular morphology consistent with β -Ni(OH)₂ indicating the successfully chemical precipitation from the waste. The major elements Ni, Cu and Fe quantified by EDX and ICP-OES shows the consistence in the chemical composition. Overall, this study enhances our understanding of β -Ni(OH)₂ synthesis and properties, crucial for its potential applications, and suggests avenues for further research to optimize synthesis conditions and explore specific applications. These findings underscore the efficacy of the chemical precipitation method for synthesizing Ni(OH)₂ and highlight lime as a promising precipitating agent for future applications in the production of high-quality nickel hydroxide compounds. The precipitation process using Ca(OH)₂ for Ni(OH)₂ preparation from the waste (chloride media) enables effective recycling and re-use of Nickel, which provide with the economic method for high efficient utilization of waste (acidic chloride media).

Acknowledgments: The authors wish to extend heartfelt thanks to Mintek for their financial support granted through Science Vote grant number: ASR-00002313 (HM-05), as well as for granting permission to publish this research.

Supporting Information: The utilisation of the advanced analytical techniques and high resolution instrument are essential for synthesis of nickel hydroxide from waste solution using Ca(OH)₂ precipitation from a chloride media. The supporting information provided in Figure S1 and S2 in support of the comprehensive analysis of the PSD and elemental composition of the sample by ICP-OES.

References

- [1] F. Odegbemi, G. A. Idowu, and A. O. Adebayo, "Nickel recovery from spent nickel-metal hydride batteries using LIX-84I-impregnated activated charcoal," *Environ. Nanotechnology, Monit. Manag.*, vol. 15, no. March, p. 100452, 2021, doi: 10.1016/j.enmm.2021.100452.
- [2] K. Watanabe, T. Kikuoka, and N. Kumagai, "Physical and electrochemical characteristics of nickel hydroxide as a positive material for rechargeable alkaline batteries," *J. Appl. Electrochem.*, vol. 25, no. 3, pp. 219–226, 1995, doi: 10.1007/BF00262959.
- [3] M. J. Avena, M. V. Vazquez, R. E. Carbonio, C. P. De Pauli, and V. A. Macagno, "A simple and novel method for preparing Ni(OH)₂ Part I: Structural studies and voltammetric response," *J. Appl. Electrochem.*, vol. 24, no. 3, pp. 256–260, 1994, doi: 10.1007/BF00242893.
- [4] C. Fierro, A. Zallen, J. Koch, and M. A. Fetcenko, "The Influence of Nickel-Hydroxide Composition and Microstructure on the High-Temperature Performance of Nickel Metal Hydride Batteries," *J. Electrochem. Soc.*, vol. 153, no. 3, p. A492, 2006, doi: 10.1149/1.2161577.
- [5] T. N. Ramesh and P. V. Kamath, "Synthesis of nickel hydroxide: Effect of precipitation conditions on phase selectivity and structural disorder," *J. Power Sources*, vol. 156, no. 2, pp. 655–661, 2006, doi: 10.1016/j.jpowsour.2005.05.050.
- [6] S. Cabanas-Polo, K. S. Suslick, and A. J. Sanchez-Herencia, "Effect of reaction conditions on size and morphology of ultrasonically prepared Ni(OH)₂ powders," *Ultrason. Sonochem.*, vol. 18, no. 4, pp. 901–906, 2011, doi: 10.1016/j.ultsonch.2010.11.017.
- [7] N. Solomane, P. A. Ajibade, and B. Omondi, "Crystal structure of sodium morpholine-4-," pp. 27–29, 2019.
- [8] J. A. Matthews, "Chemical Precipitation," *Encycl. Environ. Chang.*, vol. 3, pp. 141–142, 2014, doi: 10.4135/9781446247501.n624.
- [9] Q. Song, Z. Tang, H. Guo, and S. L. I. Chan, "Structural characteristics of nickel hydroxide synthesized by a chemical precipitation route under different pH values," *J. Power Sources*, vol. 112, no. 2, pp. 428–434, 2002, doi: 10.1016/S0378-7753(02)00396-8.

- [10] R. D. Ludwig, R. G. McGregor, D. W. Blowes, S. G. Benner, and K. Mountjoy, "A permeable reactive barrier for treatment of heavy metals," *Ground Water*, vol. 40, no. 1. Pp. 59–66, 2002. Doi: 10.1111/j.1745-6584.2002.tb02491.x.
- [11] M. Endo, E. Yoshikawa, Y. Tamaki, A. Hara, K. Hikichi, and A. Sasaki, "Variations in the Concentration of Dissolved Metal Ions and their Buffering Effect in an Acidified River Environment," *J. Water Environ. Technol.*, vol. 10, no. 4, pp. 463–471, 2012, doi: 10.2965/jwet.2012.463.
- [12] K. C. Wanta *et al.*, "Synthesis and Characterization of Nickel Hydroxide From Extraction Solution of Spent Catalyst," *Metalurgi*, vol. 35, no. 3, p. 111, 2020, doi: 10.14203/metalurgi.v35i3.572.
- [13] L. Hidmi and M. Edwards, "Role of temperature and pH in Cu(OH)₂ solubility," *Environ. Sci. Technol.*, vol. 33, no. 15, pp. 2607–2610, 1999, doi: 10.1021/es981121q.
- [14] H. M. Mabowa, A. Mkhohlakali, S. Mokoena, J. Tshilongo, and L. Chimuka, "Removal of Nickel from Nickel Sulfite-Fire Assay Dissolution Filtrate Through Precipitation," *ACS Omega*, 2023, doi: 10.1021/acsomega.3c07623.
- [15] I. Nozari and A. Azizi, "An Investigation into the Extraction Behavior of Copper from Sulfate Leach Liquor Using Acorga M5640 Extractant: Mechanism, Equilibrium, and Thermodynamics," *Mining, Metall. Explor.*, vol. 37, no. 5, pp. 1673–1680, 2020, doi: 10.1007/s42461-020-00280-z.
- [16] M. Younas, S. Druon-Bocquet, J. Romero, and J. Sanchez, "Experimental and Theoretical Investigation of Distribution Equilibria and Kinetics of Copper(II) Extraction with LIX 84 I and TFA," *Sep. Sci. Technol.*, vol. 50, no. 10, pp. 1523–1531, 2015, doi: 10.1080/01496395.2014.978943.
- [17] H. Basturkcü and N. Acarkan, "Selective nickel-iron separation from atmospheric leach liquor of a lateritic nickel ore using the para-goethite method," *Physicochem. Probl. Miner. Process.*, vol. 53, no. 1, pp. 212–226, 2017, doi: 10.5277/ppmp170118.
- [18] S. Kettaf *et al.*, "Electrochemical measurements of synthesized nanostructured β -Ni(OH)₂ using hydrothermal process and activated carbon based nanoelectroactive materials," *SN Appl. Sci.*, vol. 1, no. 1, pp. 1–12, 2019, doi: 10.1007/s42452-018-0038-3.

- [19] Z. Qin, Y. Wang, X. Huang, W. Shen, J. Yu, and J. Li, "A Facile Synthesis of Three Dimensional β -Ni(OH)₂ Composed of Ultrathin Nanosheets for High Performance Pseudocapacitor," *J. Inorg. Organomet. Polym. Mater.*, vol. 30, no. 6, pp. 2089–2097, 2020, doi: 10.1007/s10904-019-01360-4.
- [20] R. Thimmasandra Narayan, "Effect of Crystallinity of β - and β bc -Nickel Hydroxide Samples on Chemical Cycling ," *Indian J. Mater. Sci.*, vol. 2015, no. Ii, pp. 1–7, 2015, doi: 10.1155/2015/820193.
- [21] T. Asakai and T. Suzuki, "Reliability in Standardization of Iron(III) and Titanium(III) Solutions in Volumetric Analysis," *ACS Omega*, vol. 6, no. Iii, pp. 21147–21152, 2021, doi: 10.1021/acsomega.1c03074.

4.3 PAPER IV

This paper entitled “A comparative study of sol-gel prepared and solvent extracted NiO from fire assay waste: Structural characterization and insights into VOCs sensing application” Published, Environmental Advances, (16) 2024,

<https://doi.org/10.1016/j.envadv.2024.100531>

Highlights

- ◇ LX63-70 showed high efficiency for loading Cu and liberating Ni from FA-NiS waste.
- ◇ Lime is an excellent precipitating agent for Ni(OH)₂ from Ni-raffinate at pH 6.5.
- ◇ High crystallinity was observed in chemical precipitated NiO.
- ◇ NiO based sensor could sense up to 1.5 ppm ethanol at room temperature.
- ◇ NiO sensor demonstrated maximum response of 1.58 towards 45 ppm ethanol at 150 °C.

Authors Contributions

Happy Mothepane Mabowa - The main author conceptualized the methodology, validation, writing the original draft, led the design of the methodology, supervising data collection and analysis, ensured compliance with ethical standards, securing funding, and maintaining communication with collaborators and funding agencies.

Andile Mkhohlakali - Contributed to Formal analysis, Investigation, Data curation, Writing original draft.

James Tshilongo – Contributed to data collection, Supervision, editing, visualization, and acquire funding.

Luke Chimuka - Supervision, data curation, and statistic validation.

Comparative study of sol-gel process and chemical precipitation of NiO from fire assay waste: Structural characterization and insights into VOCs sensing application

Happy Mothepane Mabowa^{1,2}, Andile Mkhohlakai¹, Luke Chimuka², James Tshilongo^{1,2}

¹Analytical Chemistry Division, Mintek, 200 Malibongwe Drive, Randburg 2194, South Africa

²School of Chemistry, University of the Witwatersrand, Johannesburg, 2050, South Africa

Corresponding author: Andilem@mintek.co.za; happyc@mintek.co.za

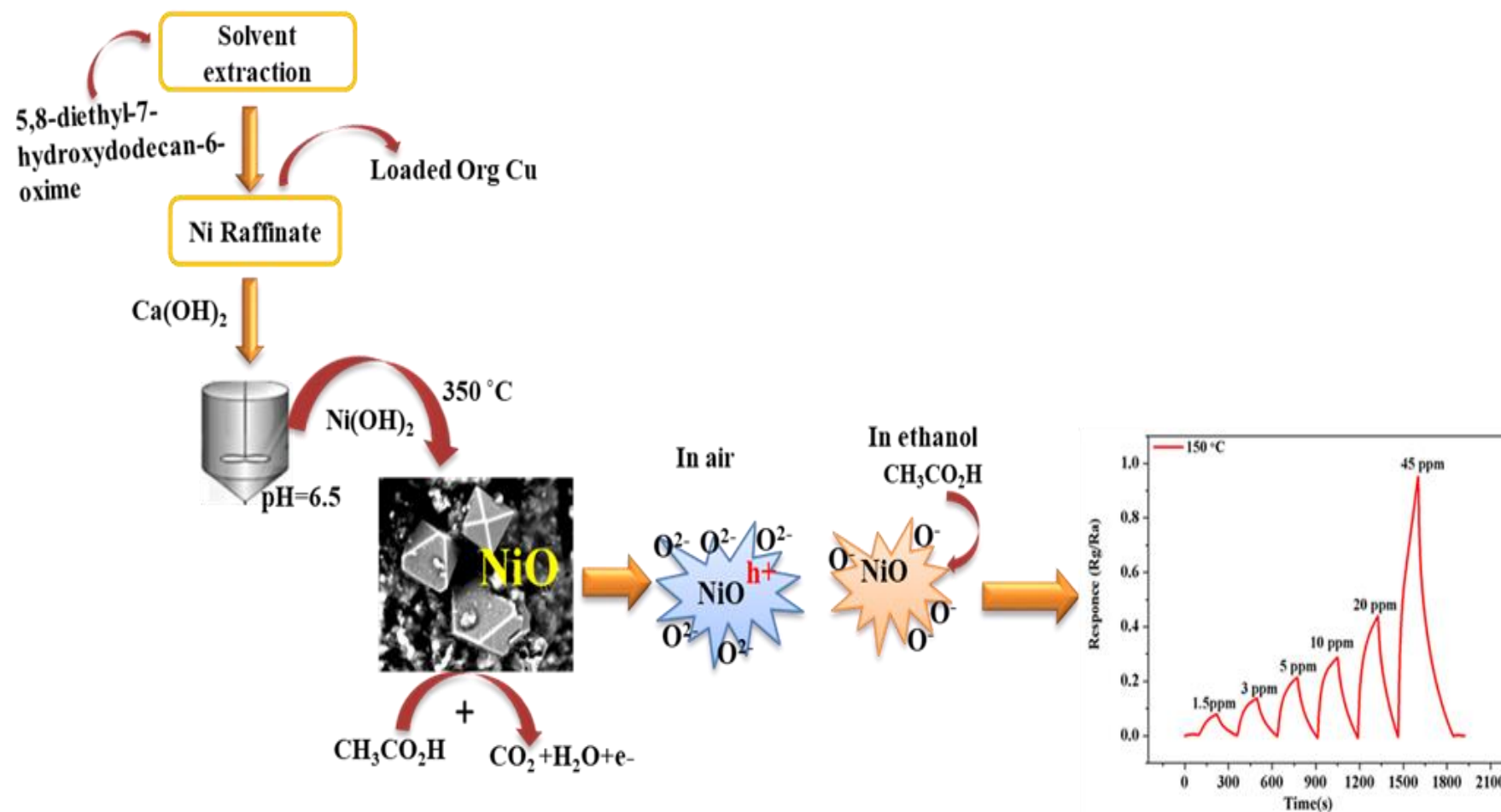
Abstract

This study compares nickel oxide (NiO) derived from fire assay waste nickel sulphide (FA-NiS) and chemical precipitation and sol-gel process. This work reports the first time NiO prepared through chemical precipitation from the waste for VOCs sensing purpose. Additionally, herein we provide insights into compare the properties of NiO obtained through different methods and their potential for environmental sensing applications. Structural, morphological, and elemental characterizations are conducted, alongside preliminary investigation into their volatile organic compounds (VOCs) sensing application. After Cu extraction with 5,8-diethyl-7-hydroxydodecan-6-oxime, the nickel (Ni) raffinate was precipitated using lime (Ca(OH)₂) at pH 2.5 and 6.5 conditions. Scanning electron microscope (SEM) -energy dispersive spectroscopy and X-ray photoelectron spectroscopy confirmed nickel and oxygen (O₂) presence at pH 6.5, and iron (Fe), Ni, and O presence at pH 2.5. X-ray diffraction revealed a cubic crystal structure and high average crystalsize of (39 - 41 nm) for both sol-gel process and chemical precipitation of NiO. SEM showed uniform, spherical particles for sol-gel process while chemical precipitation displayed aggregated layered granules. NiO precipitated at pH 2.5 exhibited coalesced hexagonal particles with predominant Fe and Ni presence. Developed analytical methods for inductively coupled plasma

optical emission and X-ray fluorescence demonstrated high purity NiO ($\approx 75\%$) with low relative standard deviation (RSD $< 0.05\%$) and 90% recovery using certified reference material. The NiO from fire assay waste demonstrated clear sensing responses at both 25°C and 150°C , with recovery times of 80 and 120 seconds, even at the lowest concentration (1.5 ppm). The highest response ($R_g/R_a = 1.198$ for 45 ppm ethanol) occurred at 150°C , indicating the potential NiO from the fire assay waste as a futuristic device for VOCs sensing under ambient conditions.

Keywords: Solvent extraction, NiO, sol-gel process, chemical precipitation, volatile organic compounds sensing

Graphical Abstract



1. Introduction

Every year, tons of waste is produced by pyrometallurgical and extractive metallurgical processes during the minerals and ore recovery process (Kalisz et al., 2022), (Matinde et al., 2018). Metals and their oxide wastes are widely available from industries like metal manufacturing, electronics, battery materials, printed circuit board waste (PCBs) (Łukomska et al., 2022), and mineral processing (Meng et al., 2022). The waste contains valuable metals and other toxic compounds, if improperly retrieved, might seriously threaten the environment and if not recycled may contribute to the depletion of natural resources (Matinde et al., 2018). Mining companies are exploring novel methods to retrieve high-grade nickel (Ni), a coveted base metal. Prolonged exposure to metals like Ni, cobalt (Co), copper (Cu), and others can result in a range of health concerns, including respiratory infections, typhoid fever, lung fibrosis, as well as kidney and cardiovascular disorders (Basturkcü & Acarkan (2017). In addition, the demand and prices of commodity and strategic critical minerals are expected to rise due to their importance in various high-technology industries such as electronics, and energy sources (Han et al., 2023). Thus, extensive research on the recovery and precipitation of critical minerals from alternative sources including wastewater streams, fire assay nickel sulphide (NiS) waste and refuse piles (Krishnan et al., 2021).

It is well known that removing Ni is a challenging and hence scientific task. Numerous treatment methods, including chelating resins, adsorption on activated carbon, chemical precipitation, microfiltration, and ion exchange on zeolites, have been proposed for the removal of Ni from aqueous waste streams (Krishnan et al., 2021; Pohl, 2020; Dermentzis, 2010). Some of these techniques have limitations due to their tendency to generate large amounts of sludge. This not only leads to secondary environmental pollution but also results in high effluent treatment costs and increased energy consumption (Zinicovscaia et al., 2020). Chemical precipitation using precipitating agents such as lime (Ca(OH)_2) and sulphide is the most economical and widely used method for treating industrial effluents containing heavy metals, although it can lose its effectiveness when significant

complexing agents are present (Dermentzis et al., 2016; Kartal et al., 2023). The chemical precipitation uses an alkaline agent such as Ca(OH)_2 or sodium hydroxide (NaOH) which increases the pH and subsequently decreases the solubility of the metal ion which results in their precipitation in the form of metal hydroxide from solvent according to the following general mechanism (Pohl, 2020) in equation 1:



These developments have inspired researchers to play a pivotal role in synthetic and recycling technologies to produce and recover valuable metals and metal oxide. Metal oxides have attracted considerable interest due to their potential application in numerous fields, including electronics, energy conversion, bio-sensing, volatile organic chemicals sensing and energy storage (Altammar, 2023). The base metal oxides such as copper oxide (CuO) and nickel oxide (NiO) are n-type and p-type semiconductors with 1.24 and 2.4 to 3.5 eV band gaps respectively (Singh et al., 2022; Sabirin et al., 2013). Their intriguing properties such as band gap indicate the potential application for gas sensing, with high sensitivity, and selectivity for VOC sensing. The sensing properties of the metal oxide (MeO) depend on chemisorption of the oxygen species in negative charge (O^{2-} , O^{-} and O^{-2}) in the air due to charge transfer between the analyte (Oxygen) and MeO surface which depends oxygen vacancies, electron density and electrical conductivity (Sharma & Kumar, 2024). The key factors influencing the properties of metal oxide that control oxygen vacancies are the synthesis technique, processing, and operating conditions (Al-hashem et al., 2019; Katoch et al., 2013).

There are several methods reported in the literature for the fabrication of metal oxides and recovery of these metals from waste such as waste PCBs (Chavali et al., 2019) by optimizing temperature conditions and type of solvent used during extraction. The precipitation approach is one of the best ways to prepare metal oxides out of all of these synthetic processes. Compared to other ways, the precipitation method is the most straightforward and least expensive way to grow metal oxides at low temperatures while maintaining size control (Mala et al., 2023).

In addition, recovery methods for metals and their oxide include extractive metallurgy and pyrometallurgical methods which utilise the long-chain polymeric solvent and high-temperature furnace respectively. Among the preparation methods for metal oxides (MOs), the sol-gel technology has garnered significant interest owing to its straightforward preparation method, high degree of homogeneity, low cost and the possibility of forming small particles at room temperature (Parashar et al., 2020). Other advantages of MOs form a chemiresistive phenomenon with metal oxide-based sensors where oxygen molecules are adsorbed on MOs surface to form a hole-electron accumulation (Goel et al., 2023). The extensive search on synthetic processes and recovery of MO from waste for re-purpose and to cushion the environment issues by removal of toxic metal in the waste streams and sensing of toxic gases.

Herein, we compare the NiO extracted and precipitated from fire assay (NiS) waste and NiO prepared from the sol-gel process as a reference for chemical properties. To the best of the author's knowledge, there is no study reported on the recovery process of NiO from fire assay waste for re-use, purpose in VOC sensing. Herein, we report the recovery and precipitation of NiO from PGM collector (NiS) waste and compare it to sol-gel prepared NiO. The elemental, statistical analysis, and structural characterization employed are ICP-OES, XRF, and analysis of variance (ANOVA) tool, XRD, SEM-EDS, FTIR and XPS. In addition, the preliminary analysis of NiO towards VOCs sensing application towards ethanol was conducted.

2 Experimental details

2.1 Materials and reagents

In this method, the following chemicals and reagents that were used for the experiment, are Nickel acetate ($\text{Ni}(\text{CH}_3\text{COO})_2$) obtained from Sigma Aldrich (South Africa), ethanol (EtOH) 99.9% from Merck, nitric acid 65% (w/w) from Merck, Acetic acid (CH_3COOH) (Merck), sodium hydroxide (NaOH), and Hydrochloric acid (Merck), oxime (BASF) was used. NiS waste was collected from the

Analytical Chemistry Laboratory at Mintek in Randburg South Africa. All reagents were analytical grade and were used without further modification. Throughout the studies, the Milli-Q system Type 1 water (Merck) was used to prepare ultrapure water (18.2 MΩ cm).

2.2 Preparation methods

2.2.1 Sol-gel process

NiO was synthesized using a sol-gel process by mixing 0.5 g of $\text{Ni}(\text{CH}_3\text{COO})_2$ and 40 mL of EtOH in a 200 mL beaker. The solution was stirred using the magnetic stirrer bar for 1h and the viscous green solution was formed. Thereafter, 1M hydrochloric acid (HCl) was added dropwise and the solution was stirred, and then the temperature was adjusted to 60 °C and the gel was formed. After 2h, the gel was heated to 100 °C for 1h and the crystals formed were crushed using mortar and piston. The green powder was calcined for 3h at 350 °C. Fig 1 summarizes the synthetic route and step-wise of the sol-gel process.

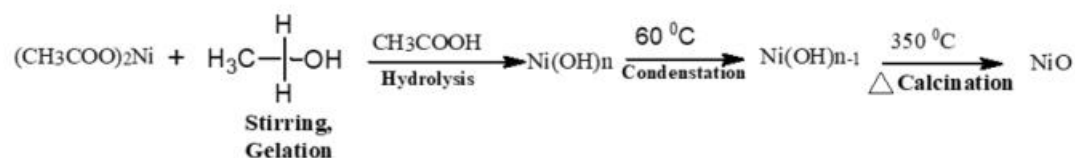


Fig.1. Schematic synthetic route of sol-gel process of NiO

2.2.2 Solvent extracted and selective precipitation of NiO

As summarized in the schematic in Fig 2, the pregnant leach solution (PLS) was made by sampling NiS waste into a 250 mL flask. The PLS was stirred for 30 min. Then, the solution was added in a 500 mL separating funnel, then a 1:5 ratio of the extracting solvent 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX 63-70) was added and the solution was shaken gently to form a loaded organic phase ($\text{Org}_{\text{Loaded}}$). The $\text{Org}_{\text{Loaded}}$ and aqueous phase solution was separated and the Ni-raffinate settled at

the bottom and was collected in the aqueous phase as explained in literature Mabowa et al. (2024). Thereafter, lime $\text{Ca}(\text{OH})_2$ was introduced to the Ni-raffinate for the chemical precipitation process. The pH was adjusted to 2.5 and 6.5 to precipitate $\text{Fe}_2\text{O}_3/\text{Ni}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ respectively.

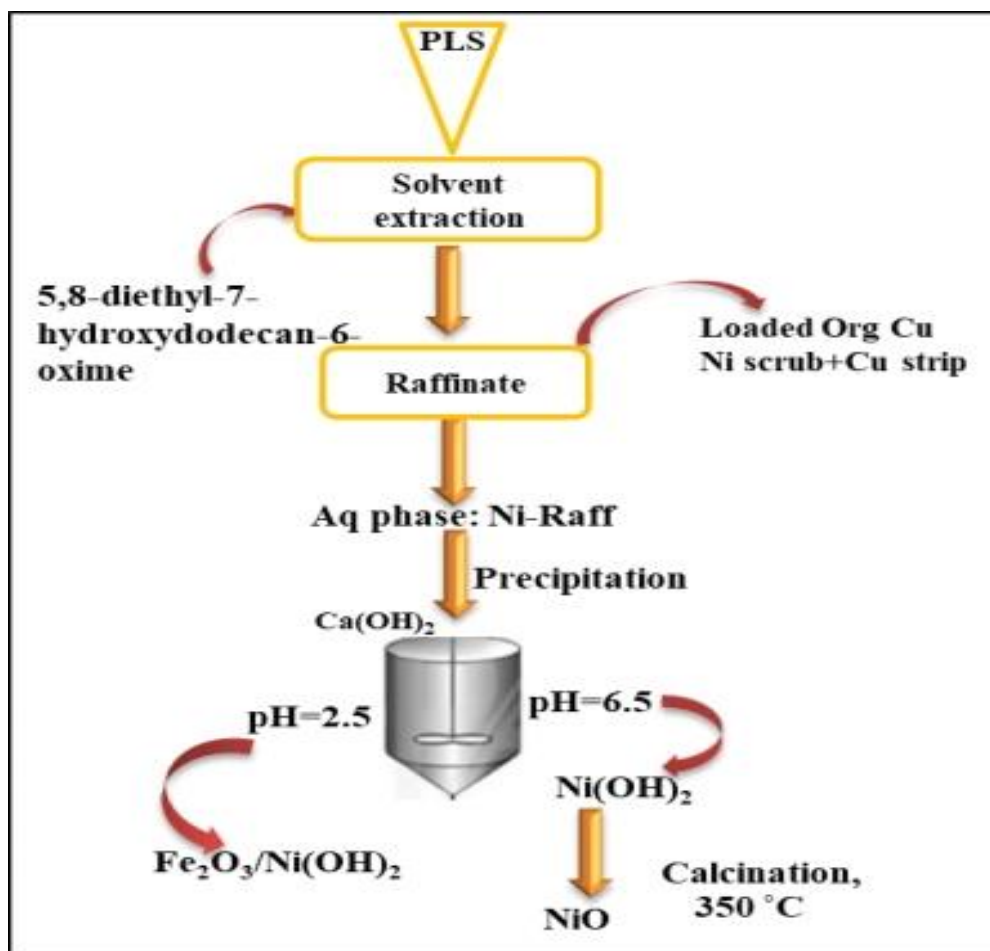


Fig. 2. Schematic diagram showing solvent extraction and chemical precipitation $\text{Ni}(\text{OH})_2$ and $\text{Fe}_2\text{O}_3/\text{Ni}(\text{OH})_2$

2.3 Characterization

This work used the following high-resolution instrumentation and advanced analytical techniques to examine the structure, morphology and elemental composition. Fourier-transform infrared spectroscopy (FTIR), Bruker vertex 70 technique was used to analyse the bond stretching frequencies of NiO-based compounds. The structure and crystallinity phase of NiO-based materials were

determined using powder X-ray diffraction (XRD, Bruker D8 advance diffractometer, Cu-K radiation, $\lambda = 1.54060 \text{ \AA}$, operated at 20 kV and 40 mA). The patterns were obtained at 2θ between $10\text{--}90^\circ$ at the scan rate of 2°min^{-1} . Field emission scanning electron microscopy (FE-SEM) was performed using JEOL JSM-7800F with an EDX detector for elemental composition. X-ray photoelectron spectroscopy (XPS), elemental composition or metal concentration is determined using Agilent 5510 Vertical dual view (VDV) ICP-OES, and HITACHI, XRF analyser (x-met 8000 expert Geo).

3 Results and discussion

Fig. 3 (a), and 3 (b) illustrate the FTIR spectrum of NiO prepared through chemical precipitation, and sol-gel process respectively, indicating calcined chemical precipitation NiO,. In all the FTIR spectra, there is a prominent and broad peak around 3400 cm^{-1} that is attributed to $\nu(\text{OH})$ stretching vibration which is the characteristic feature of $\beta \text{ Ni}(\text{OH})_2$ (Qin et al., 2020) (Mala, Nazir Ahmad, S, Sivakumar, 2021) formed before the calcination process. The spectral peak around $550\text{--}620 \text{ cm}^{-1}$ is assigned to $\nu(\text{NiO})$ stretching mode. The vibration peak observed around 1422 cm^{-1} and 1622 cm^{-1} could be assigned to $\delta(\text{-OH})$ bending vibration and stretching of carboxylic $\nu(\text{CO}_3^{2-})$ respectively (Singh et al., 2022) (Qin et al., 2020). The transformation of $\beta \text{ Ni}(\text{OH})_2$ to NiO through calcination is confirmed by the drastic peak intensity reduction around 3400 cm^{-1} .

There is an apparent wavenumber shift from 3400 cm^{-1} ($\text{Ni}(\text{OH})_2$) to 2969 cm^{-1} of NiO (insert) which indicates the transformation of functional group. Furthermore, the lack of $\delta(\text{OH})$ bending mode around 1622 cm^{-1} from water is attributed to high NiO crystalline, with less water held by hydrogen bonding (Mabowa et al., 2024). Noteworthy, the stretching vibration for calcined NiO shifted to a higher wave number (from 630 to 786 cm^{-1}) which indicates the phase ($\text{Ni}(\text{OH})_2$) to NiO transformation. Likewise, NiO from sol-gel was prepared to exhibit similar results as calcined NiO. Similar to the sol-gel procedure, the FTIR spectrum shows NiO distinctive peaks, confirming the effective transformation. These findings strongly

correlate with the literature (Fazlali et al., 2019).

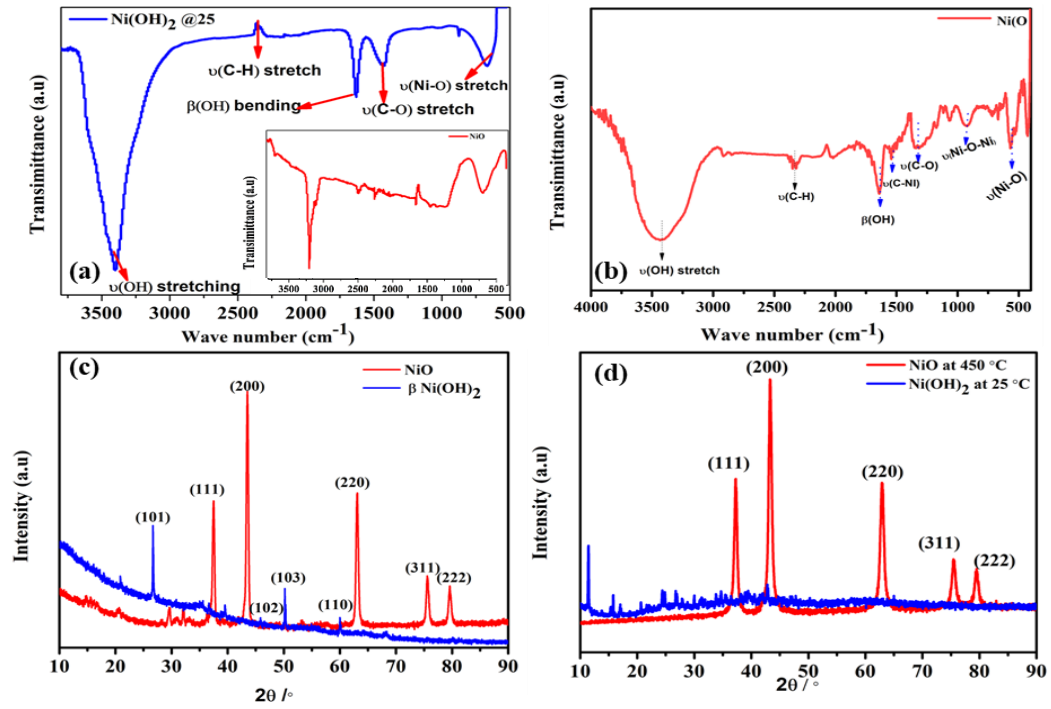


Fig. 3. FTIR spectrum of NiO from chemical precipitation (a) and sol-gel process (b), XRD pattern of chemical precipitation NiO (c), and (d). sol-gel process NiO

Table 1. Summary of Ni(OH)₂ and NiO functional groups

Functional group	Wave number (cm ⁻¹)	Assignment
ν(NiO)	550-620	Stretching mode of O-Ni-O
β (-OH)	1422	OH bending of Ni(OH) ₂
ν C-O,	1622	Stretching vibration of carboxylic species
ν(OH)	3400	OH stretch vibration of H ₂ O
ν(C-H)	2800	Stretch vibration of carbon species

In Fig. 3 (c-d), XRD represents the NiO precipitated from the sol-gel process and chemical precipitation. The transformation of Ni(OH)₂ to NiO was observed upon the calcination process at 350°C. Evidently in Fig 3 (c), the diffraction peaks depict

the β -Ni(OH)₂ formed during the precipitation process. All diffraction peaks for room temperature chemical precipitation Ni(OH)₂ confirms the β -Ni(OH)₂ hexagonal phase and the peaks indexed 2θ values 24°, 29°, 30°, 45°, 50°, and 60° corresponding to (001), (100), (101), (102), (103), (110) respectively which is in agreement with the literature (Qin et al., 2020), (Thimmasandra Narayan, 2015). The results indicate that crystalline Ni(OH)₂ was precipitated successfully. Furthermore, for the un-calcined sol-gel process Ni(OH)₂ in Fig 3 (d) indicates the amorphous phase. Both calcined sol-gel process NiO and chemical precipitation exhibit a similar XRD pattern indexed at 35°, 44°, 65°, 75°, and 80° corresponding to (111), (200), (220), (311) and (222) planes, respectively which is attributed to NiO cubic crystal structure and matches with the Joint Committee on Powder Diffraction (JCPDS0: #73-1520) standard. In addition, XRD results are in strong agreement with FTIR results (Fig. 3). Using the Debye-Scherrer equation as described in literature (Etape et al., 2017), chemical precipitated NiO exhibited higher crystalline size (41.1 nm) as compared to sol-gel process (38.5 nm). The results are summarized in Table S4 (supporting information).

X-ray photoelectron spectroscopy (XPS) analysis was used to characterize the electron surface of NiO. Fig 4 (a) depicts the NiO spectra survey which displays the prominent peak around 880 eV, 540 eV and 250 eV binding energy, corresponding to Ni2p, O1s and C1s respectively. The results confirm the high purity of NiO with low impurity as indicated by low carbonaceous peak (C1s). Fig 4 (b) displays the spectrum of Ni2p with doublet peaks situated at 860 eV and 880 eV binding energy which are attributed to Ni2p (2/3) and Ni2p (1/2) respectively. The higher O1s for metal oxide in Fig 4 (c) than O1s of carbonaceous peak confirms the strong bond between Ni and oxygen and indicates the purity of NiO. Likewise, in Fig 4 (d-f) the XPS spectra survey chemical precipitated NiO exhibit a similar chemical composition, except for the Calcium (Ca) and Chloride (Cl) impurities. These impurities are due to the HCl matrix of fire assay waste and Ca from the Ca(OH)₂ neutralizing agent. There are two prominent peaks around 858 and 873 eV separated by its satellite around 862 eV, which correspond to Ni2p(3/2), and Ni2p (1/2) respectively. The later results confirms the presence of NiO (Huang et al., 2017).

The prominent O1s peak indicates high oxygen vacancies which could be MO with enhanced gas-sensing properties. Furthermore, the chemical oxidation states of the as-prepared NiO are summarized in Table S2 (supplementary information).

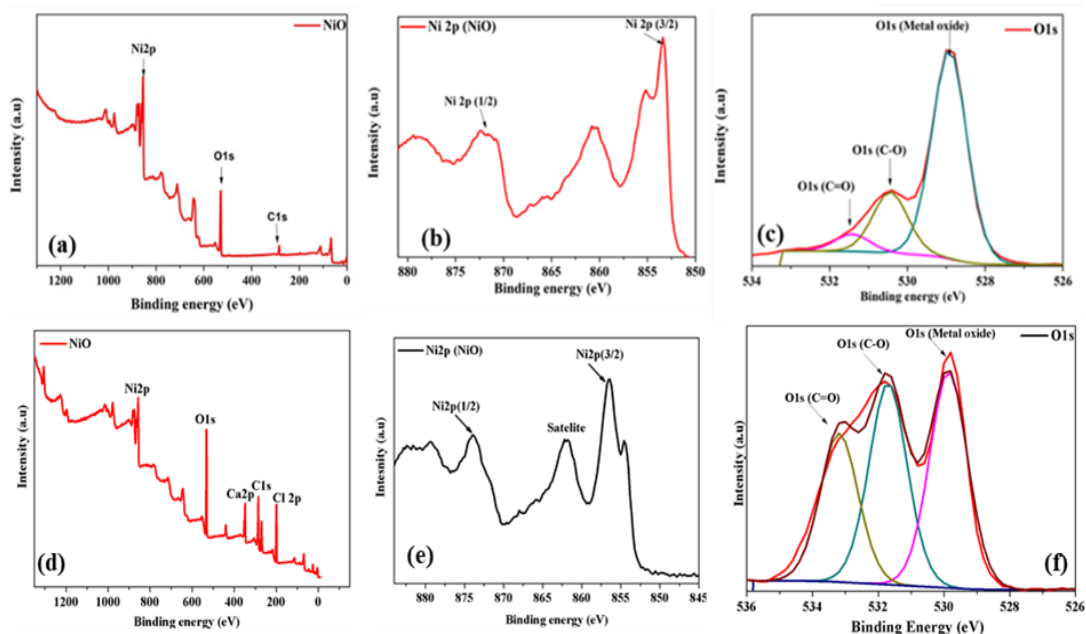


Fig. 4. XPS spectra survey, Ni2p and deconvoluted O1s of sol-gel process NiO (a-c) and of chemical precipitated NiO (d-f).

SEM and EDS were used to examine the surface morphology and to profile the elements of chemical precipitation at different pH (2.5 and 6.5) and compare them to NiO prepared via sol-gel process. Fig 5 (a-c) represents the SEM image of NiO at pH 6.5, 25°C and 350°C. As discussed by this group in the literature (Mabowa et al., 2024), Fig (5a) revealed the rough and agglomerated NiO particles which are in agreement with the literature (Zunaidi et al., 2022). Whereas Fig 5 (b) exhibits the flat surface and reduced particle size. These later results are due to the loss of water and other impurities during the calcination at 350°C. Fig. 5(g) displays aggregated spherical particles in the NiO sol-gel, in contrast to chemical precipitation. The results are ascribed to the typical sol-gel process of metal oxide (Kessler & Seisenbaeva, 2023),(Arya et al., 2021). Fig. 5 (d) illustrates the precipitation of Fe₂O₃/Ni(OH)₂ at 6.5 as described by this group in previous studies (Mabowa et al., 2024), showing layered rough granules which typical goethite (α -FeOOH) which

corroborated with the literature (Satyananda et al., 2017). However, the calcination process liberated the typical hexagonal α -Fe₂O₃ particle shape in strong agreement with literature (Woo et al., 2019), (Lin et al., 2014). The shape confirms the improved crystallinity of Fe₂O₃ after the loss of carbonaceous and H₂O impurities. Fig 5 (c) displays the EDS which indicates the existence of Ni and O. The high Ca is attributed to Ca(OH)₂ utilised for precipitation. In comparison to the sol-gel process, NiO reveals the existence of Ni and O at high purity as displayed in Fig 5 (f). Fig 5 (f) indicates the significant loss of Ni and dominance of Fe at pH 2.5, the loss is discussed in literature (Wang et al., 2011). The later results confirm the loss of Ni at pH above 4 in goethite. The EDS spectra lines have improved the intensity for the calcined precipitate at pH 6.5 and pH 2.5 as compared to un-calcined materials displayed in Fig S1 and Fig S2 (supplementary information).

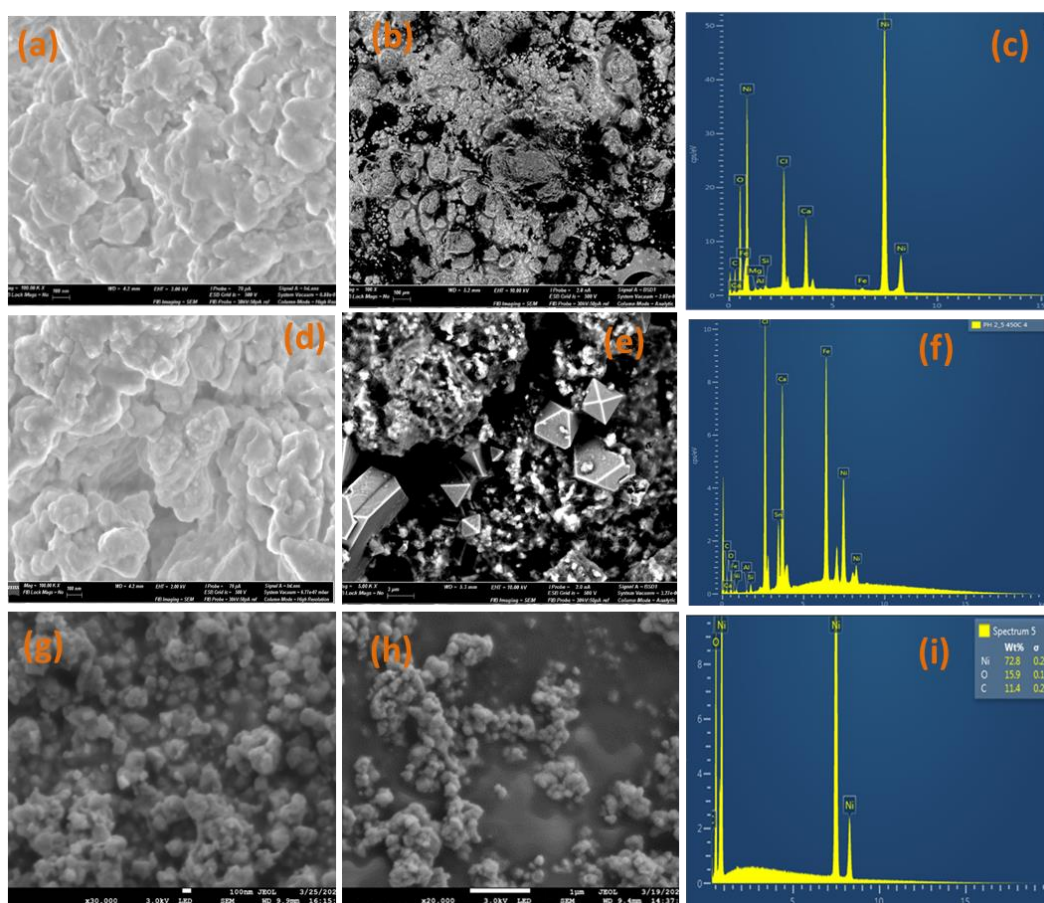
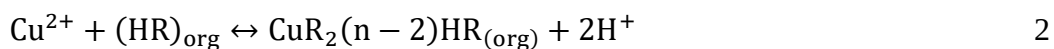


Fig. 5. (a-c) SEM micrograph and EDX of NiO from chemical precipitation pH 6.5 and (d-f) chemical precipitation at pH 2.5 (g-i) and sol-gel process NiO

The latter results indicate improved crystallinity and less impurity. The ICP-OES analysis was employed to determine the concentration of major elements such as Ni, Fe, Co, and Cu to name a few to profile the Fe and Ni loss and recovery from PLS, raffinate and the precipitated material at different pH conditions. The results for elemental concentration are summarized in Table 2. For precipitated samples, alkaline fusion was used followed by acid digestion using hydrochloric acid (HCl) as described in literature (Uchida et al., 2005), with slight changes. Whereas the liquid sample from raffinate was digested using HCl. Before analysis, the instrument was calibrated using the multi-element 1000 ppm stock solution. The known concentration solutions were used as quality control systems (QCs) and certified reference materials (CRM); AMIS 56 and 51/71 were also analysed for quality control. It was observed that the Ni concentration was increased when the pH is adjusted to 6.5 and there is significant Ni loss when the pH decreases which is consistent with EDS (Fig 5). While the pH decreases up to 2.5 during precipitation, Fe content increases which promotes the mixture of Ni and goethite (α -FeOOH) precipitation as described in literature (Basturkcu & Acarkan, 2017). The findings are consistent with XRF results in Table S3 (supplementary information) and EDS results (Fig 5). As observed in Table 1, there is a significant drop of Cu from the head solution (PLS), to raffinate (3.87 ppm to 0.81ppm) which corresponds to Cu-loaded organic (Cu-LIX 63-70). This is due to coordinating of Cu with the nitrogen atom of the oxime group as indicated by Fig 1 and expressed in the following equation 2 (Shakibania et al., 2020),(Elizalde et al., 2019).



The XRF analysis was used to examine the elemental composition of the precipitate at different pH (2.5 and 6.5). As illustrated in Table S3 (supplementary information), all samples including the certified reference material (CRM; AMIS 56 and SARM 33) were analysed in duplicate and expressed in two decimals. The results from XRF show the consistence with EDS results displayed in Fig 5. It was observed that the sol-gel process NiO indicates the highest Ni and O content which confirms the formation of NiO. Furthermore, chemical precipitation NiO

precipitated at acidic conditions (pH 2.5) exhibited a slight decrease of Ni from and higher Fe_2O_3 . The results are comparable with the findings from $\alpha\text{-FeOOH}$ precipitation in an acidic environment as explained in the literature (Davey & Scott, 1976), (Basturkcu & Acarkan, 2017).

Table 2. ICP-OES results for major elements.

Materials	Elements		
	Ni (%)	Fe(%)	Cu(%)
PLS	62.3	4.72	3.87
SX Ni-raffinate	50.29	2.58	0.81
Precipitate pH 2.5	6.08	7.12	3.4
Precipitate pH 6.5	28.24	0.12	0.17
CRM: amis56	0.196	7.008	0.151
Accurate value	0.2	7.02	0.14
SARM 33	0.27		0.23
Accurate value	0.28		0.29

4 Sensing application

Before the sensing experiment commenced, the gas flow test was conducted at different temperatures as displayed in Fig S5 (supplementary information). In Fig 6 (a-d) and Table S5 (supplementary information), NiO showed an increase and clear linear response up to 1.198 of ethanol gas concentration ranging from 1.5ppm to 45 ppm. Interestingly, the NiO sensing type indicates the transformation of p-type NiO to n-type NiO as depicted in Fig S6 (supplementary information) which could be due to the adsorption of oxygen species (O_2^-) of ethanol with NiO, creating a higher electron density upon the electron-hole accumulation as explained in literature (Nkosi, S.S, Mkwae et al., 2022). Additionally, the NiO shows the sensing ability at room temperature, however with a higher response. As indicated in Fig 6, the resistance is decreasing with increase in temperature from 25°C to 250°C. The increase in resistance is attributed to the decline of NiO hole upon the chemisorption of oxygen species (O_2^- (ads) and O^- (ads) which they donate the electron back to NiO's conduction band. As illustrated in Table S5 (supplementary information) and Fig 7, the sensing response of NiO varies with temperature. The response initially increases with temperature, reaching its highest value at 150°C, and then decreases

at higher temperatures, such as 250°C. The optimum temperature is identified as 150 °C, where the response is maximized. This variation indicates that while higher temperatures generally improve the sensor's performance up to a certain point, excessive temperatures may reduce the response due to factors such as the desorption of ethanol or changes in the sensor's active sites.

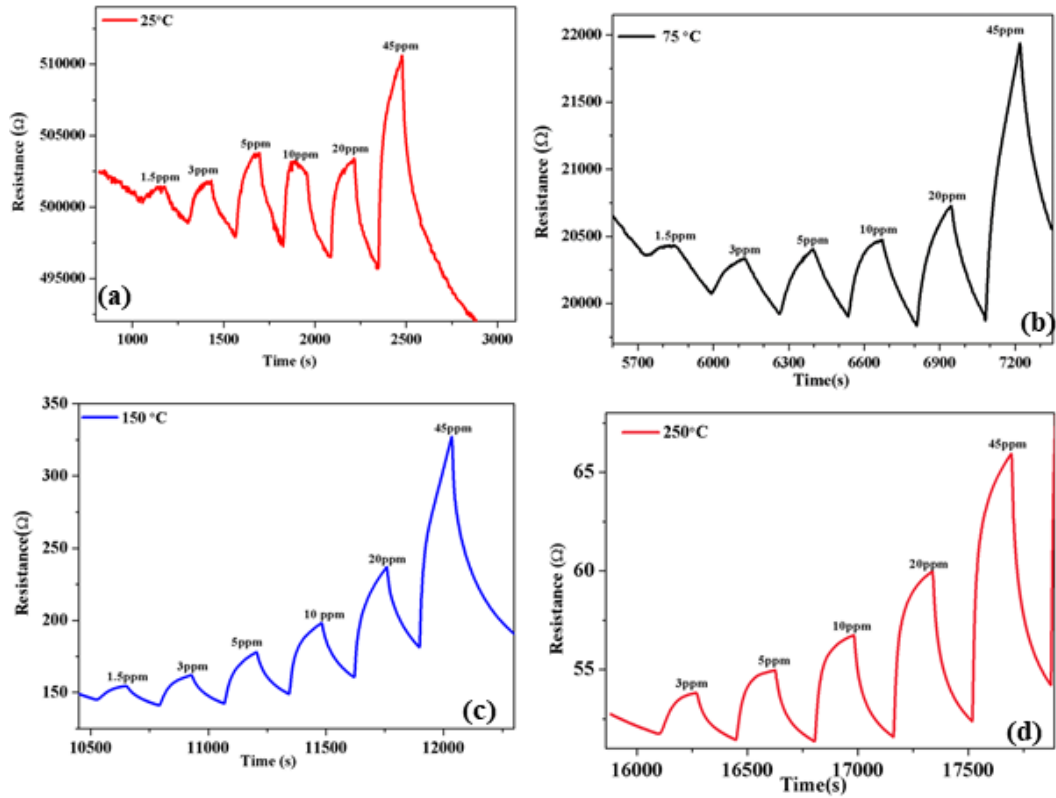


Fig. 6. Sensing resistance of NiO towards ethanol, exposed in various time intervals at different concentrations (1.5 ppm, 3 ppm, 5 ppm, 10 ppm, 20 ppm, 45 ppm) at 25 °C, 75 °C and 150 °C and 250 °C.

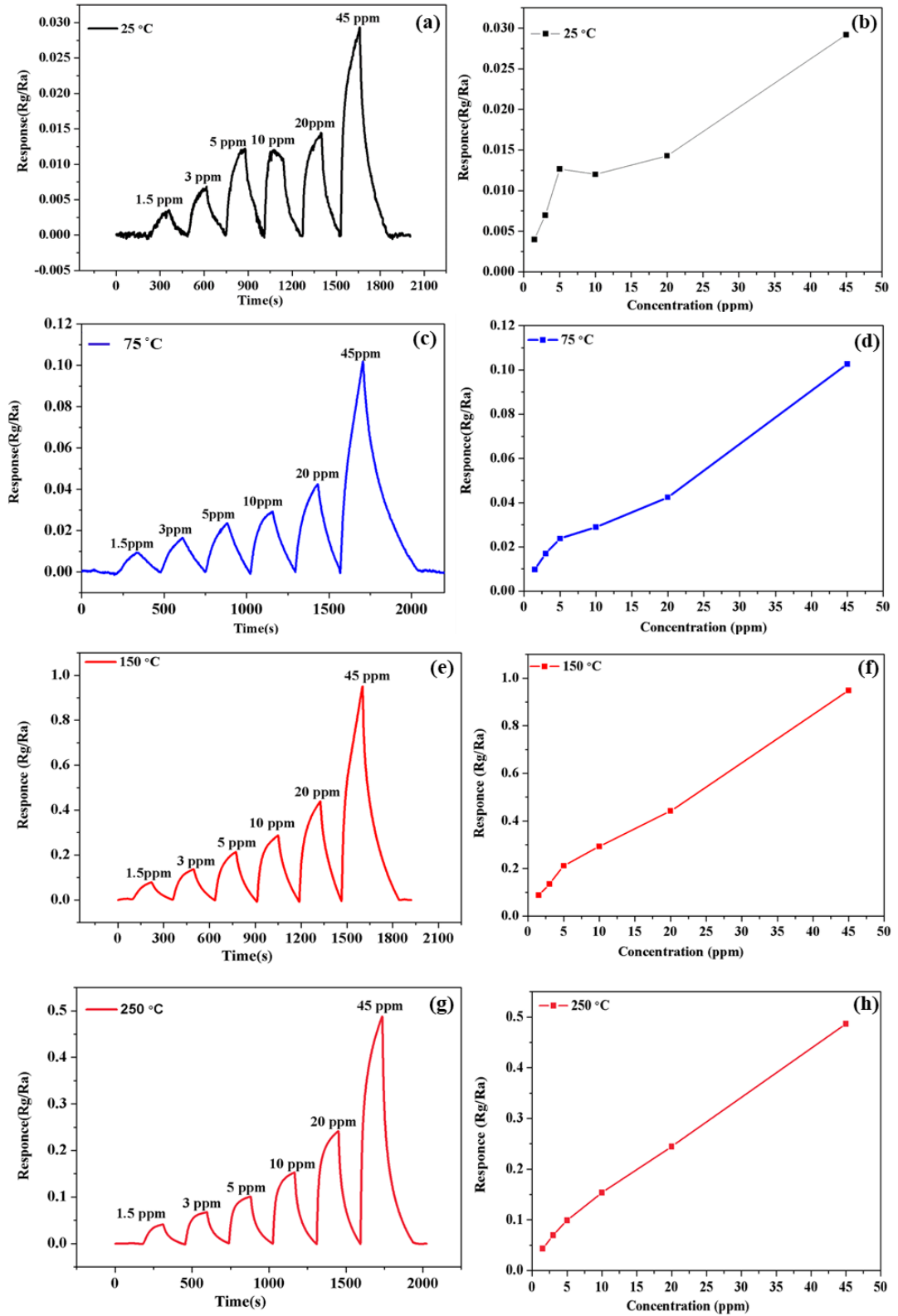
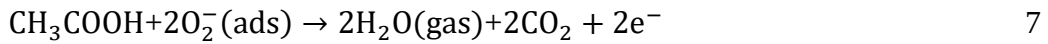


Fig. 7. Sensing response of NiO towards ethanol at different exposure time at various concentrations (1.5 ppm, 3 ppm, 5 ppm, 10 ppm, 20 ppm, 45 ppm) (a-b) at 25 °C, (c-d) 75 °C, (e-f) 150 °C and (g-h) at 250 °C.

4.1 NiO fundamental gas sensing mechanism

The ethanol sensitivity of the NiO predominantly depended on the gas adsorption on the NiO surface. NiO is the p-type semiconductor, however, according to the above response exhibits the n-type gas sensing properties. When NiO material is exposed to air, O₂ molecules are adsorbed onto the surface and form ionic O₂ species (O₂⁻, O⁻, O₂²⁻) by trapping electrons (e⁻) from the conduction band of NiO. This process increases the electron density in NiO, as the trapped electrons recombine with holes, reducing the number of holes and affecting the material's electronic properties. It was observed that resistance increased and current increased. Since electrons make up the majority of MOSs' charge carriers, exposure to reducing gas (Ethanol) causes n-type Metal oxide conductance to increase. When ethanol is exhausted the O₂ gas molecules get re-adsorbed to the surface of the materials. The general mechanism can be expressed by different equations 3-7;



Additionally, when the examined polar volatile organic compounds (VOCs) are adsorbed on reduced surfaces, there is very little interaction between the pre-adsorbed oxygen species and the VOCs. Because the free electrons are trapped, a surface electron depletion layer is formed, which lowers the NiO conductivity and carrier concentration (Ahmed et al., 2017).

Conclusion

Sol-gel process was employed to synthesize NiO. Additionally, Ni(OH)_2 was recovered from NiS waste, and upon calcination, Ni(OH)_2 was converted to NiO was done successfully. 5,8-diethyl-7-hydroxydodecan-6-oxime reveals high efficiency in liberating Ni to the aqueous raffinate phase while efficiently loading the Cu in the organic phase. Ni(OH)_2 and $\text{Fe}_2\text{O}_3/\text{Ni(OH)}_2$ were precipitated with Ca(OH)_2 at pH 6.5 and 2.5 respectively as confirmed by physicochemical characterization and elemental analysis. The predominance of Ni, O at pH 6.5 enhances the sensing performance of NiO. The calcination process removed the impurity and improved the crystallinity. The elements analysis using ICP-OES and XRF are in strong agreement with the S-curve precipitation, exhibiting the loss of Ni at lower pH. The results 5,8-diethyl-7-hydroxydodecan-6-oxime and Ca(OH)_2 are classical and efficient reagents to remove toxic and critical elements from waste streams. In addition, the reference NiO exhibits detected ethanol at room temperature with a clear response at low concentrations. These findings highlight the potential of NiO as a futuristic device for sensing the VOC at ambient conditions. The results indicate the extracted NiO from NiS waste shows the potential for sensing VOCs, because of the intriguing properties. Recycling and repurposing of NiS waste have a high potential of realizing critical minerals and mitigating the environment while contributing to a circular economy.

Acknowledgements

The authors wish to extend heartfelt thanks to Mintek for their financial support granted through Science Vote grant number: ASR-00002313 (2023/2024), as well as for granting permission to publish this research.

Supplementary information

The utilisation of the advanced analytical techniques and high resolution instrument are essential for evaluating the effectiveness of the solvent extraction pre-treatment

in mitigating Cu loss during precipitation to understand the composition and structure of the precipitated material. The supplementary information provided in Fig S1, S2, S3 and S4, S5, S6 in support of the comprehensive analysis of the surface morphology and elemental composition of the sample by EDX , XPS analysis, gas flow and response as function of time.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability statement: The corresponding author will make the data contained in this work available upon request.

References

- Ahmed A. Abokifa, Kelsey Haddad, John Fortner, Cynthia S. Lo, and P. B. (2017). Sensing Mechanism of Ethanol and Acetone at Room Temperature by SnO₂ Nano- columns Synthesized by Aerosol Routes: Theoretical Calculations Compared to Experimental Results. *Journal of Materials Chemistry A*, DOI <https://doi.org/10.1039/C7TA09535J>
- Al-hashem, M., Akbar, S., & Morris, P. (2019). Sensors and Actuators B : Chemical Role of Oxygen Vacancies in Nanostructured Metal-Oxide Gas Sensors : A Review. *Sensors & Actuators: B. Chemical*, 301(July), 126845. <https://doi.org/10.1016/j.snb.2019.126845>
- Altammar, K. A. (2023). A review on nanoparticles : characteristics , synthesis , applications , and challenges. *Frontier in Microbiology*, April, 1–20. <https://doi.org/10.3389/fmicb.2023.1155622>
- Arya, S., Mahajan, P., Mahajan, S., Khosla, A., Datt, R., Gupta, V., Young, S.-J., & Oruganti, S. K. (2021). Review—Influence of Processing Parameters to Control Morphology and Optical Properties of Sol-Gel Synthesized ZnO

- Nanoparticles. *ECS Journal of Solid State Science and Technology*, 10(2), 023002. <https://doi.org/10.1149/2162-8777/abe095>
- Basturkcu, H., & Acarkan, N. (2017). Selective nickel-iron separation from atmospheric leach liquor of a lateritic nickel ore using the para-goethite method. *Physicochemical Problems of Mineral Processing*, 53(1), 212–226. <https://doi.org/10.5277/ppmp170118>
- Chavali, M. S., Nikolova, M. P., & Silver, A. (2019). Metal oxide nanoparticles and their applications in nanotechnology. *SN Applied Sciences*, 1(6), 1–30. <https://doi.org/10.1007/s42452-019-0592-3>
- Davey, P. T., & Scott, T. R. (1976). Removal of iron from leach liquors by the “Goethite” process. *Hydrometallurgy*, 2(1), 25–33. [https://doi.org/10.1016/0304-386X\(76\)90011-6](https://doi.org/10.1016/0304-386X(76)90011-6)
- Dermentzis, K. (2010). Removal of nickel from electroplating rinse waters using electrostatic shielding electrodialysis/electrodeionization. *Journal of Hazardous Materials*, 173(1–3), 647–652. <https://doi.org/10.1016/j.jhazmat.2009.08.133>
- Dermentzis, K. ., Marmanis, D. I., Christoforidis, A. K., Kokkinos, N. C., & Stergiopoulos, D. K. (2016). Recovery of metallic nickel from waste sludge produced by electrocoagulation of nickel bearing electroplating effluents. *4th International Conference on Sustainable Solid Waste Management*, 23–25.
- Elizalde, M. P., Rúa, M. S., Menoyo, B., & Ocio, A. (2019). Solvent extraction of copper from acidic chloride solutions with LIX 84. *Hydrometallurgy*, 183(1), 213–220. <https://doi.org/10.1016/j.hydromet.2018.12.013>
- Etape, E. P., Ngolui, L. J., Foba-tendo, J., Yufanyi, D. M., & Namondo, B. V. (2017). Synthesis and Characterization of CuO, TiO₂, and CuO-TiO₂ Mixed Oxide by a Modified Oxalate Route. *Hindawi Journal of Applied Chemistry*, 2017, 1–10.
- Fazlali, F., Mahjoub, A., & Abazari, R. (2019). A new Route for Synthesis of Spherical NiO Nanoparticles via Emulsion Nano- Reactors With Enhanced Photocatalytic Activity A new route for synthesis of spherical NiO nanoparticles via emulsion nano-reactors with enhanced photocatalytic activity. *Solid State Sciences*, 48(September 2015), 263–269.

<https://doi.org/10.1016/j.solidstatesciences.2015.08.022>

- Goel, N., Kunal, K., Kushwaha, A., & Kumar, M. (2023). Metal oxide semiconductors for gas sensing. *Engineering Reports*, 5(6), 1–22. <https://doi.org/10.1002/eng2.12604>
- Han, S., Zhenghao, M., Meilin, L., Xiaohui, Y., & Xiaoxue, W. (2023). Global supply sustainability assessment of critical metals for clean energy technology. *Resources Policy*, 85(PB), 103994. <https://doi.org/10.1016/j.resourpol.2023.103994>
- Huang, W., Ding, S., Chen, Y., Hao, W., Lai, X., & Peng, J. (2017). 3D NiO hollow sphere / reduced graphene oxide composite for high- performance glucose biosensor. *Scientific Reports*, 1–11. <https://doi.org/10.1038/s41598-017-05528-1>
- Kalisz, S., Kibort, K., Mioduska, J., Lieder, M., & Ma, A. (2022). Waste management in the mining industry of metals ores , coal , oil and natural gas - A review. *Journal of Environmental Management*, 304(September 2021), 114239. <https://doi.org/10.1016/j.jenvman.2021.114239>
- Kartal, L., Şen, A., & Timur, S. (2023). The removal of heavy metals from refinery effluents by sulfide precipitation. *Acta Montanistica Slovaca*, 28(1), 214–225. <https://doi.org/10.46544/AMS.v28i1.17>
- Katoch, A., Sun, G., Choi, S., Byun, J., & Kim, S. S. (2013). Competitive influence of grain size and crystallinity on gas sensing performances of ZnO nanofibers. *Sensors & Actuators: B. Chemical*, 185, 411–416. <https://doi.org/10.1016/j.snb.2013.05.030>
- Kessler, V. G., & Seisenbaeva, G. A. (2023). Molecular mechanisms of the metal oxide sol-gel process and their application in approaches to thermodynamically challenging complex oxide materials. *Journal of Sol-Gel Science and Technology*, 107(1), 190–200. <https://doi.org/10.1007/s10971-023-06120-y>
- Krishnan, S., Zulkapli, N. S., Kamyab, H., Taib, S. M., Din, M. F. B. M., Majid, Z. A., Chaiprapat, S., Kenzo, I., Ichikawa, Y., Nasrullah, M., Chelliapan, S., & Othman, N. (2021). Current technologies for recovery of metals from industrial wastes: An overview. *Environmental Technology and Innovation*,

- 22, 101525. <https://doi.org/10.1016/j.eti.2021.101525>
- Lin, M., Tng, L., Lim, T., Choo, M., Zhang, J., Tan, H. R., & Bai, S. (2014). Hydrothermal synthesis of octadecahedral hematite (α -Fe₂O₃) nanoparticles: An epitaxial growth from goethite (α -FeOOH). *Journal of Physical Chemistry C*, 118(20), 10903–10910. <https://doi.org/10.1021/jp502087h>
- Łukomska, A., Wiśniewska, A., Dąbrowski, Z., Lach, J., Wróbel, K., Kolasa, D., & Domańska, U. (2022). Recovery of Metals from Electronic Waste-Printed Circuit Boards by Ionic Liquids, DESs and Organophosphorous-Based Acid Extraction. *Molecules*, 27(15). <https://doi.org/10.3390/molecules27154984>
- Mabowa, H. M., Mkhohlakali, A., Mokoena, S., Tshilongo, J., & Chimuka, L. (2024). Removal of Nickel from Nickel Sulfite-Fire Assay Dissolution Filtrate Through Precipitation. *ACS Omega*. <https://doi.org/10.1021/acsomega.3c07623>
- Mala, Nazir Ahmad, S, Sivakumar, K. M. B. and E. H. R. (2021). Efficient , highly stable Zn²⁺ doped NiO nanoparticles with enhanced magnetic and supercapacitor applications. *Materials Technology*, 37(10), 1375–1387.
- Mala, N. A., Dar, M. A., Rather, D., Reshi, B. A., Sivakumar, S., Batoo, K. M., & Ahmad, Z. (2023). Supercapacitor and magnetic properties of NiO and manganese-doped NiO nanoparticles synthesized by chemical precipitation method. *Journal of Materials Science: Materials in Electronics*, 34(6), 1–16. <https://doi.org/10.1007/s10854-023-09907-5>
- Matinde, E., Simate, G. S., & Ndlovu, S. (2018). Mining and metallurgical wastes: A review of recycling and re-use practices. *Journal of the Southern African Institute of Mining and Metallurgy*, 118(8), 825–844. <https://doi.org/10.17159/2411-9717/2018/v118n8a5>
- Meng, S., Wen, S., Han, G., Wang, X., & Feng, Q. (2022). Wastewater Treatment in Mineral Processing of Non-Ferrous Metal Resources: A Review. *Water (Switzerland)*, 14(5). <https://doi.org/10.3390/w14050726>
- Nkosi, S.S, Mkwae, S., Ogundipe, A., Leshabane, N., Revaprasadu, N., & Kroon, R. E. (2022). Abnormal p-type to n-type switching during nitric oxide gas sensing : Ni (OH)₂ nanoplatelets on amorphous NiO seed layers. *Vacuum*, 200, 111032. <https://doi.org/https://doi.org/10.1016/j.vacuum.2022.111032>

- Parashar, M., Kumar, V., & Ranbir, S. (2020). Metal oxides nanoparticles via sol – gel method : a review on synthesis , characterization and applications. *Journal of Materials Science: Materials in Electronics*, 31(5), 3729–3749. <https://doi.org/10.1007/s10854-020-02994-8>
- Pohl, A. (2020). Removal of Heavy Metal Ions from Water and Wastewaters by Sulfur-Containing Precipitation Agents. *Water, Air, and Soil Pollution*, 231(10). <https://doi.org/10.1007/s11270-020-04863-w>
- Qin, Z., Wang, Y., Huang, X., Shen, W., Yu, J., & Li, J. (2020). A Facile Synthesis of Three Dimensional β -Ni(OH)₂ Composed of Ultrathin Nanosheets for High Performance Pseudocapacitor. *Journal of Inorganic and Organometallic Polymers and Materials*, 30(6), 2089–2097. <https://doi.org/10.1007/s10904-019-01360-4>
- Sabirin, A., Zamharir, M., Abdul, R., Zhen, J., Balendhran, S., Zhuiykov, S., Latham, K., Wlodarski, W., & Kalantar-zadeh, K. (2013). Sensors and Actuators B : Chemical Nanostructured copper oxides as ethanol vapour sensors. *Sensors & Actuators: B. Chemical*, 185, 620–627. <https://doi.org/10.1016/j.snb.2013.05.042>
- Satyananda, P., Kumar, A., & Rayasam, V. (2017). The effect of particle size on green pellet properties of iron ore fines. *Journal of Mining and Metallurgy A: Mining*, 53(1), 31–41. <https://doi.org/10.5937/jmma1701031s>
- Shakibania, S., Mahmoudi, A., Mokmeli, M., & Rashchi, F. (2020). The effect of the chloride ion on chemical degradation of LIX 984N extractant. *Minerals Engineering*, 159(June), 106628. <https://doi.org/10.1016/j.mineng.2020.106628>
- Sharma, N., & Kumar, R. (2024). Materials Today : Proceedings Ethanol sensing performance of sol gel driven spin coated TiO₂ thin film. *Materials Today: Proceedings*, June 2023. <https://doi.org/10.1016/j.matpr.2023.08.348>
- Singh, A., Goyal, V., Singh, J., Kaur, H., Kumar, S., Mujasam, K., Gaur, J., Pal, M., Rawat, M., & Hussain, S. (2022). Structurally and morphologically engineered single-pot biogenic synthesis of NiO nanoparticles with enhanced photocatalytic and antimicrobial activities. *Journal of Cleaner Production*, 343(February), 131026. <https://doi.org/10.1016/j.jclepro.2022.131026>

- Thimmasandra Narayan, R. (2015). Effect of Crystallinity of β - and β bc -Nickel Hydroxide Samples on Chemical Cycling . *Indian Journal of Materials Science*, 2015(Ii), 1–7. <https://doi.org/10.1155/2015/820193>
- Uchida, S., Tagami, K., & Tabei, K. (2005). Comparison of alkaline fusion and acid digestion methods for the determination of rhenium in rock and soil samples by ICP-MS. *Analytica Chimica Acta*, 535(1–2), 317–323. <https://doi.org/10.1016/j.aca.2004.11.065>
- Wang, K., Li, J., McDonald, R. G., & Browner, R. E. (2011). The effect of iron precipitation upon nickel losses from synthetic atmospheric nickel laterite leach solutions: Statistical analysis and modelling. *Hydrometallurgy*, 109(1–2), 140–152. <https://doi.org/10.1016/j.hydromet.2011.06.009>
- Woo, Y., Hyun, K., & Park, S. (2019). Microstructural and Magnetic Characterization of Iron Oxide Nanoparticles Fabricated by Pulsed Wire Evaporation. *Electronic Materials Letters*, 15(6), 665–672. <https://doi.org/10.1007/s13391-019-00164-5>
- Zinikovscaia, I., Yushin, N., Grozdov, D., Vergel, K., Popova, N., Artemiev, G., & Safonov, A. (2020). Metal removal from nickel-containing effluents using mineral–organic hybrid adsorbent. *Materials*, 13(19), 1–21. <https://doi.org/10.3390/ma13194462>
- Zunaidi, M. A., Setiawan, I., Oediyani, S., Irawan, J., Rhamdani, A. R., & Syahid, A. N. (2022). Iron Removal Process From Nickel Pregnant Leach Solution Using Sodium Hydroxide. *Metalurgi*, 37(3), 113–118. <https://doi.org/10.14203/metalurgi.v37i3.665>

4.5 PAPER V

This paper entitled “Optimization of Impurity Removal from Pregnant Nickel Solution Using Lime Precipitation: pH Control and Analytical Characterization.”
Submitted

Highlights

- ◇ Successful precipitation of Fe^{3+} at pH 2.0-3, demonstrating effective impurity removal from pregnant nickel solution.
 - ◇ Efficient Mn and Cu precipitation at pH 5.5-6 and 4-6 respectively, emphasizing the importance of pH control for optimal impurity removal.
 - ◇ Confirmation of impurity removal efficacy through elemental composition analysis using ICP-OES and EDX techniques.
 - ◇ Method performance evaluation with certified reference materials ensures reliability and accuracy of analytical techniques.
-

Authors Contributions

Happy Mothepane Mabowa - The main author played a central role in the research process, leading the design of the methodology, supervising data collection and analysis, ensuring compliance with ethical standards, securing funding, and maintaining communication with collaborators and funding agencies.

Andile Mkhohlakali - Contributed to data collection, interpretation, and manuscript revision.

James Tshilongo - Contributed to data collection, interpretation, supervision, and manuscript revision.

Luke Chimuka - Contributed to data collection, interpretation, supervision, and manuscript revision.

Optimization of Impurity Removal from Pregnant Nickel Solution Using Lime Precipitation: pH Control and Analytical Characterization.

Happy Mothepane Mabowa^{1,2}, Andile Mkhohlakai¹, Luke Chimuka², James Tshilongo^{1,2}

¹Analytical Chemistry Division, Mintek, 200 Malibongwe Drive, Randburg 2194, South Africa

²School of Chemistry, University of the Witwatersrand, Johannesburg, 2050, South Africa

Corresponding author: happyc@mintek.co.za

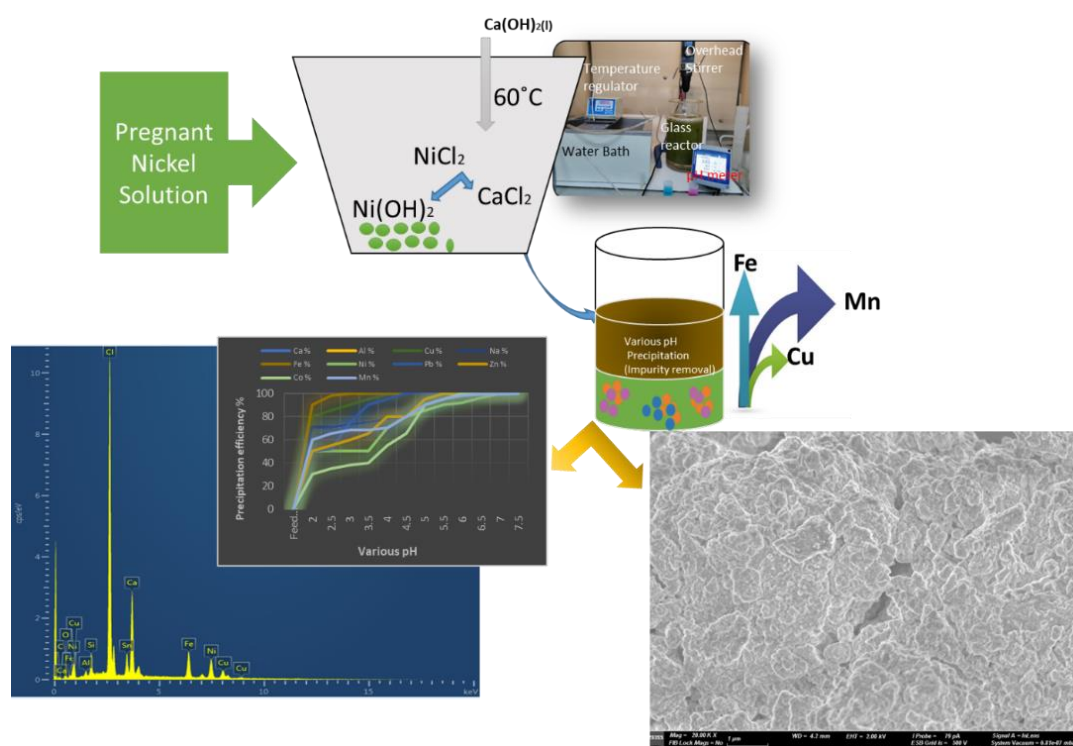
Abstract

This study reports on an investigation of the precipitation process of impurities from pregnant waste solution (PWS) across various pH levels, focusing on impurity removal efficiency and its impact on nickel concentration. Lime was utilised as a precipitation agent, targeting impurities such as Fe, Mn, and Cu. Results demonstrate successful Fe³⁺ precipitation within the pH range of 2.0-3, consistent with the literature. A decrease in nickel concentration is observed from pH 2.02, suggesting chemical precipitation mechanisms. Efficient Mn and Cu precipitation occurs at pH 5.5-6 and 4-6, respectively, aligning with established behaviours. These findings highlight the importance of pH control for optimising impurity removal from PWS, offering insights into the enhancement of nickel recovery processes in industrial contexts. Additionally, inductively coupled plasma optical emission spectroscopy (ICP-OES) and energy-dispersive X-ray spectroscopy (EDX) analysis confirm the presence of Fe, Cu, Ni, Sn, Si, Al, Ca, and (OH⁻) species, providing comprehensive elemental composition data for the precipitate sample. The study also utilised a reference material to evaluate method performance, demonstrating acceptable repeatability, reproducibility, precision, and accuracy. Detection limits and method stability are also evaluated, with results indicating robust detection sensitivity and methodology resilience over time. Furthermore, morphological investigations reveal distinctive structures in the Fe-

Ni hydroxide nanostructures precipitate, shedding light on its formation mechanism and potential applications.

Keywords: precipitation process, impurities, pregnant nickel solution (PWS), pH control

Graphical Abstract



1. INTRODUCTION

The recovery of valuable metals from waste streams has become increasingly imperative in the pursuit of sustainable resource utilisation and environmental stewardship. Among these metals, nickel (Ni) has particular significance because of its widespread industrial applications and economic value. In various hydrometallurgical processes aimed at nickel extraction, pregnant waste solutions (PWS) emerge as critical intermediates, embodying both the promise of resource recovery and the challenge of managing trace elemental impurities.

The PWS originate from the treatment of diverse waste sources, including spent batteries, electronic scrap, industrial effluents, and mining tailings. These solutions represent complex matrices containing dissolved Ni along with a spectrum of impurities derived from the original feedstock and the extraction process itself. Understanding the composition and concentration of trace elemental impurities in these solutions is essential for optimizing recovery processes, mitigating environmental risks, and ensuring the quality of recycled Ni products. In this review the analytical strategies employed for characterising trace elemental impurities in PWS derived from fire assay nickel sulphide collection waste streams are explored. By examining the methodologies and challenges associated with impurity determination and the implications for downstream processing and product quality, this review provides insights into the complex interplay between analytical science, metallurgical engineering, and environmental management in the context of Ni recovery from secondary overlooked resources. Through a deeper understanding of these dynamics, researchers and practitioners can develop more robust analytical methodologies and process optimisation strategies to enhance the sustainability and efficiency of Ni recycling operations.

Due to its outstanding properties, such as corrosion resistance, conductivity, and catalytic activity, Ni is a versatile metal broadly applied in industrial processes [1]. The demand spans various sectors, such as metallurgy, electronics, aerospace, and energy storage. However, the purity requirements vary significantly depending on the intended application. For instance, producing advanced electronic devices and high-performance batteries necessitates high purity to minimise impurities that could impair functionality and durability. Conversely, lower grades may suffice for alloying purposes in sectors such as steel manufacturing. To address these divergent needs, industry standards and regulatory frameworks establish guidelines for Ni purity, specifying acceptable concentrations of contaminants and impurities.

The London Metal Exchange (LME) is a prominent authority in setting standards for metals trading including Ni. The exchange delineates the criteria for different grades of Ni, outlining permissible levels of contaminants such as sulphur (S), phosphorus (P), and iron (Fe) [2]. Adherence to these standards is imperative for ensuring product quality, reliability, and market acceptance [2]. Analytical techniques play a crucial role in verifying compliance with these standards, enabling precise characterisation of Ni samples and the detection of trace-level impurities [3]. Various analytical techniques have been applied for the determination of trace impurities in high-purity Ni or Ni salts, including atomic absorption spectrometry (AAS) [4], inductively coupled plasma optical emission spectrometry (ICP-OES) [5], and inductively coupled plasma mass spectrometry (ICP-MS) [6].

In this context, ICP-OES emerges as a powerful analytical tool for assessing the elemental composition of Ni and quantifying contaminants at trace levels. By subjecting the samples to high-temperature plasma excitation, the equipment enables the emission-based detection of elemental constituents with exceptional sensitivity and precision. The spectral analysis obtained facilitates the identification and quantification of contaminants, thereby facilitating quality control measures production and processing of Ni. This study aimed to investigate the presence and concentration levels of contaminant in Ni using ICP-OES analysis. Specifically, the study sought to determine the elemental composition, including both major constituents and trace contaminants. Secondly, the aim was to quantify the concentrations of contaminant in Ni samples across different grades and finally to highlight the utility of ICP-OES as a reliable analytical technique for quality control and assurance in the Ni industry.

2. MATERIAL AND METHODS

2.1 Reagents, Standard Solutions, and Certified Reference Materials

Nitric acid (HNO_3) of analytical grade, with a concentration of 65% (w/w) and certified to ACS and ISO standards was acquired from Merck in Johannesburg, South Africa. Additionally, sodium hydroxide (NaOH) and sodium peroxide (Na_2O_2) were obtained from Merck in Johannesburg. Single-element standard solutions, each containing 1000 mg/L concentrations of Mg, Al, Si, Ti, Cr, Mn, Fe, Co, Cu, As, Cd, Zn, and Pb and meeting ICP grade AccuStandard specifications were sourced from both Stargate and LGC in Johannesburg, South Africa. Ultrapure water, boasting a resistivity of 18.2 M Ω cm, was consistently generated utilizing a Milli-Q system Type 1 water purification system from Merck and was utilized throughout all experimental procedures. Certified reference materials (CRMs), specifically AMIS 56 were obtained from Modderfontein, Johannesburg, South Africa and were employed for validation purposes and SARM 42, Analytical Chemistry Division, Mintek, Randburg South Africa.

2.2 Sample Preparation, Preparation of Calibration Standards, and Instrumentation

2.2.1 Solid samples: Precipitate preparation

The sample mass and CRMs were weighed to a zirconium crucibles. The sample is fused using an automatic fusion apparatus with alkali salts and mixed until a complete melt was achieved. The melt was leached in a beaker containing distilled water and concentrated hydrochloric acid (HCl) was added to the mixture and stirred with a plastic rod. Excess peroxide was boiled off by heating on the hot plate until the small bubbles were no longer observed. The solutions were quantitatively transferred into a volumetric flasks containing scandium (Sc) which were then filled up to the mark with ultrapure water.

2.2.2 Solution samples: Precipitate preparation

The sample preparation process involved the use of an auto dilutor for dilution. Following this, an amount of and internal standard solution were added to the flask. The flask was then filled to the mark with ultrapure water. The prepared solution was analysed with ICP-OES, with immediate processing deemed necessary. The summary of calibration results used for the analysis are detailed calibration curves in **Figure S1**. The study employs a systematic approach to analyse Ni samples of high purity.

The Ni samples sourced from the fire assay nickel collection production were prepared for analysis following established protocols to ensure sample homogeneity and representativeness. The instrument was calibrated using certified reference materials and QC standards to validate the accuracy and precision of measurements as shown in **Table S1**.

During analysis Ni samples underwent digestion to solubilize the metallic matrix, facilitating the release of elemental constituents for detection by ICP-OES. The instrument operated under optimized conditions, including plasma power, nebulizer flow rate, and analytical wavelengths, to achieve optimal sensitivity and resolution. Spectral data obtained from the instrument were processed using appropriate software for peak identification, integration, and quantification. Concentration levels of contaminants in Ni samples were determined through comparison with calibration curves constructed using standard reference solutions in **Figure S1**.

3. RESULTS AND DISCUSSION

3.1 Calibration of ICP-OES

The process of constructing linear calibrations involved systematically preparing standard solutions with known concentrations of each elemental impurity. These solutions were then analysed using the Agilent 5110 ICP-OES, a highly sensitive analytical instrument capable of detecting trace elements in solution. The resulting data presented graphically in **Figure S1** showcase the relationship between the concentration of each impurity and the corresponding intensity of the detected signal. The correlation coefficients, exceeding 0.9995 for all elemental impurities, indicate a strong linear relationship between the concentration of impurities and the signal intensity measured by the ICP-OES. This high degree of correlation underscored the reliability and accuracy of the calibration curves generated for each element. Moreover, the peak shapes displayed in the spectra provide additional insight into the analytical performance of the instrument. By examining the characteristics of these peaks, such as their width and symmetry, analysts can assess the precision and resolution of the measurements obtained.

Overall, the results demonstrate the excellent sensitivity and performance of the Agilent 5110 ICP-OES in accurately quantifying elemental impurities across a wide range of concentrations. This

capability is essential for various applications, including quality control, environmental monitoring, and research in fields such as metallurgy, chemistry, and materials science.

3.2 Chemical Analysis of ICP-OES

Figure 1 displays recoveries for the Certified Reference Material CRM namely Amis56 used at the listed concentrations, with all recoveries found to be within 10%. This confidently confirms the capacity of the instrument to accurately measure these elements at low concentration levels. The CRMs are indispensable for addressing methodological, laboratory, and run biases. These precisely characterized materials come with a statement of uncertainty, ensuring their traceability to international standards. Consequently, CRMs serve as invaluable tools for establishing traceability in analytical measurements, calibrating equipment and methods when necessary, monitoring laboratory performance, validating methods, and enabling method comparison. Certified Reference Material (CRM) are crucial because of their rigorous requirements for precision and comprehensiveness, which establish a dependable foundation for validating methods and ensuring quality control [7-8].

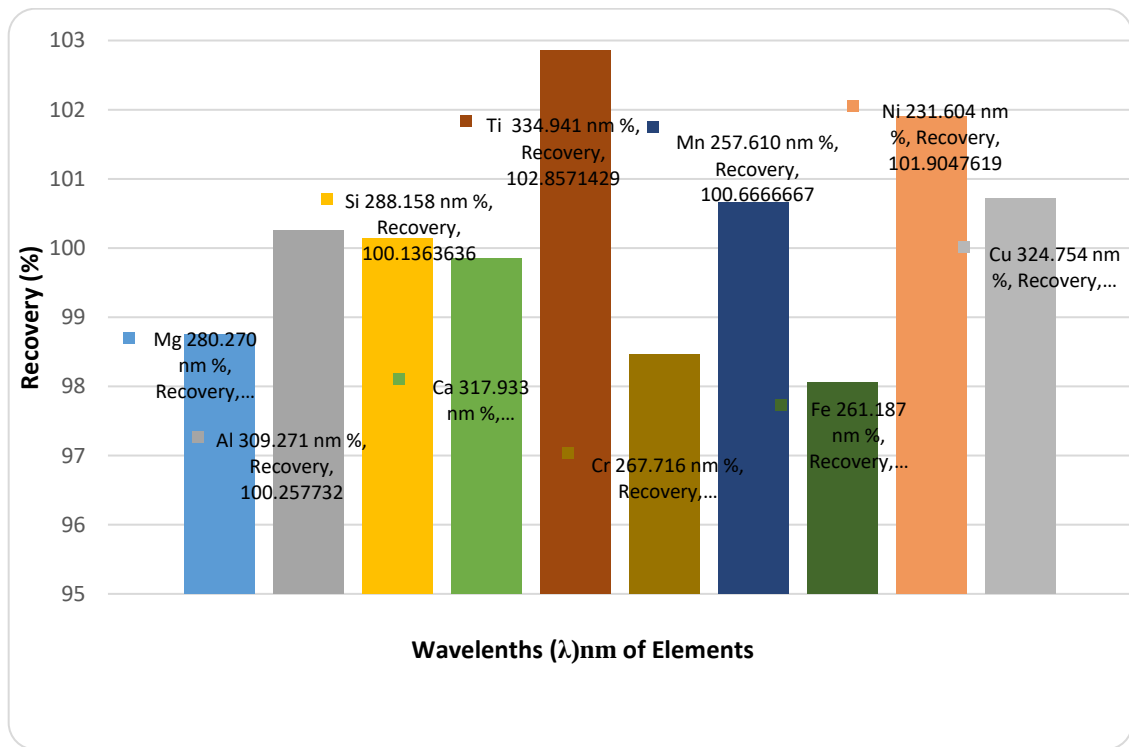


Figure 1: Recovery of certified reference (CRM) against the method of analysis

The method detection limits were calculated as three times the standard deviation of three consecutive measurements, ensuring a robust assessment of the detection sensitivity. Following the determination of accuracy, the stability of the methodology was evaluated by monitoring both the internal standard signal and the performance of the certified reference material (CRM). The obtained results, depicted in **Figure 2**, exhibit a variation of less than 5% when normalized to the initial reading, indicating the robustness and stability of the analytical approach over time.

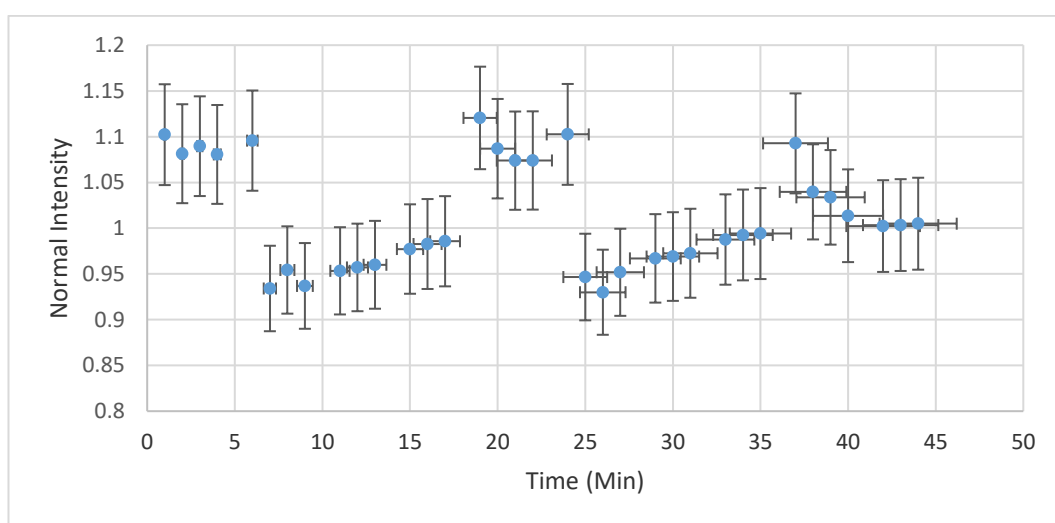


Figure 2: Stability of Internal standard scandium (Sc)

In this study, the AMIS56 CRM which encompasses representative base metals matrices was utilized to evaluate the performance of the method in determining PWS. Analytical data, including the average of 3 replicates, along with various statistical parameters obtained for these samples, were presented in **Table S1**. The samples were dried, pulverised and prepared for ICP-OES analysis illustrated in **Table S1**. The results display repeatability, reproducibility, precision, and accuracy, with acceptable thresholds established as follows: repeatability characterised by a relative standard deviation (RSD) below 2%, reproducibility with an RSD below 3%, precision with an RSD below 1.5%, and accuracy within $\pm 5\%$ of the certified value. The analysis was prepared and analysed three times for the samples. The results of this study demonstrate satisfactory repeatability, reproducibility, precision, and accuracy as indicated by acceptable relative standard

deviation (RSD) values. The analysis was conducted three times for each sample, ensuring robustness and reliability of the findings. The precipitation of Fe^{3+} impurities from PWS samples treated at pH 2.5 yielded 100% efficiency, confirming the effectiveness of the method. The literature by [9] reported the Fe^{3+} is precipitated at pH of 2.5 and Fe^{2+} at pH of 8 indicating the effectiveness of 98.82 % for Fe^{3+} at a pH of 3.6 for sample Fe precipitate at. **Figure 3** and **Table S1** efficiency is confirmed by [10] who reported an efficiency of 100% at pH 2.5 using lime.

The ICP-OES results showed significant variations in impurity concentrations across PWS samples at different pH levels. The impurities including Mg, Na, Al, and Ca spiked in PWS samples treated with $\text{Ca}(\text{OH})_2$, indicating the influence of precipitation agents on impurity levels. The method was found to be effective in removing Fe impurities from PWS as complete precipitation of Fe^{3+} impurities was achieved at pH 3. These findings contribute to the existing knowledge on impurity removal processes and provide valuable insights for optimizing precipitation conditions in industrial settings.

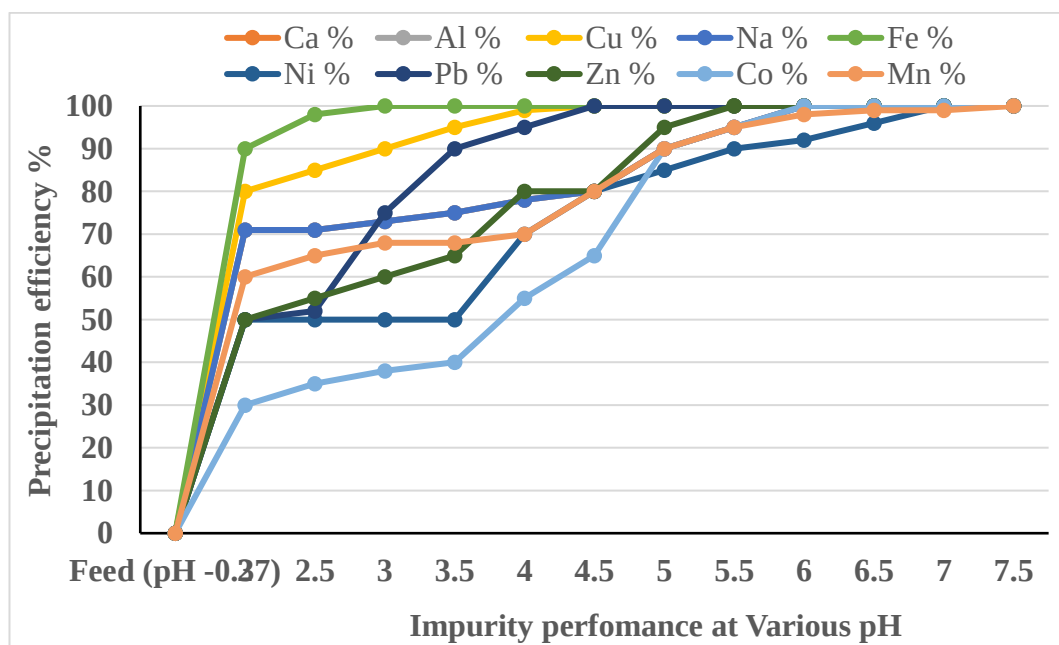


Figure 3: Efficiency of Chemical precipitation

The observed reduction in nickel (Ni) concentration within the PWS at a pH of 2.02 can perhaps be attributed to initial losses during the process. However, it is important to note that Ni precipitation does not occur to a substantial extent until the pH reaches approximately 6.5. According to previous research [10], the precipitation of copper (Cu) initiates at a pH of 5.5. In contrast, manganese (Mn) exhibits precipitation behaviour within a pH range of 5.5 to 9, resulting in a precipitation efficiency of 89.49% as reported in reference [11]. According to the data presented in Figure 3, the removal effectiveness of Mn is around 60% at a pH of 2, with a notable increase observed as the pH level increases. The data demonstrate a significant enhancement in the effectiveness of Mn removal, with a peak value of around 98% seen at pH 6. This finding indicates that the process of Mn precipitation has enhanced efficacy at elevated pH values, specifically in the vicinity of pH 5.5 and beyond.” Hence, it is probable that the decrease in Ni concentration observed at lower pH levels is not attributable to its own precipitation, but rather to early-stage interactions or co-precipitation with other metals such as Cu and Mn as the pH is modified.

The research conditions are indicative of the fact that the efficiency of precipitation was successful. Moreover, Cu precipitation from the solution exhibits maximum efficacy between pH 4 and 6, corroborating established literature as shown in **Table S2**. Earlier investigations suggest Cu precipitation initiates at pH values surpassing 4 culminating in complete precipitation at pH 6. The precipitation efficiency for Cu is impressively high, as evidenced by the 99.3% efficacy depicted in **Figure 3**. Nonetheless, the potential for losses during the precipitation process merits consideration, potentially arising from metal adsorption by the $\text{Fe}(\text{OH})_3$ precipitate reported by [10] and indicates a phenomenon supported by the EDX analysis depicted in **Figure 4(a)**. These findings highlight the critical importance of elucidating the intricate mechanisms underlying precipitation processes while also emphasizing potential challenges inherent in achieving optimal metal recovery, emphasising the need for careful examination of factors that could impact the efficiency and effectiveness of the process.

The results depicted in **Figure 4(a)** and the ICP-OES data in **Table S1** of the iron (Fe) precipitate sample exhibit remarkable agreement with the findings of EDX analysis, thereby validating the presence of various elements reported by ICP-OES. Specifically, the analysis confirms the existence of Fe, Cu, Ni, Sn, Si, Al, Cl, Ca, and hydroxyl within the precipitate sample indicating the determination of impurities that are precipitated at pH 2.5 [10]. This concurrence between the experimental results in **Table S1** and the EDX analysis in **Figure 4 (a)** underscores the reliability and accuracy of the characterization process, further enhancing our understanding of the elemental composition of the Fe precipitate.

The morphological investigation of impurities in the Fe-Ni hydroxide nanostructures precipitate at pH 2.5 obtained through the scanning electron microscopy (SEM) technique in **Figure 4(b)** reveals a layered structure of Fe-Cl-hydroxide with multi-component layers. This layered structure suggests the presence of distinct layers composed of Fe, Cu, Ni, Sn, Si, Al, Cl, Ca, and hydroxyl groups (OH). The layered arrangement indicates a sequential deposition of different components during the precipitation process possibly influenced by the pH and the relative concentrations of the different ions in the solution. The multicomponent layers imply the coexistence of Fe, Ni, and Cl species within the precipitate, which could have significant implications for understanding the formation mechanism and properties of the precipitate. Further characterization techniques, such as EDX and SEM, as provided in Figure 4 (a&b), offered additional insights into the elemental composition and morphology of the multicomponent layers of the sample. These insights obtained from complementary techniques, aided in the comprehensive understanding of the multicomponent Fe-Ni hydroxide precipitate.

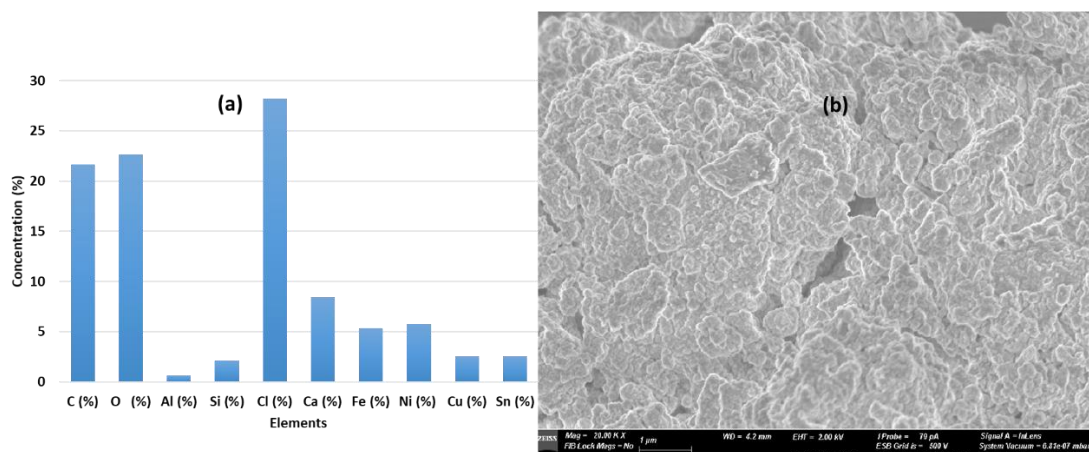


Figure 4: (a) EDX results at pH 2.5; (b) SEM results at pH 2.5

The results of the analysis in Figure 5 (a) confirm the findings from the ICP-OES data in Table S1 for the Ni precipitate sample **Figure 5 (a)** depicts the EDX findings, which exhibit a strong correlation with the ICP-OES outcomes, thereby substantiating the existence of diverse components inside the precipitate sample and demonstrating the thorough elimination of contaminants at a pH level of 6.5. This validates the presence of various elements reported by ICP-OES, such as Ni, Cl, Ca, and hydroxyl groups (OH) within the precipitate sample.

The scanning electron microscopy (SEM) technique used and represented in **Figure 5(b)** to investigate the morphological impurities in the Ni hydroxide nanostructures precipitate at pH 6.5 reveals a cauliflower-like structure of Ni-hydroxide, consistent with previous reports by [10]. The magnified image of the coarse structure further demonstrates that Ni(OH)_2 precipitates are aggregated together to create a cauliflower-like appearance. The aggregation of Ni(OH)_2 into cauliflower-like structures creates a rough and textured surface with multiple hierarchical levels, enhancing the surface area and providing numerous micro/nanostructures as previously reported by [12]. Moreover, the irregular morphology of the cauliflower-like structures ensures that the surface remains rough and textured even after exposure to various environmental conditions. Overall, the presence of cauliflower-like structures in the coarse morphology is instrumental in facilitating the formation of a hierarchical structure. Further characterization techniques, such as EDX

provided in **Figure 5(a)**, offer additional insights into the elemental composition. This aids in the comprehensive understanding of the Fe-Ni hydroxide precipitate.

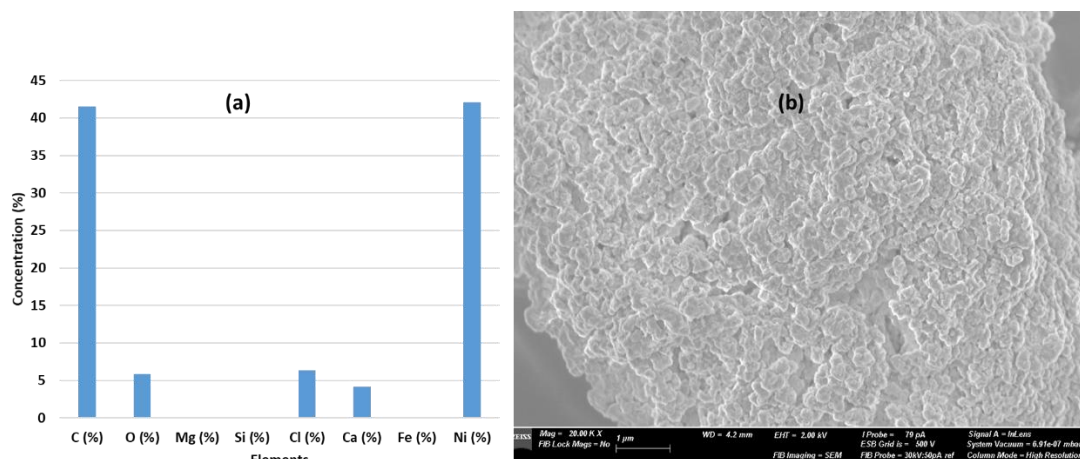


Figure 5: (a) EDX results at pH 6.5; (b) SEM results at pH 6.5

4. CONCLUSION

This study provided valuable insights into the precipitation process of impurities from PWS and its impact on Ni concentration. By utilizing lime as a precipitation agent, the successful removal of impurities such as Fe, Mn, Cu and other impurities was achieved across various pH levels. The observed Fe^{3+} precipitation within the pH range of 2.0-3, along with efficient Mn and Cu precipitation at pH 5.5-6 and 4-6, respectively, underscores the importance of pH control in optimizing impurity removal from PWS. The findings highlight the potential for enhancing Ni recovery processes in industrial contexts through precise pH manipulation. Moreover, the elemental composition analysis conducted via ICP-OES and EDX provided comprehensive data on impurity content, further validating the effectiveness of the precipitation process. Method performance evaluation using certified reference materials demonstrated the reliability and accuracy of the analytical techniques employed. The morphological investigations unveiled distinctive structures in the Fe-Ni hydroxide nanostructures precipitate, offering valuable insights into its formation mechanism and potential applications. Overall, this study contributes to advancing our understanding of impurity removal processes in Ni recovery and

underscores the importance of precise control and characterization techniques in optimizing industrial processes.

ACKNOWLEDGEMENTS

The authors wish to extend heartfelt thanks to Mintek for their financial support granted through Science Vote grant number: ASR-002508 (HM-05), as well as for granting permission to publish this research.

SUPPORTING INFORMATION

The results of these analytical techniques are essential for the determination of impurities in a pregnant solution. The supporting information is provided in Table S1 and S2 in support of the elemental composition of the sample by ICP-OES.

CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflicts of interest in relation to the publication of this research.

5. REFERENCES

- [1] Hart, T. (2015). *The use of nickel based particles in the electronics industry*. Wombourne: Hart Materials Limited.
- [2] Exchange, T. L. (2023). Special Contract Rules for Primary Nickel. London, England.
- [3] Bulska, E., & Ruszczyńska, A. (2017, May). Analytical Techniques for Trace Element Determination. *Physical Sciences Reviews*, 2(5), 2017-8002. doi:10.1515/psr-2017-8002
- [4] Elci, L., Soylak, M., Uzun, A., Buyukpatir, E., & Dogan, M. (2000). Determination of trace impurities in some nickel compounds by flame atomic absorption spectrometry after solid phase extraction using Amberlite XAD-16 resin . *Fresenius' Journal of Analytical Chemistry*, 368(4), 358-361.
- [5] Kujirai, O., & Yamada, K. (1994). Simultaneous determination of seven trace impurities (Al, As, Cr, Fe, Ti, V and Zr) in high-purity nickel metal and nickel oxide by coprecipitation and inductively coupled plasma-atomic

emission spectrometry. *Fresenius' Journal of Analytical Chemistry*, 11, 719-723.

- [6] Cheng, Y. (2008). Determination of trace elements in high-purity nickel by inductively coupled plasma mass spectrometry with microwave digestion. *Metallurgical Analysis*, 28(3), 9-13.
- [7] Magnusson, B., & Örnemark, U. (2014). *Eurachem Guide: The Fitness for Purpose of Analytical Methods—A Laboratory Guide to Method Validation and Related Topics* (2 ed.). United Kingdom: Eurachem: Teddington.
- [8] Thompson, M., Ellison, S., & Wood, R. (2002). Harmonized guidelines for single-laboratory validation of methods of analysis. *Pure and Applied Chemistry*, 74, 835-855. doi:DOI: <https://dx.doi.org/10.1351/pac200274050835>.
- [9] Xinchao, W., Roger, C., Viadero, J., & Karen, M. (2005). Recovery of Iron and Aluminum from Acid Mine Drainage by Selective Precipitation. *Environmental Engineering Science*, 22(6), 745-755.
- [10] Mabowa, H., Mkhohlakali, A., Mokoena, S., Tshilongo, J., & Chimuka, L. (2024). Removal of Nickel from Nickel Sulfite-Fire Assay Dissolution Filtrate Through Precipitation. *ACS Omega*, 9, 5592-5600. doi:<https://doi.org/10.1021/acsomega.3c07623>
- [11] Balintova, M., & Petrilakova, A. (2011). Study of pH Influence on Selective Precipitation of Heavy Metals from Acid Mine Drainage. *14th International Conference on Process Integration, Modelling and Environmental Engeneering*. 25, pp. 345-350. Slovakia: Technical University of Kosice, Civil Engineering Faculty, Institute of Building and. doi:DOI:10.3303/CET1125058
- [12] Du, H., Wang, Y., Yuan, H., & Jiao, L. (2016). Facile synthesis and high capacitive performance of 3D hierarchical Ni(OH)₂ microspheres. *Electrochimica Acta*, 84-91. doi:10.1016/j.electacta.2016.02.190

CHAPTER FIVE: CONCLUSION AND RECOMEDATIONS

This chapter presents a detailed and conclusive analysis based on the results of the conducted experiments. The research comprehensively outlines the work carried out, including the accomplished objectives. Furthermore, this chapter provides a clear explanation of the potential outcomes that may arise from the research in the future.

5.1 Conclusion

As the demand for electric vehicles (EVs) and energy storage systems continues to rise, the manufacturing of high-quality battery-grade nickel sulphate (NiSO_4) is becoming more and more important. As South Africa aims to solidify its place in the global supply chain for this vital material, this research emphasises the critical need of attaining high-purity NiSO_4 to improve battery performance and lifespan. Impurity control and purification are fundamental to manufacturing NiSO_4 that satisfies rigorous industry standards, and the main findings highlight the complexity of these processes.

The manufacturing of NiSO_4 places a premium on efficient impurity management. When used in battery applications, contaminants like magnesium (Mg), arsenic (As), and other trace elements can greatly impact NiSO_4 's quality and performance. Beyond conventional analytical procedures, the research reveals that improved purification techniques are necessary to overcome these obstacles. A recurrent issue throughout the study is the necessity of novel techniques to achieve the high purity levels demanded by the business.

Producing high-purity NiSO_4 requires the use of cutting-edge extraction and refining technologies in conjunction with exacting analytical procedures, as shown in the study. The separation of nickel (Ni) from other metal ions and the successful management of contaminants rely on crucial processes including solvent extraction and hydroxide-based precipitation. Ensuring effective and precise extraction while minimising impurity levels requires conducting these operations under controlled conditions of temperature and pH. Furthermore, a crucial step in attaining the targeted NiSO_4 purity is the controlled re-dissolution of nickel hydroxide ($\text{Ni}(\text{OH})_2$) in sulphuric acid (H_2SO_4).

To back the expansion of the battery sector, it is essential to solve the problems of impurity removal and uphold high purity standards. To keep up with the growing

demand for battery-grade NiSO_4 and keep the environment safe, the research highlights the importance of continuously improving and inventing new extraction and purification processes. To ensure materials that not only fulfil performance needs but also comply with regulatory norms, it will be crucial to concentrate on improving these procedures as the sector develops.

Improving NiSO_4 manufacturing requires a multidisciplinary strategy. Modern developments in analytical procedures, quality control, separation technology, and efficient production processes should all be incorporated into this strategy. In line with sustainability goals, efforts to cut energy consumption, implement eco-friendly processes, and minimise waste creation further emphasise the necessity of creative manufacturing methods. To fulfil the needs of the battery industry while preserving resources and being mindful of the environment, it is essential to purify nickel hydroxide thoroughly and create sustainable production methods.

A thorough comprehension of Ni processing and analysis was enhanced by the research's insightful contributions, which are presented in several important publications as such the S-Curve precipitation's efficacy in Ni recovery from industrial waste streams was the primary emphasis of the first paper. Consistent to study the efficacy of this method, the experimental results showed that parameters might be optimised to increase the efficiency of nickel extraction. In the second paper, the different ways to analyse trace elements while purifying high-purity NiSO_4 was investigated from synthetic samples. The FAAS was compared with portable handheld EDXRF in particular. Results demonstrated how well these approaches worked for online monitoring and control of purification for plant performance, answering the call for trustworthy analytical methods for impurity detection.

Paper III reported the investigation from the novel approaches towards studying several ways of synthesising nickel oxide (NiO) and characterising its properties by annealing the hydroxide precipitate at various temperatures. This provided insights into potential alternative strategies for Ni recovery and purification. The purpose of

Paper IV was to contribute to the mission of comprehending the synthesis of Ni compounds through precipitation processes by studying the synthesis and characterisation of γ -Nickel hydroxide (Ni(OH)_2). The examining impurity precipitation processes was achieved through Paper V which examined the impurity precipitation from pregnant waste solution (PWS) at various pH levels, highlighting the significance of pH management in impurity removal.

Collectively, these research projects improve the knowledge of Ni purification, extraction methods and make substantial strides in creating environmentally friendly refining procedures towards NiSO_4 battery grade. The environmental responsibility while supporting the growth of the battery sector was ensured in this research indicated that it is vital to address impurity removal, maintain high purity requirements, and integrate eco-friendly techniques. Meeting industrial demands while promoting resource conservation and environmental stewardship requires a focus on comprehensive purification and the development of efficient, sustainable production processes, according to this research.

5.2 Recommendations

Through an extensive analysis of the research articles, a number of significant recommendations have been discovered to enhance the production processes of nickel sulphate (NiSO_4) batteries and promote the development of sustainable energy storage technologies. Integration of data from several scholarly articles is necessary in order to cultivate a comprehensive comprehension of the nickel recovery and purification procedure, encompassing the transformation of waste streams into materials suitable for battery applications. Future enhancements to recovery and purification procedures should leverage the knowledge acquired from Papers I and V, with a focus on investigating innovative approaches to improve both efficiency and purity. Drawing upon the findings presented in Paper II, it is imperative to enhance and authenticate analytical methodologies employed in the determination of impurities. This may involve the integration of supplementary techniques to facilitate a thorough study. Expanding upon the conclusions drawn in Papers III and IV, it is imperative to direct future investigations into nickel

compounds towards the examination of their crystal structure and electrochemical performance. This will enable a comprehensive evaluation of their appropriateness for battery-grade applications. Furthermore, the optimisation of the re-dissolution of nickel hydroxide (Ni(OH)_2) in sulphuric acid (H_2SO_4), as elucidated in the scholarly articles, is crucial for enhancing both purity and process efficiency. The assessment of the environmental consequences associated with nickel recovery procedures, particularly in relation to sustainability and green chemistry, is of utmost importance in order to adhere to the principles of the circular economy. Facilitating cooperative research endeavours among researchers, industry collaborators, and relevant stakeholders will effectively tackle obstacles and expedite the advancement of battery-grade NiSO_4 . Furthermore, the application of DEHPA-impregnated resin (LewatitVPOC1026) for the purpose of reducing calcium impurities to a concentration below 20 mg/L within a specified pH range effectively tackles the specific challenges related to impurity management that were found in the study. The recommendations presented in this study are based on empirical research and are intended to boost the efficiency of nickel processing methods, promote environmental stewardship, and facilitate the advancement of sustainable energy technologies. Future studies that involve thorough comparison with various sample matrices, temperatures and methods used to analyse and interpret the results will be used to contribute to the robustness and formulation of the methods.

APPENDIX : Supporting Information for PAPER I-V

This chapter describes the supplementary information that has already been discussed in papers I, III, IV, and V.

APPENDIX A: Paper I Supplementary Information

The Removal of Nickel from Nickel Sulfite-Fire Assay (NIS-FA) Dissolution Filtrate through Precipitation

Happy Mothepane Mabowa^{1,3*}, Andile Mkhohlakali¹, Sam Mokoena², James Tshilongo^{1,3}, Luke Chimuka³

¹Analytical Chemistry Division, MINTEK, 200 Malibongwe Drive, 2155, South Africa

²Hydrometallurgy Division, MINTEK, 200 Malibongwe Drive, 2155, South Africa

³School of Chemistry, University of the Witwatersrand, Private Bag 3, PO WITS, 2050, South Africa

SUPPORTING INFORMATION

^{1,3*}Corresponding Author: Happy Mothepane Mabowa, Email: happyc@mintek.co.za

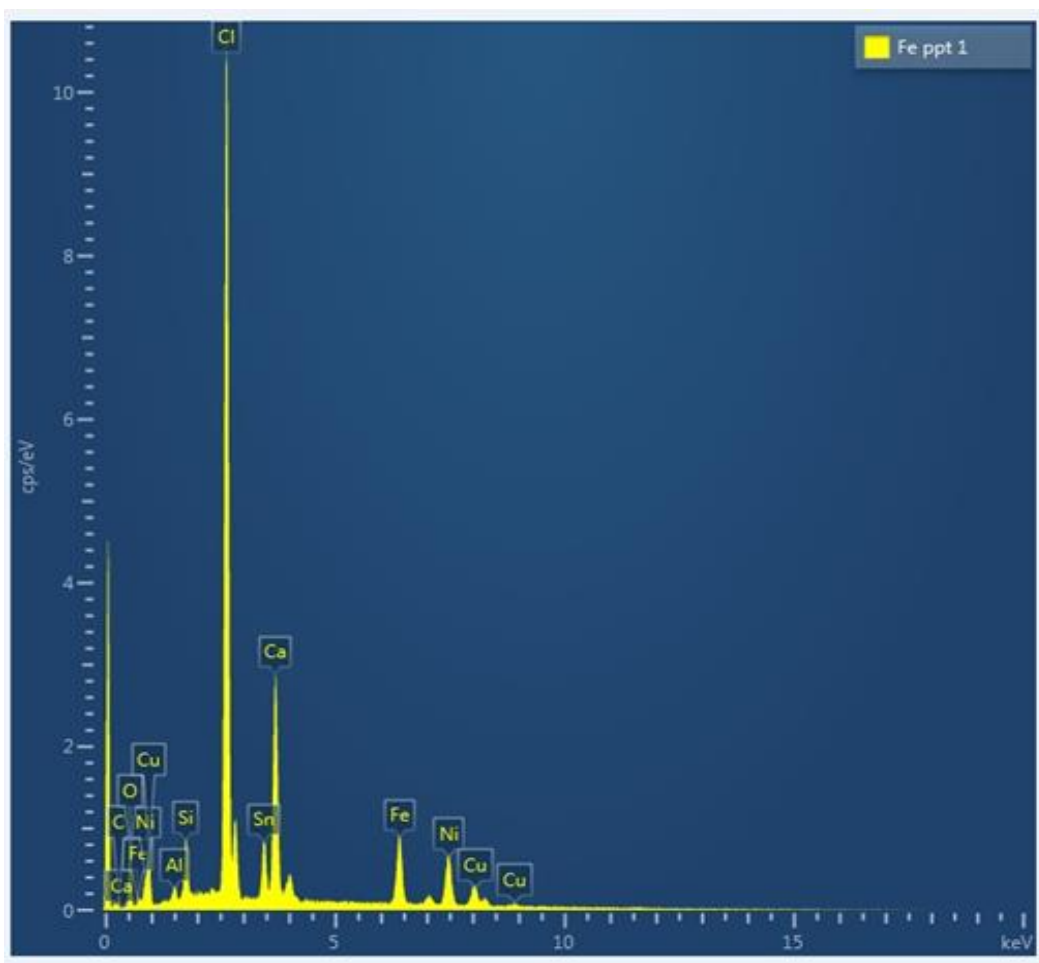


Figure S1. EDX spectra of $\text{Fe}_2\text{O}_3/\text{Ni}(\text{OH})_2$

Table S1. EDX results of Fe₂O₃/Ni(OH)₂ precipitate at pH 2.5

Label	C	O	Al	Si	Cl	Ca	Fe	Ni	Cu	Sn
Fe ppt 1	21.68	22.69	0.65	2.14	28.24	8.43	5.34	5.75	2.56	2.52
Fe ppt 2	36.73	38.19	0.87	1.82	12.61	3.87	2.4	1.72		1.79
Fe ppt 3	18.58	6.34	0.41	1.91	36.2	15.04	8.01	8.17		5.32
Fe ppt 4	29.4	38.01	0.67	4.49	14.27	4.53	3.76	2.38		2.5
Fe ppt 5	35.76	40.3	0.8	1.91	11.96	3.77	1.91	1.78		1.8
Statistics										
Max	36.73	40.3	0.87	4.49	36.2	15.04	8.01	8.17	2.56	5.32
Min	18.58	6.34	0.41	1.82	11.96	3.77	1.91	1.72	2.56	1.79
Average	28.43	29.11	0.68	2.45	20.65	7.13	4.29	3.96	2.56	2.79
Standard Deviation	8.16	14.55	0.18	1.15	10.96	4.82	2.47	2.88	0	1.46

Table S2. EDX results of Ni(OH)₂ precipitate at pH 6.5

Label	C	O	Mg	Si	Cl	Ca	Fe	Ni
Ni PPT 1	25.7	14.73			25.02	9.85	0.4	24.31
Ni PPT 2	71.69	7.62			3.69	2.14		14.87
Ni PPT 3	76.42	8.56			3.38	1.55		10.1
Ni PPT 4	40.7	30.4	0.41	0.16	13.62	5.07		9.64
Ni PPT 5	62.51	18.07			9.28	3.38		6.77
Statistics								
Max	76.42	30.4	0.41	0.16	25.02	9.85	0.4	24.31
Min	25.7	7.62	0.41	0.16	3.38	1.55	0.4	6.77
Average	55.4	15.87	0.41	0.16	11	4.4	0.4	13.14
Standard Deviation	21.54	9.2	0	0	8.91	3.33	0	6.89

Table S3. XPS results of Ni(OH)₂ precipitate at pH 6.5

Name	Peak BE	FWHM (eV)	Atomic %
C12p ³ (metal chloride)	198.3	1.5	5.1
C1s (C-C)	284.8	1.2	44.8
C1s (C-O)	286.2	1.1	10.3
C1 (C=O)	288	1.1	1.5
C1s (O-C=O), carbonate	288.7	1.2	7.4
Ca 2p (CaCO ₃)	347.6	1.5	1.4
O1s (Metal Oxide)	530.5	1.6	1.3
O1s (C-O; Carbonate)	531.5	1.6	14.7
O1s (C=O)	533.2	1.6	9.9
Ni2p (Ni(OH) ₂)	855.8	2.4	3.7

Table S4. XPS results of Fe₂O₃/Ni(OH)₂ precipitate at pH 2.5

Name	Peak BE	FWHM (eV)	Atomic %
C12p ³ (metal chloride)	198.5	1.4	8.8
C1s (C-C)	284.8	1.2	40.2
C1s (C-O)	286.2	1.1	9.1
C1 (C=O)	288	1.1	1.6
C1s (O-C=O), carbonate	347.8	1.2	5.9
Ca 2p (CaCO ₃)	487	1.5	1.4
Sn 3d (SnO, SnO ₂)	530.5	1.5	0.8
O1s (Metal oxide)	530.3	1.5	2.9
O1s (C-O; Carbonate)			15.3
O1s (C=O)	533.2	1.6	8.9
Fe2p (FeOOH)	712	4.4	2.2
Ni2p (Ni(OH) ₂)	856.4	2.1	1.9

APPENDIX B: Paper IV Supplementary Information

A comparative study of sol-gel prepared and chemical precipitation NiO from fire assay waste: Structural characterization and insights into VOCs sensing application

Happy Mothepane Mabowa^{1,2}, Andile Mkhohlakai¹, Luke Chimuka, James Tshilongo^{1,2}

¹Analytical Chemistry Division, Mintek, 200 Malibongwe Drive, Randburg 2194, South Africa

²School of Chemistry, University of the Witwatersrand, Johannesburg, 2050, South Africa

Corresponding author: Andilem@mintek.co.za

SUPPLEMENTARY INFORMATION

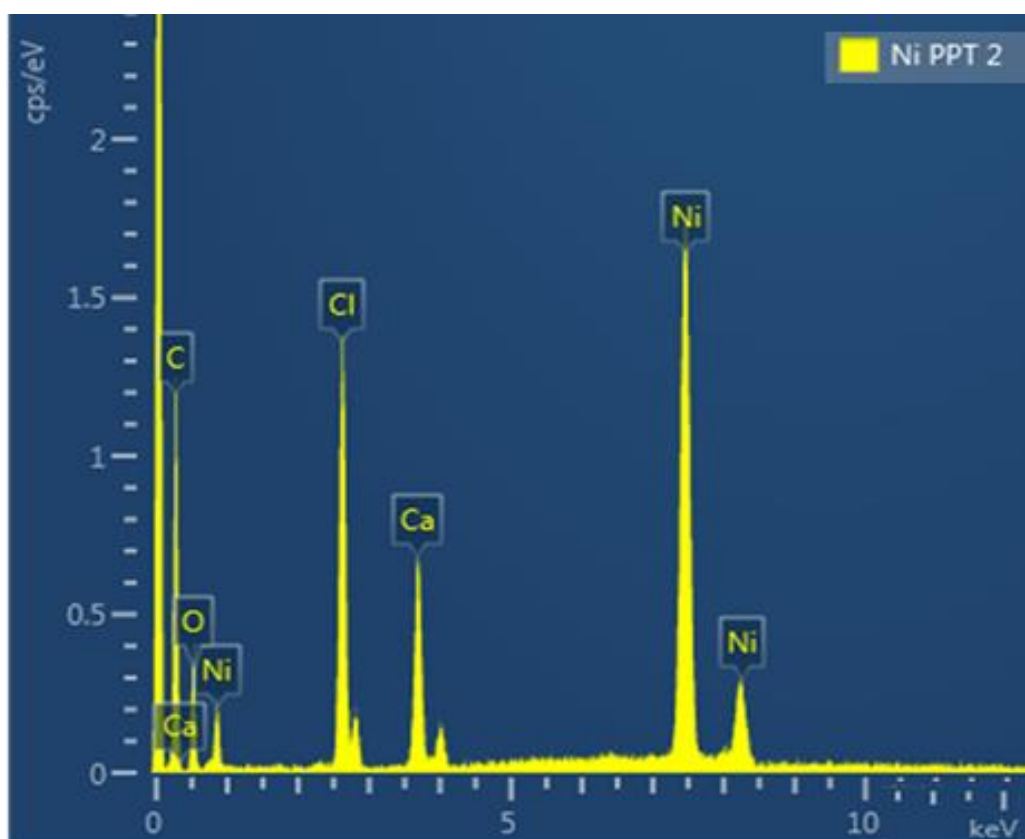


Fig S1. EDS spectra of Ni(OH)₂ at pH 6.5, 25 °C

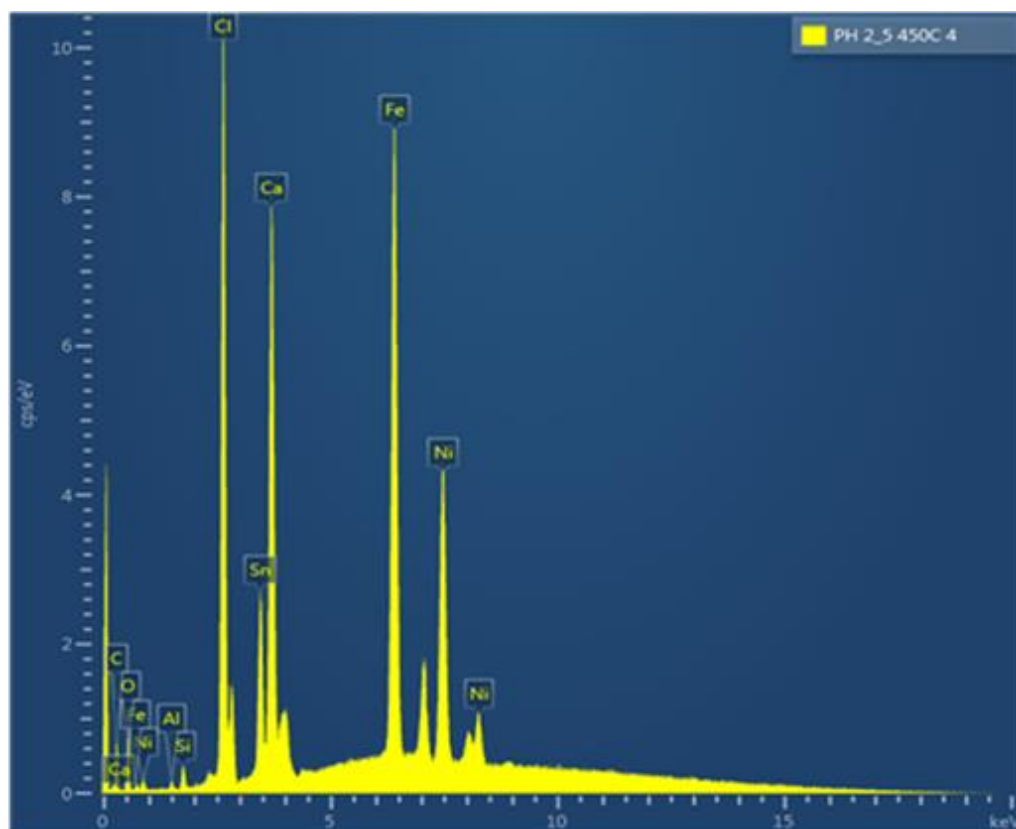


Fig S2. EDS spectra of $\text{Fe}_2\text{O}_3/\text{Ni}(\text{OH})_2$ at pH 2.5, 25 °C

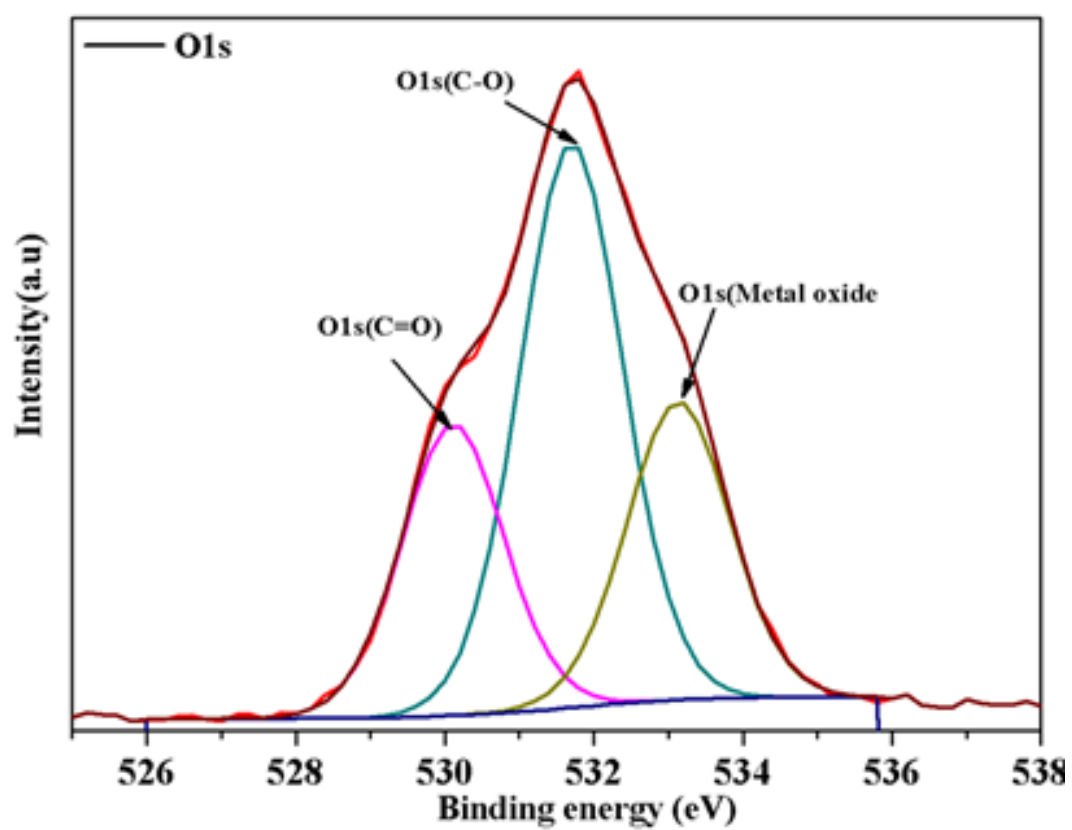


Fig S3. XPS spectrum of Fe₂O₃ at pH 2.5

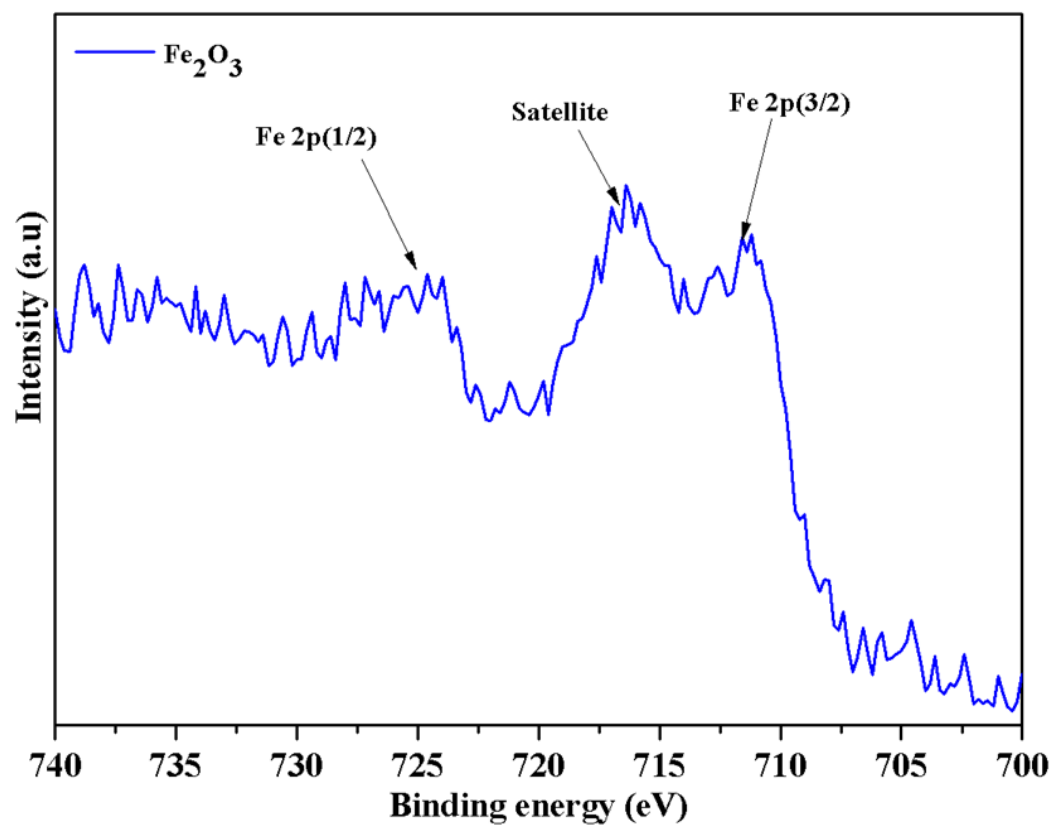


Fig S4. XPS spectrum of Fe_2O_3 at pH 2.5

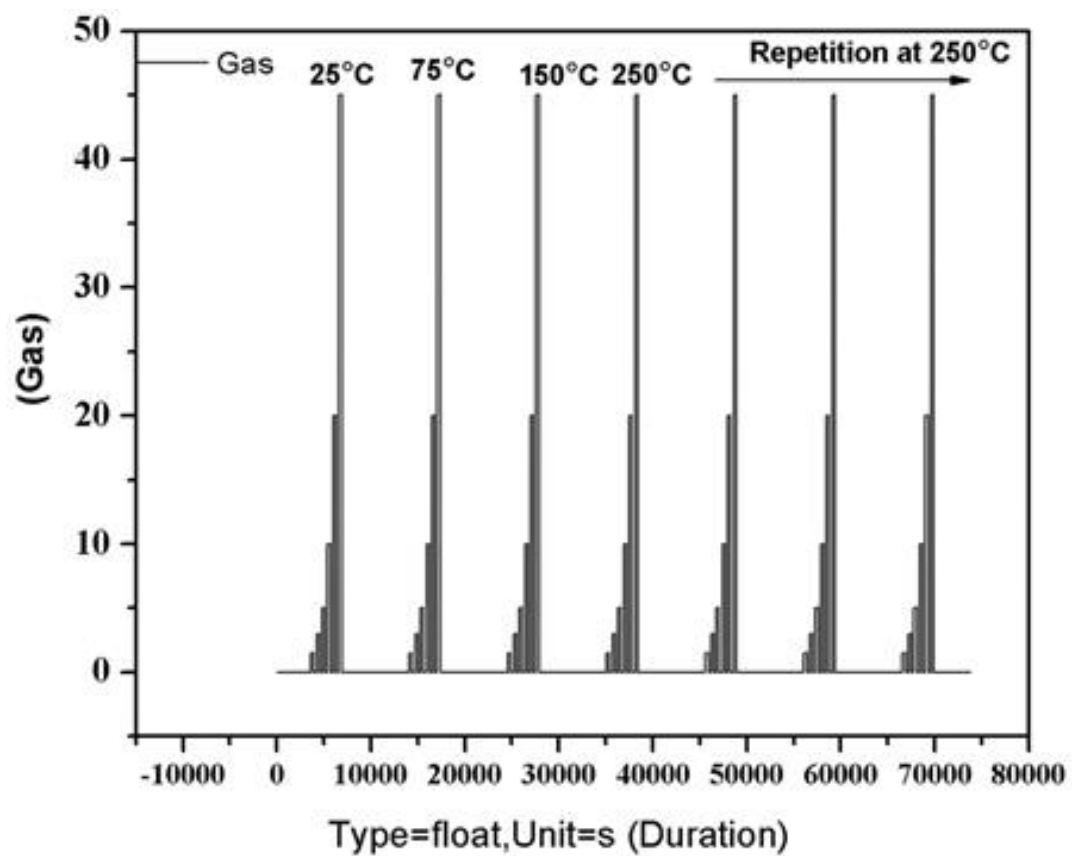


Fig S5. Gas flow test at different temperature in the NiO presence.

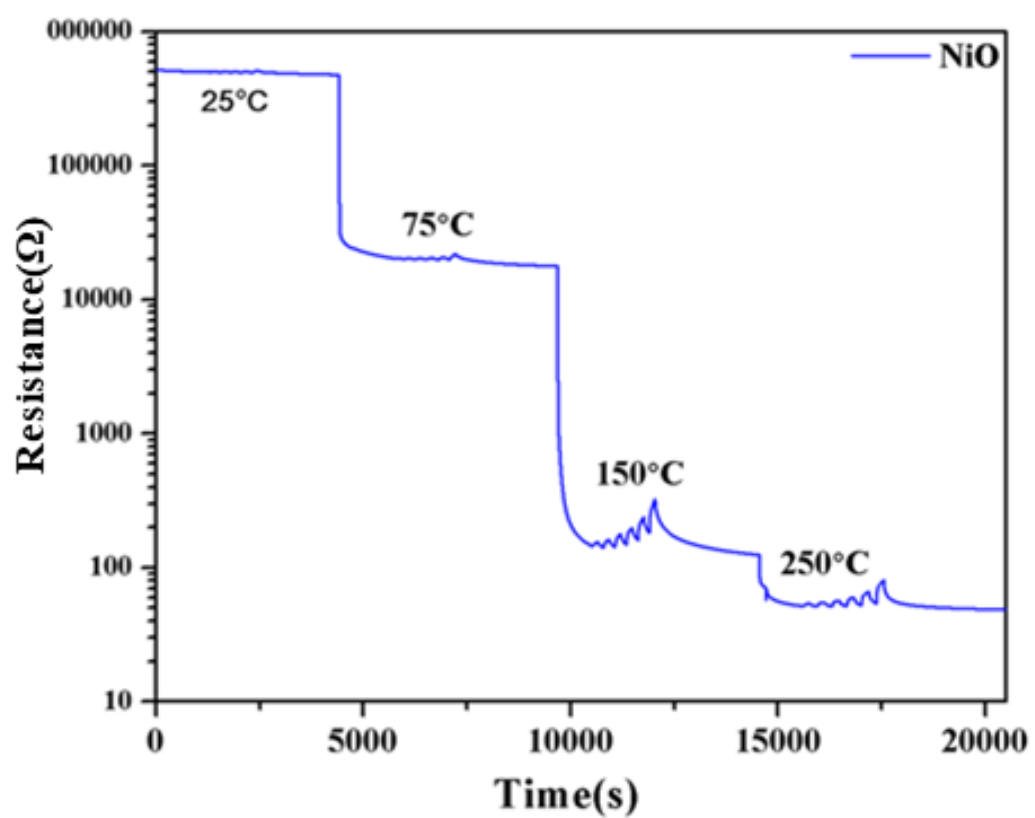


Fig S6. NiO sensing response towards ethanol at different temperatures

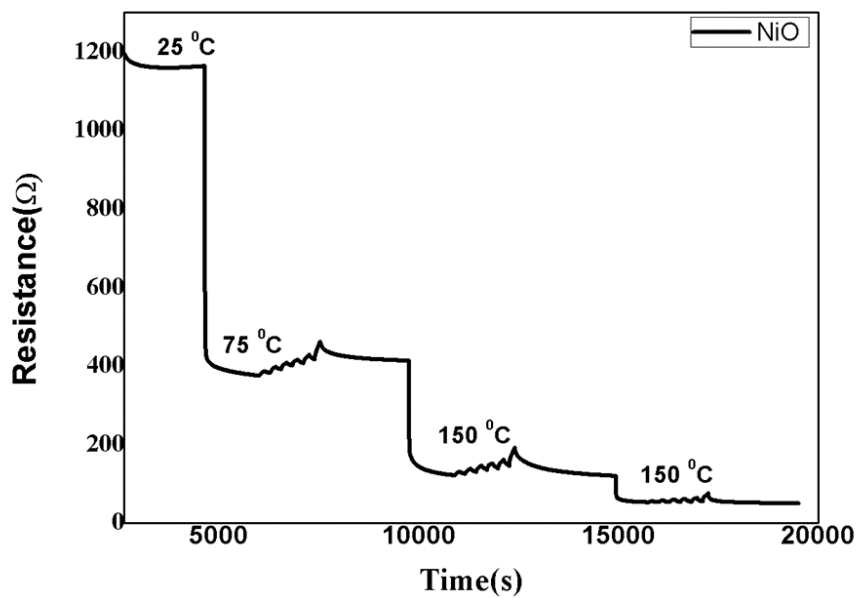


Fig S7. Sol-gel process NiO sensing response towards ethanol at different temperatures

Table S1. Crystallinity results of NiO material

Materials		Av. crystalline size(nm)
NiO sol-gel		38.5
NiO	chemical precipitation	41.1

Table S2. The chemical state and binding energy of NiO at pH 6.5 and Fe₂O₃/Ni(OH)₂ at pH 2.5

Process	Materials	Species	Binding energy(eV)	Oxidation state
Chemical precipitation	NiO at 6.5	Ni2p(3/2)	856	Ni ²⁺
		Ni2p(1/2)	874	N ³⁺
		Satallite1	862	-
		Satellite2	880	-
		O1s O ²⁻ of NiO	529	-
		O1s O ₂ of Ni(OH) ₂	531	-
		C=O	533	-
	Fe ₂ O ₃ /Ni(OH) ₂	Ni2p(1/2)	872	Ni ³⁺
		Ni2p(3/2)	855	Ni ²⁺
		Satallite	861	
		O1s O1s (Metal oxide)	533	-
		O1s O ²⁻ of FeO ₂ O ₃	531	-
		O1s O ₂ of FeO ₂ O ₃	530	-
		Fe (1/2)	724	Fe ³⁺
		Fe(3/2)	711	Fe ²⁺

	Satellite	716	
	Ni2p(1/2)	880	Ni³⁺
	Ni2p(3/2)	860	Ni²⁺
	Satellite1	863	-
Sol-gel process NiO	O1s (Metal oxide)	535	-
	O1s O²⁻ of NiO	537	-
	O1s O₂ of Ni(OH)₂	544	-

Table S3. ICP-OES results for Concentration of NiO at pH 2.5 and Fe₂O₃ at pH 2.5

Sample ID	Ni	Conversion factor	NiO	Fe	Conversion Factor	Fe₂O₃
pH 2.5 A	10.66	1.2725	13.565	12.192	0.6994	8.53
pH 2.5 B	11.04		14.05	12.25		8.57
Average	10.85		13.807	12.221		8.547
Standard deviation (SD)	0.27		0.343	0.041		0.028
RSD%	2.48		2.482	0.333		0.333
pH 6.5 A	41.3	1.2725	41.301	0.243	0.6994	0.17
pH 6.5 B	40.82		41.301	0.242		0.169
Average	41.06		41.301	0.242		0.169
Standard deviation (SD)	0.34		0	0		0
RSD%	0.83		0	0.146		0.146
CRM-51/71 A	4.658	1.2725	5.927	-		-
CRM-51/71 B	4.584		5.833	-		-
Accurate value	5.54		5.54	-		-
Average	4.621		5.88	-		-
Standard deviation(SD)	0.052		0.067	-		-
RSD%	1.134		1.134	-		-

Table S4. ICP-OES results for major elements sol-gel process NiO

Element	Concentration (%)
Ni	55 g/L
CRM: AMIS56	0.20
Accurate value	0.21

Table S5. Sensing parameters of sol-gel NiO towards ethanol

Concentration (1.5 ppm)				
Temperature (°C)	25	75	150	250
Resistance (Ω)	156.4	-4.26	154.2	-
Response (Rg/Ra)	0.002	-0.006	0.049	-
Concentration(3ppm)				
Temperature (°C)	25	75	150	250
Resistance (Ω)	161.8	-0.0026	160.95	53.85
Response (Rg/Ra)	0.0029	-0.0021	0.1	0.0338
Concentration (5ppm)				
Temperature (°C)	25	75	150	250
Resistance	178.86	-0.0016	176.16	55.05
Response (Rg/Ra)	0.0065	-0.0006	0.2022	0.059
Concentration (10ppm)				
Temperature (°C)	25	75	150	250
Resistance (Ω)	198.62	0.002	196.84	56.96
Response (Rg/Ra)	0.0055	0.0015	0.365	0.0897
Concentration (20ppm)				
Temperature (°C)	25	75	150	250
Resistance (Ω)	236.2	0.0145	234.57	65.86
Response (Rg/Ra)	0.006	0.074	0.598	0.27
Concentration (45 ppm)				
Temperature (°C)	25	75	150	250
Resistance (Ω)	325.31	0.073	325	65.86
Response (Rg/Ra)	0.02	0.074	1.198	0.27

Table S6. EDX results of as-prepared NiO

Materials	Major elements	Molecular weight (%)
Chemical precipitated NiO	Ni	72.35
	O	
	Ca	25.05
	Cl	
	C	7.62
		16.44
Sol-gel process NiO		2.62
	Ni	72.8
	O	15.9
	C	11.4

For the % loading of Cu, there is a need to understand the concentration change of Cu and use it to determine the percentage of Cu that has been loaded onto the organic phase or removed from the solution.

From the information provided:

- Initial Cu concentration: 3870 ppm (before pre-loading)
- Final Cu concentration: 801 ppm (after pre-loading)
- Precursor solution concentration: @ pH 2.5 501 ppm

The % loading of Cu can be calculated based on the reduction in concentration from the initial solution to the precursor solution:

% Loading of Cu =

$$\left(\frac{\text{Initial Cu concentration}(3870 \text{ ppm}) - \text{Precursor Cu concentration}(801)}{\text{Initial Cu concentration} (3870)} \right) \times 100$$

The loss of Ni was calculated as ~9.73% which was calculated as follows for the concentrations provided in Table 2:

$$\% \text{ Total loss} = \left(\frac{\text{Total Ni Loss} (6100 \text{ ppm})}{\text{Initial Ni concentration}(62700 \text{ ppm})} \right) \times 100$$

And the ~90.27 % recovery of Ni was calculated as follows:

% Recovery

$$= \left(\frac{\text{Initial Ni concentration (62700 ppm)} - \text{Final Ni concentration (6100 ppm)}}{\text{Initial Ni concentration (62700 ppm)}} \right) \times 100$$

- NiO Sensing Methodology

The NiO used in the sensing experiments was prepared via two methods: sol-gel and chemical precipitation. In the sol-gel method, nickel nitrate dissolved in ethanol formed a gel, which was calcined at 350°C and 450°C to yield NiO. In the chemical precipitation method, nickel sulfate was precipitated, filtered, washed, and calcined at the same temperatures. Both methods produced NiO with properties suitable for gas sensing. The NiO was then used in sensors to detect ethanol gas concentrations ranging from 1.5 ppm to 45 ppm at temperatures of 25°C, 75°C, 150°C, and 250°C.

APPENDIX C: Paper III Supplementary Information

Separation and Characterisation of Nickel Hydroxide from Waste Solution using $\text{Ca}(\text{OH})_2$ Precipitation In Chloride Media

Happy M. Mabowa^{1,2*}, Andile Mkhohlakali¹, James Tshilongo^{1,2}, Luke Chimuka²

¹Analytical Chemistry Division, MINTEK, 200 Malibongwe Drive, 2155, South Africa

²School of Chemistry, University of the Witwatersrand, Private Bag 3, PO WITS, 2050, South Africa

*Corresponding author's email: happy@mintek.co.za

SUPPORTING INFORMATION

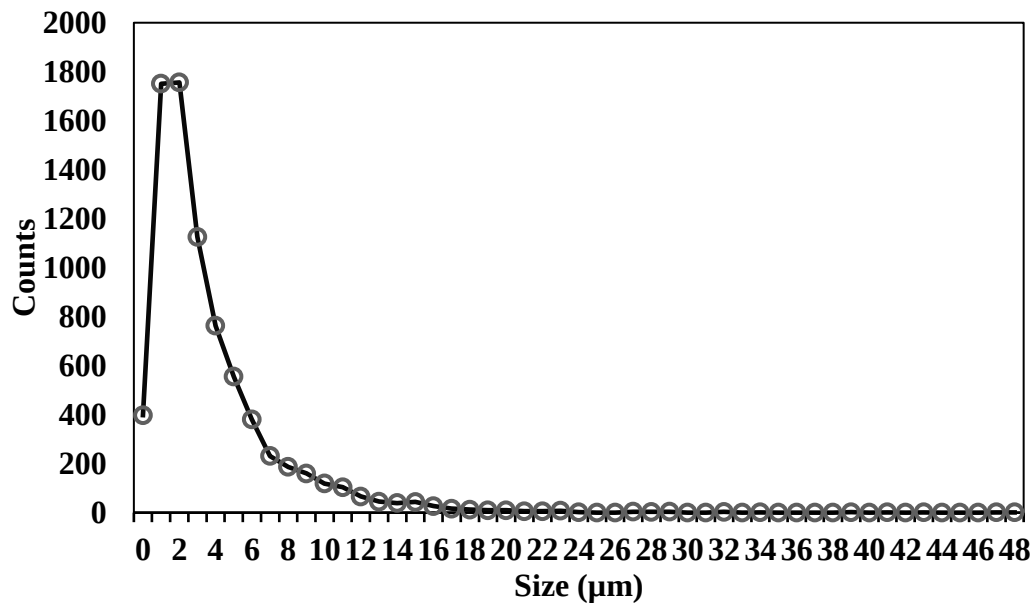


Figure S1. Particle Size Distribution (PSD) Ni(OH)₂

- ✚ **From (μm):** The particle sizes ranged from 0 μm to 48 μm, with a mean of 24 μm.
- ✚ **Counts:** The number of particles per size range had a mean of 160.06, a minimum of 0, and a maximum of 1756.
- ✚ **Percent:** The cumulative percentage ranged from 5.07% to 100%, with a median of 99.73% and a mean of 92.53%.

The quartiles of the distribution indicate that:

- ✚ 25% of the particles are smaller than 12 μm.
- ✚ 50% of the particles are smaller than 25 μm.
- ✚ 75% of the particles are smaller than 37 μm.

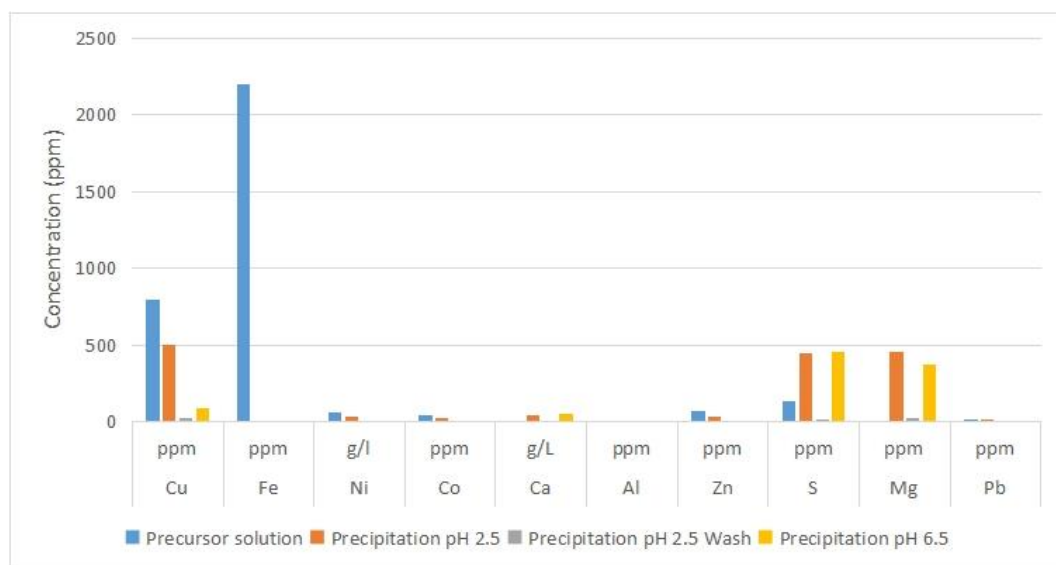


Figure S2. Elemental composition of the sample by ICP-OES $\text{Ni}(\text{OH})_2$

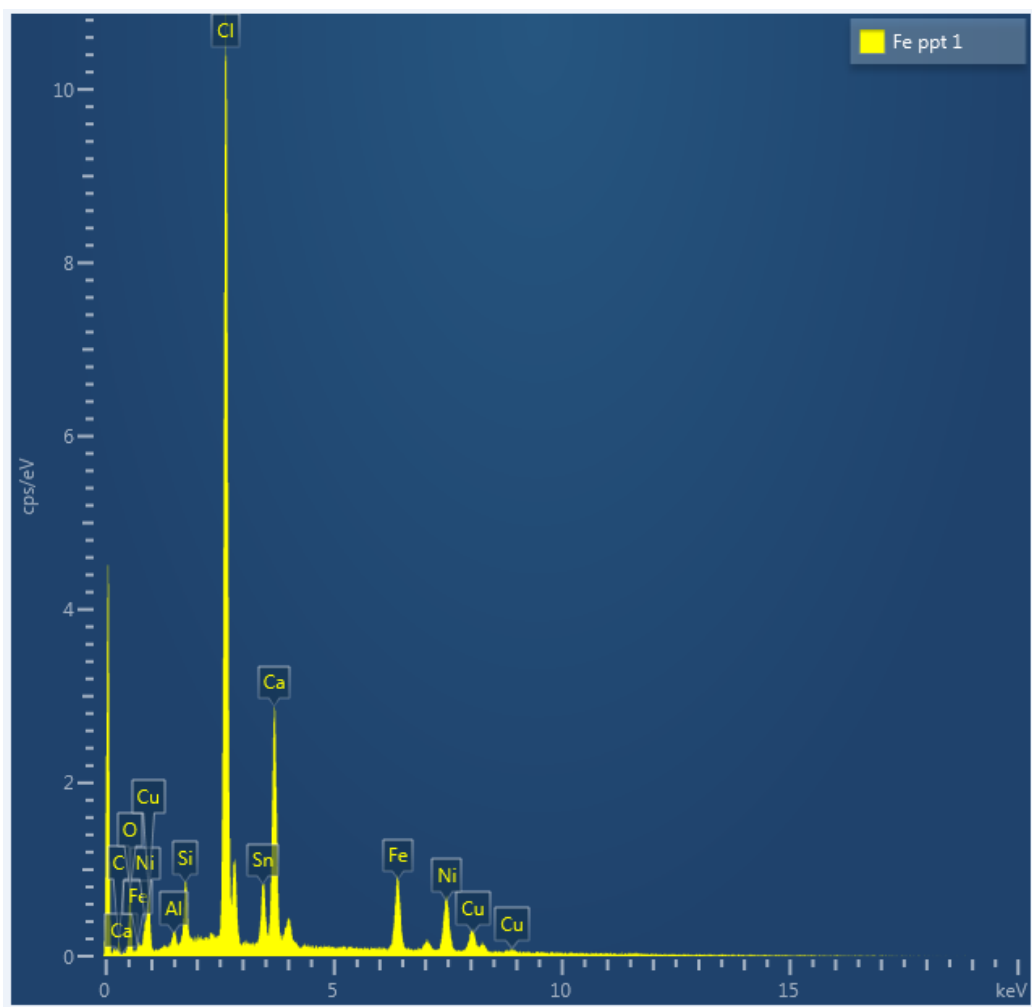


Figure S3. EDX precipitate at pH 2.5

Table S1: Concentration of Cu in the organic phase in consequent stages.

Element,	Pregnant Solution	Cu-Loaded Organic	Precursor solution, (ppm)	Wash solution, (ppm)
Cu (ppm)	3900	3097.96	801	7.43

APPENDIX D: Paper V Supplementary Information

**Optimization of Impurity Removal from Pregnant Nickel Solution Using Lime
Precipitation: pH Control and Analytical Characterization.**

Happy M. Mabowa^{1,2*}, Andile Mkhohlakali¹, James Tshilongo^{1,2}, Luke Chimuka²

*Corresponding author's email: happyc@mintek.co.za

¹Analytical Chemistry Division, MINTEK, 200 Malibongwe Drive, 2155, South
Africa

²School of Chemistry, University of the Witwatersrand, Private Bag 3, PO WITS,
2050, South Africa

SUPPORTING INFORMATION

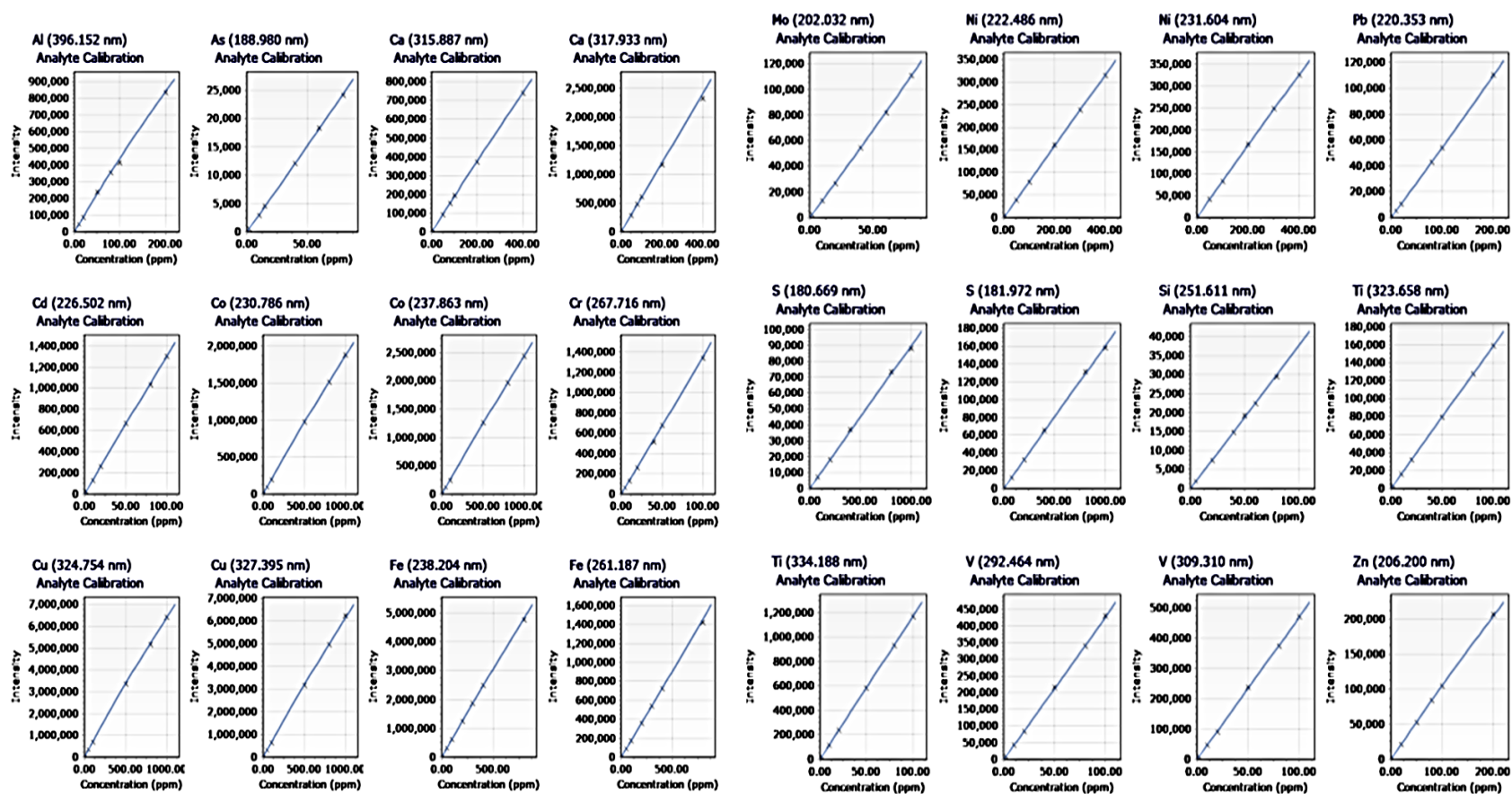


Figure S1: Calibration curves for (Ni, Co, Mn, Mg, S, Fe, Cu, V, Zn, Ti, Cd, Mo, Ca, Al and Pb)

Table S1: Results for the solid precipitate from the pregnant nickel solution

Solution	Mg	Si	Ca	Ti	V	Cr	Mn	Co	Cu	Zn	Pb	Al	As	Fe	Li	Mg	Ni
	280.270	288.1	317.9	334.9	290.8	267.7	257.6	230.7	324.7	206.2	220.3	394.4	188.9	261.3	670.7	285.2	222.4
Label	nm %	58	33	41	81	16	10	86	54	00	53	01	80 nm	82	83	13	86
		nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	%	nm	nm	nm	nm
		%	%	%	%	%	ppm	%	%	ppm	ppm	%		%	%	%	%
AMIS56	10.576	21.14	8.328	0.144	0.009	0.128	0.15	0.009	0.141			3.8	-0.003	6.88	0.027	11.12	0.209
													u			9	
Amis56 Acc Value	10.71	22	8.34	0.14	0.01	0.13	0.15		0.14			3.88		7.02		10.7	0.2
51/71	8.019	11.75	1.203	0.06	0.005	0.131		0.11	2.596			0.725	-0.003	19.88	0.023	8.28	5.053
													u				
51/71 Accuracy Value						0.14		0.13	2.87								5.54
SARM42							780		17.15	43.55	12						
SARM42 Accuracy						800			17	44	10						

te																	
Value																	
FE-	0.086	6.24	6.938	0.078	0.003	0.017	8.96	0.003	0.344	88.93	30.48	1.071	0.003	7.34	0.015	0.099	6.156
PPT/A																	
FE-	0.085	6.17	7	0.078	0.003	0.014	8.06	0.002	0.342	86.21	30.57	1.084	0.002	7.42	0.017	0.1	6.012
PPT/B																	
FE-	0.098	6.69	7.01	0.077	0.003	0.016	8.65	0.003	0.356	86.76	29.54	1.08	0.003	7.31	0.017	0.133	5.986
PPT/C																	
Mean	0.086	6.24	7	0.078	0.003	0.016	8.65	0.003	0.344	86.76	30.48	1.08	0.003	7.34	0.017	0.1	6.012
RSD	0.007	0.282	0.039	0.001	0.000	0.002	0.457	0.001	0.008	1.438	0.570	0.007	0.001	0.057	0.001	0.019	0.092
%																	
Ni-	0.189	0.47	9.212	0.007	0	-	22.66	0.01	0.151	298.9	0	0.109	0.001	0.11	0.016	0.212	26.98
PPT/A																	
Ni-	0.192	0.53	9.059	0.007	0	0	21.2	0.011	0.149	297.2	0	0.117	0.001	0.11	0.016	0.219	26.84
PPT/B																	
Ni-	0.187	0.5	9.106	0.008	0	0.001	21.36	0.011	0.144	306.4	0	0.113	0.001	0.1	0.017	0.208	27.34
PPT/C																	
Mean	0.189	0.5	9.106	0.007	0	0	21.36	0.011	0.149	298.9	0	0.113	0.001	0.11	0.016	0.212	26.98
RSD	0.00251	0.03	0.078	0.000	0	0.001	0.800	0.000	0.003	4.902	0	0.004	0	0.005	0.000	0.005	0.258
%	66		37	58			75	58	61	9				77	58	57	91

Table S2: Results for the solution samples at different precipitate pH

	pH	K	Na	Al	Ca	Cu	Fe	Mg	Ni	Pb	S	Si	Zn	Ag	Ca	Cd	Co	Cr	Mn
Description		ppm	ppm	ppm	g/L	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Nickel ppt Feed	0	22.5		7.37		3870	4720	2.69	62300	10.1	162	4.04	73.9	0.25	4.53	0.23	9.8	3.5	6.7
Nickel ppt Feed	0	22.5		7.3		3860	4720	2.73	62700	10.2	162	4.11	74.1	0.25	4.87	0.24	9.78	3.51	6.7
Mean		22.5		7.335		3865	4720	2.71	62500	10.15	162	4.075	74	0.25	4.7	0.235	9.79	3.505	6.7
RSD %		0.00		0.05		7.07	0.00	0.03	282.84	0.07	0.00	0.05	0.14	0.00	0.24	0.01	0.01	0.01	0.00
Nickel ppt pH 2.026	2.02	35.1	184	207	50.2	2390	238	501	33400	5.7	127	93.3	45	0.16		0.02	6.87	0.22	2.37
Nickel ppt pH 2.726	2.73	25.1	192	48	50.2	2100	1.87	491	33200	5.13	122	32.9	43.4	0.15		0.02	6.39	0.09	2.13
Nickel ppt pH 3.020	3.02	24.7	190	31.7	50.3	1770	0.3	490	32900	4.91	124	36.3	42.8	0.15		<0.02	6.39	0.02	2.07
Nickel ppt pH 3.567	3.57	24.7	193	12.5	49.7	501	0.56	506	33800	3.36	127	23.4	41.9	0.15		0.02	6.28	0.15	2.09
Nickel ppt pH 4.023	4.02	25.1	183	11.2	52.4	155	0.09	507	31700	1.8	1.27	18.6	40.1	0.15		0.02	6	0.05	2.08
Nickel ppt pH 4.023	4.02	25.1	184	11.2	53.2	155	0.06	507	0	1.73	127	19.4	40.2	0.14		0.02	6.02	0.03	2.06
Mean		25.1	183.5	11.2	52.8	155	0.075	507	31700	1.765	127	19	40.1	0.14		0.02	6.01	0.04	2.07

RSD %	0	0.71	0.00	0.57	0.00	0.02	0.00	0.00	0.05	0.00	0.57	0.07	0.01		0.00	0.01	0.01	0.01	
Nickel ppt	4.54	26	209	11.6	53.5	22.8	0.2	524	29600	<0.02	129	23.8	36.1	0.15		0.02	5.64	0.07	2.14
pH 4.544																			
Nickel ppt	5.04	26.7	207	11.6	55.3	3.96	<0.02	524	28200	<0.02	128	14.1	11.2	0.13		<0.02	4.82	0.02	2.02
pH 5.037																			
Nickel ppt	5.51	26	198	12.8	58.5	2.19	0.02	533	18900	<0.02	123	4.22	0.5	0.1		<0.02	1.36	0.02	1.47
pH 5.508																			
Nickel ppt	6.04	26.5	185	13.3	66.9	0.23	0.42	546	3200	<0.02	119	3.05	0.33	0.05		<0.02	0.54	0.1	0.54
pH 6.042																			
Nickel ppt	6.51	26.4	191	13.5	65.7	0.49	0.59	531	600	<0.02	119	2.88	0.58	0.04		<0.02	0.43	0.08	0.14
pH 6.507																			
Nickel ppt	6.51	26.4	191	13.5	65.7	0.47	0.45	531	604	<0.02	120	2.69	0.54	0.04		<0.02	0.43	0.14	0.14
pH 6.507																			
Mean	26.4	191	13.5	65.7	0.48	0.52	529	602			119	2.78	0.56	0.04			0.43	0.11	0.14
RSD %	0	0.00	0.00	0.00	0.01	0.10	2.12	2.83			0.71	0.13	0.03	0.00			0.00	0.04	0.00

APPENDIX E: Battery Grade Nickel Sulphate from Ni(OH)_2 Dissolution