

Investigation on the Synergistic Effect of Using Calcium Hypochlorite and Sodium Chloride During the Leaching of Silver from PCB e-waste

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Abstract: *This study applied Response Surface Methodology (RSM) to investigate the interaction between Calcium Hypochlorite (HTH) concentration, Sodium Chloride (NaCl) concentration and contact time on the leaching of silver (Ag) from PCB e-waste. A Central Composite Design (CCD) was generated by Minitab, which was used to guide the experimental procedure and optimize the process parameters. The outcome of the experimental results highlight that the extraction of silver relies on the chloride ion concentration and contact duration. The contour plot and surface plots demonstrated minimal silver extraction (<0.05) at low NaCl concentrations (<2.0 M) and short contact times (<150 min), while optimum extraction (0.18 - 2.0, ~ 20% recovery) occurred at NaCl = 2.5 - 3.0 M, HTH = 0.20 - 0.25 M, contact time = 200 – 250 min. Beyond these ranges, the response plateaued, suggesting equilibrium controlled kinetics.*

The observed trends align with chloride complexation mechanisms involving the formation of AgCl₂-2 and AgCl₂-3 species. The results confirm that chloride-based systems enhance silver dissolution efficiency while reducing the environmental footprint compared to cyanide leaching. Overall, the RSM approach effectively optimized the process parameters, establishing a robust foundation for future scale up and integration of chloride-assisted silver recovery within sustainable metallurgical processing frameworks.

Keywords: *E-waste, Silver, Leaching, Calcium Hypochlorite, and Sodium Chloride*

I. Introduction

The pursuit of sustainable development necessitates industrial processes that are not only economically viable but also ecologically durable. This requires a shift into circular economy, emphasizing 100% end of life waste recovery, recycling and reuse to enhance resource efficiency and minimize waste generation (Hagelken, Lee-Shin, Carpentier & Heron, 2016). End-of-life waste from electrical and electronic equipment (WEEE or e-waste) represents a critical sector for implementing circular economy principles. Often termed “urban mining”. E-waste recycling is crucial due to the rich concentration of valuable minerals it contains (Hagelken & Meskers, 2009).

E-waste is one of the fastest-growing waste streams globally, with annual generation estimated at millions of tonnes, a figure that continues to rise with technological advancement and reduced device lifespans (Balde et al., 2014). A significant and valuable component of e-waste is the printed circuit board (PCB), which, despite constituting only about 3% of the total weight of e-waste, contains a highly complex mixture of materials, including a substantial fraction of precious and base metals (Goosey & Keller, 2003). They concentrate an estimated 40% of its economic value, harbouring a complex mixture of metals like copper, tin, nickel, and most notably, precious metals such as gold and silver (Vakilchap

& Mousavi, 2022). The recovery of these metals is crucial for creating a circular economy, reducing the immense environmental footprint of virgin mining, and improving the economic viability of recycling operations.

Silver (Ag) is a key valuable metal found in PCBs, prized for its high electrical conductivity and corrosion resistance. Efficient recovery of these metals is essential not only for economic gain but also to mitigate the environmental hazards associated with their disposal in landfills or through informal recycling (Cui & Zhang, 2008). For instance, studies focusing on mobile phone PCBs have found significant and highly variable concentrations of silver, highlighting its economic importance as a target metal (Vats & Singh, 2025). The efficient and environmentally sound recovery of metals from PCBs is therefore essential for closing the material loop, reducing the environmental footprint associated with virgin mining and improving the economic viability of e-waste recycling operations.

This proposed synergy of chemicals is in line with the industry's goal of innovatively developing simpler and robust recovery methods. A study conducted by Pietrantonio et al., (2025) on leaching waste from discarded mobile phones indicated the simplicity in which the leaching reactions occur.

Conventional hydrometallurgical methods for metal recovery from e-waste often involve strong acids (e.g., nitric acid, aqua regia) or cyanide, which are highly effective but generate toxic gaseous emissions and hazardous liquid effluents, posing significant environmental and safety concerns (Jadhav & Hocheng, 2015). In response to these concerns, research has explored alternative methods such as the use of thiourea, which produced high recoveries however, it is an expensive process, which requires high chemical consumption and tends to decompose, and these are some of its limitations (Sanberg & Huiatt, 1986a). In addition to this alternative method, an emerging technology including the use of chloride-based leaching systems is being explored, such as the application of ferric chloride in the digestion of silver from various sources (IstroOdziejci, 1998; Sanberg & Huiatt, 1986b). The chemistry involved in chloride-based systems include the formation of chloride complexes, which have high stability and can prevent the passivation that can impede other processes (Maudos et al., 1966).

To enhance the effectiveness of a chloride-based system, an oxidant is commonly used. Recent publication has indicated the capability of acid chloride heap leaching to extract a wide range of metals, including precious metals (Dreisinger et al., 2015). Hypochlorite, commonly used as an oxidant can enhance the dissolution properties of the sample by effectively breaking down refractory components and liberating precious metals (Norris et al., 2017). Due to these abilities, this method has demonstrated potential application in the recovery of valuable metals from complex matrix systems such copper anode slimes (Dong et al., 2020) and newer waste streams like solar panels (Wongnaree et al., 2020).

However, using hypochlorite alone as the leaching lixiviant occurs to be an expensive process due to its high reagent consumption and non-selective reactions. To address this issue, the synergist effect of hypochlorite (HTH) and a salt, sodium chloride (NaCl) in this case is explored, providing avenue for research. The chloride ions form a complexation with the target metal, enabling the solubility of silver as silver chloride. Hypochlorite provides highly oxidative environment enabling the breakdown of material components. By investigating the interaction between these two chemicals, this study aims to develop a predictable and effective process that uses readily available chemicals to address the uncommon challenge of e-waste, paving the way to further investigate other methods that aim to address the same problem.

The fundamental research gaps that have been identified include studies that do not explore the explicit investigation on synergistic effect of using calcium hypochlorite and sodium chloride during the leaching of silver and the precise reaction mechanism that occurs

2. Methodology

2.1. Equipment & Chemical Required

The equipment used included: Personal Protective Equipment (PPE), Reaction vessel, Magnetic Stirrer, Thermometer, pH meter, Vacuum filtration, Atomic Adsorption Spectroscopy (AAS), Scanning Electron Microscopy (SEM), and X-Ray Diffractometer (XRD). The chemicals used were: Sodium Chloride (NaCl), Deionized water (H₂O), Calcium Hypochlorite (HTH), Concentrated Nitric Acid (HNO₃) for acid digestion, and Hydrochloric Acid (HCl) for acid digestion.

2.2. Preparation of E-waste & Leaching Experiments

The PCB e-waste was prepared and characterized. For quantification of the head sample, a 5g sample of >2 mm PCBs was digested in 100 ml Aqua Regia in a 500 ml beaker. Digestion conditions were 3hrs, 180 rpm, and 110°C, following a ratio of 5g PCB/100ml aqua regia. The solution was then analyzed using Atomic Adsorption Spectroscopy (AAS).

For the leaching experiments, a 2 g sample mass of PCB was used. A 25 ml leach solution was prepared with varying concentrations of NaCl (1.5, 2.5, & 3.5 M) and HTH (0.1, 0.2, & 0.3 M). The leaching was conducted at T=25°C and 300 rpm for varying contact times (1, 3.5, & 6 hrs). After solid-liquid separation, the pregnant solution was analyzed using AAS, and the solid residue was characterized using Scanning Electron Microscopy to determine if silver was removed or if a passivation layer was present.

2.3. Experimental Design for Statistical Analyses and Optimization

Response surface methodology was applied in selecting the parameters used to determine the optimal combination that would produce the highest silver extraction and the statistical software Minitab was used. The design type was selected to be Central Composite Design (CCD) which was used to establish the design of experiments (DOE) for optimal silver recovery from the synergistic combination. The table below illustrates the selected manipulated variables which were HTH concentration, NaCl concentration and contact time. All selected manipulated variables were studied using two levels (-1 and 1) on the CCD. The output variable was recorded as silver extraction. The manipulated variables and their levels are shown in the table below.

TABLE I: UPPER AND LOWER LIMITS OF THE PARAMETERS

Variable	Parameter	Units	-1	1
A	HTH concentration	M	0.1	0.3
B	NaCl concentration	M	1.5	3.5
C	Contact time	Hours	1	6

HTH concentration

Range: 0.1 – 0.30 M

Justification: Small concentrations (0.1 M) enable researcher to observe leaching kinetics at low concentration (Almeida & Amarante, 1995). Simultaneously, high concentration of oxidant (0.30 M) certifies that the leaching kinetics do not rely on the amount of oxidant available (Dong et al., 2020). This demonstrates stages where oxidant availability in the system no longer limits the occurrence of reactions. Using oxidation concentration higher than 0.3 M can lead to unwanted material being oxidized too, facilitating their breakdown such as base metals and organic components. The oxidation of unwanted material increases reagent consumptions and impedes the process (Almeida & Amarante, 1995; Dong et al., 2020)

NaCl concentration

Range: 1 – 3 M

Justification: The selection of the lower bound value is based on the significance that it provides excess amount of chloride ions beyond stoichiometric requirement to form AgCl_2^- or AgCl_3^{2-} , which prevents formation of passivation by AgCl (s) (Maudos et al., 1996).

The higher bound numerical value was selected to supplement for salt ions that may dissolve in water. Using strong salt solutions has proven to be effective in the recovery of metals out of sulfides.

Contact time

Range: 60 – 360 minutes

Justification: The use of the lower bound value is important because it enables the operator to observe the speed at which the target metal dissolves initially before a protective layer could form on the surface or the oxidant becomes weaker. The higher bound is necessary to enable the entire dissolution of Ag from the sample, it allows for maximum recovery to occur, where overtime the leaching kinetics begin to slow down only

recovering little extra silver.

TABLE II: ANOVA ANALYSIS OF VARIANCE

Analysis of Variance					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	2	1161034	580517	150,93	0,000
Error	117	450020	3846		
Total	119	1611055			

The ANOVA results provides a P-value that is equal to zero, which suggests that the synergistic system is a highly efficient method in leaching Ag from PCB e-waste. The observed value of P demonstrates that the differences that occur across various tested experimental treatment are not due to random chances. Furthermore, the F-value of 150.93, which provides information on the variations that are observed when changes in reagent formulation are induced, is greater than the inherent experimental error. This further demonstrated that contact time and the synergistic blend of the two reagents, are a major determinant in the leaching process, confirming the core hypothesis that these reagents interact in a way that directly and powerfully affect silver dissolution.

3. Results and Discussion

3.1. Characterization of the leachate

The leach solution after leaching tests were conducted, was analysed using Atomic Adsorption spectroscopy (AAS) as mentioned in the methodology, where the table below lists the respective Ag % recoveries for each experimental run as per Minitab design of experiment (DOE). According to the table, the highest % yield was recorded at 13,9687037 % with a predicted % yield of 6,367762095 %, which suggested that the actual % recovery was more or less double the predicted % yield. This was one of the rare cases where the difference between the actual and predicted % values exceed the common difference which can be attributed to the fixed but uncontrolled temperature variations under the fume hood that are influenced by unstable room temperature induced through weather conditions.

Table 3 below demonstrates the difference in the actual experimental values and the model predicted values, where the average difference between the actual value and predicted value was calculated to be

0.04, which suggested that the fitted Response Surface Methodology model was able to establish a substantial and reliable relationship between the factors that play a role in the leaching system.

TABLE III: ACTUAL AND PREDICTED YIELD % AG

HTH Concentration	NaCl Concentration	Contact time	Silver Extraction (mg/L)	Ag % Actual	Predicted Yield	Ag % Predicted
0,2	2,5	210	0,132863149	1,32863149	0,128925051	1,28925051
0,2	3,5	210	0,014439119	0,14439119	0,10110437	1,011043702
0,1	3,5	60	0,035010528	0,350105278	0,039280089	0,392800887
0,2	2,5	210	0,032351755	0,323517546	0,128925051	1,28925051
0,1	1,5	360	0,022412527	0,224125274	0,092062701	0,920627009
0,3	3,5	360	0,014649876	0,146498755	0,140274033	1,402740329
0,2	2,5	210	0,040421505	0,404215045	0,128925051	1,28925051
0,2	2,5	210	1,17530918	11,7530918	0,128925051	1,28925051
0,3	2,5	210	1,20296371	12,0296371	0,441656905	4,416569053
0,2	2,5	360	0,009242147	0,092421472	0,053569928	0,535699284
0,2	2,5	210	0,032479543	0,324795432	0,128925051	1,28925051
0,2	1,5	210	0,034881704	0,348817036	0,044933634	0,449336338
0,2	2,5	210	0,026551999	0,265519992	0,128925051	1,28925051
0,1	1,5	60	0,018348077	0,183480773	0,10997495	1,099749505
0,2	2,5	210	0,025895003	0,258950032	0,128925051	1,28925051
0,3	1,5	360	0,004421495	0,044214954	0,002546936	0,025469359
0,3	1,5	360	0,004421495	0,044214954	0,002546936	0,025469359
0,1	3,5	60	0,035010528	0,350105278	0,039280089	0,392800887
0,2	2,5	210	0,024658701	0,246587005	0,128925051	1,28925051
0,1	3,5	360	0,069159314	0,69159314	0,099387309	0,993873091
0,3	3,5	60	1,39687037	13,9687037	0,636776209	6,367762095
0,3	1,5	60	0,034060728	0,340607278	0,153250191	1,532501914
0,2	1,5	210	0,026990568	0,269905683	0,044933634	0,449336338
0,1	1,5	360	0,003696426	0,036964258	0,092062701	0,920627009
0,2	2,5	210	0,032107681	0,32107681	0,128925051	1,28925051
0,3	2,5	210	0,018553373	0,185533725	0,441656905	4,416569053
0,3	3,5	60	0,040096238	0,400962383	0,636776209	6,367762095
0,1	3,5	360	0,001769817	0,017698174	0,099387309	0,993873091
0,2	3,5	210	0,014439119	0,14439119	0,10110437	1,011043702
0,1	1,5	60	0,018348077	0,183480773	0,10997495	1,099749505
0,1	2,5	210	0,003044857	0,030448567	0,190213663	1,902136634
0,2	2,5	60	0,01383007	0,138300695	0,093662334	0,936623342
0,2	2,5	360	0,009242147	0,092421472	0,053569928	0,535699284
0,2	2,5	210	0,023451308	0,234513078	0,128925051	1,28925051
0,2	2,5	210	0,018762048	0,187620483	0,128925051	1,28925051
0,3	3,5	360	0,014649876	0,146498755	0,140274033	1,402740329
0,1	2,5	210	0,017588235	0,175882354	0,190213663	1,902136634
0,2	2,5	210	0,025430666	0,254306663	0,128925051	1,28925051
0,2	2,5	60	0,026279485	0,262794849	0,093662334	0,936623342
0,3	1,5	60	0,008133646	0,081336461	0,153250191	1,532501914

3.2.Characterization of Computer PCBs

The results of XRF analysis of computer PCBs are illustrated in the table below, showing the complex multi-metal matrix of the feedstock, including a measurable content of Ag₂ O at 0.1937% by mass. Other metal elements such as Sn are present in significant amounts (7.7376%) in the sample however, due to the objectives of this experiment, the synergistic effect of the system was designed to target Ag as it a scarce metal. This is further supported by its minimal existence in the sample, therefore, the development of innovative recycling methods need to be established, which supports the goal of this project. Table 4 below provides the X-Ray fluorescence analysis of the PCB sample.

3.3. Atomic adsorption spectroscopy

To further confirm the presence of Ag in the PCB sample, Atomic Adsorption spectroscopy on the prepared aqua regia solution confirmed a further concentration of Ag as 10 ppm. The extraction efficiencies were calculated according to the

10-ppm head grade. Below, is a table that demonstrates the recorded AAS value during analysis of the head grade. Table 5 Head grade of the aqua regia sample

In Atomic Adsorption spectroscopy, the head grade sample went through three resample processes to ensure that the recorded mean value of 10.6466188 mg/L was accurate. However, this value is the corrected concentration, with an actual concentration of 0.967874467 mg/L.

3.4. Scanning Electron Microscopy

The SEM/EDS was used to analyse the PCB sample, however due to the effect of mass, only the prominent elements were detectable on the EDS results. The SEM/EDS was able to detect other metals such as Pt, Al, Cu and Sn which existed in significant amounts in comparison to Ag which existed at about 0.1937% according to the XRF results. The presence of Ag was further confirmed by AAS results on the aqua regia head sample analysis. Further confirmation was established through the recorded experimental on Table x above.

TABLE IV: X-RAY FLUORESCENCE OF THE SAMPLE

Component	Unit	Result	Component	Unit	Result
Na2O	mass%	0.0000	Co2O3	mass%	0.0516
MgO	mass%	1.5174	NiO	mass%	1.3117
Al2O3	mass%	3.9015	CuO	mass%	4.3530
SiO2	mass%	13.4890	ZnO	mass%	5.0341
P2O5	mass%	1.5504	Br	mass%	6.3871
SO3	mass%	1.6992	SrO	mass%	0.3388
Cl	mass%	0.5840	Ag2O	mass%	0.1937
K2O	mass%	0.1529	SnO2	mass%	7.7376
CaO	mass%	2.3773	I	mass%	1.2021
TiO2	mass%	1.1042	BaO	mass%	1.0602
Cr2O3	mass%	0.2736	PbO	mass%	2.7833
MnO	mass%	7.2978	Bi2O3	mass%	0.1390
Fe2O3	mass%	35.4604			

TABLE V: AQUA REGIA AAS

Sample ID	Mean	SIGNAL	Rsd	FLAGS	CONC.	CORRECTED CONC.	TIME
Aqua regia 1	Resample 1 of 3	0.0352453627	%		mg/L		12:36:59 6/22/2010
Aqua regia 2	Resample 2 of 3	0.0442072898					12:37:04 6/22/2010
Aqua regia 3	Resample 3 of 3	0.0447797962					12:37:08 6/22/2010
Aqua regia	Mean	0.0195006467	36.6277122		0.967874467	10.6466188	
Aqua regia 1	Resample 1 of 3	0.0234234687					12:40:00 6/22/2010
Aqua regia 2	Resample 2 of 3	0.0238222219					12:40:04 6/22/2010
Aqua regia 3	Resample 3 of 3	0.0112562496					12:40:08 6/22/2010

3.5. Leaching Results

The surface plot below provides quantitative insight into the experimental outcomes for silver recovery. The paired factors in the first case include Calcium Hypochlorite (HTH) and Sodium Chloride (NaCl) which were tested between ranges 0.1 to 0.3 M and 1.8 to 3 M respectively where across all these parameters values the silver (Ag) recovery remained at a minimum of approximately 0.05 to a maximum around 0.45. This visual representation demonstrates the possible variabilities that influence process efficiency across the experimental domain (Almeida & Amarante, 1995).

Maximum Ag recovery at ~ 0.45 was observed in regions where the HTH concentration was near its highest pre-determined level at approximately 0.3 M while NaCl concentration were low at values around 1.8 M to 2.4 M. Additionally, low extraction efficiencies were recorded at regions where both the NaCl and HTH concentration were high, which suggested a complex interaction between the factors rather than a linear response to increased reagent concentration.

Based on the observed results, the synergistic system stands as a potential replacement for toxic recovery methods and potential for industrial application. The synergistic combination offers a safer alternative in comparison to cyanide leaching systems. This demonstration is consistent with already

existing literature where multiple metals were recovered using similar robust chloride systems (Dong et al., 2020).

The contour plot above visually demonstrates the dependence of silver extraction on both the reagents (HTH and NaCl) as oxidant and complexation agents respectively. The model outcomes are demonstrated as lowest and highest efficiencies ranging from 5% (blue region) to 50% (dark green region) which suggested an overall improvement of ~45% points. The dissolution of silver was observed to be at a minimum when HTH concentrations that range between 0.12 to 0.18 and moderate NaCl levels at around 2.0 to 3.0 were tested, which emphasised the importance of oxidation process as a rate-limiting factor. Additionally, increasing the concentration of HTH to ~0.26 and NaCl to ~ 3.2 has demonstrated the improvement on extraction to roughly 46% which corresponds to ~ 475% in silver recovery compared to baseline.

The most prominent finding based on the above contour plot is demonstrated by the diagonal orientation of the contour lines, which suggest that the simultaneous increase of both reagents produce a non-additive, enhanced effect. This observation supports existing literature in that silver solubilization in chloride-based systems depend on the simultaneous oxidation and complexation reactions, where the mechanism of the system is based on the ability of HTH to provide an oxidative environment and the Cl ions from NaCl enhance the complexation of silver ions, continuously driving the dissolution equilibrium forward (Sandberg & Huiatt, 1986b). The curvature of the contour lines demonstrated that at upper reagent concentrations, the dissolution rate becomes limited by secondary factors such as mass transfer or the precipitation of silver chlorides.

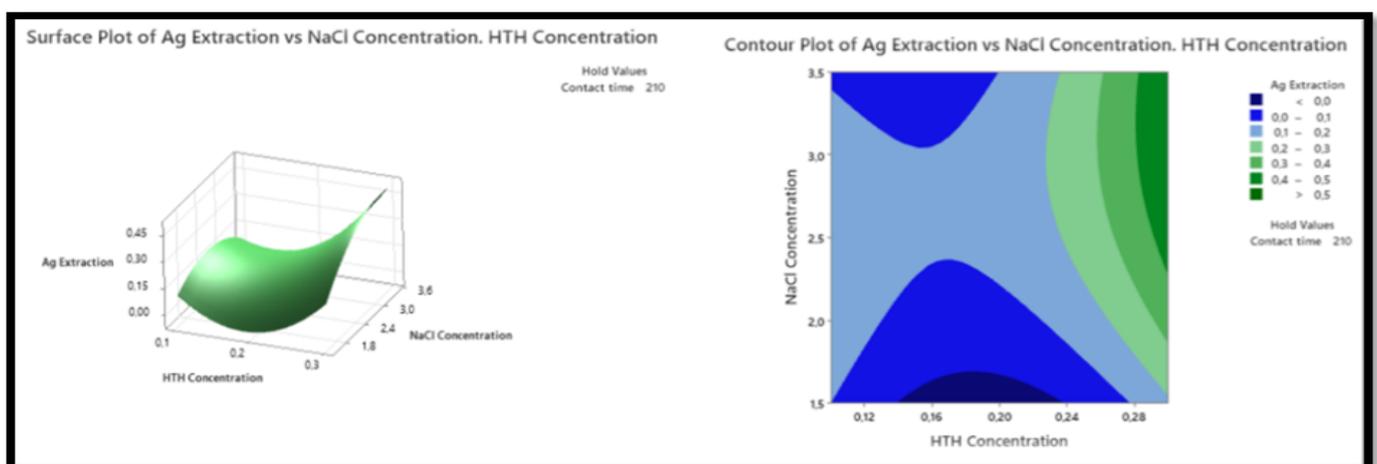


Fig. 1: NaCl vs HTH concentration surface and contour plots respectively

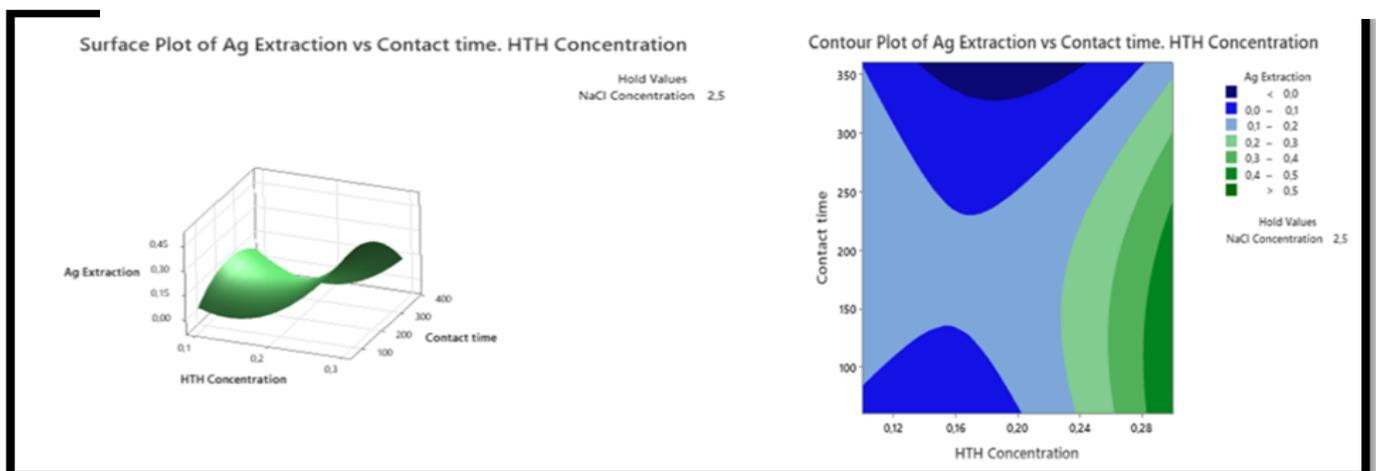


Fig. 2: Contact vs HTH concentration surface and contour plots respectively

The surface plot and contour plot illustrated below are based on the extraction of Ag as a function of HTH concentration and contact time at a fixed NaCl concentration of 2.5, which indicated a non-linear but significant improvement on the recovery of silver as the oxidant concentration increased simultaneously with contact time. It was observed that at contact times below 150 min and low HTH concentrations, the dissolution of Ag remained below 10% represented visually by the dark blue region in the contour map. When both parameters were increased, it was observed that the efficiency improved to ~ 45% to 50% at HTH concentration of ~ 0.26 to 0.28 while contact time increased from 300 to 350 minutes, which signified an increased recovery of silver in comparison to the baseline region. The concave-up curvature of the surface plot suggests that a second order interaction between the parameters exists, which is typical for RSM optimization models reflecting on the synergistic kinetics between the two parameters

The tendency of the oxidizing agent (HTH) to penetrate deeper into particle matrices, was enhanced when contact time was increased which facilitated improved Ag dissolution. This is contrary to conditions where HTH concentrations were low and contact duration were short, where the oxidation process was not allowed sufficient time to occur resulting in insufficient oxidation to overcome kinetic limitations, which resulted in poor Ag recovery %. These findings are supported by Almeida and Amarante (1995) and Maudos et al., (1996), where longer contact durations in oxidative conditions increased the probability of Ag-Cl complex formation, particularly AgCl_2^- and AgCl_3^{2-} , stabilizing dissolved silver in solution.

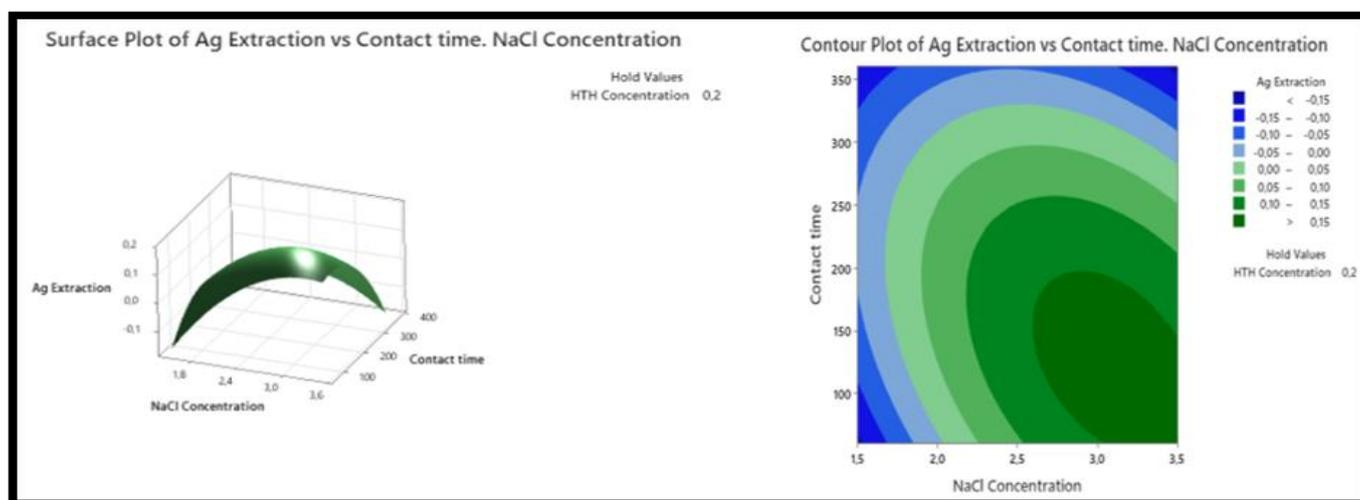


Fig. 3: NaCl vs. Contact time surface and contour plots respectively

In comparison to all available parameter combinations, the NaCl concentration and contact time combination produced the best results with the optimum range being visually demonstrated. It can be observed that at low NaCl concentrations (1.5 - 2M) and short contact duration (<150 min), the yield % produced was negligible or slightly negative (<-0.05), which suggested minimal effect of the synergistic combination or due to possible formation of passivated layer. However, as the NaCl concentration increases (2.5 - 3M) simultaneously with contact time (200 – 250 mins), an improvement in the extraction of Ag was observed to approximately 0.15-0.20 which suggests an increase of 20 - 25% in dissolution efficiency. At values beyond 3 M or 300 min, the surface plots become flattened, indicating that equilibrium conditions and diminishing returns prolonged leaching.

These results agree with conclusions from chloride mediated complexation mechanisms. Studies by Almeida and Amarante (1995) and Maudos et al., (1996) concluded that silver dissolution in chloride media is possible through the formation of AgCl_2^- and AgCl_3^{2-} complexes. The results obtained in regions where the NaCl concentration was around 0.28 M, support Almeida (1995) and

Maudos (1996) conclusions, as moderate chloride levels enhance the complex stability and ionic strength without excessive AgCl re-precipitation (Fuerstenau & Wang, 1997; IstroOdziej, 1988). Furthermore, in the light green regions, it is where the system's optimal conditions were observed, with extraction efficiency changing from 0.1 to 0.2, demonstrating an estimated 100% improvement compared to the blue region (<0.05).

Contact duration plays a secondary but crucial role in kinetics. At contact duration of 100 min, the silver recovery is significantly low at values below 0.05 across all pre-determined NaCl levels, which suggested a reaction-controlled system. The slope of the surface plot was observed to increase between contact duration of 200 – 250 min, which suggested that the system at this level was diffusion-controlled, this observation is supported by similar findings from articles by Sandberg and Huiatt (1986a) and Dong et al., (2020) on chloride heap leaching. Overall, the conditions recommendable to achieving maximum recovery lie around NaCl concentration of 2.5 to 3 M and contact times between 200 – 250 minutes, producing a recovery of up to 0.2 which is equivalent to ~ 20% of total recoverable Ag under hydrometallurgical chloride leaching systems

The outcome of the study demonstrates that the combination of the two reagents stands as a potential replacement method. The evidence is guided by the applied Response Surface Methodology which aimed to optimize process parameters of the system and confirmed that the interaction between the two reagents is synergistic rather than additive. Across all contour plots, the recovery of Ag has increased gradually when the reagent concentrations and contact duration were optimized. At NaCl concentration of 2.5 - 3.0 M, HTH concentrations of 2.0 - 2.5 M, and contact time of 200 min – 250 min, the recovery reached 0.18 to 0.20, which suggested an improvement of up to 200% when compared to low-parameter zones (<0.05). These optimal regions confirm the formation of stable Ag complexes such as AgCl_2^- and AgCl_2^{2-} that enhance the solubility and mass transfer of chloride media.

4. Conclusion

The above results confirm that the synergistic effect of the system is a feasible idea such that it promotes silver dissolution under moderately oxidizing conditions, in agreement with earlier findings by Almeida and Amarante (1995) and Maudos et al., (1996). Extended leaching duration has proven to improve extraction up to equilibrium, where beyond this period a plateau occurred, which suggested diffusion-controlled kinetics and solid-liquid interfacial limitations also reported by Sandberg and Huiatt (1986a) and Dong et al. (2020). The applied parameter ranges also considered the risk of re-precipitation of AgCl and surface passivation, hence they were kept as minimum as possible. This highlighted the need for controlled reagent balance during hydrometallurgical operation.

The mechanism of the system is based on a dual-action process where HTH as an oxidant serves to provide an oxidative environment while NaCl chloride ions facilitate the complexation of metallic silver into soluble complexes such as AgCl_2^- and AgCl_2^{2-} . This synergistic combination continues to drive forward the dissolution equilibrium while effectively preventing passivation through AgCl (s) layer formation.

Overall, the RSM contour plot demonstrated NaCl concentration as the most influential parameter, followed by HTH concentration and then contact time. The results of the project support the goal of transitioning into clean hydrometallurgy by offering an environmentally viable and efficient method for silver recovery from complex or secondary sources (Dong et al., 2020; Pietrantonio et al., 2025). These findings offer a data supported foundation for process optimization and potential industrial scale-up of chloride-based silver extraction systems.

5. Acknowledgment

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