

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMICAL ENGINEERING
(PROCESS ENGINEERING STREAM)

**SILVER RECOVERY AND OPTIMIZATION FROM WASTE X-
RAY PHOTOGRAPHIC FILM USING SODIUM HYDROXIDE
STRIPPING.**

By

Mekurialem Demelash Erku

DECEMBER, 2014

ADDIS ABABA, ETHIOPIA

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMICAL ENGINEERING
(PROCESS ENGINEERING STREAM)

**SILVER RECOVERY AND OPTIMIZATION FROM WASTE X-RAY
PHOTOGRAPHIC FILM USING SODIUM HYDROXIDE STRIPPING**

A thesis submitted to the research and graduate school of Addis Ababa University, Addis Ababa Institute of Technology, Department of Chemical Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in chemical engineering (Process Engineering stream)

Candidate: Mekurialem Demelash

Advisor: Dr-Ing. Abubeker Yimam

DECEMBER, 2014
ADDIS ABABA, ETHIOPIA

ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSTITUTE OF TECHNOLOGY
DEPARTMENT OF CHEMICAL ENGINEERING
(PROCESS ENGINEERING STREAM)

**SILVER RECOVERY AND OPTIMIZATION FROM WASTE X-RAY
PHOTOGRAPHIC FILM USING SODIUM HYDROXIDE STRIPPING**

A thesis submitted to the research and graduate school of Addis Ababa University, Addis Ababa Institute of Technology, Department of Chemical Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in chemical engineering (Process Engineering stream)

By: Mekurialem Demelash Erku

Approved by the Examining Board:

Chairman, Department's Graduate Committee

Advisor

Internal Examiner

External Examiner

ACKNOWLEDGMENT

My special thanks go to Dr. Abubeker Yimam for giving me his priceless advice and supervision throughout this study. I also would like to take this opportunity to express my thanks to Ato Anteneh Maregn and Ato Demisew Lema for giving me the subject for the thesis and idea that is valuable for the work. Special thanks must go to the technical assistants, Yosan, Hintsu, Nebiyu, Alene and Azeb for their help throughout the experimental work in showing the equipment and devices that I required and in making the setup for the processes. Last but not least, thanks also to my family for their patience, support and always ready to offer a helping hand. Above all, I thank God for this unreserved help to finalize this thesis.

Table of content

ACKNOWLEDGMENT	i
Table of content	ii
List of Acronyms	iv
List of tables	v
List of figures	vi
ABSTRACT	vii
1 INTRODUCTION	1
1.1 Background	1
1.2 Problem Statement	2
1.3 Objective of the Research.....	3
1.3.1 General objective.....	3
1.3.2 Specific objectives.....	3
1.4 Scope	3
1.5 Significant of the Thesis.....	4
2 LITERATURE REVIEW	5
2.1 About Silver	5
2.1.1 Characteristics	5
2.1.2 Isotopes.....	6
2.1.3 Chemical Properties and it's Compounds	7
2.1.4 Applications.....	9
2.1.5 Occurrence and Extractions.....	9
2.1.6 Human Exposure and Consumption.....	10
2.2 Silver in X-Ray Film	10
2.3 Silver in Photographic Waste (Waste X-Ray Photographic Film).....	13
2.4 Environmental Effects of Silver	13
2.5 The Most commonly used Technologies for Silver Recovery:	14

2.5.1	Electrolysis	14
2.5.2	Metallic Replacement.....	15
2.5.3	Chemical Precipitation	17
2.5.4	Other Recovery Process.....	17
3	MATERIALS AND METHODS.....	20
3.1	Material	20
3.2	Methods.....	21
3.2.1	Preparation of the Film:.....	21
3.2.2	Reagents Preparation:	22
3.2.3	Recovery of Silver	23
3.2.4	Quantitative Determination of Silver using Preliminary Experiments	25
3.3	Experimental Factors and Responses	26
3.3.1	Study Factors:.....	26
3.3.2	Measured Response.....	29
4	RESULTS AND DISCUSSION	31
4.1	Recovery of the recovered silver.....	31
4.2	Interpretation of the Result Using Experimental Design Software:	33
4.2.1	Pre- Analysis of Main Effects through Simple Plots.....	34
4.2.2	Pre- Analysis of Interaction Effects through 3D & contour-Surfaces.....	37
4.2.3	Screening of Factors.....	39
4.2.4	Diagnostic.....	42
4.2.5	Optimization.....	43
4.3	Characterization of the Product.....	44
5	CONCLUSION.....	48
6	RECOMMENDATION	50
7	REFERENCE.....	51
	Annex-1: Table of randomized design (actual) values.....	53
	Annex-2: Table of R ² values.	54
	Annex-3: Analytical result: percent & weight (g).....	54

List of Acronyms

3D- three-dimensional

MRC- metallic recovery cartridge

CRS- chemical recovery cartridge

XRF- x-ray fluorescence

KeV- kilo electron volts

RSM- response surface methodology

FCI- fixed capital investment

TPC- total product cost

ROI- returns on investment

List of Tables

Table	Page
Table 2.1: Comparison of Silver Recovery Methods	19
Table 3.1: Factors and the corresponding ranges and levels	27
Table 3.2: Combination of factors and levels	28
Table 4.1: Factors and determined response	32
Table 4.2: Design summary	33
Table 4.3: ANOVA for recovery of silver	40
Table 4.5 : Model coefficient for silver recovery or yield.	41
Table 4.6: constraints of optimization.....	43
Table 4.7: possible optimized solution.....	44
Table 4.8: Analytical Result and weight (g)	44
Table 4.9: Results ($\mu\text{g/g}$) for the trace impurities in the recovered silver and in comparison to some results for high purity silver in the literature	46

List of Figures

Figure	Page
Figure 2.1: Time trend of silver production	9
Figure 2.2: Exposed x-ray photographic film	10
Figure 2.3: Schematic Diagram for Typical Electrolytic Silver Recovery Process	15
Figure 2.4: Schematic Diagram for Metallic Replacement Process Using MRCs	16
Figure 3.1: Film preparation.....	21
Figure 3.2: Recovery process flow sheet.....	23
Figure 3.3: Laboratory setup for stripping the black silver from the film	24
Figure 3.4: The recovered sample.....	29
Figure 3.5: smelting of the dried black silver in a furnace.....	30
Figure 4.1: Effects of concentration on silver recovery.	35
Figure 4.2: Effects of stripping time on silver recovery (yield).....	36
Figure 4.3: Effects of temperature on silver recovery (yield).....	37
Figure 4.5: 3D & contour surface for time – concentration interaction	38
Figure 4.6: 3D & contour surface for interaction of temperature and concentration.....	38
Figure 4.7: 3D & contour surface for the interaction of temperature and time.....	39
Figure 4.8 : Predicted versus actual values for silver yield.....	42
Figure 4.9: Sample image on the purity-analyzing instrument.	44
Figure 4.10: Spectrum of silver on XRF instrument.....	45

ABSTRACT

Silver is a depleted precious resource and in the near future it all be used up. In addition to this, our country is not produced the metal at this moment. Extracting silver from enough silver-containing wastes like used X-ray photographic film will considerably save the foreign currency to import this metal. This work reports on a novel, simple, fast and cheap method to utilize waste x-ray film for recovering silver using sodium hydroxide stripping. In this study, the silver recovery was optimized against the stripping temperature, stripping time and sodium hydroxide concentration. Firstly, the film was washed, dried, cut and weighed. Then, the silver was stripped at three different factor's level i.e. sodium hydroxide concentration (0.5M, 1.5M and 2.5M), temperature (50 °C, 70 °C and 90°C) and time (1 min, 10.5 min and 20 min.). Finally, silver was recovered by precipitation using sodium sulphide. The yield or recovery was then determined using XRF. A maximum silver recovery of 54% w/w and a purity level of 98.02% were obtained. The experimental results were then analyzed using Design Expert Software (version 7.0.0) to determine the optimum operating conditions. The optimum operating conditions found to be a stripping temperature of 70.81°C, stripping time of 10.90 minute and NaOH concentration of 1.46M. It is concluded that waste x-ray photographic film can be stripped by NaOH and precipitated by Na₂S successfully and in most economical way.

Keywords: Silver recovery, waste photographic film, sodium hydroxide.

1 INTRODUCTION

1.1 Background

'Silver is one of the precious and noble metals used in large quantities for many purposes, particularly in the photographic industry. The waste X-ray/photographic films containing black Metallic silver spread in gelatin are very good source for silver recovery compared to other types of film. The amount of silver in the X-ray film varies between 1.5 and 2.0% (w/w). It has been reported that 25% of the world's silver needs are supplied by recycling out of which 75% is obtained from photographic waste. With an increasing demand for silver in the world, recent attention is focused on X-ray/photographic films as one of the secondary sources of silver owing to the considerable amount of silver present in them [1].

Various studies have been carried out to recover the silver from photographic/X-ray film wastes and following methods are reported in literature: (a) burning the film directly, (b) oxidation of the metallic silver following electrolysis, and (c) stripping the gelatin- silver layer using different solutions. Recovery of silver by burning the films directly, a conventional method used at present is the most primitive method and generates undesirable foul smell. The method causes environmental pollution and polyester film on which emulsion of silver and gelatin is coated cannot be recovered. The second and third methods have been used more extensively for the recovery of silver than the first method. In general, the methods reported for the recovery of silver from films involve two steps; the first is the separation of the silver from the film base, and the second the recovery of the silver by smelting or electrolysis. The first step is commonly leaching, which may be either chemical or microbiological. The use in chemical methods of reagents such as sodium cyanide, nitric acid or organic compounds causes environmental problems. Microorganisms can be used, but this process is slow. All methods have been broadly described in the literature [2-6].

This paper reports on a novel method for recovering high-purity silver from waste x-ray films using sodium hydroxide. The method is effective by following the stripping step and the recovery step of the silver recovery process by smelting.

1.2 Problem Statement

Researches show that silver-containing wastes like used X-ray photographic film are toxic and considered as hazardous wastes. Even if it was hard to know the exact amount of used x-ray films were disposed, it was possible to know the used film produced in black line hospital per day. As the hospital was reported around 5kg per day used films were collected excluding the film that handed by the patient. Other 50 hospitals in Addis Ababa (health indicators, FMOH: EFY 2001), if each releases 2kg per day, the total amount that has been deposited in Addis Ababa only become 105kg per day. However, our country's hospitals, clinics, and medical laboratories dispose these wastes without the knowledge of their toxicity. So, the Environmental Protection Agency (EPA) will require silver recyclers, hospitals and clinics to follow certain rules regarding used X-ray film disposal. Even if the used film is considered as personal information, which shows medical status of a patient, it must be destroyed since the silver and the other chemicals with in the film are toxic to human being and the environment. Therefore, recovering silver from X-ray phototgraphic waste, prevent the metal from entering the environment, and will has both environmental and economic benefit.

Since silver is a depleted precious resource and in the near future it all be used up and also not produced in our country, extracting silver from enough silver-containing wastes like used X-ray photographic film will save foreign currency to import this metal. This heavy metal is a valuable resource for manufacturing and economic trade. Recovering the silver from used film help keep it in the market place and out of the landfills, serving as an economic boost and helping the environment. Its sale can help hospitals, clinics and recyclers reduce the cost of disposal, earn extra income. Several technologies exist to recover silver from used X-ray photographic film such as burning the film, electrolysis, metal replacement, bacterial, and enzymatic methods and chemical precipitation. Except chemical methods, the other methods are expensive and time consuming to recover the silver. However, using the chemical method does not need much time, not expensive technology, fast and simple. The research that was done by Nuri Nakiboglu et.al, 2003 showed that recovery-using NaOH (chemical method) is more advantageous but they did not show the economical ways of silver recovery. Thus the intention of this paper is to optimize the different parameters that affect silver recovery using NaOH.

1.3 Objective of the Research

1.3.1 General objective

The main objective of this thesis work is to recovery silver from waste X-ray photographic film using NaOH and to optimize the process conditions.

1.3.2 Specific objectives

The specific objectives are-

- To investgate the stripping efficiency of NaOH silver from waste X-ray photographic film.
- To determine the dominant factors that affects the process.
- To optimization the process parameters, like temperature, concetration of NaOH, and contact time between the film and NaOH.
- To determine the amount of silver recovered and its purity.
- To determine trace metal impurities

1.4 Scope

This study covers the analysis of silver recovery from waste x-ray film using NaOH as a stripping agent and Na₂S as precipitating agent and identifying the trace metal impurities. Other potential sources such as photographic wastes like fixer and developer solutions, from which silver can be extracted, were not analyzed and the effect of other stripping and precipitating agents were not studied.

1.5 Significant of the Thesis

This thesis work has shown that there are different directions through which waste materials generated from medical centers used to recover valuable products in addition to make the environment safe. The interest in the technology of the recovery of silver has developed, as it has a wide range of applications. Recovering silver from photographic film waste has many importance both to the society and the country as a whole. First of all silver is a heavy metal that affects the environment if it is disposed even in trace amount. In addition since silver is among those metals used for ornamental purpose it's recovery will be economically beneficiery. Besides, this precious metal is brought to the country through foreign currency (0.49 dollar per gram), which is scarce now adays, thus the recovery will help to retain a big deal of foreign currency which could be expended otherwise. The availability of the waste raw materials and the alternative acheivable methods make the research more significant.

To summerize the points, the recovery has been significant:-

- To save the environment
- To reuse the silver for different purpose.

2 LITERATURE REVIEW

2.1 About Silver

Silver is a chemical element with the chemical symbol Ag and atomic number 47. A soft, white, lustrous transition metal, it possesses the highest electrical conductivity of any element and the highest thermal conductivity of any metal. The metal occurs naturally in its pure, free form (native silver), as an alloy with gold and other metals, and in minerals such as argentite and chlorargyrite. Most silver is produced as a byproduct of copper, gold, lead, and zinc refining.

Silver has long been valued as a precious metal, used in currency coins, to make ornaments, jewelry, high-value tableware and utensils (hence the term silverware) and as an investment in the forms of coins and bullion. Silver metal is used industrially in electrical contacts and conductors, in mirrors and in catalysis of chemical reactions. Its compounds are used in photographic film and dilute silver nitrate solutions and other silver compounds are used as disinfectants and micro biocides (oligodynamic effect). While many medical antimicrobial uses of silver have supplanted by antibiotics, further research into clinical potential continues.

2.1.1 Characteristics

Silver is produced from lighter elements in the Universe through the r-process, a form of nuclear fusion believed to take place during certain types of supernova explosions. This produces many elements heavier than iron, of which silver is one [7].

Silver is a very ductile, malleable (slightly harder than gold), monovalent coinage metal, with a brilliant white metallic luster that can take a high degree of polish. It has the highest electrical conductivity of all metals, even higher than copper, but its greater cost has prevented it from being widely used in place of copper for electrical purposes. An exception to this is in radio-frequency engineering, particularly at VHF and higher frequencies, where silver-plating to improve electrical conductivity of parts, including wires, is widely employed. During World War II in the US, 13,540 tons were used in the electromagnets used for enriching uranium, mainly because of the wartime shortage of copper [8].

Among metals, pure silver has the highest thermal conductivity (the nonmetal carbon in the form of diamond and superfluid helium II are higher) and one of the highest optical reflectivity [9]. (Aluminum slightly outdoes silver in parts of the visible spectrum, and silver is a poor reflector of ultraviolet). Silver is the best conductor of heat and electricity of any metal on the periodic table. Silver also has the lowest contact resistance of any metal. Silver halides are photosensitive and are remarkable for their ability to record a latent image that can later be developed chemically. Silver is stable in pure air and water, but tarnishes when it is exposed to air or water containing ozone or hydrogen sulfide, the latter forming a black layer of silver sulfide which can be cleaned off with dilute hydrochloric acid [10]. The most common oxidation state of silver is +1 (for example, silver nitrate, AgNO_3); the less common +2 compounds (for example, silver(II) fluoride, AgF_2), and the even less common +3 (for example, potassium tetrafluoroargentate(III), KAgF_4) and even +4 compounds (for example, potassium hexafluoroargentate (IV), K_2AgF_6) [11] are also known.

2.1.2 Isotopes

Naturally occurring silver is composed of two stable isotopes, ^{107}Ag and ^{109}Ag , with ^{107}Ag being slightly more abundant (51.839% natural abundance). Silver's isotopes are almost equal in abundance, something that is rare in the periodic table. Silver's atomic weight is 107.8682(2) g/mol.[12]

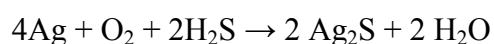
Twenty-eight radioisotopes have been characterized, the most stable being ^{105}Ag with a half-life of 41.29 days, ^{111}Ag with a half-life of 7.45 days, and ^{112}Ag with a half-life of 3.13 hours. This element has numerous Meta states, the most stable being $^{108\text{m}}\text{Ag}$ ($t_{1/2} = 418$ years), $^{110\text{m}}\text{Ag}$ ($t_{1/2} = 249.79$ days) and $^{106\text{m}}\text{Ag}$ ($t_{1/2} = 8.28$ days). All of the remaining radioactive isotopes have half-lives of less than an hour, and the majority of these have half-lives of less than three minutes.

Isotopes of silver range in relative atomic mass from 93.943 (^{94}Ag) to 126.936 (^{127}Ag); [13]the primary decay mode before the most abundant stable isotope, ^{107}Ag , is electron capture and the primary mode after is beta decay. The primary decay products before ^{107}Ag are palladium (element 46) isotopes, and the primary products after are cadmium (element 48) isotopes.

The palladium isotope ^{107}Pd decays by beta emission to ^{107}Ag with a half-life of 6.5 million years. Iron meteorites are the only objects with a high-enough palladium-to-silver ratios to yield measurable variations in ^{107}Ag abundance. Radiogenic ^{107}Ag was first discovered in the Santa Clara meteorite in 1978. The discoverers suggest the coalescence and differentiation of iron-cored small planets may have occurred 10 million years after a nucleosynthetic event. ^{107}Pd – ^{107}Ag correlations observed in bodies that have clearly been melted since the accretion of the solar system must reflect the presence of unstable nuclides in the early solar system [14]

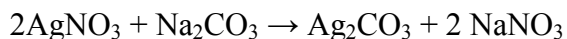
2.1.3 Chemical Properties and it's Compounds

Silver metal dissolves readily in nitric acid (HNO_3) to produce silver nitrate (AgNO_3), a transparent crystalline solid that is photosensitive and readily soluble in water. Silver nitrate is used as the starting point for the synthesis of many other silver compounds, as an antiseptic, and as a yellow stain for glass in stained glass. Silver metal does not react with sulfuric acid, which is used in jewelry making to clean and remove copper oxide fire scale from silver articles after silver soldering or annealing. Silver reacts readily with sulfur or hydrogen sulfide H_2S to produce silver sulfide, a dark-colored compound familiar as the tarnish on silver coins and other objects. Silver sulfide Ag_2S also forms silver whiskers when silver electrical contacts are used in an atmosphere rich in hydrogen sulfide.



Silver chloride (AgCl) is precipitated from solutions of silver nitrate in the presence of chloride ions, and the other silver halides used in the manufacture of photographic emulsions are made in the same way, using bromide or iodide salts. Silver chloride is used in glass electrodes for pH testing and potentiometric measurement, and as a transparent cement for glass. Silver iodide has been used in attempts to seed clouds to produce rain [7]. Silver halides are insoluble in aqueous solutions and are used in gravimetric analytical methods. Silver (Ag_2O), produced when silver nitrate solutions are treated with a base, is used as a positive electrode (anode) in watch batteries. Silver carbonate (Ag_2CO_3) is precipitated when silver nitrate is treated with sodium carbonate (Na_2CO_3) [15].





Silver fulminate (AgONC), a powerful, touch-sensitive explosive used in percussion caps, is made by reaction of silver metal with nitric acid in the presence of ethanol ($\text{C}_2\text{H}_5\text{OH}$). Other dangerously explosive silver compounds are silver azide (AgN_3), formed by reaction of silver nitrate with sodium azide (NaN_3), and silver acetylide, and formed when silver reacts with acetylene gas [16].

Latent images formed in silver halide crystals are developed by treatment with alkaline solutions of reducing agents such as hydroquinone, metol (4-(methylamino) phenol sulfate) or ascorbate, which reduce the exposed halide to silver metal. Alkaline solutions of silver nitrate can be reduced to silver metal by reducing sugars such as glucose, and this reaction is used to silver glass mirrors and the interior of glass Christmas ornaments. Silver halides are soluble in solutions of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) which is used as a photographic fixer, to remove excess silver halide from photographic emulsions after image development

Silver metal is attacked by strong oxidizers such as potassium permanganate (KMnO_4) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and in the presence of potassium bromide (KBr); these compounds are used in photography to bleach silver images, converting them to silver halides that can either be fixed with thiosulfate or redeveloped to intensify the original image. Silver forms cyanide complexes (silver cyanide) that are soluble in water in the presence of an excess of cyanide ions. Silver cyanide solutions are used in electroplating of silver [15].

Although silver normally has oxidation state +1 in compounds, other oxidation states are known, such as +3 in AgF_3 , produced by the reaction of elemental silver or silver fluoride with krypton difluoride [17].

Silver artifacts, primarily, undergo three forms of deterioration. Silver sulfide is the most common form of silver degradation. Silver chloride is purple to silvery-yellow colored, and projects slightly from the surface of the artifact or coin. The precipitation of copper in ancient silver can be used to date artifacts [18].

2.1.4 Applications

Many well-known uses of silver involve its precious metal properties, including currency, decorative items, and mirrors. The contrast between its bright white color and other media makes it very useful to the visual arts. It has also long been used to confer high monetary value as objects (such as silver coins and investment bars) or make objects symbolic of high social or political rank. Silver salts have been used since the middle Ages to produce a yellow or orange color to stained glass, and more complex decorative color reactions can be produced by incorporating silver metal in blown, kiln formed or torch worked glass [19].

The most common applications are :- Currency, jewelry and silverware, dentistry, Photography and electronics, mirrors and optics, other industrial and commercial applications, biology, medicine, investing, clothing.

2.1.5 Occurrence and Extractions

Silver is one of the basic elements that make up our planet. Silver is rare, but occurs naturally in the environment as a soft “silver” colored metal. It also occurs in powdery white (silver nitrate and silver chloride) or dark-gray to black compounds (silver sulfide and silver oxide). Silver found at hazardous waste sites in the form of these compounds mixed with soil and / or water. Photographers use silver compounds to make photographs. Photographic materials are the major sources of the silver that released into the environment. Another source is mines that produce silver and other metals [20].



Figure 2.1: Time trend of silver production

Silver is found in native form, as an alloy with gold (electrum), and in ores containing sulfur, arsenic, antimony or chlorine. Ores include argentite (Ag_2S), chlorargyrite (AgCl) which includes horn silver, and pyrargyrite (Ag_3SbS_3). The principal sources of silver are the ores of copper, copper-nickel, lead, and lead-zinc then, the metal is primarily produced as a byproduct of electrolytic copper refining, gold, nickel, and zinc refining, and by application of the Parks process on lead metal obtained from lead ores that contain small amounts of silver. Commercial-grade fine silver is at least 99.9% pure, and purities greater than 99.999% are available [20].

2.1.6 Human Exposure and Consumption

Silver plays no known natural biological role in humans, and possible health effects of silver are a disputed subject. Silver itself is not toxic to humans, but most silver salts are. In large doses, silver and compounds containing it can be absorbed into the circulatory system and become deposited in various body tissues, leading to argyria, which results in a blue-grayish pigmentation of the skin, eyes, and mucous membranes. Argyria is rare, and although, as far as known, this condition does not otherwise harm a person's health, it is disfiguring and usually permanent. Mild forms of Argyria are sometimes mistaken for cyanosis [10].

2.2 Silver in X-Ray Film

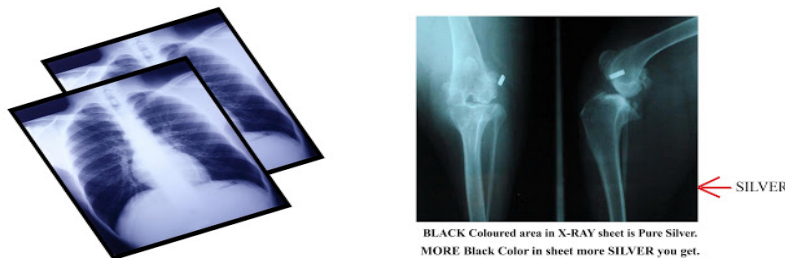


Figure 2.2: Exposed x-ray photographic film

A photographic film that consists of a radiation sensitive emulsion coated on one or both sides of a thin transparent base (Fig.2.2). The base consists of a thin plastic sheet, which is only necessary to give support to the emulsion. The base designed to provide a flexible, but strong support such

that it can conveniently and repeatedly snapped into a view box. Second, the base must withstand any geometric distortion due to the heat of the developing process. Finally, the base must provide a uniform, highly transparent, optical background.

Historically, photographic glass plates were used as the X-ray film base. After World War I cut off the supply of photographic glass from Belgium, cellulose nitrate, used as a base for photographic film was adapted for use with X-ray film. A cellulose triacetate base was developed in 1924 to avoid the highly flammable nature of cellulose nitrate. Finally, a stronger, thinner, more dimensionally stable film base made of polyester was developed in 1960 [21].

The X-ray film emulsion is composed of a form of gelatin and a silver halide, typically silver bromide. The gelatin for X-ray film is made from cattle bone. The gelatin serves as a matrix, which keeps the silver halide grains well dispersed and prevents their clumping. The developing and fixing solutions can penetrate the gelatin very rapidly without changing the strength or permanence of the gelatin. Finally, gelatin can be obtained in large quantities with uniform quality.

Small crystal grains of silver halide about 1.0 to 1.5 microns in diameter comprise the light sensitive substance in the emulsion. These grains, known as silver-iodo-bromide, are typically between 90 and 99% silver bromide and between 1 and 10% silver iodide. The grains are suspended in the gelatin of the film emulsion. The atoms in the silver-iodo-bromide crystal are arranged in a cubic lattice and each crystal contains many point defects, where a silver ion is displaced and is free to move through the crystal. The mobility of these silver ions contributes to the formation of the latent image. In the process of film exposure, the energy from absorbing a photon of light is sufficient to liberate an electron from a bromide ion in the crystal. The electron travels freely through the crystal until it is trapped at a site of crystal imperfection such as a dislocation defect or a sensitivity speck composed of a AgS molecule. A free silver ion is attracted to the negative charge and combines with the charge (is reduced) to form an atom of metallic silver (which is optically black). The single atom of silver acts as an electron trap for

another electron and then attracts another atom of silver, which is then reduced to metallic silver. This process continues while the exposure to light continues.

In general, the emulsion and the base do not adhere to each other. For this reason, the emulsion must be attached to the film base using a thin layer of adhesive. To protect the emulsion, which would be easily scratched and damaged by normal handling, a very thin outer protective layer is applied.

Although conventional photographic film is usually coated with emulsion on only one side, radiographic film is usually double coated (coated on each side of the base) to be used with intensifying screens. The reason for this double coating is easy to understand. The great majority of X-ray film exposure comes from optical photons created by interaction of each X-ray photon with the intensifying screen. The thicker the screen, the greater the fraction of the X-ray beam that will be stopped and converted to light photons. Thus, increasing the thickness will increase the sensitivity of the image detection. Unfortunately, the light photons are emitted in all directions from the point of interaction of each X-ray with the atoms of the screen. Thus, the thicker the screen, the greater will be the distance that the light photons can travel before striking the X-ray film. Thus, thick screens can result in a spreading or blurring of detail because of the lateral movement of the light photons before striking the film. For a given screen thickness, the blurring can be minimized by placing the X-ray film in the center of the intensifying screen. Thus, by placing screen plates above and below the film, the sensitivity of double screen thickness can be obtained while at the same time suffering the blurring equivalent to that of a single screen thickness

Photographic waste is the waste generated by the photographic processing machine in paper and printing industries. X-ray film is one of the photographic wastes generated by hospital and biochemical lab and used X-rays made of a polyester film coated in emulsion layers made of gelatin and contain silver. Photographic wastes contain silver that is the main material used to transfer image. The light-sensitive properties of silver compounds are the key to most photographic processes, and the basis of most of the waste produced. Like the compounds of many others heavy metals, they are highly toxic, and classified as special wastes. Along with the

decreasing amount of silver deposited, the cost of silver productions has risen rapidly and the price of silver in the market has increased constantly. Every country has focused on the recovery of silver from silver-containing wastes [21].

2.3 Silver in Photographic Waste (Waste X-Ray Photographic Film)

The primary sources of recoverable silver from photographic processing solutions are the ‘fix’ and the ‘bleach-fix’ solutions [22]. Many photographic and X-ray wastes contain silver thiosulfate. Wastes having a silver concentration of 5 parts per million (ppm) or more are hazardous because they display the characteristic of toxicity. Wastes that typically contains silver in concentration greater than 5ppm includes;

- I. Fixer solution
- II. Rinse water following water baths
- III. Solution from cleaning developer tanks (cleaner dissolved precipitated silver)
- IV. Film, negative and paper.

Most photographic films and papers carry as light sensitive agents silver halides embedded in a layer of gelatin. In this “emulsion”, a single photon of light can sensitize by catalytic action a billion silver atoms. The sensitization of the silver halide, predominantly silver bromide, is accomplished by exposing the emulsion to light through the lens of a camera or by means of a projector or a transparency, to X-rays or as accomplished only recently by means of computerized laser beams [23]. The photographic and X-ray wastes have to manage well to prevent harm to human health and the environment.

2.4 Environmental Effects of Silver

Toxicity is the measure of adverse chemical effects on an organism and governed by several factors, including the form and amount of the chemical present in the organism. Different forms of silver display different degree of toxicity. This toxicity is the basis of regulations on discharge of silver compounds. Some silver compounds release ionic silver very slowly due to very low solubility (e.g., silver sulfide) or complexation of the silver (e.g., silver thiosulfate). These compounds are over 15,000 times less toxic than silver nitrate to aquatic organisms. Because of the tendency for silver to form nearly insoluble compounds in natural waters and sediments,

the chance for organism to be affected long term is minimal [24].

Soluble silver salts, especially AgNO_3 , are lethal in concentrations of up to 2g (0.070 oz). Body tissues, with the consequent bluish or blackish skin pigmentation (argiria), can slowly absorb silver compounds. Liquid or vapor may be irritating to skin, eyes, throat, or lungs. Intentional misuse by deliberately concentrating and inhaling the contents of this product can be harmful or fatal.

2.5 The Most commonly used Technologies for Silver Recovery:

2.5.1 Electrolysis

Electrolysis is the most common used technology to recover silver. Recovery of metals from aqueous solution of their salts by electrolysis can be realized by two methods. The first method consists of the electrolysis of solutions obtained after leaching of the corresponding metal from ores or concentrated with the use of insoluble anodes. The second method consists of the electrolytic refining of the metal [25].

In the process of electrolysis, or commonly known as electrolytic silver recovery, a direct current is passed through a silver-rich solution between a positive electrode (the anode) and a negative electrode (the cathode). During this electrolytic process, an electron is transferred from the cathode to the positively charged silver, converting it to its metallic state, which adheres to the cathode [26].

In a simultaneous reaction at the anode, an electron is taken from some species in solution. In most silver-rich solution, this electron usually comes from sulfite. One advantage of electrolysis is that the silver it collects on the cathode is 90% or more pure. Here the crude metal to be refined serves as the anode and the pure metal is deposited at the cathode. This is a better method for noble metal recovery [25].

Electrolysis recovery process produces nearly pure metallic silver, contaminated only slightly by some surface reactions that also take place. The plated silver should be greater than 90 percent pure [24, 26].

A drawback of the method is that it requires substantial capital outlay. Another disadvantage of electrolysis is that extending the time the electrodes are in solution in attempt to maximize the

silver recovered and produce an inferior substance on the plating.

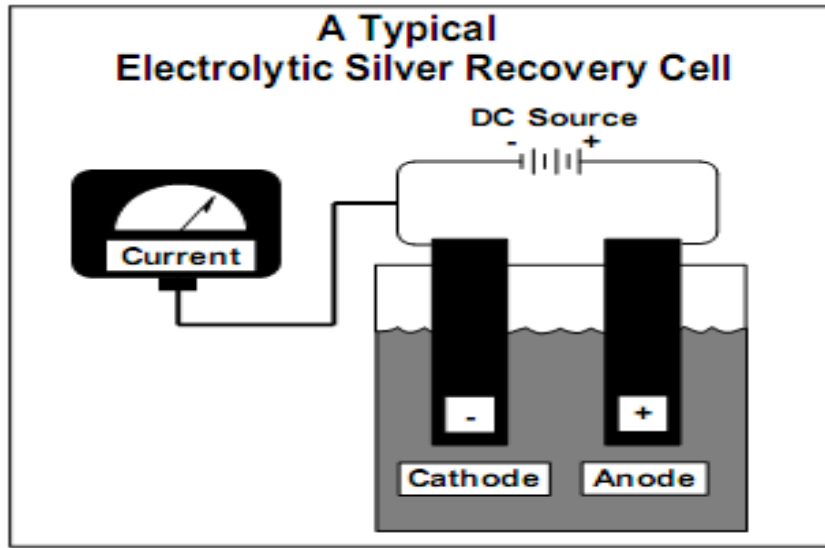
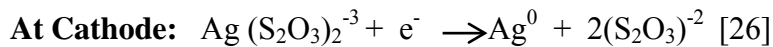
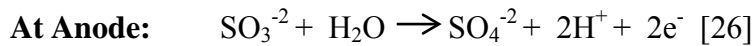


Figure 2.3: Schematic Diagram for Typical Electrolytic Silver Recovery Process [24, 26]

Figure three shows that the typical electrolysis cell for silver recovery process. An overview of the reactions is:



Silver Thiosulfate Complex + Electron \rightarrow Metallic Silver + Thiosulfate



Sulfite + Water \rightarrow Sulfate + Hydrogen Ions + Electron

Here the crude metal to be refined serves as the anode and the pure metal is deposited at the cathode. This is a better method for noble metal recovery. Electrolysis recovery process produces nearly pure metallic silver, contaminated only slightly by some surface reactions that also take place [25].

2.5.2 Metallic Replacement

Metallic replacement is a process that involves passing a silver-bearing solution through a container filled with metal, typically steel wool. Sometimes other materials are used, such as

iron-impregnated resins or iron screens, and commercial operators typically use a “metallic recovery cartridge.” When silver meets the metal, settles at the bottom of the container or deposits on the metal inside. The silver-bearing deposits are refined further. Initial capital costs for metallic replacement are modest and the equipment is easy to install, but it may not always reduce silver to legally acceptable level.

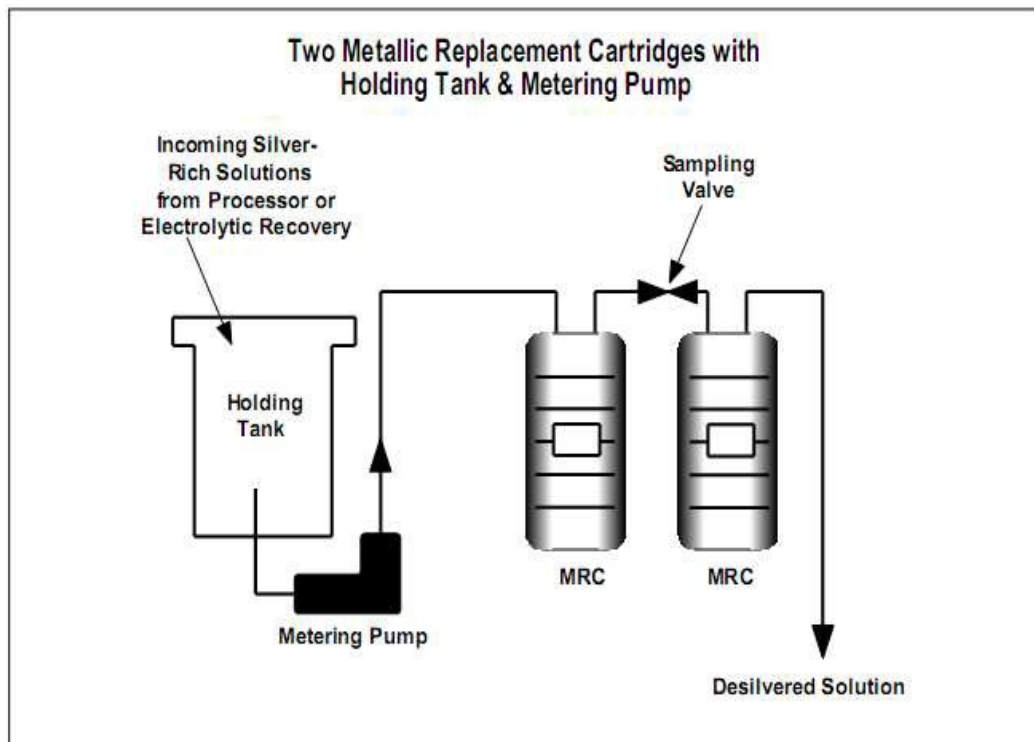


Figure 2.4: Schematic Diagram for Metallic Replacement Process Using MRCs [24, 26]

Silver is also recovered from photographic processing solution by replacing the silver with another metal such as zinc by electrolysis or by chemical precipitation with chemicals such as sodium hydroxide or sodium sulphide [25].

The commercial equipment commonly used for the recovery is often referred to as Metallic Recovery Cartridges (MRCs) or Chemical Recovery Cartridges (CRCs). The most common source of iron is fine steel wool, chosen for its surface area. The steel wool is wound on a core or chopped up and packed into a cartridge. The silver rich solutions are slowly metered into the cartridge and through the iron medium. The silver is left behind in the cartridge while iron is

solubilized and carried out by the solution. Like the electrolytic process, metallic replacement is a reduction- oxidation process.



Silver Thiosulfate Complex + Metallic Iron \rightarrow Metallic Silver + Ionic Iron + Thiosulfate
Flow rate, iron surface area, contact time, pH, original silver concentration, thiosulfate concentration, and the volume passing through the cartridge affect the final silver concentration. If the MRC is operating properly, the silver concentration may be reduced to less than 5 mg/L [26]

2.5.3 Chemical Precipitation

Another option is chemical precipitation with sodium sulfide, sodium borohydride or sodium dithionite. This can remove virtually 100 percent of the silver and most other metals from photographic effluent. With the addition of alkaline sodium sulfide and the resulting precipitation of silver sulfide, levels of soluble silver below 0.1 mg/L are possible. However, the more difficult part of the process is the separation of the precipitate from the liquid. Total silver levels of 0.5 to 1.0 mg/L usually obtained due to filtration limitations. This process requires only small capital expenditure and uses chemicals, which are relatively inexpensive. It is not as widely used as the electrolytic or metallic replacement methods because of the inconvenience of handling large amounts of chemicals, the separation process required, and the problem of concentrating finely precipitated silver sulfide particles into a sludge that can be dried and refined. In addition, careful pH control is required to avoid generation of highly toxic hydrogen sulfide gas [25].

Therefore, Silver can precipitated out of solution to very low levels using chemicals like alkaline sodium sulfide. This method has the advantage of being able to recover nearly 100% of the silver.

2.5.4 Other Recovery Process

Ion exchange generally used for effective recovery of silver from rinse water or other dilute solutions of silver. The ion exchange method involves the exchange of ions in the solution with ions of a similar charge on the resin. The soluble silver thiosulfate complex exchanged with the anion on the resin. This exhaustion step and is accomplished by running the solution through a column containing the resin. For large operations, the next step is the regeneration step in which

the silver is removed from the resin column with a silver complexing agent such as ammonium thiosulfate. This step includes several backwashes to remove particulate matter and excess regenerant before the next exhaustion step initiated. Silver is then recovered from the thiosulfate regenerant with an electrolytic recovery cell. For smaller operations, an alternative to performing the regeneration step onsite would be to remove the resin from the column and send it to a refiner for silver reclamation. Important factors in considering an ion exchange system for silver recovery are; selection of the resin, flow rate of the silver-bearing solution, column configuration, and selection of the regenerant. It has been demonstrated that the use of ion exchange can reduce the silver concentration in photographic effluent to levels in the range of 0.5 to 2 mg/L and can recover over 98 percent of the available silver. If this method used as a tailing method after primary recovery by electrolysis, levels in the range of 0.1 to 1 mg/L can be obtained. Reverse osmosis (RO) is also used for dilute solutions. RO uses high pressure to force the silver-bearing solution through a semipermeable membrane to separate larger molecules, such as salts and organics, from smaller molecules like water. The extent of separation is determined by membrane surface chemistry and pore size, fluid pressure, and wastewater characteristics. For removal of silver, after-fix rinse water is flow-equalized, filtered, and pumped through an RO unit. Once the silver is separated from the water in this manner, it can be recovered by conventional means such as metallic replacement, electrolytic recovery or chemical precipitation. Operating problems include fouling of the membrane and biological growth.

In distillation recovery process, the photographic processing effluent is captured in a vessel and heated to evaporate the water. In some apparatus, the solution is actually boiled, the steam being condensed. In others, the solution is merely heated and released into the air (by a fan) to discharge evaporating moisture. Although some pieces of equipment may be capable of producing a solid block from the effluents, the energy requirements can be prohibitive, and heated photo processing effluents tend to give off pungent, unpleasant odors. We may need an air emission discharge for this type of equipment. For evaporation recovery process, vacuum distillation or cool temperature evaporation is a process by which a vacuum drawn on a vessel containing the photographic processing effluents. At a sufficiently low pressure, the solution will boil and the water vapor drawn from the vessel, condensed, and collected. These evaporators can generally reduce the effluent volume by up to 90 percent, but the initial equipment expense is relatively high [26].

Table 2.1: Comparison of Silver Recovery Methods

Recovery method	Advantages	Disadvantages
Electrolysis (In-line)	<ul style="list-style-type: none"> • Obtain >90% pure silver • Re-circulate fixer • Reduce chemical use £50% - 70% and mixing labor 	<ul style="list-style-type: none"> • Used for fixers and high-silver solutions only • Can damage fixer if not properly maintained
Electrolysis (Terminal)	<ul style="list-style-type: none"> • Low refining costs • Moderate capital costs • Able to determine silver recovered 	<ul style="list-style-type: none"> • Cannot achieve 5 mg/L alone • Used for high-silver solutions only • Sulfide precipitation possible
Evaporation Distillation	<ul style="list-style-type: none"> • Up to 90% waste reduction 	<ul style="list-style-type: none"> • Moderate to high capital costs • Messy sludge
Ion Exchange	<ul style="list-style-type: none"> • 98 – 99.99% removal efficiency from dilute solutions 	<ul style="list-style-type: none"> • High capital costs • Fouling problems • May require use of hazardous chemicals • Works best on dilute solutions • Monitoring required for replacement or regeneration
Metallic Replacement	<ul style="list-style-type: none"> • Available for all silver-rich solutions • Low capital costs • Low maintenance • 99% removal possible with 2 units 	<ul style="list-style-type: none"> • Channeling at flows £0.5 gpd • Low concentration reduces lifespan • Cannot re-circulate fixer • Cannot determine amount of silver until refined • High smelting and refining costs • Monitoring required for replacement
Chemical method (precipitation)	<ul style="list-style-type: none"> • >99% consistent removal possible • Moderate capital costs • Little maintenance 	<ul style="list-style-type: none"> • Higher smelting cost than electrolytic • Ongoing chemical usage • Moderate to high operation costs
Reverse Osmosis	<ul style="list-style-type: none"> • Up to 90% efficiency on dilute streams • No treatment chemicals required 	<ul style="list-style-type: none"> • High capital costs • Frequent maintenance required • Works best on dilute solutions • Large installations noisy

From table 2.1, the chemical method had a lot of advantages but less disadvantage when it compared with other recovery methods. Its simplistic operation, more than 99% recovery, easily availability of chemicals and equipment, less operation time and cost encourages conducting this research.

3 MATERIALS AND METHODS

3.1 Material

The raw materials used were:

- Used x- ray photographic film which were obtained from Addis Ababa Medical faculty.
- Distilled water, it was prepared in technology faculty.
- Analytical grade reagents such as NaOH, Na₂S, ethanol, HCl, Borax and sodium carbonate obtained from Lion pharmacy, Neway, Sara and Wise chemical importers, Emenda chemical and stationery trade.

Equipment and instruments used in the lab were:

- Motor with Stirrer
- EDXRF 2008 Spectrometer (XRF)
- Beakers, volumetric flasks, pipette , burettes , disicator, P^H meter
- Analytical weigh balance, precise to two digets
- Wash bottle, funnel
- Oil bath
- Oven
- Goggles for eyes protection, protective gloves for hand
- Cleanol, filter paper watt man 540
- Thermometer, furnace.

Experimental procedures were employed during the research

- ✓ Used X-ray film, were collected, washed with distilled water and wiped with cotton impregnated with ethanol.
- ✓ The films were dried in an oven at 40°c for 30min.
- ✓ The film were measured (25 cm by 29 cm) and cut into required pieces.
- ✓ Sodium hydroxide solution were prepared in 0.5M, 1.5M and 2.5M

- ✓ The beakers were put into an oil bath at different oil and solution temperature.
- ✓ The prepared films were weighed and put into a 1000 ml solution (sodium hydroxide) at different concentration in a 3000 ml beaker.
- ✓ The sample was heated at different temperature and time with continues stirring to stripe the silver.
- ✓ The stripped gelatinous solutions were decanted and the films were rinsed thoroughly and discard after rinsing.
- ✓ Sodium sulphide solution was added into the stripped solution to precipitate the silver.
- ✓ The precipitated black silver was separated from the solution using decantation.
- ✓ The precipitates had been washed repeatedly with distilled water until the P^H became 7.
- ✓ The precipitate (black sludge) was dried in an oven at 500°c for 30 min.
- ✓ The dried black silver was cooled in a desiccator and weighed.
- ✓ The dried black silver was mixed with borax and sodium carbonate in a 1:2 ratio.
- ✓ The mixtures were put in to a graphite crucible and inserted in to a furnace at 950°c for 1:30
- ✓ The smelted pure silver was poured into a mold.
- ✓ The molded pure silver had been collected after an hour
- ✓ The product using was characterized using XRF instrument

3.2 Methods

3.2.1 Preparation of the Film:

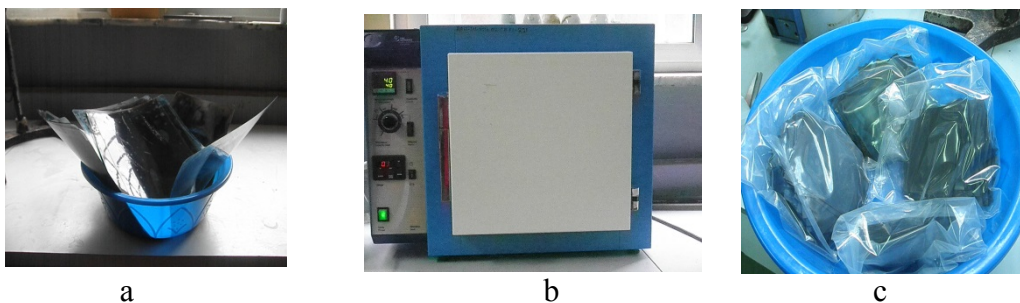


Figure 3.1: Film preparation

The used X-ray photographic films collected from Black Lion medical faculty, Addis Ababa University. The collected X-ray photographic films were washed with distilled water and wipe with cotton impregnated with ethanol, and were cut into required pieces after being dried in an oven at 40°C for 30 min [27].

3.2.2 Reagents Preparation:

1. NaOH (Sodium Hydroxide analytical grade) 0.5M, 1.5M and 2.5M were prepared to strip the gelatin-silver layer from the film base [28, 29].
2. Na₂S (sodium sulfide, analytical grade) proportional to NaOH were prepared to precipitate the silver from the stripped solution [23].
3. HCl (hydrochloric acid analytical grade) 11.65M were prepared to check whether the stripping is completed or not and to check the presence of silver in the solution [30].
4. Equal mixture of Borax and sodium carbonate were prepared [30].

3.2.3 Recovery of Silver

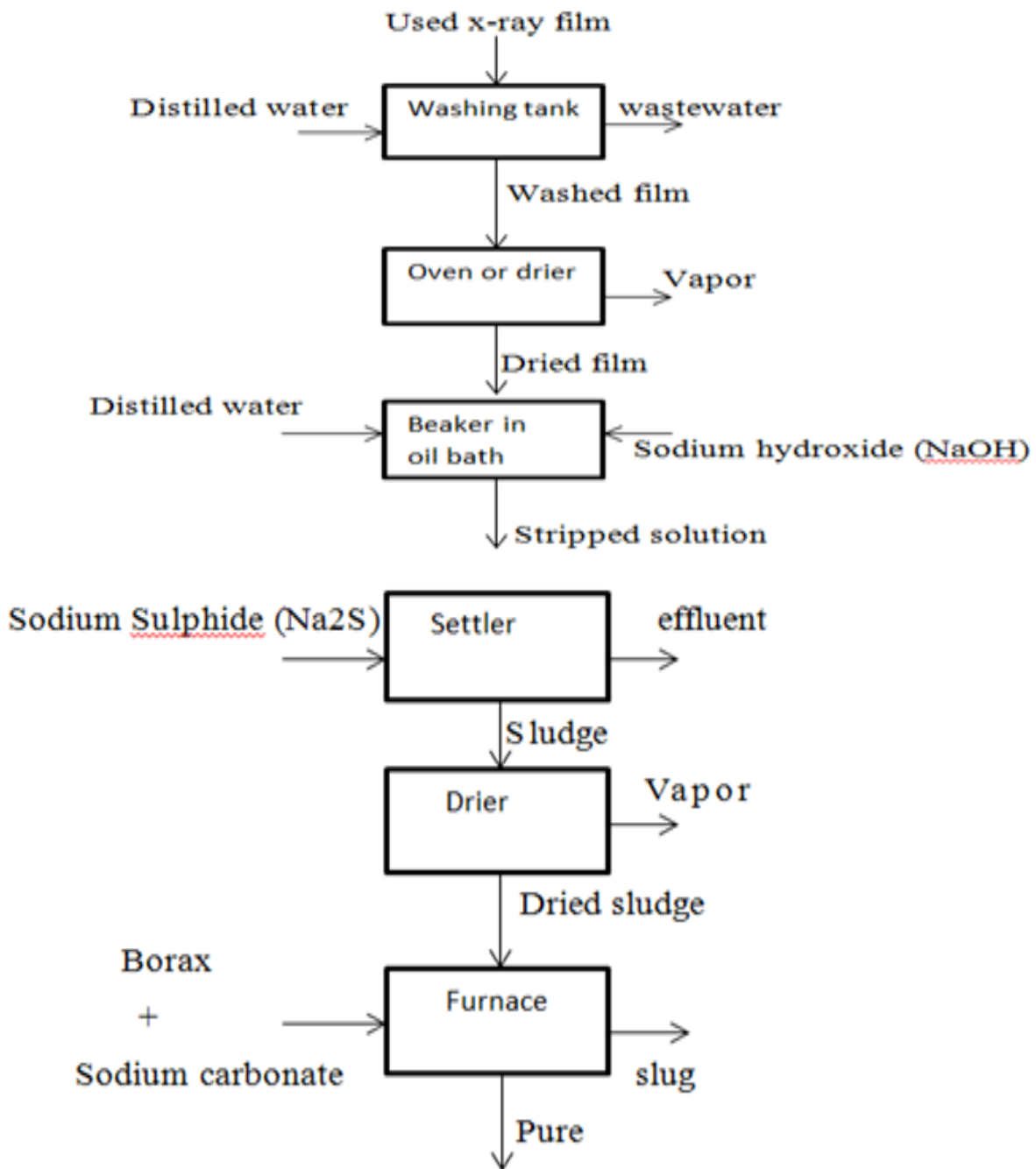
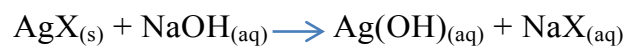


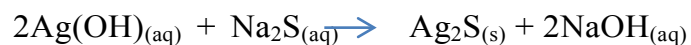
Figure 3.2: Recovery process flow sheet

From the above flow sheet, there was a chemical reaction at stripping and precipitating stages.

At stripping process the following reaction was occurred.



At precipitation stage (addition of sodium sulphide), this reaction was takes place.



Where X: halides

(s): represents solid form

(aq): aquaous (solution) form

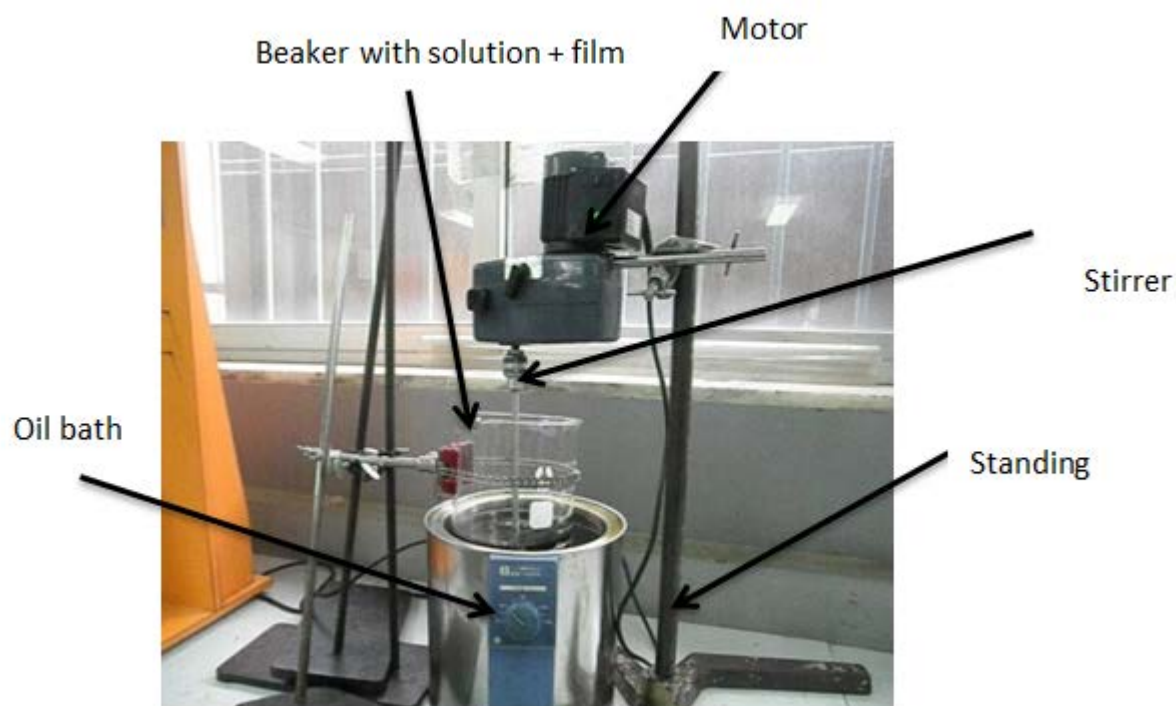


Figure 3.3: Laboratory setup for stripping the black silver from the film.

3.2.4 Quantitative Determination of Silver using Preliminary Experiments

Preliminary experiments were done to check whether silver could be recovered or not. Therefore, two experimental runs were carried out to know the best procedures, equipment, facilities, available and applicable chemicals. During the trial, 8.68g and 6.32 g silver were recovered from 90 and 80 plates used x-ray film respectively. Using these preliminary experiments, oil bath was selected rather than water bath. Because the oil bath have large heat capacity than water bath and the water easily boiled at a temperature of 92°C. It was difficult to maintain the temperature of the water bath when water level minimized due to vaporization. The best precipitating reagents were selected from the available hydrogen peroxide and sodium sulphide reagents. The second one was best to precipitate the silver ion within 30 minutes but hydrogen peroxide was taken longer time (about one day) to precipitate the suspended silver ion in the stripped solution. The levels and ranges of the variables were identified practically by considering . The research were done by Nuri Nakiboglu et.al, 2003 said that the best temperature range is 70-80°C and NaOH concentration is 1.5M and time of 3.5minute. So, parameters ranges were considered beyond these values in the experiments by selecting three levels for each parameter.

After the trials were done, the experimental runs were carried out. For each run, twenty pieces of prepared films were measured, cut, weighed and inserted in a beaker (3-liter capacity). The beaker contains 1 liter of sodium hydroxide solution with a concentration of 0.5M, 1.5M and 2.5 M. The temperature was varied in three levels (i.e. 50°C, 70°C, and 90°C). To keep the temperature at the required level, an oil bath was used for the experimental work. Time was also varied in three different levels (i.e. 1 minute, 10.5 minutes and 20 minutes). Once the silver was stripped in black colloidal form from the film, the resulting solution was mixed with Na₂S. The amount of Na₂S that was added should be in a proportion of 1:2 to the amount of NaOH. The mixture were stirred together and due to common ion effect the silver were precipitated. A black sludge containing the silver was observed at the bottom of the beaker.

The precipitated black sludge was separated from solution by decantation and the residue

were put on the filter paper to neutralize it by washing. Then, the residue was dried and weighed. Before the dried black silver inserted into the furnace, equal amount of Borax and sodium carbonate, were prepared and mix with the dried sludge in a ratio of 2:1. Because the borax and sodium carbonate were contribute the purity and increasing heat capacity of the sample respectively. After this, the mixture were put inside the furnace using graphite crucible for 1:30 hr. while keeping the temperature of the furnace at 950⁰C. Finally, the smelted black silver was poured in to the prepared molder to collect the pure silver.

3.3 Experimental Factors and Responses

3.3.1 Study Factors:

The study factors were selected by referring some literatures and it was checked by carried out preliminary experiments. During the preliminary experiments, the factors, their ranges, and effects were observed on the silver recovery amount. Therefore, there was no need to go beyond this level.

The effects of the factors listed below on the amount of silver recovery and its purity studied.

- ❖ Stripping temperature
- ❖ Concentration of NaOH
- ❖ Stripping time

The three factors were analyzed against three levels (low [-1], medium [0] and high [+1]), that is the 3³ design. About (3*3*3 =27) runs were done and analysis was carried out to know the interaction effects between the factors and their effect on the amount of recovered silver. However, the Response Surface Miscellaneous (RSM) design for three levels duplicates the center point five times and the run became 32, only 27 replicated runs were carried out.

Table 3.1: Factors and the corresponding ranges and levels

Factors	Range	Levels		
		Low (-1)	Medium(0)	High(+1)
Temperature in degree centigrade	50-90	50	70	90
Concentration in Molar	0.5-2.5	0.5	1.5	2.5
Stripping time in minute	1 - 20	1	10.5	20

Since only 27 replicated runs were done with three levels, the lower, medium, and higher values from the above ranges were taken. This was because significant response variations observed only if a significant gap between the lower and higher levels kept. If the gap between the lower and the higher levels larger, there would be a problem of identifying whether there was an increment or decrement of the response. Therefore, medium level had been considered to see the profile of the response.

Table 3.2: Combination of factors and levels

Run	(A):NaOH conc. (M)	(B):Time (hr)	(C):Temperature (°c)	Treatment combination
1	0.5(-1)	1(-1)	50(-1)	(-)(-)(-)
2	0.5(-1)	10.5(0)	50(-)	(-1)(0)(-)
3	0.5(-1)	20(+1)	50(-1)	(-1)(+1)(-1)
4	0.5(-1)	1(-1)	70(0)	(-1)(-1)(0)
5	0.5(-1)	10.5(0)	70(0)	(-1)(0)(0)
6	0.5(-1)	20(+1)	70(0)	(-1)(+1)(0)
7	0.5(-1)	1(-1)	90(+1)	(-1)(-1)(+1)
8	0.5(-1)	10.5(0)	90(+1)	(-1)(0)(+1)
9	0.5(-1)	20(+1)	90(+1)	(-1)(+1)(+1)
10	1.5(0)	1(-1)	50(-1)	(0)(-1)(-1)
11	1.5(0)	10.5(0)	50(-1)	(0)(0)(-1)
12	1.5(0)	20(+1)	50(-1)	(0)(+1)(-1)
13	1.5(0)	1(-1)	70(0)	(0)(-1)(0)
14	1.5(0)	10.5(0)	70(0)	(0)(0)(0)
15	1.5(0)	20(+1)	70(0)	(0)(+1)(0)
16	1.5(0)	1(-1)	90(+1)	(0)(-1)(+1)
17	1.5(0)	10.5(0)	90(+1)	(0)(0)(+1)
18	1.5(0)	20(+1)	90(+1)	(0) (+1) (+1)
19	2.5(+1)	1(-1)	50(-1)	(+1)(-1)(-1)
20	2.5(+1)	10.5(0)	50(-1)	(+1) (0) (-1)
21	2.5(+1)	20(+1)	50(-1)	(+1)(+1)(-1)
22	2.5(+1)	1(-1)	70(0)	(+1)(-1)(0)
23	2.5(+1)	10.5(0)	70(0)	(+1)(0)(0)
24	2.5(+1)	20(+1)	70(0)	(+1)(+1) (0)
25	2.5(+1)	1(-1)	90(+1)	(+1)(-1)(+1)
26	2.5(+1)	10.5(0)	90(+1)	(+1)(0)(+1)
27	2.5(+1)	20(+1)	90(+1)	(+1)(+1)(+1)

3.3.2 Measured Response

3.3.2.1 Recovery of Silver

The recovery of the silver was the process of gaining the silver particles from the solution using Na_2S as a precipitating reagent from the many alternative reagents.

Na_2S were selected for precipitation purpose. Because the silver was precipitated within a short period using this chemical.

The recovery method was done in the following way:-



Figure 3.4: The recovered sample

After stripping 20 pieces of 25cm * 29 cm for each run in a liter of solution, the residue was decanted, rinsed the film by 1 liter distilled water thoroughly, and discarded the stripped film. A proportional amount of Na_2S to NaOH (1:2 ratio) was added into a cooled and stripped solution to precipitate the silver. The precipitated black sludge were separated by decantation and washed repeatedly the precipitate with distilled water until the P^{H} was about 7 and put the residue (black sludge) on the filter paper as shown in figure 3.4 above.





Figure 3.5: smelting of the dried black silver in a furnace.

The precipitate was dried in a furnace at 500°C for 30 min and cooled in a desiccator. After cooling, it was weighed to mix with purity and heat capacity increment reagent. Equal mixture of borax and sodium carbonate were added in to the dried black silver in a ratio of 2:1 in graphite crucible. The crucible was inserted inside the furnace at 950°C for 1:30 hr. The smelted silver was decanted in to the molder and the pure silver was collected as shown in figure 3.5. The purity of silver was tested in Ethiopian geological survey using XRF instrument.

Silver purity and Trace metal impurity determination.

- EDXRF Spectrometer (XRF) in Ethiopian geological survey were used to determine the purity of the recovered silver and trace metal impurities in it. This instrument is the latest to determine about 78 elements in a sample in ore, soil, and bar forms. Therefore, both purity and trace impurities in precious metal recoveries like gold and silver were detected easily using this instrument. First, the samples were put on the slide of the analyzer in the form of ore, soil, and bar and the detection was covered about 8 mm diameter and 15 mm depth of the sample. Since this research is precious metal recovery, the instrument software was setup for precious metal sample in bar form.

4 RESULTS AND DISCUSSION

4.1 Recovery of the recovered silver

To calculate the yield or recovery of silver, the weight of silver in the exposed or used films that going to be stripped were considered as an input and the amount of pure silver as an output. Therefore, the yield could be the ratio of output to input.

The silver recovered varies from film to film even if the film had the same size and type. Because the amount of the silver much depend on how much the area of the x-ray picture covers the surface of the film. Due to this, the experiments were triplicated for each run. The amounts of silver recovered were determined by taking the average weight of silver recovered divided by the average amount of silver in the film.

The average percentage recovery of silver was calculated as follows for each triplicated run.

$$\% \text{ yield or recovery} = \left(\frac{\text{weight of pure silver obtained}}{\text{weight of silver in the film}} \right) * 100$$

The first run was calculated as follows and the data had been randomized during design expert software analysis, see annex-1.

$$\% \text{ yield or recovery} = \frac{1.45}{354.7 \cdot 0.02} * 100 = 20.5\%$$

All the percentage recovery of silver for each sample run with deviation were calculated in the above way and the results were tabulated in table 4.1

Table 4.1: Factors and determined response.

Run No.	factors			Average film Weight (g)	Average Pure silver weight (g)	Average Pure silver weight/ Average Film Weight (%)	Recovery (%)
	Concentration (Mole/liters)	Time (min)	Temp. (°C)				
1	0.50	1.00	50.00	354.70 ± 0.46	1.45 ± 0.08	0.41 ± 0.02	20.5 ± 1
2	0.50	10.50	50.00	354.10 ± 1.15	2.16 ± 0.32	0.61 ± 0.06	30.5 ± 3
3	0.50	20.00	50.00	353.20 ± 0.36	2.15 ± 0.27	0.61 ± 0.04	30.5 ± 2
4	0.50	1.00	70.00	345.37 ± 0.55	2.56 ± 0.70	0.74 ± 0.02	37 ± 1
5	0.50	10.50	70.00	347.50 ± 0.79	3.09 ± 0.09	0.89 ± 0.03	44.5 ± 1.5
6	0.50	20.00	70.00	352.60 ± 2.34	3.07 ± 0.35	0.87 ± 0.03	43.5 ± 1.5
7	0.50	1.00	90.00	353.70 ± 0.46	2.30 ± 0.28	0.65 ± 0.06	32.5 ± 3
8	0.50	10.50	90.00	351.40 ± 1.65	2.85 ± 0.29	0.81 ± 0.04	40.5 ± 2
9	0.50	20.00	90.00	354.20 ± 1.31	2.55 ± 0.34	0.72 ± 0.04	36 ± 2
10	1.50	1.00	50.00	352.00 ± 1.41	2.50 ± 0.51	0.71 ± 0.02	35.5 ± 1
11	1.50	10.50	50.00	348.70 ± 0.10	2.96 ± 0.40	0.85 ± 0.04	42.5 ± 2
12	1.50	20.00	50.00	353.80 ± 0.26	2.76 ± 0.13	0.78 ± 0.07	39 ± 3.5
13	1.50	1.00	70.00	348.80 ± 0.72	3.31 ± 0.49	0.95 ± 0.04	47.5 ± 2
14	1.50	10.50	70.00	358.10 ± 0.36	3.87 ± 0.08	1.08 ± 0.01	54 ± 0.5
15	1.50	20.00	70.00	347.60 ± 1.08	3.30 ± 0.29	0.95 ± 0.06	47.5 ± 3
16	1.50	1.00	90.00	355.50 ± 0.79	2.81 ± 0.16	0.79 ± 0.04	39.5 ± 2
17	1.50	10.50	90.00	353.90 ± 0.20	3.15 ± 0.27	0.89 ± 0.08	44.5 ± 4
18	1.50	20.00	90.00	348.20 ± 0.26	2.71 ± 0.15	0.78 ± 0.04	39 ± 2
19	2.50	1.00	50.00	355.80 ± 0.95	2.46 ± 0.04	0.69 ± 0.02	34.5 ± 1
20	2.50	10.50	50.00	352.10 ± 0.62	2.75 ± 0.16	0.78 ± 0.02	39 ± 1
21	2.50	20.00	50.00	349.70 ± 2.04	2.13 ± 0.25	0.61 ± 0.05	30.5 ± 2.5
22	2.50	1.00	70.00	347.70 ± 0.35	2.78 ± 0.21	0.80 ± 0.04	40 ± 2
23	2.50	10.50	70.00	358.60 ± 0.80	3.14 ± 0.38	0.88 ± 0.03	44 ± 1.5
24	2.50	20.00	70.00	350.30 ± 0.75	2.52 ± 0.24	0.72 ± 0.07	36 ± 3.5
25	2.50	1.00	90.00	350.40 ± 0.95	2.06 ± 0.34	0.59 ± 0.09	29.5 ± 4.5
26	2.50	10.50	90.00	349.70 ± 0.85	2.20 ± 0.23	0.63 ± 0.02	31.5 ± 1
27	2.50	20.00	90.00	354.90 ± 0.96	1.60 ± 0.32	0.45 ± 0.01	31.5 ± 0.5

4.2 Interpretation of the Result Using Experimental Design Software:

For the analysis of the data, Design Expert Software (version 7.0.0) was used. Response surface methodology (RSM-miscellaneous) had been chosen than other design methods. Because it enables evaluation of the effect of several process parameters and their interactions on the response variable [31]

At each combination of the process setting, the yields of silver were recorded.

This experimental design software was made to-

- ✓ Screen out insignificant factors and identify significant factors. Get some idea about the existence of interaction effects.
- ✓ Understand main effects and get complete information about 3-factor interaction.
- ✓ Characterize how the significant factors affects the response (for optimization purposes)

The number of runs, number of factors, name and units of factors and their levels, the response name and units were entered and the following design summary table was generated.

Table 4.2: Design summary

Design summary										
Study Type	Response Surface		Runs	32						
Initial Design	3 Level Factorial		Blocks	No. Blocks						
Design Model	Quadratic									
Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded	Mean	Std. Dev.	
A	concentration	mole/liter	Numeric	0.50	2.50	-1.000	1.000	1.500	0.75	
B	Time	minute	Numeric	1.00	20.00	-1.000	1.000	10.500	7.125	
C	temperature	°c	Numeric	50.00	90.00	-1.000	1.000	70.000	15.00	
Response Y1	Name	Units	Obs	Analysis	Minimum	Maximum	Mean	Std.Dev.	Ratio	Trans
	Yield	%	32	polynomial	20.50	54.00	40.4	8.659	2.634	None

The design summary table indicates the report of the design, factors, and response information. New items were the factors and response, mean and standard deviation.

4.2.1 Pre- Analysis of Main Effects through Simple Plots

On the graph column of the following figures the variation of the factors with respect to the yield of the recovered silver.

4.2.1.1 Effects of NaOH Concentration

As shown on the figure 4.1, the graph indicates the effects of concentration on the recovery or yields of silver.

Sodium hydroxide (NaOH) concentration was the most important factor during stripping and recovery of silver in this study. Stripping of silver from the film base needed a shorter time with increasing NaOH concentration. When the concentration was lower, it was difficult to stripe all the silver particles from the film base with appropriate time and also the number of silver particles could not achieve a high value in the solution. However, further increasing the NaOH concentration would make difficult the recovery of the silver from the solution. The high concentration of NaOH could dissolve the metal and made difficult for separation. Due to this, the silver was not precipitated easily and the yield was lowered. However, at 1.5M NaOH concentration the yield or recoveries of silver were maximum value (54% recovery).

The graph was showed that concentration of sodium hydroxide had a large impact on the recovery or yields of silver. Generally, increasing the concentration of NaOH until 1.5 M increases the yield rapidly. However, further increasing the concentration, the yield was decreased by the same rate.

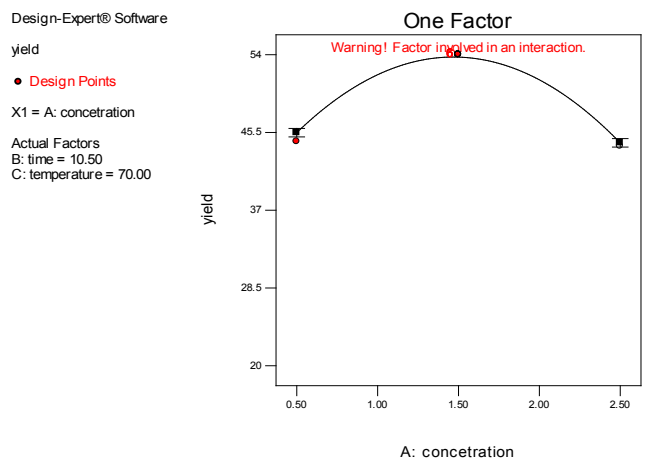


Figure 4.1: Effects of concentration on silver recovery.

4.2.1.2 Effects of Stripping Time on Silver Recovery (Yield)

The yields or recoveries of silver were increased with stripping time until 10.5 minute. This means the longer the stripping time, the higher contact between the reagent and the film base to strip all the silver from the surface of the film. However, a slight decrease of the yield was occurred when the stripping time was extended. Because NaOH with longer extraction time could dissolve the metal. Generally, increasing stripping time was increased the yield but it reaches the maximum time that all the silver particles were leached out. Then further increasing would decrease the yield slightly if the concentration of the reagent were kept high. This was observed in the figure 4.2 below and an interaction effects were occurred. The time versus yield graph below was shown the increment of the yield until 10.5 stripping time but the yield was decreased for further time increment.

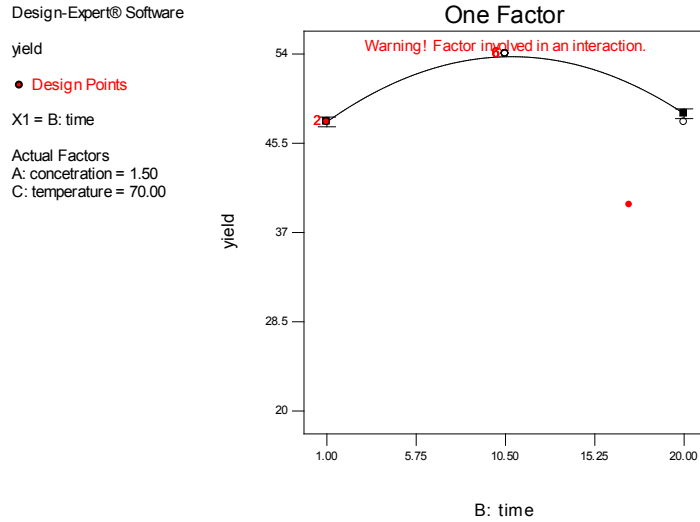


Figure 4.2: Effects of stripping time on silver recovery (yield).

4.2.1.3 Effects of Temperature on Silver Recovery

As shown in the figure 4.3, the temperatures had a significant effect on the yields of the silver. The recoveries were increased with temperature until a stripping temperature of 70°C. However, further increasing would decrease the yield due to the interaction effects of the other factors. The silver was leached into the solution when the temperature had been increased progressively to a certain value. Because the collagen that made stacked the silver with the plastic had, loosen its sticking strength when the temperature was increased. Therefore, the gelatinous substances with silver were easily detached from the film base during this time. When the temperature was increased, the silver was dissolved by NaOH and suspended in the solution. At this time, it was difficult to precipitate the suspended very fine silver particles. Due to this the recovery was decreased as shown in the figure 4.3.

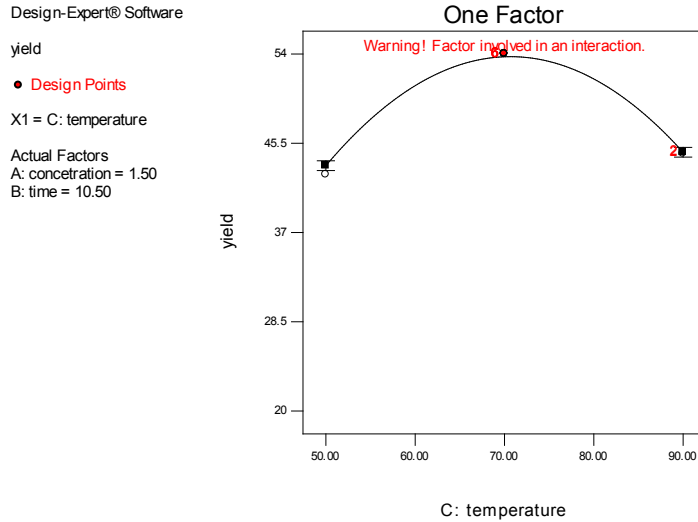


Figure 4.3: Effects of temperature on silver recovery (yield).

4.2.2 Pre- Analysis of Interaction Effects through 3D-Surfaces

The 3-D & contour response surface curves were plotted to understand interaction between the variables and to determine the optimum levels of each variable for maximum response.

4.2.2.1 Interaction Effects of Concentration and Time

As shown on figure 4.5, the 3D & contour surfaces showed that the interaction effects of concentration and time with respect to silver yield.

The interaction graphs were shown that the yield of silver was increased until 10.5 minute and 1.5M NaOH concentration with maximum recovery of 54% at center of contour. However, it was decreased beyond this time and concentration value. Higher stripping time, favor complete stripping of silver from the film in to solution. However, when the striping time was extended, the silver had been dissolved with NaOH and this was made the silver to suspend rather than settling. This condition was difficult to decant and separate the silver from the solution. Thus, the higher stripping time may favor dissolving of silver with increasing concentration. Generally, increasing time and concentration beyond some value will decrease the yields (recovery) of silver.

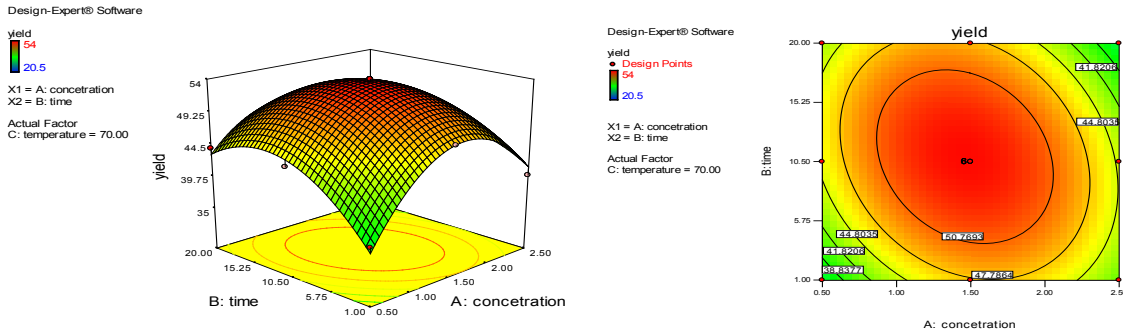


Figure 4.5: 3D & contour surface for time – concentration interaction

4.2.2.2 Interaction Effects of Temperature and Concentration

From figure 4.6, a higher yield of silver was obtained (54% at center point of the contour) at 1.5M NaOH concentration and at 70°C temperature. This was clearly due to the reason that at higher values of NaOH concentration more silver was dissolved and unable to settle for separate from the solution. By this case, the yield was lowered at higher concentration. However, the temperature favors higher extraction at higher value and more silver were available in the solution. In the opposite side the increased temperature with concentration leads to lower yield since silver was dissolved at higher temperature and NaOH concentration.

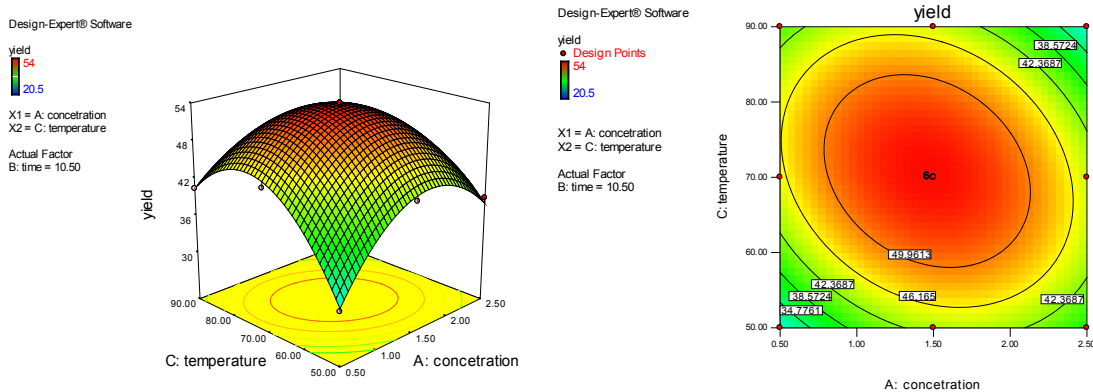


Figure 4.6: 3D & contour surface for interaction of temperature and concentration.

4.2.2.3 Interaction effects of Temperature and Time

Higher values of temperature and time were increased the yields of silver. This was the reason that the silver stripped completely from the film when the stripping time was increased. The temperature also made the collagen favorable for stripping and the silver easily detached from the film base. The recovery (yield) maximum at 70°C and 10.5 minutes stripping temperature and time respectively (54% at center of contour surface). From the figure 4.7 below, the yield was increased rapidly until the temperature was 70°C but it was decreased rapidly above this value. The yield with time was shown a slightly increment until 10.5 minute but the recovery was decreased beyond this value due to interaction effect.

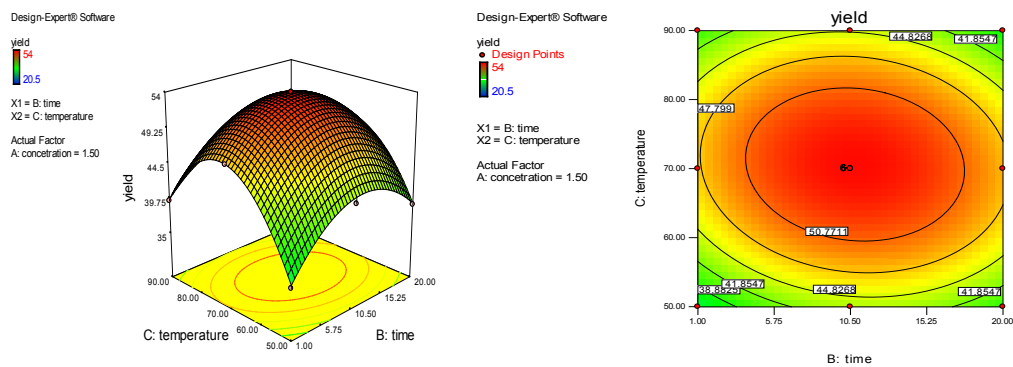


Figure 4.7: 3D & contour surface for the interaction of temperature and time.

4.2.3 Screening of Factors

From figure 4.1-4.7 above, the graphs were shown that all the factors were significant during the analysis of the result. Each one and combined factor effects were shown more significance. The significant effects of the factors were determined using the analysis of variance and the predicted versus actual graph. From the ANOVA table 4.3, all the factors have values of “prob > F” less than 0.05. From design expert, this indicates that all the factors were significant during the recovery of silver.

4.2.3.1 Analysis of Variance for Silver Recovery (Yield)

Response 1 yield

Backward Elimination Regression with Alpha to Exit = 0.100

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Table 4.3: ANOVA for recovery of silver

Source	Sum of Square	df	Mean Square	F value	p-value Prob > F	
Model	2702.51	9	300.28	631.62	< 0.0001	Significant
A-concentration	5.56	1	5.56	11.69	0.0025	
B-time	2.72	1	2.72	5.73	0.0257	
C-temperature	7.35	1	7.35	15.45	0.0007	
AB	114.08	1	114.08	239.97	< 0.0001	
AC	204.19	1	204.19	429.50	< 0.0001	
BC	18.75	1	18.75	39.44	< 0.0001	
A ²	555.82	1	555.82	1169.15	< 0.0001	
B ²	241.86	1	241.86	508.74	< 0.0001	
C ²	677.44	1	677.44	1424.96	< 0.0001	
Residual	10.46	22	0.48			
Lack of Fit	10.46	17	0.62			
Pure Error	0.000	5	0.000			
Cor Total	2712.97	31				

The Model F-value of 631.62 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A², B², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. This means the insignificant model terms that had been rejected during design software analysis were not affect the mathematical model equation.

As shown on annex-2, The "Pred R-Squared" of 0.9907 is in reasonable agreement with the "Adj R-Squared" of 0.9961. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 86.37 indicates an adequate signal. This model can be used to navigate the design space.

Based on the above significant factors, the coefficients for the model were estimated.

Table 4.5 : Model coefficient for silver recovery or yield.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	53.73	1	0.23	53.25	54.21	
A-concentration	-0.56	1	0.16	-0.89	-0.22	1.00
B-time	0.39	1	0.16	0.052	0.73	1.00
C-temperature	0.64	1	0.16	0.30	0.98	1.00
AB	-3.08	1	0.20	-3.50	-2.67	1.00
AC	-4.13	1	0.20	-4.54	-3.71	1.00
BC	-1.25	1	0.20	-1.66	-0.84	1.00
A ²	8.81	1	0.26	-9.35	-8.28	1.10
B ²	-5.81	1	0.26	-6.35	-5.28	1.10
C ²	-9.73	1	0.26	-10.27	-9.20	1.10

Final Equation in Terms of Coded Factors:

$$\text{Yield} = + 53.73 - 0.56 * A + 0.39* B + 0.64 * C - 3.08* A * B - 4.13* A * C - 1.25* B * C - 8.81* A^2 - 5.81 * B^2 - 9.73* C^2$$

Where A: is concentration of NaOH in mole per liter

B: is the stripping time in minute

C: is the stripping temperature in °c.

From the above equation, the yield to be maximized the coefficient should be positive but the coefficients which were negative would minimize the recovery amount. Therefore, concentration, had inverse relationship with our target (i.e maximum yield or recovery). The amount of silver to

be recovered was minimized when the concentration was increased. The high concentration were dissolved the metal to be precipitated and make difficult for separation that was the reason why it was inversely proportional to the recovery. However, time and temperature had a positive coefficient and they were directly proportional to the yield. Increasing time would allow the silver stripped completely from the film base and the temperature also should activate and exposed the stucked silver to be leached out. The interaction and square of these factors have inversely proportional to the yield or recovery.

4.2.4 Diagnostic

Parity plots were prepared to investigate the agreement between experimental (actual) values and model predictions. Model prediction was generated by the software which was compared with the real experiment that had been done in the lab and to show development of empirical equation for the actual experiment.

On the parity plot below (figure 4.8) the actual values and the predicted values were compared. The actual value was the measured response data for particular run, y_i , and the predicted value was also the value generated and predicted from experimental design software model equation and compared with the response data that inserted into the model. This plot was shown that the agreement between experiments and models were satisfactory. The experimental and the predicted values fall on the 45 degree line, this was indicated that the predicted values were agreed with the experimental one.

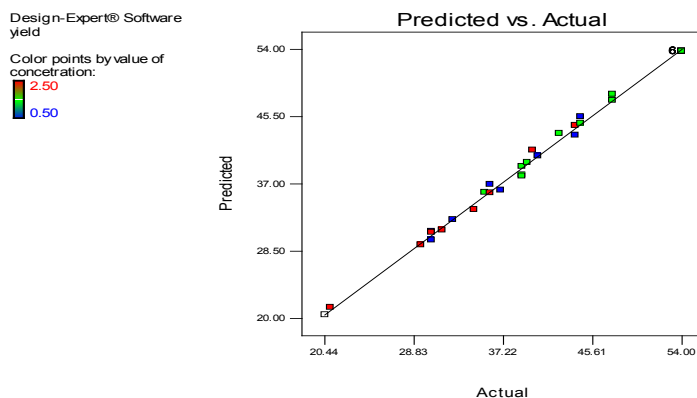


Figure 4.8 : Predicted versus actual values for silver yield.

4.2.5 Optimization

Optimization may be interpreted as the way to find those values of controllable independent variable that give the most desired value of the dependent variable.

Numerical optimization was carried out considering each value of the response and the goal of silver recovery or yield is set to maximize. Results of optimization based on our target give certain set of solutions and they are tabulated below.

Constraints

Table 4.6: constraints of optimization

Name	Goal	Lower Limit	Upper limit	Lower Weight	Upper Weight	Importance
Concentration	is in range	0.5	2.5	1	1	3
Time	is in range	1	20	1	1	3
Temperature	is in range	50	90	1	1	3
Yield	maximize	20.5	54.0	1	1	3

Below was the output from the design expert statistical software. It analyzed the input data from the experimental work, predicts one possible solution found and suggested this as an optimum value. The optimum yield was 53.77%. This value was obtained at a concentration of 1.45 mole/liter, stripping time 10.90 min. and temperature of 70.81°C. Using this optimum value, the average silver content of the waste x-ray film was 0.26 mg/cm². This result was supported by the 0.37 mg/cm² of the literature [3].

The average yield of the method was 54% according to silver content based on the finding of 0.26 mg/cm². The variations of the yields in different NaOH concentrations were attributed to the differences in silver content of the waste photographic film.

Table 4.7: possible optimized solution

Number	Concentration (M)	Time (min)	Temperature (°c.)	Yield (%)	Desirability	
1	1.45	10.90	70.81	53.77	0.993	Selected

4.3 Characterization of the Product

The recovered silver was identified and characterized using XRF EDX 2800 instrument, annex-3. At the same time, the purity and its trace impurities had been recognized and quantified. These characteristics of the product were compared with the result in the literature [3, 32]. The following results were obtained using XRF instrument.



Figure 4.9: Sample image on the purity-analyzing instrument.

Table 4.8: Analytical Result and weight (g)

No.	Field no.	Lab no.	Weight	Cu	Zn	Ag	Au	Pd	Cd	Sn
			Grams	%	%	%	%	%	%	%
1	M-14	8175/14	2.52	<0.01	0.30	98.28	<0.01	0.52	0.30	<0.01
2		duplicate	1.61	<0.01	0.30	97.77	<0.01	0.52	0.30	0.54

The X-Ray Fluorescence (XRF) instrument covers about 0.8 mm diameter and about 15 mm depth of the samples. Therefore, the instrument can generate a representative average composition of the sample. The purities of the silver at any run was the same because purity of the silver was depend on the amount of borax and sodium carbonate that was added to the dried black silver to be smelted. Therefore, no matter which samples were taken for purity measurement.

From table 4.8, the purity of the first sample is 98.28 % the second duplicated one is 97.77% purity. The average purity of the two samples became 98.03 %. This result was very encouraging because it had less than 2% impurities inside it. This value was agreed with the literatures that have an average purity 99.24%. However, even if the method was the same with literature, there was a 1.21 % difference [32].

The purity difference between the literature and the proposed method was due to chemicals that were used in the lab could have different grade even if they were labeled as if they are analytical grade. In addition to this, distilled water that was used for the experimental work was not triply distilled due to unavailability of enough distiller machines in the institute (only one they had). However, the literature was recommended to use triply distilled water for the experiment. Therefore, this was the main reason for the difference of the result from the literature.

The silver produced locally and available in the market was not more than 80 % purity. Due to this, most customers were interested to buy the imported once.

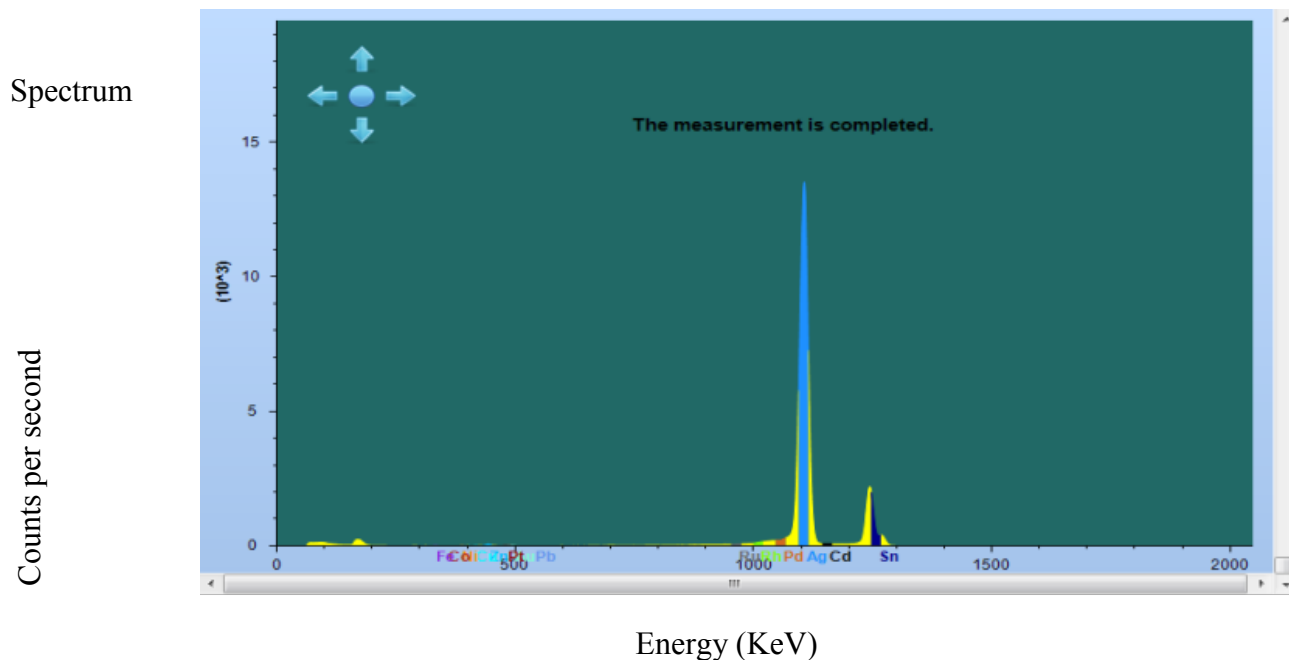


Figure 4.10: Spectrum of silver on XRF instrument.

Using the instrument, each trace impurities composition had been identified and quantified based on the instrument counts per second conversion. Figure 4.10 was shown the completion of software setup for precious metal trace impurities detection and measurement.

Table 4.9: Results ($\mu\text{g/g}$) for the trace impurities in the recovered silver and in comparison to some results for high purity silver in the literature [3, 32].

Element	Silver recovered using the proposed method	Silver recovery using NaOH in literature [32]	Silver recovered by the enzymatic method [3]	EM946 5	EM9343	FS 14
Fe	-	2.3	20.01	1.85	0.26	47.6
Cu	< 0.01	0.047	1.714	0.132	0.078	61.8
Mg	-	0.011	0.033	0.087	0.0640	-
Cr	-	0.499	0.671			-
Pb	-	<0.001	0.010	0.597	0.011	33.8
Al	-	0.024	4.620	0.082	0.024	-
Mn	-	0.003	0.021	0.011	0.007	-
Co	-	1.16	20.89	0.002 4	-	-
Ni	-	0.362	9.962	0.011	0.007	53.9
Sn	< 0.2	0.044	0.021	0.006	0.039	44.0
Cd	< 0.3	<0.001	<0.001	0.018	0.012	
Zn	0.3	2.3	-	-	-	-
Au	< 0.01	0.047	-	-	-	-
Pd	0.52	0.011	-	-	-	-

EM9465; high-purity silver containing 5'9 grade silver, EM9343; high-purity silver containing 6'9 grade silver, Fine silver FS 14: NIST SRM 8171.

From table 4.9, the proposed method is the best that could remove the trace metal impurities than the high-grade silver in the literature. As were observed in the table Mg, Cr, Pb, Al, Mn, Co, Ni and Fe were not observed in the proposed method because during smelting most of the impurities were removed with the slug but the literature was not followed smelting step and not used this instrument for impurities measurement. Instead of XRF, the researcher was used Inductively

Coupled Plasma Mass Spectrometry (ICP-MS) method. The ICP-MS instrument was measured the impurities in the precipitate and it could introduce a lot of interfering species. However, Zn, Au and Pd were detected which were not found in the high-grade silver in the literature due to the instrument highest detection capacity.

5 CONCLUSION

This study has demonstrated the stripping and recovery of silver from used X-ray photographic film by sodium hydroxide (NaOH) and sodium sulphide solution for stripping and precipitation of silver respectively. A full factorial design (3^3) for the factors, stripping temperature at (50 °c, 70 °c, and 90 °c), stripping time at (1 min, 10 min, and 20 min.) and sodium hydroxide concentration at (0.5M, 1.5M, and 2.5M) was developed for the experiment.

The stripping of silver were carried out for each factor levels combination. Blackish metallic silver in colloidal form in a NaOH solution had been observed. This observed colloidal form converted to sludge by adding Na_2S to precipitate the silver and the sludge were separated easily by decantation. The yield were increased at the lower levels and it reaches its maximum value at the medium factor levels but decreases towards its highest level. The maximum silver recovery (yield) was 54%. This was obtained at a NaOH concentration of 1.5M, stripping time of 10.5 min. and stripping temperature of 70°C. The silver yields were determined by XRF and 98.03% average purity was recorded. The average silver content of waste x-ray film was 0.26 mg/cm².

The experimental data were put into design expert software to develop yield equation and significant factors were identified. Therefore, from optimization, best condition were obtained to achieve high silver recovery by using Design expert software. The optimal recovery conditions of silver was stripping temperature of 70.81°C, stripping time of 10.90 minutes and concentration of sodium hydroxide (NaOH) 1.45 M. Under this particular conditions 53.77% silver recovery is obtained.

Moreover, in the process of silver recovery, the order of factors influencing the stripping was : stripping temperature > stripping time > and concentration of sodium hydroxide.

In addition, regarding the effect of operating conditions on the final product the following two points are concluded.

- ✓ The amount of the silver stripped from the film base can be increased by increasing the stripping agents (sodium hydroxide, stripping time and temperature) within the range studied.

- ✓ The recovery or yield is much dependent on the precipitating reagent concentration (sodium sulphide) and the stripping reagent sodium hydroxide. Due to common ion effect between sodium sulphide and sodium hydroxide, for maximum recovery of silver, the ratio (sodium sulphide/sodium hydroxide) should be 1:2. In addition, higher concentrations of sodium hydroxide were observed to dissolve the silver and made the separation or precipitation difficult and decrease the yield.

Generally, from this study, it is concluded that silver can be recovered from waste x-ray photographic film effectively and economically using NaOH for stripping and Na₂S for precipitation.

6 RECOMMENDATION

In the laboratory experiments, many ideas were identified which need consideration for the result to be very refined.

1. In the stripping process the parameter, solid to aqueous ratio and dosage of sodium sulphide shall be varied and the optimum result should be selected to have a better number of silver particles in a solution and a good amount of solvent that could strip the silver efficiently from the given area of film. In this thesis work the solid to aqueous ratio and dosage of sodium sulphide were not considered as parameter but the aqueous fixed at 1 liter and sodium sulphide 1:2 ratio to sodium hydroxide. This was because studying more than three parameters at three levels is very difficult task, especially on the laboratory work. But, they can be investigated separately.
2. The stripping and recovery of silver needs a medium under which the stripping and recovery or separation are takes place. The medium may be an aqueous solvent or organic solvents. These solvents have an effect on the reaction. The best solvent should be selected based on its activity towards the reaction, its cost and so on. It would be better if the various solvents are tested and each other are compared from different angles.
3. It would be better if triply distilled water could be used, whereas once distilled water had been used throughout the experiment.

7 REFERENCE

1. W. Dahne, *Schriftenr. GDMB*, 63 231-247 (1990).
2. T. W. Ewell and J. Piper, *Ind. Water*, 7 (11), 30-32 (1970)
3. Y. Sun, J. Mierzwa, C. Lin, T. I. Yeh and M. Yang, *Analyst*, 122, 437-440 (1997)
4. V.I.E. Ajiwe and I.E. Anyadiegwu, *Separation and purif. Tech.* , 18, 89-92 (2000)
5. S. Syed, S. Suresha, L.M. sharma and A.A. Syed, *Hydrometallurgy*, 63, 277-280(2002).
6. N. Fujiwara. , T . Tsumiya, T. Katada T.T. Hosobushi and K. Yamamoto, *process Biochim.* , 24(4), 155-156 (1989).
7. Jump up ^Hansen, C. J.; Primas, F. (20 10). "Silver Stars". *Proceedings of the International Astronomical Union* 5: 67. doi:10.1017/S1743921310000207.
8. Nichols, Kenneth D. (1987). *The Road to Trinity*. Morrow, New York: Morrow. p. 42. ISBN 0-688-06910-X.
9. Edwards, H.W.; Petersen, R.P.; Petersen (1936)."Reflectivity of evaporated silverfilms".*Phys.Rev.*9(9):871.Bibcode:1936PhRv...50..871E.
doi:10.1103/PhysRev.50.871
10. Hammond, C. R. (2000). *The Elements*, in *Handbook of Chemistry and Physics* 81st edition. CRC press. ISBN 0-8493-0481-4.
11. Riedel, Sebastian; Kaupp, Martin (2009). "The highest oxidation states of the transition metal elements". *Coordination Chemistry Reviews* 253 (5–6): 606–624. doi:10.1016/j.ccr.2008.07.014.
12. "Atomic Weights of the Elements 2007 (IUPAC)". Retrieved 11 November 2009.
13. "Atomic Weights and Isotopic Compositions for Silver (NIST)". Retrieved 11 November 2009.
14. Kelly, William R.; Wasserburg, G. J. (1978). "Evidence for the existence of ¹⁰⁷Pd in the early solar system". *Geophysical Research Letters* 5 (12): 1079. Bibcode:1978GeoRL...5.1079K. doi:10.1029/GL005i012p01079.
15. Bjelkhagen, Hans I. (1995). *Silver-halide recording materials: for holography and their processing*. Springer. pp. 156–166. ISBN 3-540-58619-9.
16. Meyer, Rudolf; Köhler, Josef and Homburg, Axel (2007). *Explosives*. Wiley–VCH. p. 284. ISBN 3-527-31656-6.
17. A. Earnshaw; Norman Greenwood (1997). *Chemistry of the Elements* (2nd ed.). Elsevier. p. 903. ISBN 9780080501093.
18. citeweb|url=http://events.nace.org/library/corrosion/Artifacts/silver.asp
19. "A Riot of Effects; Kilnforming". *Bullseyeglass.com*. 3 February 2011. Retrieved 22 May 2013.
20. Agency for Toxic Substances and Disease Registry (RTSDR),1999.

21. Zhouxiang, Silver Recovery from waste fixer solution and X-ray (1999).
22. Pollet et al, Recovery of silver from photographic waste electrolysis behavior, 2000.
23. MasserSchemidt, H. 1988. Method of recovering silver from waste photographic film and paper. American patent, 4759914 (CI 423-39)
24. Kodak , 1999b, The technology of silver recovery for photographic processing facilities : Publication no; J-212 Rochester; N.Y. ,Eastman Kodak Company. Available at: <http://www.kodak.com> (retrieval date: July 2003)
25. Ajiwe, V.I.E. and Anyadiegwu, I.E. 2000. Recovery of silver from industrial wastes, cassava solution effects. Separation Purif. Tech. 18: 89-92
26. Kodak , 1999a, Recovering silver from photographic processing solutions, Publication no; J-215 Eastman Kodak Company. Available at: <http://www.kodak.com> (retrieval date: July 2003)
27. S. G. Treshkova and E.A. Prodan, Tekh. Kino Telev. 5, 14-18 (1988).
28. G. Nisli, D. Toscali, B. Yenigul and C. Duran, VIIIth National symposium on Chemistry and Chemical Engineering, Istanbul, 1, 341-345 (1992).
29. J. Guo and W. An, Huaxue Shijie, 28(4), 174-175 (1987).
30. Ato Demis Lema, Ethiopian geological survey laboratory manual.
31. G.E.P. Box, K.B. Wilson, On the experimental attainment of optimum conditions, J. R. Stat. Soc. Ser. B-Stat. Methodol. 13 (1951) 1-45.
32. Nikiboglu, Toscali, D., Nisli, G., 2003. A novel silver recovery method from waste photographic films with NaOH stripping. Turk. J. Chem. 27, 127-133.

Annex-1: Table of randomized design (actual) values

Run no.	Factor			Average Yield or recovery (%)
	Concentration (mole/liter)	Time (min)	Temperature (°c.)	
6	0.50	1.00	50.00	20.5
29	1.50	1.00	50.00	35.5
8	2.50	1.00	50.00	34.5
16	0.50	10.50	50.00	30.5
25	1.50	10.50	50.00	42.5
9	2.50	10.50	50.00	39
10	0.50	20.00	50.00	30.5
11	1.50	20.00	50.00	39
30	2.50	20.00	50.00	30.5
27	0.50	1.00	70.00	37
26	1.50	1.00	70.00	47.5
20	2.50	1.00	70.00	40
23	0.50	10.50	70.00	44.5
18	1.50	10.50	70.00	54
1	2.50	10.50	70.00	44
14	0.50	20.00	70.00	44
28	1.50	20.00	70.00	47.5
12	2.50	20.00	70.00	36
17	0.50	1.00	90.00	32.5
3	1.50	1.00	90.00	39.5
2	2.50	1.00	90.00	29.5
31	0.50	10.50	90.00	40.5
13	1.50	10.50	90.00	44.5
19	2.50	10.50	90.00	31.5
7	0.50	20.00	90.00	36
22	1.50	20.00	90.00	39
4	2.50	20.00	90.00	21
32	1.50	10.50	70.00	54
24	1.50	10.50	70.00	54
15	1.50	10.50	70.00	54
5	1.50	10.50	70.00	54
21	1.50	10.50	70.00	54

Annex-2: Table of R² values.

Std. Dev.	0.69	R-Squared	0.9961
Mean	40.03	Adj R-Squared	0.9946
C.V. %	1.72	Pred R-Squared	0.9907
PRESS	25.35	Adeq Precision	86.37

Annex-3: Analytical result: percent & weight (g)


Geological Survey of Ethiopia; Geoscience Laboratory Directorate
 Geochemical Laboratory Gold Analysis Report Format Form G0001
 File ID:8175/14GOV Originator MEKURIALEM DEMELASH(AAU)
 Sample type:SILVER INGOT
 Sample preparation: not needed
 Number of Sample:1 Date submitted 5/20/2014
 Analytical method : XRF EDX 2800

Analytical Results:PERCENT & Weight(g)


No.	FIELD NO	LAB NO	Weight	Cu	Zn	Ag	Au	Pd	Cd	Sn
			grams	%	%	%	%	%	%	%
1	M-14	8175/14	2.52	<0.01	0.30	98.28	<0.01	0.52	0.30	<0.01
2		DUPLICATE	1.61	<0.01	0.30	97.77	<0.01	0.52	0.30	0.54

NotE: Cu=COPPER Zn=ZINC, Ag= Silver, Au=Gold
 Pd=PALADIUM Cd=CADIMIUM

Analysts
 Kedir B.

CHECKED BY

 Kedir Bedasso
 Analytical Process Quality Monitoring
 Case Team Co-ordinator

QUALITY CONTROL
 DATE REPORTED
 5/20/2014



Declaration

I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, hereby submitted by me titled “recovery of silver from waste x-ray photographic film”, is my original work and has not previously been submitted for a degree at this or any other University, and that all reference materials contained therein have been duly acknowledge.

Mekurialem Demelash Erku

Name

Signature

Date

This is to certify that above declaration made by the candidate is correct to the best of my knowledge.

Abubeker Yimam (Dr.Ing.)

Name

Signature

Date