

# Hydrometallurgical Recovery of Zinc from Zinc Ash, Silver from Waste X-ray and Photographic Films

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**Abstract**—The world's reserves of silver-bearing and zinc-bearing ores are depleting rapidly. The wastes from the medical sector and zinc metallurgical industries create adverse impacts on the environment and on human health. This research work focuses on different approaches for recovery of silver from waste radiographic and photographic films, and zinc from zinc ash. Novel, fast, less expensive and relatively pollution-free methods have been investigated for the recovery of silver from X-ray and photographic films by using NaOH stripping, Plantain Ash Solution (PAS) and Thiosulphate leaching. Similarly, methods for the recovery of zinc from zinc ash by sulphuric acid leaching and electrolysis of zinc ash and domestic sewage mixture were investigated. Hydrometallurgical methods proved more favourable yielding 2.95% (NaOH stripping) and 3.53% (Thiosulphate leaching) of silver by weight and 67.73% of zinc by weight through sulphuric acid leaching. The results obtained are in tune with literature. The attempt at electrolytic recovery of zinc from the zinc ash-domestic sewage mixture using copper electrodes failed to yield metallic zinc after 1.5h of electrolysis time but reduced the total pollution load of the mixture. The recovered metals were tested using AAS, XRD and EDX analyses. Optimum conditions for metal recovery were chosen for the hydrometallurgical methods based on literature. This study paves the way for identification of appropriate recovery methodologies and to economize the process if adopted on an industrial scale. There is further scope for future investigations into combined methods for valuable and non-toxic recovery of these metals from secondary sources.

**Keywords**—*hydrometallurgy; metal recovery; photographic films; secondary sources; secondary wastes; silver; X-ray films; zinc; zinc ash (key words)*

## I. INTRODUCTION

The consistently increasing global demand for metals together with the decreasing production of metals from ores results in two issues. Firstly, the increase in processing of metals from mineral resources and secondly, the consequent increase in metal production from secondary sources. Recycling of secondary raw materials is a crucial part of industrial audit feedback in developing countries. Additionally, the characteristic pollution caused by the secondary wastes and the useful components that can be recovered from these wastes further speak in favor of production of metals from secondary sources.

Silver as a metal has high photosensitivity and electrical conductivity. Owing to this, silver is extensively used in the field photography and in the electrical industry. Approximately 40-50% of the silver production is consumed

for radiography and photographic films/papers. It is reported that 25% of the world's silver needs are supplied by recycling and that 75% of this is obtained from photographic waste [1]. Two-third of the silver obtained from mines is the by-product from the production of Cu, Au, Pb and Zn. Most of the world's silver is recovered from scraps such as photographic films, X-ray films and jewelry. Zinc is an important base metal required for various applications in metallurgical, chemical and textile industries. It is mainly recovered from primary sulphide concentrates. At present, approximately 70% of the zinc produced worldwide originates from mined ores and 30% from recycled zinc or secondary zinc [2]. In thermal zinc coating industry, the process results in zinc ash which contains 80% zinc [3],[4].

Silver production results in large emissions of mercury to air, soil and water which may lead to mercury poisoning. Silver sticks to fish gills, potentially choking fish to death. It also hinders the process of cleaning sewage because it interrupts bacterial activity [5]. Zinc may also increase the acidity of water, may cause biomagnification, may interrupt the activity in soils and retards the degradation rate of organic matter [6]. Silver compounds may be slowly absorbed by the body tissues resulting in bluish or blackish skin pigmentation, known as argiria. When silver enters the human body, it gets deposited around the nerves and also in deeper skin layers and may lead to permanent skin damage. Zinc being a trace element is essential for human health. Zinc deficient people appear 'dwarf like' with too little zinc, may people experience loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Very high levels of zinc damages pancreas, disturbs protein metabolism and cause arteriosclerosis. In the work environment, in industries zinc contagion can lead to a flu-like condition known as metal fever [6].

Many methods are established to recover silver from photographic wastes such as precipitation, electrolysis, solvent extraction and ion-exchange. Numerous approaches including adsorption, biosorption, precipitation, reverse osmosis, filtration and other membrane separations are employed to treat metal plating wastewaters. Precipitation of heavy metals is seen most effective and economical method with muffle ash recovery. Although chemical coagulation technique is considered to be effective, it shows high cost and may produce side-products as secondary pollutants [7]. Electrolysis alone is not suitable for dilute concentration. Chemical infiltration also

causes difficulty in transferring and disposing sludge and neutralizing the effluent, which is non-practical [7].

Hydrometallurgy is seen to be more promising and a more suitable alternative, offering the advantage of small quantities of sludge with a low zinc concentration [8]. Hydrometallurgy is part of the field of extractive metallurgy involving the use of aqueous chemistry involving the recovery of metals from ores, concentrates and residual materials. It typically consists of solvent extraction, leaching, precipitation, ion exchange and purification. In addition to metal recovery methods, we also intended to find hybrid treatment systems to recover silver and zinc from wastes.

## II. MATERIALS AND METHODS

### A. Recovery of silver

The films (x-ray and photographic) were procured from a local major health care facility situated in Mysore city, Karnataka, India.

1) *Recovery by NaOH Stripping* [9]: Used X-ray films were washed with single distilled water and wiped with cotton impregnated with ethanol. The films were dried in a hot air oven at 40°C for 30 minutes. Two films were taken and shredded into pieces of size 4cmx4cm. The cut portions were segregated into pieces containing majority black portions (containing more silver) and pieces with more grey and white areas. The portion of films containing a majority of black areas was taken in a series of beakers containing 80mL of NaOH solution in two strengths of 2M and 1M. The beakers containing NaOH solutions were kept at high temperature using a water bath at 70-80°C and the films were stirred continuously till the gelatin layer was stripped off. This was observed at 23 minutes after dipping. The stripped films were removed, cleaned, dried and weighed. The resulting solution containing colloidal black metallic silver was then stirred vigorously using a magnetic stirrer and a water bath at 90-95°C till a coarse residue was obtained. The 1M NaOH solutions needed a stirring time of 1h while the 2M solution took 1.5h. The residues were tested for silver by AAS and EDX analysis.

2) *Recovery by PAS (Plantain Ash Solution) Method* [10]: Plantain (*Musa paradisiaca*) is a green to yellow boat-shaped fruit of a large shrub, widely grown in the tropics. Plantain peels have been used for the production of certain chemical like ethanol, etc.

*Preparation of PAS* - Peels of unripe plantains were sun dried for 3 days (72 hours) at ambient temperature. After sun drying, the peels were dried in a hot air oven at 100°C for 6 hours and were churned using pestle and mortar and to a fine powder. 25g of ash was dissolved in 500mL distilled water and allowed to stand for 72 hours in a cool, dry place. The solution was filtered and pH was found to be 4.75. The ash was discarded. The solution was standardized using 1M HCl and methyl orange indicator. The strength of PAS was found to be 0.0075 M.

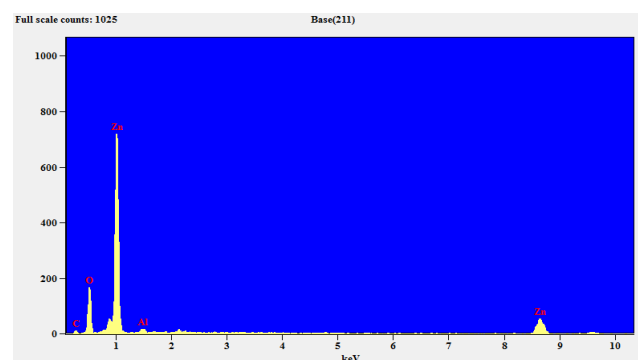
Used X-ray and photographic films were washed with single distilled water and wiped with cotton impregnated with ethanol. The films were dried in a hot air oven at 60-70°C for 30 minutes. The films were shredded into pieces of size

2cmx2cm to increase stripping area and fit the pieces in beakers. Two beakers containing 80mL of NaOH and 150mL of PAS were kept at 100°C using a water bath. The strengths of NaOH used were of 1M (for X-ray films) and 2M (for photographic films). The films were dipped and stirred continuously till the gelatin layer was stripped off which was observed at 30 minutes after dipping. The stripped films were removed, cleaned, dried and weighed. The resulting solution containing colloidal black metallic silver was then stirred vigorously using a magnetic stirrer and a water bath at 88-90°C till a coarse residue was obtained. The residue carefully transferred into an evaporating dish and heated to dryness. This was then tested for silver by AAS analysis.

3) *Recovery by Thiosulphate leaching* [11]: Reagent grade sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) and copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) were used in the study. Ammonia solution ( $\text{NH}_3$ , 25%) was used as the stock solution. The waste films were cut into 1.5cmx2cm pieces and prepared as 5g portions prior to use in the experiments. Leaching tests were performed in 250mL conical flasks. Leach solutions were prepared at the required strengths of thiosulphate (1M and 0.5M  $\text{S}_2\text{O}_3^{2-}$ ), copper (1M  $\text{Cu}^{2+}$ ), and ammonia (1M  $\text{NH}_3$ ) before the addition of the waste films (5g). The flasks were then placed in a temperature controlled (25°C) orbital shaker operating at 180 rpm. Over the experimental period, the top of the flasks were kept covered. After a leaching period of 3h, film residues were filtered and dried. They were then digested in hot concentrated nitric acid (65%  $\text{HNO}_3$ ) to determine their silver content by AAS. The pH of the residual solutions was also tested.

### B. Recovery of zinc

Zinc ash was obtained from Metal Hydroxide Private Limited, a zinc oxide manufacturing industry located in Mysore city, Karnataka, India. The obtained zinc ash sample was characterized by EDX analysis and the initial concentration of zinc was 61.44% shown in Fig. 1.



|       | Weight % | Weight %<br>Error | Atom % |
|-------|----------|-------------------|--------|
| C K   | 11.59    | ± 1.31            | 27.18  |
| O K   | 25.36    | ± 0.95            | 44.66  |
| Al K  | 1.62     | ± 0.25            | 1.69   |
| Zn K  | 61.44    | ± 4.23            | 26.47  |
| Zn L  | ---      | ---               | ---    |
| Total | 100.00   |                   | 100.00 |

Fig. 1. EDX analysis showing the peaks of constituents in the zinc ash sample

1) *Recovery by H<sub>2</sub>SO<sub>4</sub> leaching process* [12]: Zinc ash was weighed to obtain a portion of 100g. Leach solution system of 50 mL sodium chloride, 50 mL ammoniacal solution and 20mL sulphuric acid was prepared. The ash was allowed to react with this solution for a leaching time of 3h. Effervescence and fuming was not observed after the leaching period of 3h. The residue was then heated in a muffle furnace at 400–500°C for 3h. The dried sample was tested for zinc by EDX analysis.

2) *Electrolytic recover using SS (stainless steel) electrodes domestic wastewater mixture*: Zinc ash samples were mixed in varying concentrations along with domestic wastewater. The sample was collected after the screening unit at the Mysore Corporation STP 'B' located near Vidyanapuram, Mysore city. Parameters influencing the possible electrolytic recovery of zinc from this mixture were tested as shown in Table I.

An electrochemical reactor of 1.5L capacity was used for the experiment. Stainless steel electrodes having effective area of 50cm<sup>2</sup> were washed and weighed. Four electrodes were placed in the reactor with 1cm inter-electrode spacing. The reactor was filled with 1.5L with a magnetic bead placed at the bottom to maintain the homogeneity of the solution. The electrodes were connected to a DC power supply and a UPS to maintain continuous power supply to the system. Two different trials were conducted using this setup. Table II shows the characteristics of zinc and domestic wastewater mixture.

a) *Trial 1 – 100g Zn ash/ 1.6L of wastewater*

The experiment was carried out at 20V and a current of 0.1A, stirring at 400 rpm. The electrodes were weighed before and after an electrolytic run of duration 90 minutes.

b) *Trial 2 – 50g Zn ash/ 1.6L of wastewater*

The experiment was carried out at 30V and a current of 0.2A, stirring at 400 rpm. The electrodes were weighed before and after an electrolytic run of duration 90 minutes.

TABLE I. CHARACTERISTICS OF THE STP WASTEWATER SAMPLE

| Parameter                             | Value       |
|---------------------------------------|-------------|
| pH                                    | 7.24        |
| Chlorides                             | 120.96 mg/L |
| Total Alkalinity as CaCO <sub>3</sub> | 340.00 mg/L |
| COD                                   | 200.00 mg/L |

TABLE II. CHARACTERISTICS OF ZINC ASH AND DOMESTIC WASTEWATER MIXTURE

| Sample (Zn ash /1.6L of wastewater) | pH   | Chlorides (mg/L) | Alkalinity as CaCO <sub>3</sub> (mg/L) |
|-------------------------------------|------|------------------|--|
| 100g                                | 7.84 | 118.96           | 560                                    |
| 50g                                 | 7.57 | 115.96           | 400                                    |
| 25g                                 | 7.42 | 109.96           | 390                                    |

Samples were collected at regular time intervals from the reactor in both trials and were analysed for pH, alkalinity and COD.

### III. RESULTS AND DISCUSSIONS

The results obtained are categorized by metal and method as follows.

#### A. Recovery of silver

1) *NaOH Method*: Previous research by [11], demonstrated that waste X-ray films may contain 0.7-2% silver by weight on the emulsion on the polyester film base. But our sample which showed the highest loss in weight yielded 2.95% of Ag recovery by weight shown in Fig. 3. This discrepancy can be justified. When extracting a sample for EDX analysis, only 2-3g of the dry, powdered sample is taken for analysis from the bulk volume of the sample which may not be homogeneous. Considering the nature of the residue, it is possible that the Ag ions or salts were more concentrated in that portion which was extracted for sampling and hence, the higher weight % obtained. The high oxygen (61.66%) content and sodium (37.82%) is ascribed to the use of 80 mL NaOH per sample as a stripping agent. The same sample was also tested for silver using PXRD analysis (Powdered X-Ray Diffraction) and the result obtained is shown in Fig. 2. Peak for Ag nanoparticles should be at 35-40° (2θ value). The given sample showed in presence of substance having its peak within this range which confirms the presence of crystalline silver in the residual sample.

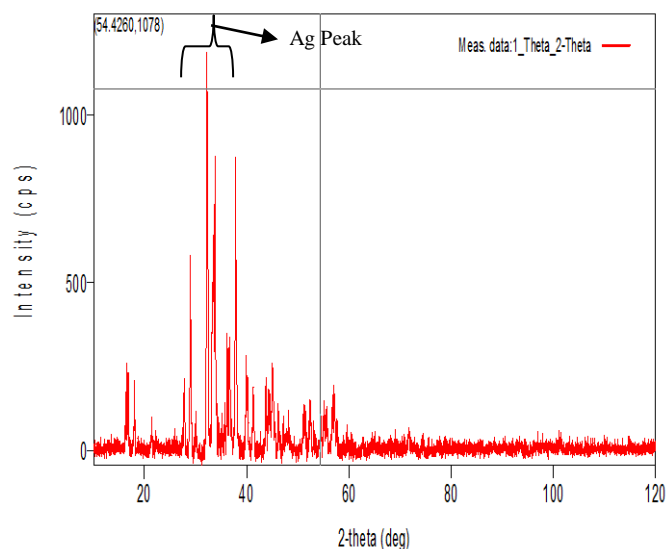
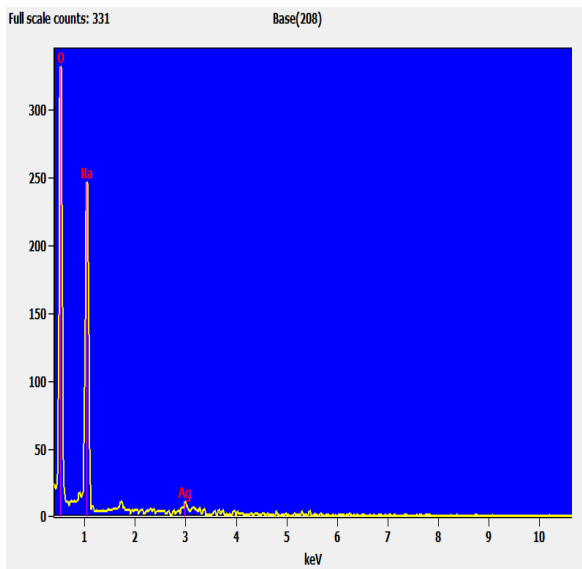


Fig. 2. XRD analysis of 1M NaOH sample confirming presence of silver nanocrystals

2) *PAS Method*: Although the solution combination stripped the films more effectively (higher weight losses) and more quickly (lesser leach time) than NaOH stripping alone, the presence of silver in the extractant (if any) was below the detection level of AAS. This could be attributed to the low concentration of the PAS solution used (0.0075M). It is possible that the solution facilitated the stripping process but hindered the recovery and extraction of silver itself by forming hydroxyl complexes.



Quantitative Results for: Base(208)

| Element Line | Weight % | Weight % Error | Atom % |
|--------------|----------|----------------|--------|
| O K          | 51.59    | ± 1.62         | 61.66  |
| Na K         | 45.47    | ± 1.34         | 37.82  |
| Ag L         | 2.95     | ± 0.69         | 0.52   |
| Ag M         | ---      | ---            | ---    |
| Total        | 100.00   |                | 100.00 |

Fig. 3. EDX analysis showing recovery of Ag by 1M NaOH as 2.95%

3) *Thiosulphate Method*: After a leaching period of 3h in the orbital shaker, the stripped films were filtered, washed and dried. The dried films were digested with  $\text{HNO}_3$  and the solution was tested for presence of silver in the form of silver nitrate by AAS analysis and results are seen in Table III.

The photographic film sample  $W_{g2}$  which yielded more silver was tested for Ag by EDX analysis shown in Fig. 5. This sample has yielded 3.53% of Ag by weight. This discrepancy can be justified as mentioned in the NaOH method. The high oxygen (66.75%) and sodium (21.36%) is ascribed to the use of sodium thiosulphate as a leaching agent. The same sample was also tested for silver using PXRD analysis. Fig. 4 shows the presence of a substance having its peak within this range which confirms the presence of crystalline silver in the residual sample.

TABLE III. SILVER CONTENT BY AAS ANALYSIS AFTER THE THIOSULPHATE LEACHING

| Film Type         | Initial Weight          | Ag by AAS (ppm)       | pH of Residual Waste Solution |
|-------------------|-------------------------|-----------------------|-------------------------------|
| X-ray Film        | $W_{b1} = 5.00\text{g}$ | Below detection level | 7.36                          |
|                   | $W_{b2} = 5.04\text{g}$ | 0.094                 | 7.84                          |
| Photographic Film | $W_{g1} = 5.00\text{g}$ | Below detection level | 6.95                          |
|                   | $W_{g2} = 5.03\text{g}$ | 0.101                 | 6.75                          |

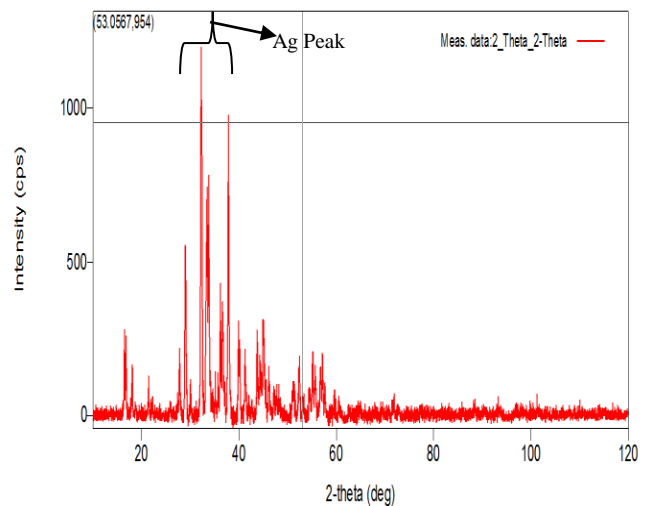


Fig. 4. XRD analysis of 0.5M thiosulphate sample showing the presence of silver nanocrystals

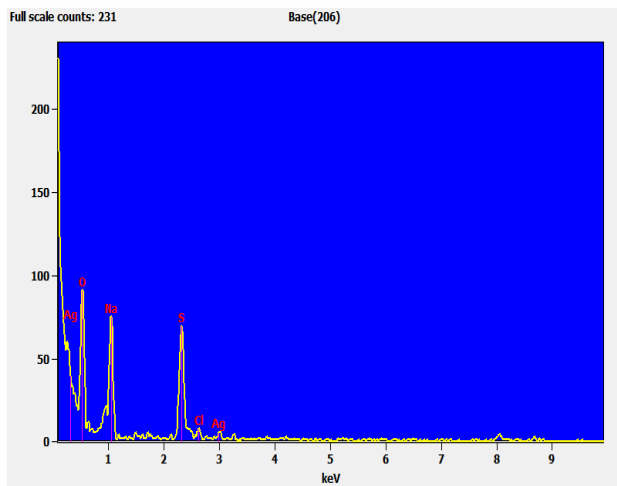
TABLE IV. COMPARISON OF THE THREE SILVER RECOVERY METHODS BY END RESULT OBTAINED

| Method Number | Main Mechanism        | Recovery (% by weight) | Result Verification       |
|---------------|-----------------------|------------------------|---------------------------|
| 1.            | NaOH Stripping        | 2.95%                  | AAS, XRD and EDX Analysis |
| 2.            | Thiosulphate Leaching | 3.53%                  |                           |
| 3.            | PAS + NaOH Stripping  | Below detection level  |                           |

4) *Comparison of the three silver recovery methods*: As seen in Table IV, the most obvious conclusion would be to choose the method that has highest recovery of silver by weight. Thus, the thiosulphate leaching process would be considered the most suitable option. Opting for this method could also be justified as the residual waste produced has pH in the range of 6.5–7.5 and the silver can be readily extracted by converting it to nitrate or chloride form.

Reference [11], adopted the Taguchi experimental design  $L_9$  ( $3^3$ ) orthogonal array tables to evaluate the influential parameters on silver recovery by thiosulphate leaching. Based on these findings, different combinations of concentration and volumes of the reagents used were utilized for 10g of films and leaching time of 3h as 10g sample + 40mL  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  + 40mL  $\text{CuSO}_4$  + 20mL  $\text{NH}_3$  (25%). The resulting samples were then tested for silver by AAS analysis shown in Table V.

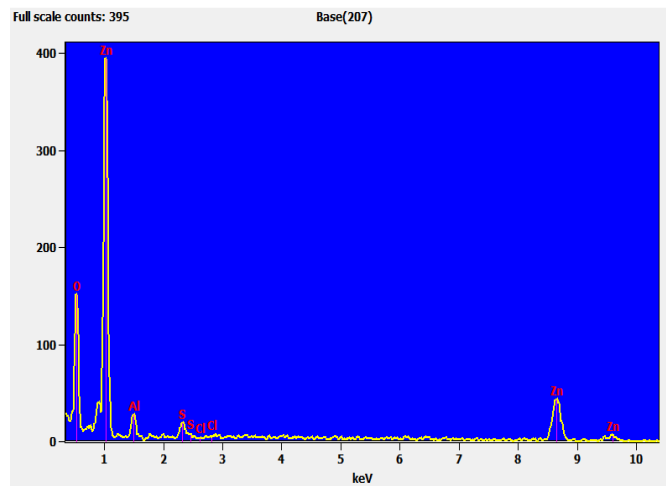
The concentration of ammonia was kept constant as it stabilizes the Cu(II) ion and concentrations of copper sulphate and thiosulphate solutions were tested. The concentration of copper ions was the most influential factor affecting recovery of silver. For the X-ray film samples, higher the concentration of copper in the solution, the higher was the silver yield. But this trend was not followed in the case of photographic films.



Quantitative Results for: Base(206)

| Element Line | Weight % | Weight % Error | Atom % |
|--------------|----------|----------------|--------|
| O K          | 53.60    | ±2.22          | 66.75  |
| Na K         | 24.65    | ±1.75          | 21.36  |
| S K          | 16.69    | ±0.95          | 10.38  |
| S L          | ---      | ---            | ---    |
| Cl K         | 1.53     | ±0.40          | 0.86   |
| Cl L         | ---      | ---            | ---    |
| Ag L         | 3.53     | ±0.91          | 0.65   |
| Ag M         | ---      | ---            | ---    |
| Total        | 100.00   | ---            | 100.00 |

Fig. 5. EDX analysis of 0.5M thiosulphate sample showing 3.53% Ag by weight recovered



Quantitative Results for: Base(207)

| Element Line | Weight % | Weight % Error | Atom % |
|--------------|----------|----------------|--------|
| O K          | 25.45    | ±1.44          | 55.51  |
| Al K         | 4.45     | ±0.54          | 5.76   |
| S K          | 2.37     | ±0.24          | 2.58   |
| S L          | ---      | ---            | ---    |
| Cl K         | 0.00     | ---            | 0.00   |
| Cl L         | ---      | ---            | ---    |
| Zn K         | 67.73    | ±5.20          | 36.15  |
| Zn L         | ---      | ---            | ---    |
| Total        | 100.00   | ---            | 100.00 |

Fig. 6. EDX analysis of zinc ash sample after sulphuric acid leaching process showing Zn as 67.73% by weight

TABLE V. RECOVERY OF SILVER BY VARYING CONCENTRATIONS OF LEACHING AGENTS

| Sl. No. | Sample            | [S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> ], M | [Cu <sup>2+</sup> ], M | [NH <sub>3</sub> ] | Recovery, mg/L (AAS) |
|---------|-------------------|---|------------------------|--------------------|----------------------|
| 1.      | X-ray film        | 0.005   | 0.025                  | (25%)              | 23.604               |
| 2.      | X-ray film        | 0.005   | 0.050                  | (25%)              | 26.349               |
| 3.      | Photographic film | 0.25  | 0.005                  | (25%)              | 0.388                |
| 4.      | Photographic film | 0.25  | 0.025                  | (25%)              | 0.071                |
| 5.      | Photographic film | 0.5   | 0.005                  | (25%)              | 0.212                |

**B. Recovery of zinc**

1) *Sulphuric acid Leaching Method:* The result of the EDX analysis of the dried sample after leaching process is shown in Fig. 6. The zinc ash normally contains its oxides and a small percent as free metallic zinc with some impurities in weight % as 60–85 Zn [12]. Hence, the recovery of zinc is well within the range of its concentration for valuable recovery. The end product of this process is zinc in zinc sulphate (ZnSO<sub>4</sub>) form. This is a valuable raw material for pharmaceutical industries

and also to make electrolytic salts for zinc electrowinning. The high percentage of zinc recovered (67.73% by weight) could be ascribed to the fact that the initial concentration of zinc in the waste itself is very high. The presence of oxygen 25.45% by weight indicates that there are significant levels of oxides in the sample. Presence of impurities like aluminium is confirmed by the EDX analysis.

2) *Electrolytic recovery of zinc using SS (stainless steel) electrodes domestic wastewater mixture:*

a) *Trial 1 – 100g Zn ash/ 1.6L of wastewater:* The zinc ash was mixed with domestic wastewater and was subject to electrolytic treatment. The parameters as tested are given in Table VI and Table VII as follows.

TABLE VI. CHARACTERISTICS OF MIXTURE DURING ELECTROLYSIS

| Time (min) | pH   | COD (mg/L) | RPM     |
|------------|------|------------|---------|
| 0          | 7.84 | 6167.6     | 390-400 |
| 15         | 7.98 | 4160       | 390-400 |
| 30         | 8.14 | 1747       | 390-400 |
| 45         | 8.21 | 915.2      | 390-400 |
| 60         | 8.17 | 2246       | 390-400 |
| 75         | 7.99 | 499.2      | 390-400 |
| 90         | 7.93 | 332.8      | 390-400 |

TABLE VII. CHARACTERISTICS OF MIXTURE BEFORE AND AFTER ELECTROLYSIS

| Parameter                       | Initial value (0 <sup>th</sup> min) | Final value (90 <sup>th</sup> min) | % Reduction |
|---------------------------------|-------------------------------------|------------------------------------|-------------|
| pH                              | 7.84                                | 7.93                               | Negligible  |
| Chlorides (mg/L)                | 118.96                              | 110                                | 7.53%       |
| Alkalinity as CaCO <sub>3</sub> | 560                                 | 372                                | 33.57%      |
| COD (mg/L)                      | 6167.6                              | 332.8                              | 94.60%      |

As seen from the data, the COD has a sudden increase at the 60<sup>th</sup> minute during electrolysis. But after the electrolytic process only COD has reduced by a significant 94%. The variation in pH from the start to end of electrolytic run showed a smooth transition with no significant end result. Alkalinity of the mixture and thus, total pollutant load of the mixture was reduced. However, metal deposition was not observed on the electrodes which justifies the presence of 59.34% of zinc as shown in Fig. 7. The difference in weights of the electrodes before and after electrolysis is given in Table VIII. Although pitting effect was observed, there was no metal deposition on the electrodes.

In the electrode arrangement, plate 4 was the cathode and plate 1 was the anode with plates 2 and 3 arranged symmetrically in between both. The pitting effect was observed on electrode plate number 4. This plate's dissolution could have contributed to the increase in COD at the 60<sup>th</sup> minute of the electrolytic operation. Metal deposition was not observed on plate number 1.

TABLE VIII. WEIGHTS OF ELECTRODES BEFORE AND AFTER ELECTROLYSIS

| Plate No. | Initial Weight (g) | Final Weight (g) | % Change (+ gain or - loss) |
|-----------|--------------------|------------------|-----------------------------|
| 1         | 17.6101            | 17.6297          | + 0.111%                    |
| 2         | 18.1612            | 18.1597          | - 0.008%                    |
| 3         | 18.9101            | 18.9139          | + 0.020%                    |
| 4         | 17.6235            | 17.5947          | - 0.163%                    |

b) Trial 2 – 50g Zn ash/ 1.6L of wastewater: A similar electrolytic run to Trial 1 was conducted but with zinc ash concentration reduced to 50g/1.6 L of wastewater sample. The parameters as tested are given in Tables IX and X. COD value increases after the 15<sup>th</sup> minute and reaches a peak after 30 minutes of electrolysis. The value of COD at the 75<sup>th</sup> minute was found to be zero which could be attributed due to human error in conducting the COD analysis by closed reflux titrimetric method or due to high concentration of interfering substances like chlorides that produce erroneous results.

Trial 1 resulted in 94.60% COD reduction while Trial 2 resulted in 51.17% COD reduction. The high COD reduction rate observed for the first sample (100g zinc ash/1.6L) is due to the high initial concentration of COD in the sample. There is a possibility that stirring by magnetic stirrer and in aerobic conditions could have also contributed in reducing the oxygen demand of the wastes.

TABLE IX. CHARACTERISTICS OF MIXTURE DURING ELECTROLYSIS

| Time (min) | pH   | COD (mg/L) | RPM     |
|------------|------|------------|---------|
| 0          | 7.51 | 4600.6     | 390-400 |
| 15         | 7.83 | 10,227.2   | 390-400 |
| 30         | 7.58 | 16,844.8   | 390-400 |
| 45         | 7.52 | 7,219.2    | 390-400 |
| 60         | 7.36 | 9,625.6    | 390-400 |
| 75         | 7.40 | 0          | 390-400 |
| 90         | 7.43 | 2,246.4    | 390-400 |

TABLE X. CHARACTERISTICS OF MIXTURE BEFORE AND AFTER ELECTROLYSIS

| Parameter                       | Initial value (0 <sup>th</sup> min) | Final value (90 <sup>th</sup> min) | % Reduction |
|---------------------------------|-------------------------------------|------------------------------------|-------------|
| pH                              | 7.51                                | 7.43                               | Negligible  |
| Chlorides (mg/L)                | 99.969                              | 90.979                             | 8.99%       |
| Alkalinity as CaCO <sub>3</sub> | 1040                                | 278                                | 73.26%      |
| COD (mg/L)                      | 4600.6                              | 2246.4                             | 51.17%      |

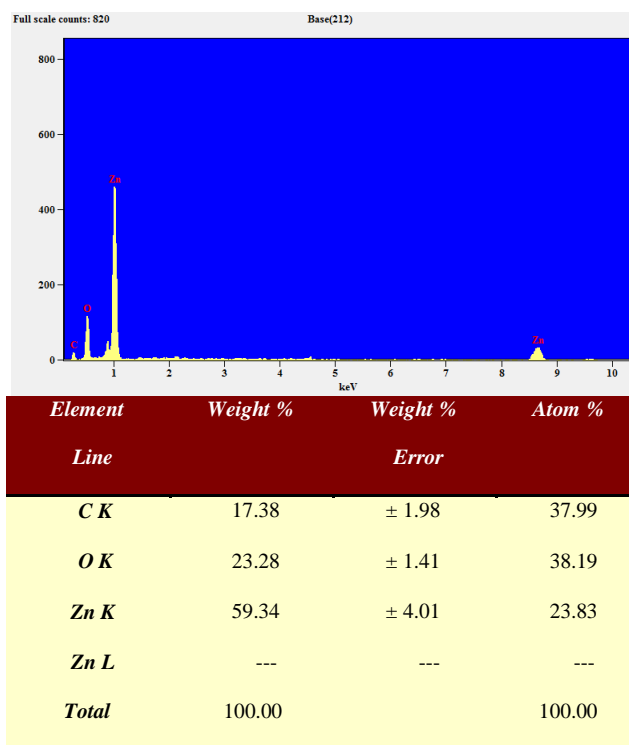


Fig. 7. EDX analysis of zinc ash sample after electrolysis

The graphical variation in pH and COD load of the mixture along with electrolysis time is shown in Fig. 8 and Fig. 9 below.

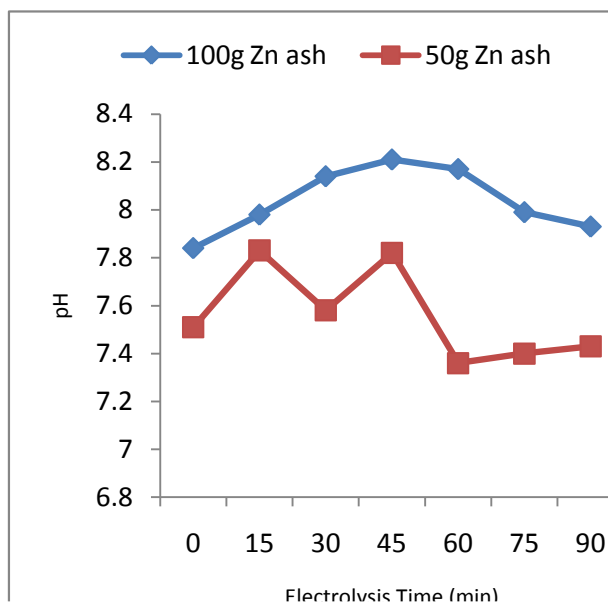


Fig. 8. Variation in pH with electrolysis time for both trials

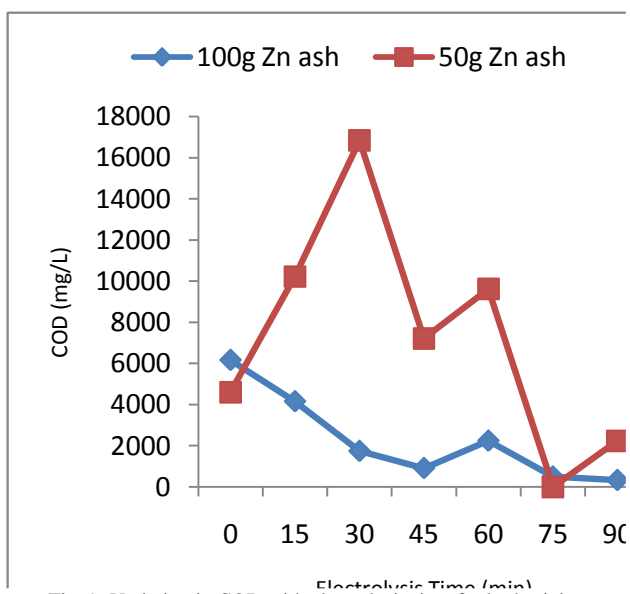


Fig. 9. Variation in COD with electrolysis time for both trials

#### IV. CONCLUSIONS

Various lab scale experiments were carried out to economically recover silver from waste photographic and X-ray films and to recover zinc from zinc oxide (ZnO) ash. Hydrometallurgical methods involving leaching and stripping for the recovery of silver as well as for the recovery of zinc showed promising results displaying high recovery rates.

The following conclusions have been drawn based on experiments carried out on batch mode:

- Silver was successfully recovered using 1M NaOH solution for stripping the waste X-ray films without any purification with a highest recovery of 2.95% by weight. The NaOH method is relatively economical

cheap as it is performed in the same container and does not require too much time (max 2h), with operations at normal temperature (70-95°C) and is relatively pollution free.

- The PAS (Plantain Ash Solution) method failed yield silver as the silver ions formed a complex with PAS ions and were not available for measurement. It follows that the faster stripping time is not a means to obtaining more silver ions. However, the silver ions have been leached from the wastes.
- The silver was successfully recovered using the 'Thiosulphate method'. Lower concentration of the principle stripping agent (0.5M) yielded more silver (0.101 mg/L and 0.094 mg/L from photographic and X-ray film samples respectively). This method yielded the highest recovery of silver (3.53% by weight). This method proves to be a relatively harmless leaching system with almost complete recovery of silver from the films.
- The 'hydrometallurgical recovery' of zinc using sulphuric acid as a leaching agent successfully yielded 67.73% of zinc as ZnSO<sub>4</sub>. The sulphuric acid leaching process for the recovery of zinc was found suitable for selective extraction of zinc from secondaries, environmentally safer, techno-economically feasible and flexible to fit several secondaries.
- An attempt on the electrolytic recovery of zinc from a mixture of zinc ash and domestic sewage using stainless steel electrodes was unsuccessful in terms of metal recovery. However the COD was greatly reduced (94% and 51.71% for 100g and 50g mixture of zinc ash per 1.6L of sewage sample).

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