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# UTILIZATION OF WASTES FROM CHEMICAL AND GALVANIZED INDUSTRIES – PREPARATION OF ZINC CHEMICALS

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Developing countries like Pakistan can ill-afford to loose so called "wastes" as sheer wastes. Beside, the dire economic necessity, the utilization of industrial wastes helps not only in minimizing the very likely hazardous impacts of these on our environemt but also in reducing the energy consumption required in shifting the wastes to disposal sites. Studies have been undertaken to prepare zinc chemicals of industrial importance from the wastes of galvanized and chemical indsutries. This paper describes details of investigations carried out into preparation of zinc chloride. Differential thermal (DTA) and thermogravimetric (TGA) analyses data indicated the product to correspond to $ZnCl_2.2H_2O$.

***Key words:*** Analysis, Developing countries, Zinc chloride, Industrial wastes, Zinc.

## Introduction

According to a survey of over 200 industries in Pakistan,34% of industrial units, including chemcial and galvanized industries, have been classified as " Most Hazardous". These industries may produce long-term accumulative health hazards and constant pollution of the ecosystem. Because of the high discharge of untreated indsutrial wastes into Deg-Nullah at Lahore (Fig. 1) which ultimately takes these to river Ravi, there has been a loss in the fish catch, approx. 200 tons per annum. Over 60% residents in the vicinity have been reported to suffer from sore eyes, throats and chronic cough caused due to polluted air contaminated with percolates (including zinc dust) and other toxic chemicals [1,2].

Besides, the utmost need for environmental protection and pollution control with regard to wastes, developing countries like Pakistan can ill-afford to loose so called "wastes" as sheer wastes. Increasing prices of land (for land fills), fuel/ power (for incineration), raw-materials, and conservation of energy and natural resources are regarded as other very positive factors for recycling and waste utilization [3]. In veiw f this, a number of processes have been developed in these laboratories to recycle and utilize industrial wastes, the detailed references of which have been quoted elsewhere [4,5].

In the present investigations, studies were carried out on the preparation of zinc chemicals from the industrial wastes from the galvanizing and chemical industries. The preparation of zinc chloride was taken up as it has a number of commercial applications in a number of industries [6], and more than 575 M tons of zinc chloride are imported in the country annually at a cost of Rs.50,00,000 in foreign exchange [7].

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## Experimental

Samples of spent acid and zinc waste were collected at the disposal site in dry weather. The acid was analysed and used as such without any pre-treatment, except where dilution was required. Zinc wastes, both in the form of lumps (Fig.2) and powder (100 mesh size B.S. standard) were washed with water and dried in open air. Thin shavings (slices) were cut from the zinc lumps prior to analyses and use.

The strength of the spent acid was determined by acid-base titration [8]. The specific gravity measurements were

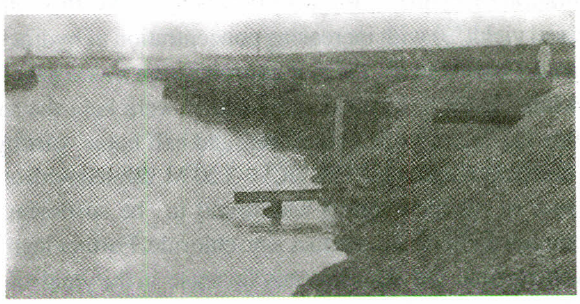

Fig. 1. Effluents discharge into Deg-Nulah, Lahore.

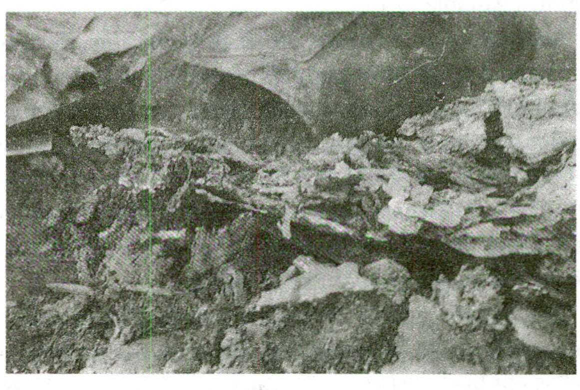

Fig. 2. Zinc waste (lumps) from galvanized industry, Peshawar.

carried out with a specific gravity bottle as well as hydrometer. The zinc content was determined volumetrically by titrating against standard potassium ferrocynide using diphenylbenzadine as the indicator [8]. The chloride content was determined by titrating against standard silver nitrate solution using 10% potassium chromate solution as the indicator [9]. Thermogravimetry (TG) and differential Thermal Analyses (DTA) were carried out in an open ceramic crucible under atmospheric pressure at a heating rate of 10°/min. on a Derivatograph (MOM) type thermobalance with automatic recording on photographic chart. All laboratory chemicals used were of reagent grade quality.

### Results and Discussions

*Study of reaction parameters.* Figure 3, Tables 1 and 2 describe the results of studies carried out with standard laboratory grade zinc and hydrochloric acid, to find out the reaction parameters for the maximum yield and recovery of the product zinc chloride. The parameters studied were mole concentration of zinc and hydrochloric acid, acid dilution and stirring time for the reaction.

Different amounts of zinc (powder/granules) corresponding to 0.50, 1.00, 1.25, 1.50 and 2.00 M were treated with 2 M hydrochloric acid diluted with equal voluem of distilled water and stired for 3 hrs. Maximum yield was observed for 1.25 M Zn (Table 1). Similar studies, carried out with different concentration of hydrochloric acid between 1-5 M, showed increased yield(%) with increasing concentration of hydrochloric acid. For this study, the zinc concentration was kept at 1.25 M while Table 1,2, others parameters were kept the same (Table 1). As shown in Table 2 one and half hours stirring of the reactants (Zinc = 1.25 M; HCl = 3.50 M, diluted with equal volume of distilled water) was found to be sufficient for maximum yield of the product zinc chloride. Further increase in stirring time did not show any increase in the yield of the product. Acid dilution study carried out by taking 1.25 M zinc, 3.50 M HCl and stirring time 3 hrs indicated that (1:1) dilution was most suitable (Table 2).

*Analyses of waste hydrochloric acid and zinc.* Results of the chemical analyses of samples of the zinc waste and spent hydrochloric acid are described in Table 3 and 4 respectively. The zinc content in the powder and lumps samples was found to be 52.11±0.01% (n=7) and 72.54±0.01% ( n = 7), respectively (Table 3). Becasue of the low zinc content in the powder waste, it was not used in the present studies. Zinc lumps were used for the preparation of zinc chloride.

The specific gravity of the spent hydrochloric acid was found to be 1.1634. By acid-base titration, the acid content in the spent hydrochloric acid was found to be 35.67 ± 0.01 (n = 5) and by argentometric method, it was found to be 27.73 q 4.73 (n = 3) (Tables 3,4).

*Preparation of zinc chloride from waste hydrochloric acid and zinc.* Having known the zinc and acid contents in the wastes, zinc chloride was prepared under the reaction conditions already determined using laboratory grade zinc and hydrochloric acid. A known amount of zinc waste, corresponding to fractions of 1.25 mole of zinc, was dissolved in

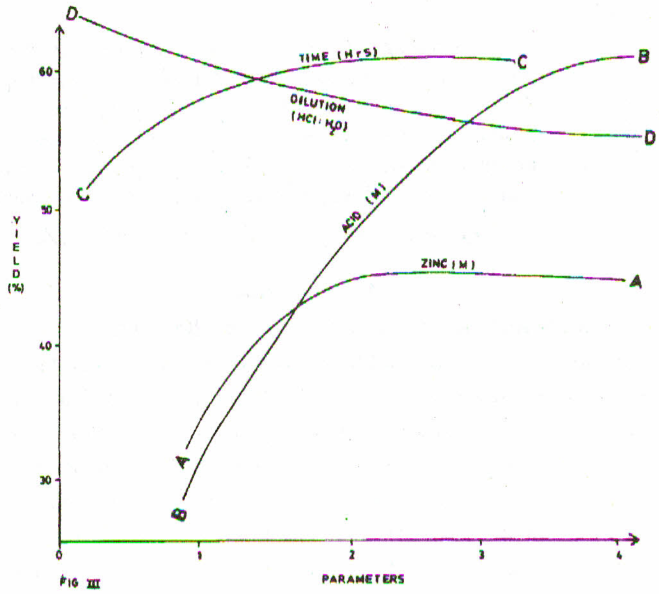


Fig. 3. Study of reaction parameters. (A) Zinc mole (B) HCl mole (C) Acid dilution (D) Stirring time.

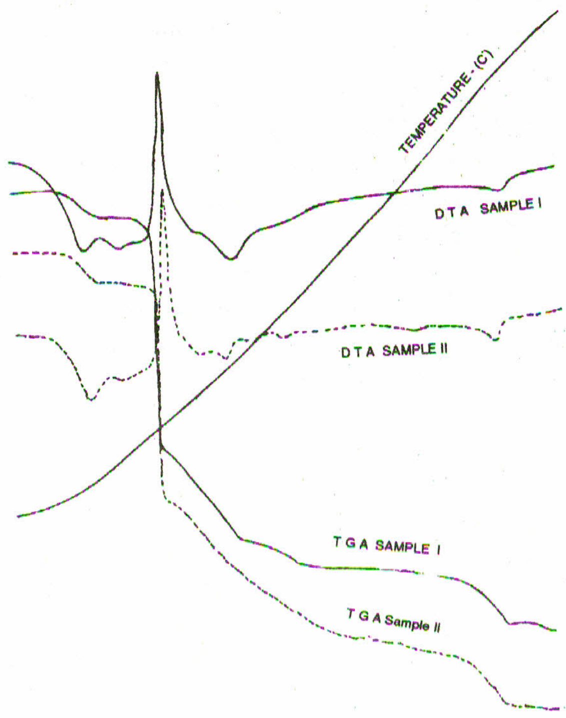


Fig. 4. Thermogrammes of impure product.

an appropriate volume of waste acid, corresponding to 3.5 M of hydrochloric acid, diluted with an equal amount of distilled water and stirred for one and a half hour. Undissolved residue was removed by filteration and washed serveral times with distilled water. The filterate was slowly evaporated on a water bath to a syrupy liquid and left overnight in a dessicater. The zinc chloride ($ZnCl_2$) product was filtered and recrystalized by dissolving in dilute nitric acid. The solution was neutralized with sodium carbonate and after filteration was again evaporated on a water-bath. A little hydrochloric acid was added to the syrupy liquid and left overnight in a dessicater. After filteration, the product was dried in an oven at 43°. Product yields with different amounts of the reactants, waste zinc and acid in the molar ratio 1.25 to 3.50 respectively, are given in Table 5. The average yield (%) was found to be 61.44 ± 2.12 (N = 9, Table 4).

Thermogravimetric (TC) and differential thermal analyses (DTA) were carried out to check the purity of the product which was found to be impure as indicated by the thermograms shown in Fig. 4. Characteristic DTA peaks and weight-losses due to water molecules and chlorine from the zinc chloride were not observed in the samples of the product studied.

Qualitative analyses of the product showed the presence of impurities, mainly iron, which could have come from steel sheet/pipes during the galvanization process.

Dean *et.al.* have utilized pH control for heavy metal removal from dilute solutions and metal recovery operations [10,11]. In the present study, removal of iron from mixtures of laboratory grade zinc chloride and ferric chloride solution of known concentrations was investigated using powdered lime for pH control. 90% recovery of zinc chloride was observed on maintaining pH 4-4.5 whereas most of iron was precipitated. Prior to recrystalization, the pH of the product solution prepared from the wastes, was adjusted to 4-4.5 with powdered lime for the removal of the impurities and TGA/DTA studies were carried out on the purified product so obtained. The results are described in Fig.5 and Table 6. Two distinct endothermic ITA peaks were obtained for both the samples studied. In the first stage, decomposition appeared to start with the elimination of water of crystalization at 225° and was completed at 360° (peak temperature = 250°) for sample A. For sample B, the observed temperatures for the first stage of decomposition were 275-400° (peak temperature = 325°). Loss in weight in this stage was found to be 19.44% and 21.28% for samples A and B respectively which was thought to be due to loss of water of crystalization from the product (expected loss in weight for $ZnCl_2 . 2H_2O$ =20.9%).The second stage of decomposition appeared to start at 450° and was completed at 600° for sample A (peak temperature = 550°)

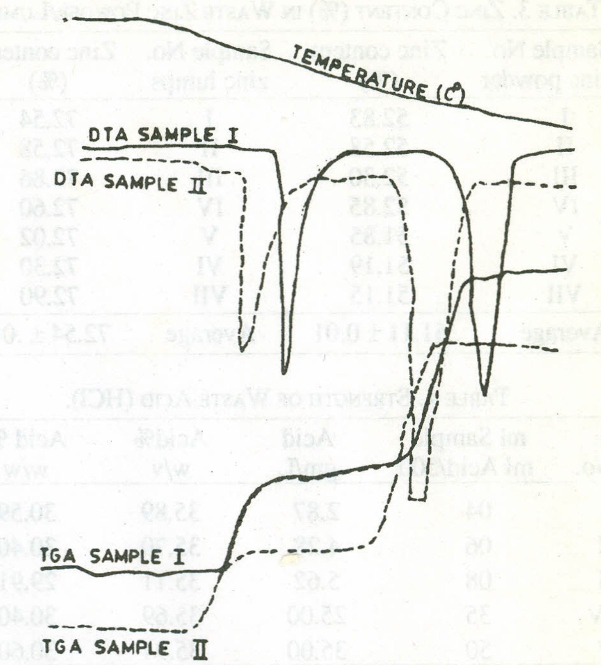

Fig. 5. Thermogrammes of purified product.

TABLE 1. STUDY OF REACTION PARAMETERS ZINC AND ACID CONCENTRATIONS (M).

| A | | B | |
|---|---|---|---|
| Zinc (M) | Zinc chloride % yield | HCl (M) | Zinc chloride % yield |
| 0.50 | 37.46 | 1.00 | 30.83 |
| 1.00 | 60.11 | 2.00 | 61.65 |
| 1.25 | 61.41 | 2.50 | 75.95 |
| 1.50 | 60.41 | 3.00 | 83.50 |
| 2.00 | 58.62 | 3.50 | 90.19 |
| — | — | 4.00 | 91.26 |
| — | — | 5.00 | 94.00 |

For A; HCl = 2M, Acid dilution = (1:1) Stirring time 3 hrs.
For B; Zn = 1.25M, Acid dilution = (1:1) Stirring time 3 hrs.

TABLE 2. STUDY OF REACTION PARAMETERS. ACID DILUTION (ACID: $H_2O$) AND STIRRING TIME (HRS).

| C | | D | |
|---|---|---|---|
| Time (hrs) | Zinc chloride % yield | Dilution (Acid : $H_2O$) | Zinc chloride % yield |
| 0.50 | 79.09 | 1 : 0 | 94.31 |
| 1.00 | 85.70 | 1 : 0.50 | 93.95 |
| 1.50 | 89.45 | 1 : 1 | 90.34 |
| 2.00 | 91.26 | 1 : 2 | 87.00 |
| 2.50 | 91.26 | 1 : 3 | 81.66 |
| 3.00 | 91.26 | 1 : 4 | 80.15 |

For C = HCl = 3.5 M; Zn = 1.25 M; Dilution (1:1)
For D = HCl = 3.5 M; Zn = 1.25 M; Stirring time = 3 hrs.

TABLE 3. ZINC CONTENT (%) IN WASTE ZINC POWDER/LUMPS.

| Sample No. zinc powder | Zinc content (%) | Sample No. zinc lumps | Zinc content (%) |
|---|---|---|---|
| I | 52.83 | I | 72.54 |
| II | 52.58 | II | 72.58 |
| III | 52.30 | III | 72.86 |
| IV | 52.85 | IV | 72.60 |
| V | 51.85 | V | 72.02 |
| VI | 51.19 | VI | 72.30 |
| VII | 51.15 | VII | 72.90 |
| Average | 51.11 ± 0.01 | Average | 72.54 ± .01 |

TABLE 4. STRENGTH OF WASTE ACID (HCl).

| S. No. | ml Sample ml Acid/500 | Acid gm/L | Acid% w/v | Acid % w/w |
|---|---|---|---|---|
| I | 04 | 2.87 | 35.89 | 30.59 |
| II | 06 | 4.28 | 35.70 | 30.40 |
| II | 08 | 5.62 | 35.11 | 29.91 |
| IV | 35 | 25.00 | 35.69 | 30.40 |
| V | 50 | 35.00 | 35.94 | 30.60 |

Average strength = 35.67 + 0.01 (w/v), Average sp. gravity = 1.1634 (n=5).

TABLE 5. YIELDS OF PRODUCT ZINC CHLORIDE.

| S. No. | Mole fraction waste zinc (gm) | Mole fraction waste acid (gm) | Product theoretical yield (gm) | Product experimental yield (gm) | Product yield (%) |
|---|---|---|---|---|---|
| 1 | 2.32 | 12.40 | 4.82 | 2.80 | 58.09 |
| 2 | 3.48 | 18.60 | 7.23 | 4.69 | 64.86 |
| 3 | 4.64 | 24.80 | 9.64 | 5.92 | 61.41 |
| 4 | 5.80 | 31.10 | 12.05 | 7.64 | 63.40 |
| 5 | 6.96 | 37.20 | 14.46 | 8.75 | 60.51 |
| 6 | 8.12 | 43.40 | 16.86 | 10.27 | 60.91 |
| 7 | 9.28 | 49.60 | 19.27 | 12.25 | 63.57 |
| 8 | 10.44 | 55.80 | 21.68 | 13.04 | 60.15 |
| 9 | 11.60 | 62.00 | 24.09 | 14.47 | 60.07 |

Average Yield = 61.44 ± 2.12 (n = 9).

TABLE 6. THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSES OF PURIFIED ZINC CHLORIDE.

| Sample | Ist Stage | | 2nd Stage | | |
|---|---|---|---|---|---|
| | Temperature (°C) | Weight loss (%) | Temperature (°C) | Weight loss (%) | Residue (%) |
| A | 225–350 *(250) | 19.44 | 450–600 *(550) | 47.22 | 33.33 |
| B | 275–400 *(325) | 21.28 | 525–690 *(640) | 46.10 | 32.62 |

* Values in parenthesis are DTA peak temperatures.

and 525° and 690° for sample B (Peak temperature = 640°) respectively. Loss in weight in the 2nd stage of thermal decomposition was found to be 47.22% and 46.10% for samples A and B respectively and this was thought to be due to elimination of chlorine from the product (Expected loss in weight for $ZnCl_2$. $2H_2O$ = 41.15%).

## Conclusion

On the basis of DTA/TGA data, the product prepared from wastes zinc and acid appeared to correspond to the composition $ZnCl_2$. $2H_2$. The low-grade product may be used in some industrial processes for which very pure zinc chloride is not required. Studies are in progress for further purification of the products by treating the product solution with an oxidizing agent (for conversion of any ferrous ion to ferric), prior to treatment with lime. However, the process economics would also have to be looked into in view of the cost of the oxidizing agent used, the energy consumption for the oxidation process and the market price for highly pure zinc chloride.

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