

RECOVERY OF ZINC FROM WASTEWATER TREATMENT SLUDGE

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ABSTRACT

Preliminary laboratory work done under a memorandum of agreement between the Bureau of Mines, Rolla Research Center and the Harrison Radiator Division of General Motors Corporation has indicated that zinc can be recovered from wastewater treatment sludges generated at the Harrison plant at Lockport, NY. The method developed at the Rolla Research Center, Rolla, MO, for extracting zinc from the sludge involves roasting, leaching-purification and electrowinning. Roasting to combust the organic fraction and leaching with H_2SO_4 to solubilize the zinc proceeded routinely. Purification and electrowinning followed standard practice for a commercial zinc electrowinning plant, but because of the large amounts of deleterious impurities coextracted with the zinc, as much as 50 times greater than normally encountered in a commercial operation, an extensive modification of the purification procedure was necessary. Zinc was electrowon with good current efficiency and deposit morphology. Residues are being characterized to determine the feasibility of recovering valuable constituents prior to disposal in an environmentally acceptable manner.

INTRODUCTION

Among the goals of the U.S. Department of the Interior, Bureau of Mines are minimizing the requirements for mineral commodities through conservation and substitution and maximizing mineral and metal recovery from primary and secondary domestic resources. Metal finishing and wastewater treatment sludges are rapidly growing secondary domestic resources. One report estimated the nationwide generation of nearly 20,000 metric tons (Mg) (dry basis) of sludge in 1975 with more than three times that annual amount expected by 1983 [1]. The magnitude of the nationwide tonnage may be low but the rate of growth is fairly accurate. The Bureau of Mines and Harrison Radiator Division, General Motors Corp., Lockport, NY, are cooperating on research to recover metal values from the company's wastewater treatment sludge. The sludge is typical of many electroplating and metal finishing operations that contain zinc, aluminum, copper, tin, chromium, nickel, etc. Handling and disposal costs have escalated dramatically in recent years. Two reasons for these increases are: (1) regulations requiring the use of secure landfill sites and (2) the large transportation distance to the approved sites. The landfilling charge alone has increased about sevenfold excluding transportation costs.

Harrison treats about $17 \times 10^3 \text{ m}^3$ (4.5 million gallons) of wastewater a day to remove oil and dissolved metals. Oil enters the wastewater stream from lubricating oils used in metalworking and machining operations associated with fabricating radiators and heat exchangers. Soldering of parts requires clean surfaces and several metal ions such as zinc and copper are introduced into the wastewater stream during these cleaning operations.

Harrison's wastewater treatment plant began operation in 1969 with the objective of removing oil and dissolved metals from their wastewater, which would enable the purified water to be recycled. All process wastewater from cleaning and soldering brass radiators, bending and forming metals, and chromating aluminum parts is treated in the plant. The blended wastewater has a pH of 3. Slaked lime is used to precipitate the hydroxides of zinc, aluminum, copper, tin, chromium, nickel, etc. The underflow from thickening is processed on rotary vacuum filters to increase the sludge solids content to approximately 25%. Approximately 4.5 Mg of zinc is present in one day's generation of sludge.

The research objective was to evaluate, on a laboratory scale, procedures to recover metallic zinc from wastewater treatment sludge. The Bureau's research was initiated on typical samples of rotary vacuum filter sludge (RVF) supplied by Harrison Radiator Division. Specific tasks to be evaluated were as follows: roasting of RVF to remove oil and organic materials; leaching of roasted RVF; purification of the zinc-rich filtrate to remove iron, copper, nickel, and other impurities deleterious to the electrowinning of zinc; electrowinning of zinc from purified solutions and characterization of the leach residue.

This paper describes the preliminary research progress since the memorandum of agreement in February 1978.

CHARACTERIZATION OF WASTEWATER TREATMENT SLUDGE

The wastewater treatment plant typically produces a lime sludge residue containing metal hydroxides, oil, other organics and water. Standard methods of analysis were used for characterizing the sludge, and the results are shown in Table 1 [2].

Several drums of wet cake were received during the research and variations

TABLE 1

Typical wastewater sludge characteristics

| | Thickener underflow | Filter cake |
|-------------------------------|---------------------|-------------|
| Solids content, % | 11-17 | 25-30 |
| Volatile solids, % | 5-8 | 11-14 |
| Nonvolatile solids, % | 6-9 | 14-16 |
| Bulk density, kg/m^3 | 1020-1050 | 1080-1100 |

TABLE 2

Partial chemical analysis of oven dried sludge

| Element | C | Zn | Ca | Al | Pb | F | Si | Sn | Mg | Cu | Fe | Cl | Ni | Na |
|---------|------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| % | 32.5 | 20.6 | 3.5 | 3.4 | 2.5 | 1.5 | 1.3 | 1.2 | 0.8 | 0.7 | 0.6 | 0.3 | 0.2 | 0.2 |

in exact analysis occurred, but results for a typical oven-dried sample are given in Table 2. The dried sludge was roasted as per the standard method, and the volatile solids content amounted to 45% and was a rough estimate of the amount of the oil and organic materials present in the RVF. The 55% nonvolatile fraction contained mostly oxides of the elements shown in Table 2 except that the carbon had been removed.

PROCESS DESCRIPTION

Roasting stage

Roasting experiments were conducted at temperatures from 600–1000° C. The oil present in the RVF pyrolyzed to carbon and hydrogen at temperatures above 900° C, and these reducing conditions caused considerable zinc volatilization. At 600–800° C the roasted product contained about 36% zinc, which is more than 99% of the zinc present in the unroasted RVF. The weight of the roasted product amounted to 14% of the wet RVF weight. This amounts to more than a sevenfold decrease in sludge weight. The bulk density of the roasted product was 320 kg/m³ with an apparent density from 5050 to 5100 kg/m³.

These promising laboratory results were utilized by Harrison Radiator Division to scale the roasting stage up to a 61 cm diameter rotary hearth furnace. The furnace was fed at 11 kg/h at various roasting temperatures. Their results indicated that 600° C was adequate for roasting the RVF, and approximately 45 kg of roasted RVF was prepared for leaching experiments. Partial chemical analysis of the roasted RVF is shown in Table 3.

TABLE 3

Partial chemical analysis of roasted rotary drum filter cake

| Element | Zn | Pb | Sn | Cu | Fe | C | Ni |
|---------|------|-----|-----|-----|-----|-----|-----|
| % | 31.1 | 2.9 | 1.5 | 1.1 | 1.1 | 0.6 | 0.4 |

Leaching stage

The sulfuric acid solubility of the zinc in the roasted RVF was determined

for laboratory and large scale roasted products. Laboratory roasted RVF had about 93% of the zinc soluble in the 200 g/l sulfuric acid. Approximately 91% of the zinc was acid soluble from the larger scale roasting tests. The balance of the zinc had probably formed zinc ferrite, which is insoluble in dilute sulfuric acid. A series of statistically designed leaching experiments was conducted to investigate temperature, solid to liquid ratios and time as independent variables. The temperature was varied from 328 K to 368 K, time from 2 to 5 hours, and from 200 to 500 g/l roasted RVF. The leach solution simulated a 200 g/l sulfuric acid and 65 g/l zinc spent electrolyte that would be generated during electrowinning. The theoretical amount of acid required to extract 100% of the zinc was 46.6 g (0.476 mole) sulfuric acid per 100 g of roasted RVF. Naturally a portion of the other oxides present in the roasted RVF reacted with the acid. A large evolution of carbon dioxide occurred during leaching experiments owing to the excess of base used in the wastewater treatment plant for precipitation of the hydroxides. The leaching reaction was exothermic and vigorous. The slurry was filtered and the filter cake washed with hot water in all leaching experiments. Linear regression analysis was used to evaluate data from the leaching tests. A three-variable polynomial equation resulted in the maximum r^2 statistic being 0.96 with 1.0 being perfect correlation. The following equation was empirically derived for the extraction of zinc from roasted RVF:

$$Z = 57.385 + 4.303 \times 10^{-2} K + 17.977 \times 10^{-2} S - 3.915 \times 10^{-4} S^2$$

where Z = total wt.% zinc extracted, S = grams solid per liter, K = temperature in degrees Kelvin.

The dependent variable Z includes the amount of zinc extracted from washing the leach residue. The wash is required because of the void space present in the leach residue. The zinc content of the actual leach liquor ranged from 110 g/l to 162 g/l. The actual zinc extraction versus the equation extraction values are shown in Table 4. Good agreement was shown at all points. The linear regression equation showed the solids concentration (mass per liter) and reaction temperature to be the prime extraction factors. The lack of time dependence indicated that extraction times of two hours were adequate. The pH of the leach liquor varied from 0.7 to 5.4. Large

TABLE 4

Comparison of empirical and actual zinc extraction results (Temperature 348 K, time 2 h)

| Wt. solids, g/l | Extraction, % | |
|-----------------|---------------|----------|
| | Actual | Equation |
| 200 | 94.3 | 92.7 |
| 350 | 86.9 | 87.3 |
| 500 | 62.3 | 64.4 |

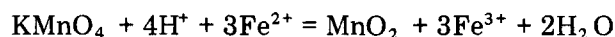
volumes (15 to 20 l) of leach liquor were produced for electrolyte purification studies. Based on the empirical equation, 300 g solids per liter, 368 K and a 2-hour reaction time were used to maximize the extraction of zinc in the leach liquor while maintaining the overall zinc extraction near 90%. The resulting leach liquor contained, in g/l, 154 Zn, 3.0 Cu, 0.6 Ni and 0.2 Fe, and had a density of 1410 kg/m³ and a pH of 1.9. The zinc content is in the range of neutral zinc solutions used for commercial zinc electrowinning; however, both the Ni and Cu concentrations are many times greater. The dried filter cake contained 18.4% zinc before washing and 5% zinc after complete washing. The tin and lead present in the roasted RVF were insoluble and were reported in the leach residue; they may be valuable byproducts if further recovery methods can be developed.

Purification

An attempt was made to purify the filtrate using the standard commercial practice of oxidation (iron purification) followed by two successive treatments with zinc dust (zinc purification). However, because of the large amount of deleterious impurities coextracted with the zinc, an extensive modification of the zinc purification procedure was necessary; e.g., the Ni concentration was approximately 50 times the amount normally encountered in commercial electrolyte.

Iron purification

During iron purification, ferrous iron was oxidized to ferric iron using 10% excess over stoichiometric of potassium permanganate, according to the following equation



The presence of Mn ions in zinc electrolyte is beneficial, and as much as 3 to 3.5 g/l are usually added to aid in forming a protective layer of MnO₂ on the lead-silver alloy anodes, which minimizes lead contamination of the cathode zinc.

After adding the KMnO₄, the solution was maintained at 363–368 K and the pH was slowly increased from 1.9 to 5.3 by adding roasted RVF sludge. The solution was held at temperature for two hours and then filtered to remove the Fe as Fe(OH)₃ precipitate as well as some, but not all, of the other impurities such as C, Cr, Pb, Si and Sn. The amount of dried residue from purifying each liter of leach liquor was 61 g. A comprehensive chemical analysis of the residue and filtrate is shown in Table 5. The concentration of Fe being less than 1 ppm indicates that iron purification was virtually complete.

TABLE 5

Analysis of residue and filtrate from iron purification

| Al | C | Ca | Cl | Cr | Cu | F | Fe | Mg | Mn | Ni | Pb | Si | Sn | Zn |
|-----------------|-----|-----|-----|-------|-----|-----|--------|-----|------|-----|-------|-----|-----|-----|
| Residue (wt. %) | | | | | | | | | | | | | | |
| 8.9 | 1.3 | 0.3 | — | 1.0 | 1.7 | 3.6 | 0.8 | 1.4 | 0.05 | 0.2 | 2.0 | 0.7 | 0.6 | 8.0 |
| Filtrate (g/l) | | | | | | | | | | | | | | |
| 1.1 | — | 0.1 | 1.2 | 0.005 | 2.3 | 0.5 | <0.001 | 5.2 | 0.2 | 0.6 | 0.003 | — | — | 156 |

Zinc dust purification — first stage

Following the practice normally employed in industrial operations, the concentrations of Cu and Ni were used to compute the Zn dust and As_2O_3 additions, respectively, for the first stage of zinc dust purification. Based on the results of extensive tests, zinc dust was added at the rate of five times the Cu concentration and As_2O_3 was added at the rate of three times the Ni concentration. Elements more noble than Zn, such as Cu and Ni, are removed from solution by zinc dust but the reaction does not occur without the presence of an activating agent such as As or Sb.

The filtrate from iron purification was heated to 363–368 K, the Zn dust and As_2O_3 additions were made and the solution was held at temperature for two hours. An additional 0.5 g/l of Zn dust was added at ½-hour intervals and the hot solution was filtered 15 min after the last addition.

The filtrate was analyzed and found to contain approximately 2 ppm each of Ni and As. In spite of repeated attempts, a method was not found that would reduce the Ni to the desired level of about 0.1 ppm or less in one treatment and it was necessary to repeat the zinc dust purification.

Zinc dust purification — Second stage

Since all the Cu was removed in first stage purification, approximately 0.3 g/l Cu was added to the filtrate prior to second stage purification. Industrial experience has shown that the cementation reaction will not work without some Cu in the solution. Other than the Cu addition, second stage purification was carried out in the same way as the first stage. A complete chemical analysis of a typical filtrate is shown in Table 6.

Spectrographic analysis of the residues from both zinc dust treatments indicated that they were predominantly zinc with minor amounts of As and Cu and traces of Al, Ca, Co, Cr, Fe, Mg, Mn, Mo, Ni, Pb and Si.

Two things are immediately apparent from the analysis of the purified neutral solution to be used for electrowinning. First, the high concentration of Mg (5.0 g/l) would be expected to cause a great deal of trouble as the concentration increased during recycling of electrolyte. Concentrations of

TABLE 6

Analysis of filtrate, in g/l, after final zinc dust purification

| Ag | Al | As | Cr | Cu | Fe | Ni | Pb | Ca | Cl | Mg | Mn | Zn |
|----------|-------|--------|--------|---------|--------|---------|--------|-----|-----|-----|-----|-----|
| < 0.0006 | 0.046 | 0.0029 | <0.001 | 0.00021 | 0.0032 | 0.00014 | 0.0001 | 0.4 | 1.2 | 5.0 | 0.2 | 160 |

Mg in the range 15 to 20 g/l displace Zn from solution and cause a noticeable decrease in current efficiency. As a general rule, if the concentration of Mg reaches 0.2% in the starting calcine, it is necessary to remove it beforehand by leaching. Lower concentrations can generally be handled by electrolytic stripping. Secondly, the high concentrations of Cl and F would probably cause sticking of the zinc deposits to Al cathodes during electrowinning. However, using zinc cathodes [3], along with the potential device for preventing solution-level corrosion developed at the Rolla Research Center [4], would eliminate this problem. Industrial attempts to substitute zinc cathodes for aluminum cathodes have all failed. Solution-level corrosion of the zinc cathode caused it to drop off into the cell. Researchers at the Rolla Research Center determined that oxygen transport from the anode was responsible. They made a significant breakthrough in developing technology that was practical, simple, and very inexpensive for the elimination of solution level corrosion of zinc cathodes [4].

The Ni analysis in the final filtrate was 0.14 ppm, which was less than that contained in samples of "good" electrolyte from two commercial plants. Even though the As concentration (0.29 ppm) was higher than desired, it was decided to proceed with electrowinning.

Electrowinning

Following standard commercial practice, glue was added to the electrolyte to smooth the deposit. Several preliminary tests were made in a 1-liter cell to determine the correct amount of glue addition. The best results were obtained when 20 mg/l glue was added to the cell and to the feed solution prior to electrowinning.

Electrolyte was prepared for the 10-liter cell by mixing the correct amount of neutral solution, H₂O and H₂SO₄ to give 60 g/l Zn²⁺ and 204 g/l H₂SO₄. Lead-dioxide-coated titanium anodes were used with 1100 alloy aluminum cathodes to electrowin zinc at 560 A/m² and 308 K. The lead-dioxide-coated titanium anodes were used in preference to the traditional lead-silver anodes to avoid the long times necessary for conditioning lead-silver anodes to prevent lead contamination of the cathode zinc.

A peristaltic pump was used to transfer neutral solution to the cell during electrowinning in an attempt to hold the zinc and acid concentrations constant. Neutral feed was pumped from the bottom of a reservoir into the bot-

tom of the electrolytic cell, and the overflow was pumped from the cell back into the neutral feed reservoir. The run was terminated after 20 hours when the concentration of the neutral feed had dropped from about 160 g/l to 70 g/l and it was no longer possible to maintain an adequate zinc concentration in the cell.

The deposit morphology was fairly good but the current efficiency was only 76%. During electrolysis the concentration of zinc in the electrolytic cell was reduced from 60 g/l to 30 g/l and the H_2SO_4 concentration increased from 180 g/l to 200 g/l, giving a zinc to acid (Z/A) ratio of 0.15. Ault et al. [5] have shown that current efficiency decreases as the Z/A ratio increases or decreases from some optimum value. The low Z/A ratio was partly responsible for the 76% current efficiency. However, there was some evidence of re-resolution of zinc at the edges of the deposit, which was probably indicative of the high As content.

Reducing the amount of As_2O_3 added during the final zinc dust purification should reduce the As in the final purified leach liquor. Also, more neutral solution available for feed would make it possible to maintain a more desirable (0.3) Z/A ratio during electrowinning.

CONCLUSIONS

This preliminary laboratory investigation has shown that zinc can be recovered from wastewater treatment sludge using the roast, leach-purification, electrowinning process described herein. The procedure is straightforward and for the most part follows accepted commercial practice for zinc electrowinning except for more extensive purification procedures necessitated by the greater than normal amount of impurities coextracted with the zinc. More work is needed to refine the procedures and to assess the effect of impurity build-up with repeated recycling of electrolyte. In addition, final disposition of the leach residues needs to be determined and an economic evaluation completed.

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