

## [BIO11] Batteries recycling process using local isolated thermophile culture

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### Introduction

Batteries are used daily in many portable electronic devices. Therefore spent batteries represent, within the wastes, an important environmental pollutant in terms of heavy metals content. Considering the risk associated with uncontrolled disposal of these batteries a legislation on disposal and recycling of spent batteries must be formulated. The development of a metal recovery processes is thus convenient from an economic and environmental point of view (i.e. high cost of landfill disposal of hazardous material, waste recycling and natural resources conservation).

Metallurgy is the science and art of extracting and refining metals. The two basic processes for recovering metals are called hydrometallurgy and pyrometallurgy.

In pyrometallurgy, the chemical action is carried out by means of heat supplied by the burning of fuel, the operation usually taking place in a furnace. The pyrometallurgical method in batteries leaching consists basically of selective volatilisation of metals at elevated temperatures followed by condensation. For example, cadmium is recovered from Ni–Cd batteries by volatilisation at temperatures around 900 °C and zinc and mercury from zinc–carbon and alkaline batteries at 1500 °C. The current commercial technology is pyrometallurgy based i.e. BATREX, RECYTEC, SNAM-SAVAN, SAB-NIFE and INMETCO (de Souza *et al.*, 2001). However, these technologies are energy consuming and produce some emissions of dust and gases (Salgado *et al.*, 2003).

Hydrometallurgical processes involve leaching the metal content from its sources in an aqueous solution, from which the metal may then be recovered. Recently, some hydrometallurgical processes have been developed to recover metals from these secondary sources. The benefits coming from a hydrometallurgical process are: complete recovery of metals at high purity, low-energy requirements, avoidance of air emissions and minimization of wastewater. In the case of hydrometallurgical treatments of waste, the

metal content in a solid material is mostly dissolved in liquid medium (acid, ferric or ammonia solution) and processed to recover metal ions. However, large amounts of chemicals are consumed, making the process uneconomical.

Bioleaching (biohydrometallurgy) refers to the use of bacteria to extract or leach metals. This technology has become increasingly important due to its simplicity, low cost and applicability to low-value metals. Bioleaching application was dominated by the mining industries. Recently, applications of bioleaching in waste detoxification have attracted a lot of scientific interest. However, the development of bioleaching applications in the industries is predicted to be limited due to the slow leaching rate (Bosecker, 1997). Sequential chemical-biological leaching approaches have been exploited in the mobilization of metals in batteries using bacteria. Application of bioleaching technology with the chemical pre-leaching step has been explored to treat a multi type of dry batteries. This technique offers the most economical, safe and efficient process for decontamination of solid waste

The bioleaching of dry cell batteries is the first project of its kind in Malaysia. The absence of this technology will lead to huge amounts of our resources of metal being left idle which can then pose a treat to the environment

### Materials and methods

#### **Batteries**

The battery used in this experiment is the C size, super heavy duty and non rechargeable type. These batteries were obtained from one of the largest local batteries producer. The C size batteries was chosen as it has been classified as schedule hazardous waste. The inner part of battery were exposed using a hammer and dried at 80°C over night. Dry weight of each batteries was then recorded.

**Total metal content**

Acid digestion test was carried out to determine the metal content in the batteries. The batteries were soaked in a 250mL aqua regia (3:1. HCl: HNO<sub>3</sub>) ratio. The mixture was then heated at 80-90°C for 5 hrs. Upon cooling, the solution was then transferred into a 1L volumetric flask. The volume was then made up to the mark using distilled deionised water (DDW). The sample was then analysed using AAS to determine the metal concentration in the sample.

The non-dissolved slurry were then dried at 80°C over night . The weight of the non-dissolved part was then recorded.

**Bacteria**

Bacteria used in this study was isolated from the slumps around the copper concentrate piles of Sg. Lembing. The concentrate contains chalcopyrite, chalcocite, copper oxide, pyrite and arsenopyrite. The concentrate was left idle due to the strict legal restriction by the Japanese Government on the arsenic limit content in roasting industries. The isolate was grown in *Thiobacillus thiooxidans* medium (Shahir, 1997), *Sulfobacillus* medium and *Sulfolobus* Medium(DSMZ, 1993). However visible growth was only observed in the *Sulfobacillus* medium

**Leaching test**

Leaching test was carried out in 2L Schott bottle containing 500ml leachate solution and a C sized battery. The inner part of the batteries were exposed using a hammer. The bottles containing the batteries and leaching solution were incubated at 200 rpm. Samples (5 ml) were periodically withdrawn from the flask. Metal analysis of leach solutions were made using Atomic Adsorption Spectrometer (AAS). Series of leaching solutions (Table 1) were used in order to compare the efficiency of the leaching process.

**Chemical leaching test**

Chemical leaching test was conducted at room temperature for 30 days using the leaching medium as described in Table 1.

TABLE 1 Leaching medium for chemical leaching test

1 Sulfuric acid (1.0 M)
2 Acid Hydrochloride (1.0 M)
3 Ferric Sulphate [Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ] (1.0 M)
4 Ferric Chloride [ FeCl <sub>3</sub> ] (1.0 M)

**Biooxidation test**

Isolate(5B), grown in *Sulfobacillus* medium was placed in a shaker, 200 rpm 70°C . The *Sulfobacillus* medium (DSMZ, Catalogue of Strain, 1993) was prepared as follows:

**Solution A (Basalt Salt):**

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (3.00 g), KCl (0.10 g), K<sub>2</sub>HPO<sub>4</sub> (0.50 g), MgSO<sub>4</sub> x 7 H<sub>2</sub>O (0.50 g), Ca(NO<sub>3</sub>)<sub>2</sub>, (0.01 g), Distilled water (700.00 ml), pH adjusted to 2.0 using H<sub>2</sub>SO<sub>4</sub> and autoclaved at 121°C for 20 minutes.

**Solution B(Iron):**

FeSO<sub>4</sub>.7H<sub>2</sub>O (1M) was prepared by adding 4.42g of FeSO<sub>4</sub>.7H<sub>2</sub>O in 300mL distilled water. The pH of the solution was adjusted to 2.0 using H<sub>2</sub>SO<sub>4</sub>, the mix was then filtered sterilised.

**Solution C(Yeast Extract):**

Yeast extract (1% w/v) solution was prepared by adding 0.2g Yeast Extract in 20mL distilled water. The solution was then autoclaved at 121°C for 20 minutes.

Solution A and B were cooled prior to mixing after which solution C was then added. Culture (5B) was then inoculated into the mixed solution and the bioleaching was conducted at 70°C for 60 days.

**Combination of chemical leaching and bioleaching test**

Leaching tests were conducted using the medium. The conditions for the test sequential have been described in Table 2A and 2B

TABLE 2A Combination of chemical leaching and bioleaching test chloride system

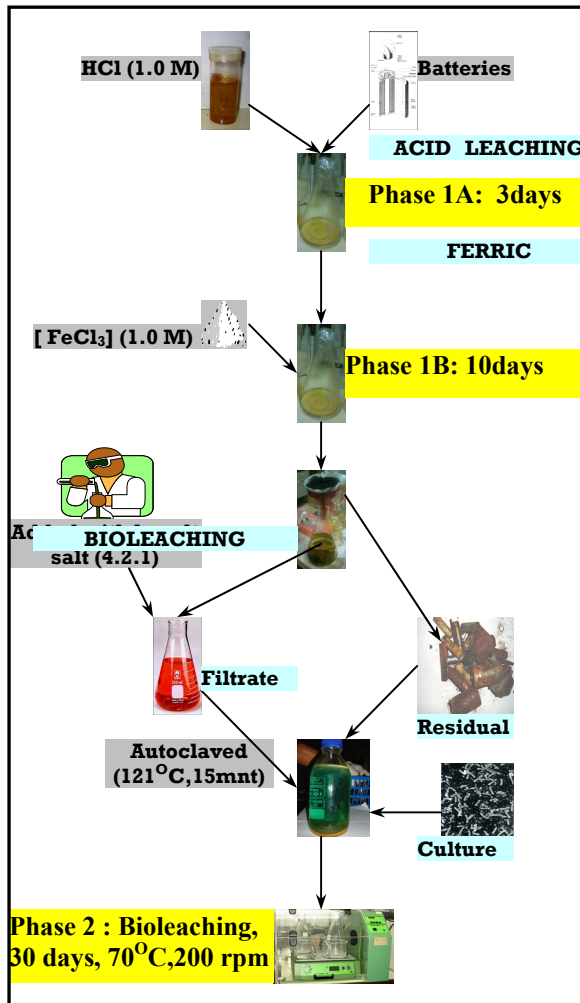
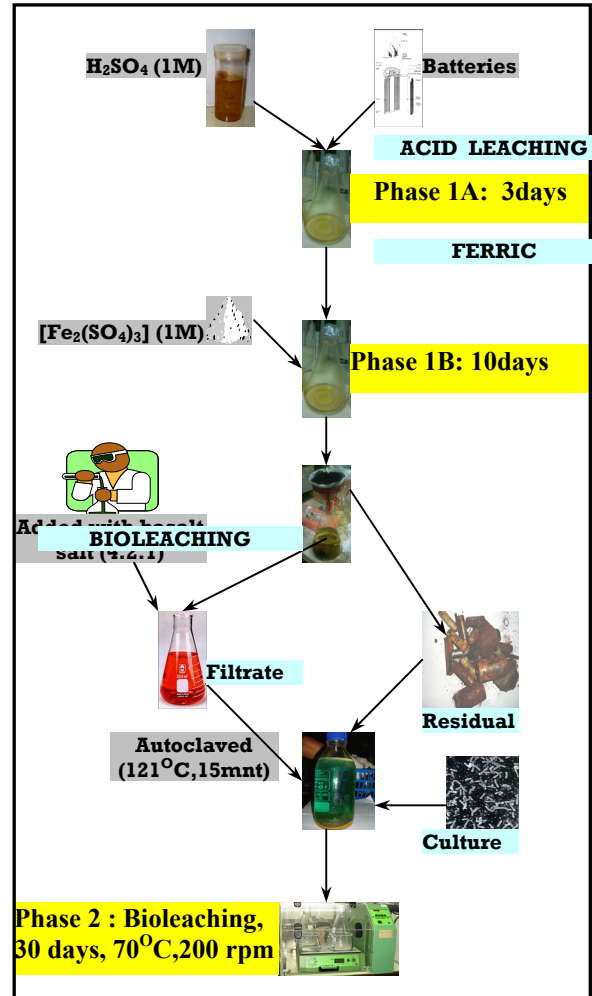


TABLE 2B Combination of chemical leaching and bioleaching test sulfate system



At the end of each tests i.e: chemical leaching , biooxidation and combination of chemical leaching and bioleaching, the mixture from each flask was filtered, the precipitate obtained was digested and the metal content was determined using AAS.

**Results and discussion**

Zinc-carbon battery was chosen in this work because of the large consumption of zinc-carbon batteries instead of alkaline batteries (Zaaba Ahmad, personal communication). Based on the collection of used dry batteries, carried out by Unit Kesihatan Dewan Bandaraya Kuala Lumpur, a large proportion of dry cell collected was the non-rechargeable type 80%, rechargeable type 12% and others 8%.

Due to its prices, rechargeable batteries are predominantly used in industrial countries such as Japan, Sweden and Switzerland. The escalating use of rechargeable batteries will lead to reduced metal usage and flow. Rechargeable batteries has a high energy capacity and many charge-discharge cycles i.e: 1000 and 600 life cycle for NiCd and NiMH type batteries respectively (Rydh and Svard, 2003)

The quantitative elemental composition of the battery is summarised in Table 3.

TABLE 3 Elemental content of batteries

Battery content	
Metal (Dissolved)	65.38%
Carbon, sulfur, paint and plastic (nondissolved)	34.62%
Percentages of metal	
Mn	45.76 %
Zn	12.78 %
Fe	2.20 %
Ni	72 ppm
Cd	6 ppm
Pb	2 ppm
Other metals (inclusive of volatile elements)	4.64 %

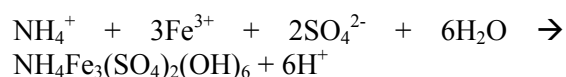
A large proportion of metal in spent batteries consists of Mn, Zn and Fe, 45.76, 12.78 and 2.20 % respectively. However, due to the economic aspect, only Mn and Zn are worthy for recycling. Zinc and Manganese have a constantly high demand and stable prices at 0.345 USD/LB and 1000 USD/MT respectively (Commission of the European Communities, 2000) .

The results shown in Table 3 also indicate that the metal content of more toxic species such as cadmium, lead and mercury\* are low, thus obeying the local government regulation\*(based on a zero mercury content which is claimed by producer)

However, it must also be stressed that battery recycling process is a non-profitable industry with the overall objective of reducing the availability of toxic heavy metals in the environment. Environmental concern is the more stringent issue in battery recycling and it will be a great challenge to develop the most appropriate treatment and disposal technique.

#### **Iron solubilization during leaching test**

Figure 1.1 shows the soluble iron profiles of the chemical leaching test on the spent batteries carried out for 30 days and the bioleaching tests which was conducted for 60 days. The iron solubilization was considered negligible for both acid leaching test using  $H_2SO_4$  and HCl. Another interesting observation was the rapid drop in iron content from 16.35% to 4.09% and 11.14% to 5.23% for the  $FeCl_3$  and  $Fe_2(SO_4)_3$  leaching tests respectively. This is probably due to the formation of iron oxide and jarosite. The formation of jarosite is given by the following reaction(Elgesma *et al*,1990). :



Precipitation rate of both is principally dependent on  $[Fe^{3+}]$ , pH and temperature (Dutrizac,1996). The stable condition for ferric leaching test was achieved at  $[Fe^{3+}]$  around 4%. Culture 5B was found able to maintain the soluble iron content. Rate of soluble iron content in the bioleaching test was slightly decreased at i.e: 0.012 %/day.

Figure 1.2 show the soluble iron profiles of the combination of chemical and biological sequential leaching test on the spent batteries.

During addition of ferric salt, the rate of soluble iron precipitate was reduced from 1.2565 %/day to 0.491 %/day and 0.594 %/day to 0.196 %/day for chloride and sulfate system respectively.

The soluble iron level was found to be low during bioleaching (Phase2) of the sequential test. Large amounts of sodium jarosite  $NaFe_3(SO_4)_2(OH)_6$  was present due to the addition of basal salt and autoclaving (Elgesma *et al*,1990). However, soluble iron level in this test was much higher compared to the bioleaching in the absence of ferric salts (Fig. 1.1).

It must be stressed that the level of soluble iron is an important indicator to predict the leaching efficiency. The overall leaching reaction was found to be dominated by chemical ferric leach (Boon, 1996). The chemical ferric leach and the bacterial oxidation of the ferrous iron are related to the redox potential, and are in equilibrium when the rate of iron turnover between the metal and the bacteria is balanced. (Breed and Hansford, 1999). The link between the chemistry and the biology of metal dissolution is shown in Figures 2 (Hansford and Vargas, 2001).

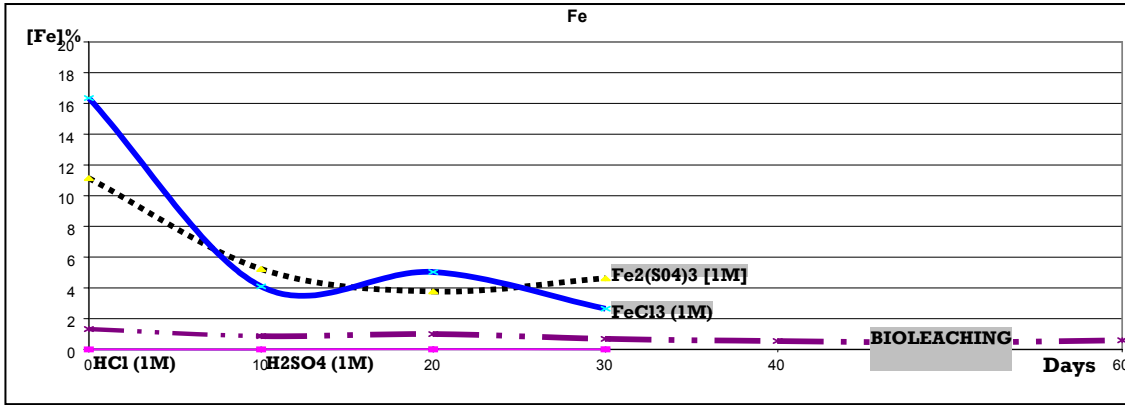


FIGURE 1.1 Iron content in a leachate solution during a chemical and bioleaching

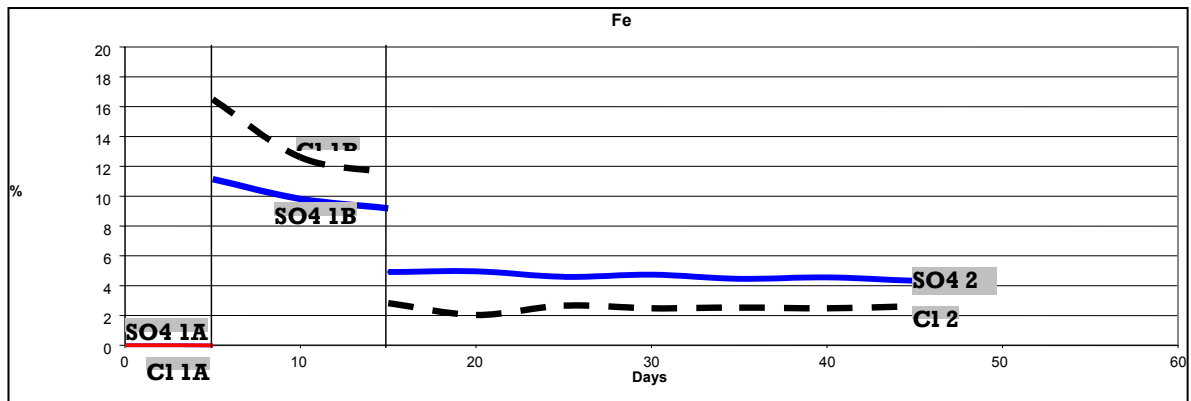


FIGURE 1.2 Iron content in leachate solution for chemical and bioleaching

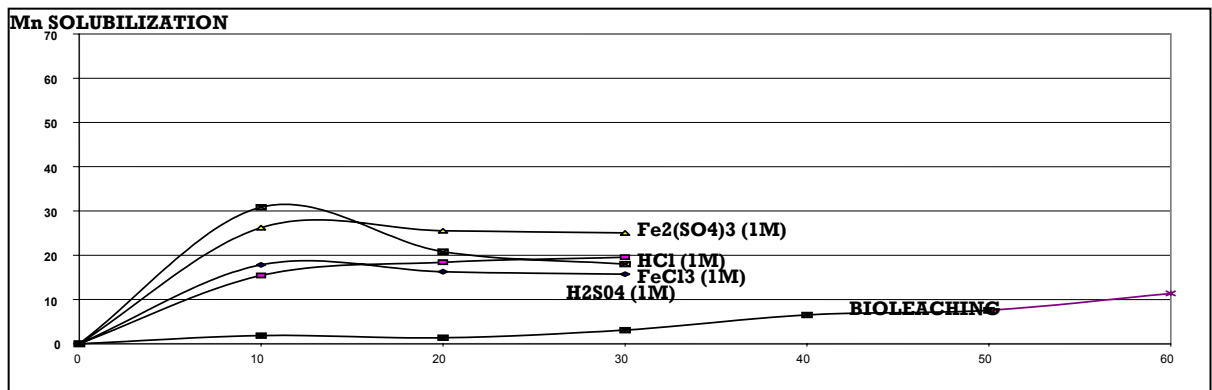


FIGURE 2.1 Manganese solubilisation profiles for chemical leaching and bioleaching.

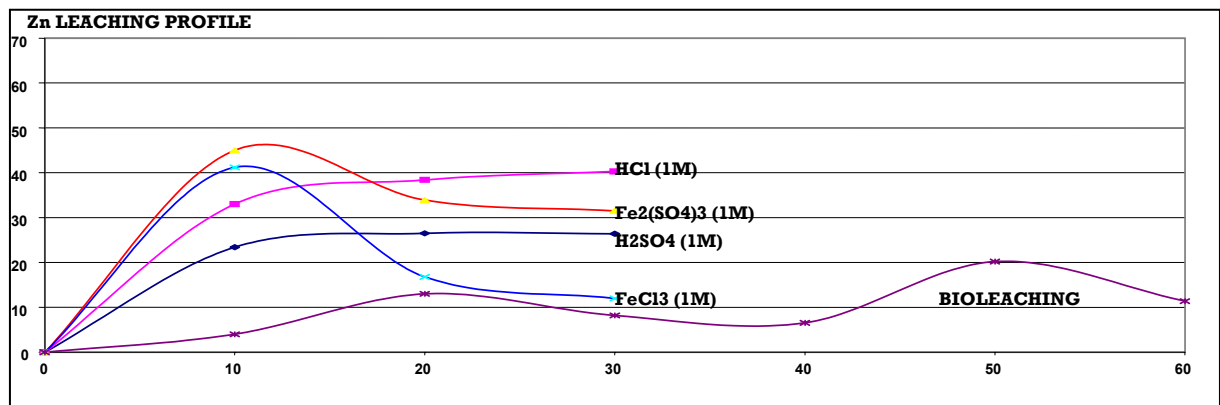


FIGURE 2.2 Zinc solubilisation profiles for chemical leaching and bioleaching.

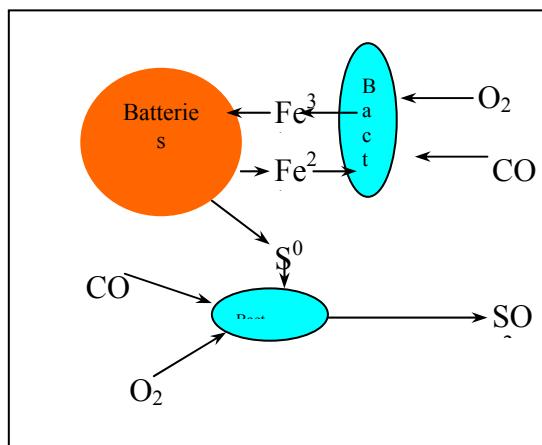


FIGURE 2 Indirect bacterial oxidation

**Leaching Behaviour**

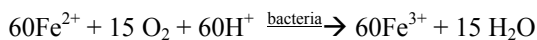
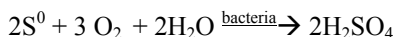
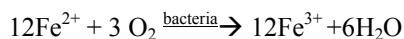
As mentioned before, the leaching tests were carried out using acid, ferric solution and bacterial oxidation. The results obtained in these tests are summarized in Figures 2.1, 2.2, where the amounts of zinc and manganese solubilized will indicate the overall leaching performance.

The Zn and Mn solubilization profiles for each set of chemical leaching test showed a drastic increase in [Zn] and [Mn]. Highest solubilization rate for the first 10 days of chemical leaching was 4.5% Zn /day and 3.084 %Mn/day obtained using 1M H<sub>2</sub>SO<sub>4</sub> and FeCl<sub>3</sub> respectively. It was also clearly shown that the initial chemical leaching rate is greater than bioleaching, i.e: 11.25 and 16.85 time folds for Zn and Mn respectively.

The [Zn] and [Mn] for FeCl<sub>3</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> leaching remained constant through out days 10 to days 30, possibly due to the presence of alkaline gangue and oxides in the batteries electrolyte, which will increase the pH value and decrease its leacheability behavior. However, the [Zn] and [Mn] decreased for the FeCl<sub>3</sub> and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, during days 10 to 30. This is probably due to the precipitation of zinc ferrite and manganese ferrite ((Elgesma et al,1990).

Culture 5B was found to maintain the rates of Zn and Mn solubilization (Figures 2.1 and 2.2). The solubilization rates Zn and Mn for bioleaching were 0.275% Zn /day and 0.181%Mn/day. This was calculated using following equation:

$$Zn\% = \frac{[Zn_{medium}]_{mg/L} \times 0.5L_{medium}}{}$$



$$\%Zn_{battery} \times Mass_{Battery}$$

$$Mn\% = \frac{[Mn_{medium}]_{mg/L} \times 0.5L_{medium}}{\%Mn_{battery} \times Mass_{Battery}}$$

Due to the slow leaching rate, the development of bioleaching applications in the batteries recycling processes is predicted to be limited. Sequential chemical-biological leaching approaches have been exploited using bacteria to mobilize metals in batteries.

Figures 3.1 and 3.2 shows the percentages of zinc and manganese leached by sequential leaching test using a combination of acid, ferric and bioleaching .

It was shown that sequential leaching was able to solubilize higher percentages of manganese and zinc compared to the other systems. Improved bioleaching was observed upon an additional chemical pre-leaching step. The leaching rates increased from 0.2747 to 1.145 %Zn/day and 0.1812 to 1.045%Mn/day. The sequential leaching system is more environmental friendly and relatively cheaper compared to the current technologies involving roasting, pressure oxidation and chemical oxidation.

**Conclusion**

The technical feasibility of recovering metals from spent batteries has been demonstrated via sequential chemical leaching and bioleaching. Considering the high cost of the ores, spent batteries can be considered as a potential source of metals, from 1 ton of spent batteries , 457.6 kg of manganese and 127.8 kg zinc can be recovered. The results obtained favours a two stage leaching process, where in the first stage, HCl (1M) and FeCl<sub>3</sub> (1M) can be used to accelerate initial leaching rates. Culture 5B can then be introduced at a later stage to enhance the oxidation effects by maintaining the high soluble iron level and promoting metal solubilization.

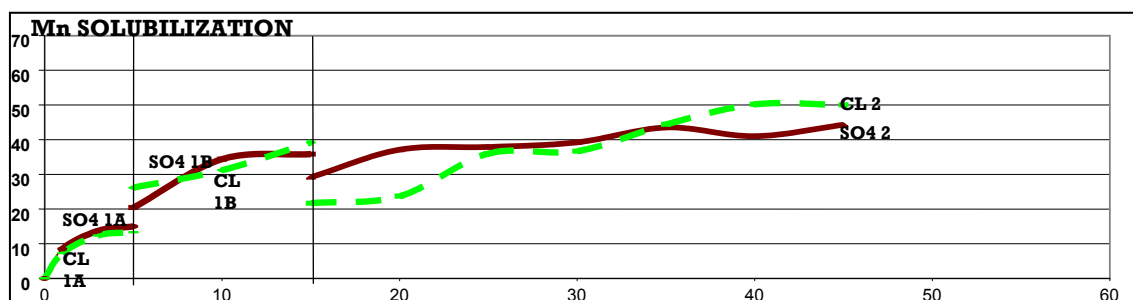


FIGURE 3.1 Zinc leached by sequential leaching test using combination of acid, ferric and bioleaching

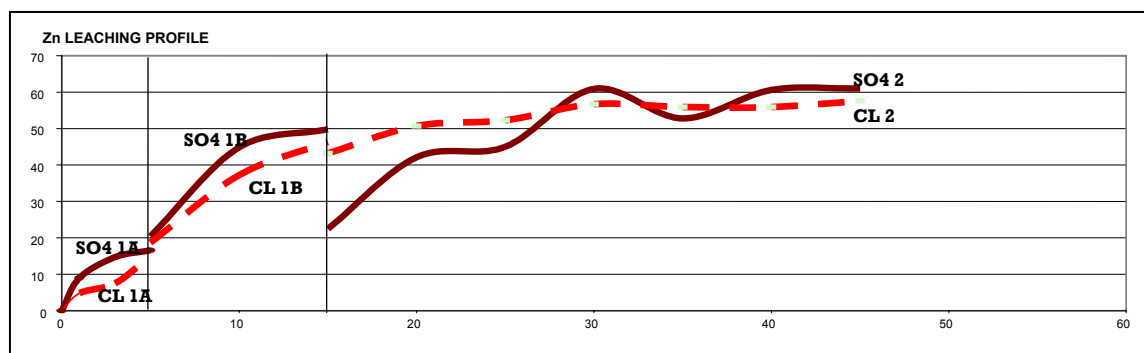


FIGURE 3.2 Manganese leached by sequential leaching test using combination of acid, ferric and bioleaching.

### Acknowledgements

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