Technoeconomic of Solar Recycling of Alkaline Batteries for Zn/ZnO Recoveries

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Introduction

In Australia, portable battery market is dominated by alkaline batteries. It was reported that alkaline batteries accounted for 198 million batteries and 9,248 tonnes that is about 57% of total annual handheld battery consumptions both on count and weight basis (1). Despite the Australian Government classifies some chemicals in the alkaline batteries as hazardous under the Hazardous Waste Act, e.g. the electrolyte (KOH) is a corrosive chemical and manganese (Mn) is a neurotoxin, the recycling rate of the portable battery in the continent were less than 5% whereas most of it thrown away together with municipal waste and ended up as landfill (2,3). Currently, the spent alkaline batteries are processed mechanically into a relatively low-value black mass powder that sold overseas. No full stream alkaline recycling facility is currently commissioned in Australia since the closure of AusZinc plant in Port Kembla at the end of 2012 (3). The strategic review of the business considered that the volume of the collected spent batteries was too low to support viable recycling business.

It is therefore reasoned that unless supportive legislation being implemented, cost of recycling being reduced, and/or value of the recycling product being multiplied, the rate of alkaline battery recycling will still stay at the current unsatisfactory rate. As Australian continent exposed to solar radiation ranging from 1500 to 1900 kWh/m^2yr (4), which is the highest compared to other continents, there is a great potential use of concentrated solar power for the recycling industry to both reduce the recycling cost and increase the recycling product value, as well as reducing the carbon footprint of the process. In the current paper, the carbothermic process to recover high value zinc/zinc oxide powder from spent alkaline black mass is studied. The study involved experimental investigation, process modelling that includes thermodynamics and mass and energy balance calculations, and techno-economic analyses. Continuous and batch-type process plants; as well as adoption of solar energy were considered in the study.

Materials and Method

In the current work, the black mass resulted from mechanical processing of spent alkaline batteries was supplied by Envirostream Pty. Ltd. According to ICP and XRD analyses, the powder composed of 28.55wt% Mn, 24.30wt% Zn, 16.78wt% C, 4.39wt% K, and 0.71wt% Fe, whereas ZnO, MnO_2, Mn_2O_3, Mn_3O_4, and carbon were the only phases present in the powder. Combined chemical thermodynamic and process flowsheet modelling were carried out to evaluate and characterise the material and energy flow during the recovery process of Zn/ZnO powder from the spent alkaline black mass through carbothermic reduction. The high temperature experimentations were carried out to confirm the thermodynamic modelling and to provide insights on yield and purity of the products that inform subsequent flowsheet modelling and technoeconomic analysis.

Spent battery black mass smaller than 100 mesh sizes were pelletised into 8mm-diameter cylindrical pellets using a hydraulic pressing machine with 1 ton of load. Pelletised samples, equates to about 34g of black mass powders were subjected to heating at 1200°C for two hours to facilitate carbothermic reduction reaction. The experiments were conducted in a horizontal tube resistance furnace made of high purity alumina under air or argon flow at various flow rates. A copper condenser was incorporated at one end of the furnace, where the exit gas outlet was situated.

An input/output model based on the Technical Cost Modelling (5-7) has been developed to asses the economic viability of the carbothermic process in producing zinc/zinc oxide powders out of the black mass. The model involving four stages and has two main components that are inputs - which are variables that directly specified in the model, and outputs – which are the results of the modelling that consist of cost and revenue estimates. The details of the stages can be found in (7-8). The revenue calculation was considering the market value of the Zn and ZnO powder with the purity and the size that obtained from the current experiments. The cost components consist of fixed capital cost and variable operational cost that includes labor, utility, materials, and maintenance costs.

The process of the Zn/ZnO powder recovery proposed in the current study i.e. through carbothermal reaction, is similar to the thermal process to produce magnesium commercially. Both processes include the reduction of the metal oxide and the condensation of the metal vapor. Due to this consideration, the fixed capital cost for equipment of the current process were approximated based on a magnesium processing plant and adjusted to the average value of Australian dollars in 2019. Two types of thermal magnesium process plants namely Mintek-thermal processing continuous process and batch-type Pidgeon process were considered as models for the development of the process.

The economics of both continuous and batch-type processes at various feed capacity were then compared with the application of solar energy, where the concept of the reactor is as follows. Essentially, the reactor has a vertical configuration and consist of two main parts that are the removable upper lid and the lower portion of feed batch. The lower portion constitutes the heating chamber of the reactor where the reduction reaction of the black mass takes place. A receiver cavity with quartz windows embedded on the domeshaped lid where the concentrated sun ray enters the reactor as heat source. The other part of the lid is connected to the cooling water to act as a condensed chamber of the vaporised Zn. The top and lower portions of the reactor are joined in a detachable manner at flange to form a sealed chamber. The reactor is connected to a gas flow (air or argon) to control the atmosphere and to ensure that the vaporised Zn emanates to the condenser. Washing chamber is installed at the gas outlet to capture the escaped Zn vapor and act as secondary condenser chamber.

Results

Upon heating to 1200°C, ZnO in the black mass was reduced by the carbon where Zn eventually leave the black mass as Zn vapour, while the manganese oxides, residual carbon, and unreacted ZnO stay in the reactor. The weight difference measurement between the initial samples and the samples after high temperature exposure under argon shown that about 50.3wt% of the black mass turned into gas phase, which is well agreed with the thermodynamics calculations result. Under argon atmosphere, the substance condensed on the copper condenser had a colour gradation. White deposits were found on the front side (closer to the hot zone) and grey deposits on the back side (closer to exit gas outlet), respectively (See Figure 1). Under air, only white substances found condensed on the quartz tube near to the hot zone. The SEM and EDS indicated that the white substance is ZnO powder while the grey substance is Zn powder. Only ZnO peaks found in the XRD signal of the white substances while Zn peaks are the only peaks found in the XRD signal of the grey substances. Overall, the condensed mixture of Zn/ZnO powders resulted from the current experiments has a purity of about 99.5% metal basis. According to the laser diffraction particle analyzer, the average particle size was in the range of 3 to 11mm, where the largest one obtained from the experiment conducted at 200 ml/h and the smallest one obtained at 1L/h gas flow rate (see Figure 2). By varying the atmosphere, carbon content, as well as gas flow rate, the current high temperature experiments demonstrated that the properties of the recovered product can be altered.

Technoeconomic analysis on the proposed plants shown that within the current alkaline battery black mass production (200 tonnes/year), both continuous and batch-process plants are economically feasible. It is expected that the generated income of the 200 tonnes/year plants are about $1.8 million and in the range of $0.5-0.6 million for Zn and ZnO recovery, respectively. Based on the feed capacity study, it was found that the continuous process plant is preferable for large capacity, and on the other hand, batch process suit for low capacity plant. The analysis also shown that the minimum annual plant capacity was expected to be 100 tonnes to ensure that the process is still economically feasible. When compared to the solar process, the solar process plant is expected to provide greater income than the batch process plant. The continuous process plant, however, is still economically superior at high feed capacity (See Figure 3a). One can see from Figure 3b, however, that the solar process plant still economically viable at a very low feed capacity when the other processes generate negative income. The solar process plant still generates positive income at an annual product capacity as low as 40 tonnes and 15 tonnes for ZnO and Zn recovery, respectively.

Figure 1. Condensed substance has whitish appearance near hot zone and greyish appearance closer to the end.

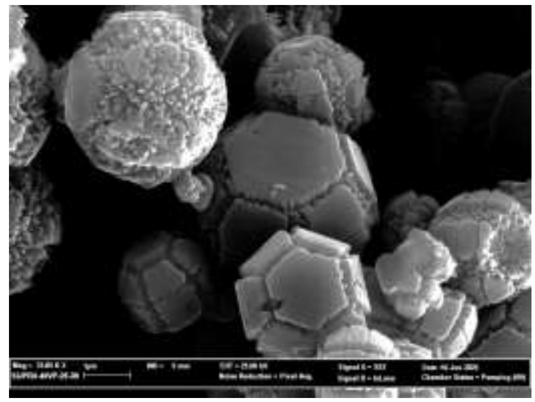

Figure 2. SEM image of the condensed substance shown the average particle size is less than 3 microns.

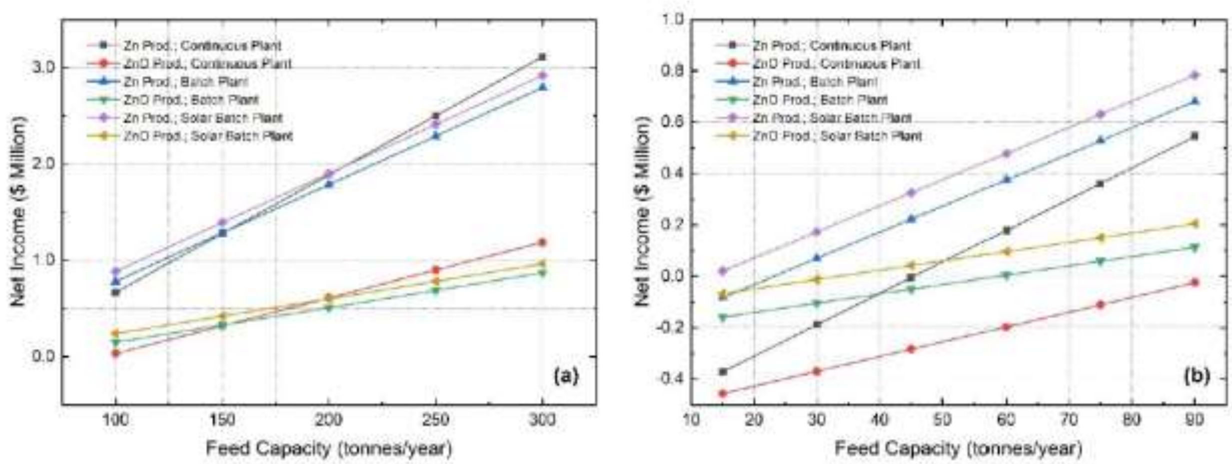

Figure 3. Impact of feed capacity on the expected annual net income at range: (a) 100 to 300 tonnes/year, (b) 15 to 90 tonnes/year

Conclusions and Future Work

The Zn/ZnO recovery process from spent alkaline batteries black mass through carbothermic reaction has been studied. The quality of the recovered powder, i.e. phase, size, yield, and purity, hence its economic value can be altered by adjusting the atmosphere of the process, the gas flow rate, and the carbon content in the black mass. The technoeconomic analysis supported by thermodynamics assessment, experimentation results, and mass and energy balance calculations shown that the proposed process plants are economically viable at a minimum black mass feed capacity of 100 tonnes/year. The realisation of the solar reactor concept will be explored further as it is expected that the process is still economically beneficial even at capacity as low as 15 tonnes, which in turns will enable a small to medium sized industry involved in the alkaline battery recycling process. The variation of the phase condensed at the condenser will also be investigated further to ensure the control of the recovered product quality can be achieved.

Acknowledgement

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