Technical Report

The Current Status on the Recycling of Lead-acid Batteries in China

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Lead-acid batteries are widely used in electric vehicles and lights. The current status of recycling of spent lead-acid batteries in China is described, including the main methods used and general trends. Current recycling of lead-acid batteries in China is mainly conducted by lead recovery companies and without direct government control. Some suggestions for improvements are made.

Keywords: Lead; Lead-acid battery; Recycling; China

1. INTRODUCTION

Worldwide, recycling rates for commonly used batteries and especially lead-acid batteries are growing, especially in industrialized countries such as Japan, the United States and countries from the European Community [1]. Recovery of the lead in these batteries after the end of their life cycle can be profitable for businesses if exploited appropriately, and is important not only for the conservation of natural resources but also for the minimization of related environmental pollution.

In the last twenty years the center of the international lead market has shifted to China, which has become not only the largest producer of raw and refined lead, but also the largest consumer [2]. In China, the lead-acid batteries are used primarily in vehicles for starting, lighting and ignition purposes, and in photovoltaic solar installations and telecommunications systems to store energy [3]. The efficiency of lead recovery from lead-acid battery recycling is lower in China than other countries [4], and the crude methods employed until recently have resulted in the release of millions of tons of lead into the environment [5], where it has the possibility to be absorbed in human body by the inhalation of dust or ingestion through contaminated food or water.

The average blood lead levels (BLLs) of Chinese children living in some industrial and urban areas, where lead levels in air, soil, dust, and food can be high, have been found to be significantly
higher than those of children in suburbs and rural areas [6]. Such children can have higher BLLs than their counterparts in other countries for the same reason. Lead pollution and its effects on children have become an important issue of public health [7], especially as children make up about one quarter of the population in China. Exposure to lead can causes harmful health effects including damage to the central nervous system, the kidneys, the cardiovascular system, and the reproductive system [8, 9]. The reality of this has been illustrated by incidences of lead poisoning reported among workers in, or residents nearby, lead-acid battery recycling and manufacturing plants during the phase of rapid industrialization in China [10]. In recent years lead recovery from spent lead-acid batteries in particular has received increasing attention. Ogunseitan and Smith estimated that Nigeria could save $1 billion every year per 50% decrease in childhood BLLs in health care costs, and the costs of lead exposure for adults is total $7 billion [11].

Studies on the adverse health effects of lead exposure in lead-acid battery manufacturing and recycling in developing countries including China and among children in nearby communities have been carried out, but none provide an overall picture or suggest any solutions to this problem. This research aimed at reducing lead emission to the land, water and air can also improve environmental health. We will investigate and analyze the data collected from various sources to control and prevent lead pollution in China.

2. LEAD-ACID BATTERIES

Typically, lead-acid batteries for vehicles contain an average of 7.94 kg lead and 5.68 liters of sulfuric acid [12]. Lead-acid batteries which are improperly disposed of can corrode, thus releasing lead and sulfuric acid which can seep into the ground and contaminate the soil and the ground water. In order to avoid this, it is necessary to promote pathways for recycling them.

The lead-acid battery is a complex industrial product constituted by several materials [13]. The main components of a lead-acid battery are [14]:

1. Active mass
   i) Anode (negative electrode) consisting of Pb
   ii) Cathode (positive electrode) consisting of PbO$_2$

2. Metallic grids, metallic connections
3. Electrolyte (aqueous solution of H$_2$SO$_4$)
4. Polypropylene casting (box)
5. Other components (wood, paper, PVC)
By a redox reaction, chemical energy is converted to electrical energy, producing insoluble PbSO$_4$ from Pb and water. The electrode reactions during discharge are following:

Negative Electrode: Pb + SO$_4^{2-}$ - 2e$^-$$\rightarrow$ PbSO$_4$

Positive Electrode: PbO$_2$ + 4H$^+$ + SO$_4^{2-}$ + 2e$^-$$\rightarrow$ PbSO$_4$ + 2H$_2$O

Important characteristics of lead-acid battery include: an ability to work effectively in a wide temperature range; a powerful recover ability; low cost; low maintenance or maintenance free; a safety seal; powerful recover ability; a long life cycle in the usage stage; a low self-discharge rate [14].

The typical elemental composition of lead-acid battery is shown in Fig. 1 [15]. Typically, a new lead-acid battery contains between 60% and 80% recycled lead and plastic [16].

3. THE APPLICATIONS OF LEAD AND LEAD-ACID BATTERIES

Lead has been widely used in electronic devices, for example, lead can be used as a major component of solders and lead oxide in the glass of cathode ray tubes (televisions and monitors), while in lead-acid batteries and in some PVC cables as stabilizers [8].

Figure 1. The composition of an average lead-acid battery

Figure 2. Bicycle Style and Scooter Style Electric Bikes (Image source: www.forever-bikes.com)
According to incomplete statistics from a Chinese government report, there were about 3000 lead-acid battery enterprises in China in 2003 [2].

**Figure 3.** Number of lead-acid battery enterprises in China (Data source: http://www.escn.com.cn)

**Figure 4.** The top ten Provinces of Lead-acid battery annual production in 2010 and 2011 (Data collected from the website: http://www.escn.com.cn)
Figure 5. The proportion of different battery types used in electric bicycles in China in 2011 (www.battery.com.cn)

Lead-acid batteries power more than 95% of all electric vehicles in China (Fig. 5), which have become a significant mode of transportation in the past decade. Because of the development of electric bicycles (Fig. 2) and tricycles, automobiles, motorcycles and buses, the demand for lead used in lead-acid batteries has been increasing rapidly (Fig. 6). With their advantages of low price, high-unit voltage, stable performance, and a wide operating temperature range, lead-acid batteries are used in rural telecommunication networks, electric power, solar and wind power energy storage systems and other areas [3, 10, 19].

Figure 6. Annual lead consumption for lead-acid batteries (Data sourced from :http://www.qqddc.com/)
However, the number declined significantly – by 50% - during from 2003 to 2008, with about 1500 enterprises closed. It is predicted that there will only be 300 enterprises in 2015, about 40 of which are large-scale enterprises (Fig. 3). The main reason is that lead pollution issues compelled government to control the number of battery enterprises [17].

In China, the manufacturers of lead-acid batteries are mainly located in Zhejiang, Guangdong, Jiangsu, Hebei, Hubei and Shandong Provinces. Fig. 4 presents the outputs of lead-acid batteries of the top ten Provinces from 2010 and 2011, which totally accounted for 90% of annual output in China [18].

4. RECYCLING OF SPENT LEAD-ACID BATTERIES IN CHINA

4.1 Methods for lead-acid battery recycling

The recycling technologies for the recovery of component materials from lead-acid batteries can be based on both hydrometallurgical and pyrometallurgical processes.

Recycling through hydrometallurgy basically consists of the acid or base leaching of scrap to put the metals in a solution. Once in a solution, metals can be recovered by precipitation, altering the pH of the solution or adding some reaction agent, or by electrolysis. The solution can also be separated by solvent extraction, using an organic solvent, which binds to the metallic ion, separating the metal from the solution. The metal can then be recovered by electrolysis or by precipitation [20]. Pyrometallurgy differs from hydrometallurgy in the stage of the treatment of the battery paste, which is contacted by thermal means in a rotary furnace in order to recover the contained lead. Both processes require expensive equipment due to the corrosive environment and cleaning systems of gas and liquid waste [14].

Comparing the two methods, the pyrometallurgical method seems more appropriate for Chinese industry, because it is a well-tested commercial method, it is simpler, and the large electric power demand of the hydrometallurgical method, combining with the shortage and high price of electric energy in China, makes the operating expense of that method significantly higher[14, 21].

4.2 The situation of recycling lead in China

There are currently about 300 lead recycling plants in China, mainly concentrated in Jiangsu, Shandong, Henan, Hubei, Hunan, Hebei and Anhui province. The total production of these factories is about 80% of all the production in China. Their capacity varies from tens to thousands of tons [22]. Many lead-acid battery enterprises have created environmental problems in recent years. Some have been reported in newspapers or on TV because of pollution problems or the high blood lead level in their workers and among children living in nearby communities. One way to reduce or even eliminate workplace exposures and emissions of lead is to take back used lead-acid batteries for proper recycling. Waste lead-acid batteries are usually recycled through the pathways as shown in Fig. 7 [2].
In China, recycled lead comes primarily from four sources [2]:
i) 72% of used lead comes from automotive batteries, e-bicycle batteries, motorcycle batteries, etc.
ii) 8.6% of used lead comes from VRLA (Valve-Regulated Lead Acid) batteries, industrial batteries, etc.
iii) 5% of used lead comes from cables, printing, etc.
iv) 14.4% of used lead comes from lead slag, lead dust, lead mud, etc.

China’s lead acid processing systems and efficiencies are very different from industrialized countries. Mao et al. [23] investigated the Chinese lead acid battery system and found that 16.2% of the lead content of a battery is lost during mining and concentrating, 7.2% lost during primary smelting, 13.6% is lost during secondary smelting and recycling processes, and 4.4% is lost during the battery manufacturing process. These loss rates reflect losses with respect to final battery production quantities, not initial lead input, and thus are very high [24]. The reasons for these high loss rates are mostly due to poor ore quality and a high proportion of lead being refined at small-scale factories using outdated technology. Traditional metallurgical techniques such as blast furnaces, reverberators and convertor metallurgy are still widely used in some regions in China. In most factories, lead was separated by hand, and then melted in traditional blast furnaces or cupolas. In some private plants, lead was melted with local methods, e.g. all of the plate and slurry melted together. The metal recovery rate for this is very low, energy consumption high, and pollution heavy. For example, in Guangdong province of south China, nearly 60-80% of families in the town of Guiyu are engaged in lead recycling operations [4]. The primitive family-run recycling centers use methods such as sorting, firing, incineration, acidic and alkaline baths, and manual assembly, open burning of wires and cables, and strong acid leaching. These operations are usually carried out with no or very little personal protection equipment or pollution control measures. In open burning of materials, fly ash particulates laden with lead and other toxic materials are usually emitted, resulting in increased human exposure,
contamination of food, soil, and surface water [8, 25]. This example occurs without any incentive from the Chinese government. Such lead recycling from lead-acid batteries is done mainly because of economical factors of interest to small businesses.

The cost of producing lead from recycling is about 38% less than from virgin, primary production, with an efficiency of about 1.9 times higher [22]. The lack of considerable primary lead resources is resulting in an increase of its price and a drive towards large scale low cost lead recovery. Therefore, waste lead recovery is booming all over the world. The official recycling rate of lead in China’s lead-acid battery industry is 31.2% [26]. However, Mao et al. estimate that the actual number is approximately double that, or 62%, because of informal, small scale recyclers [24]. More recently, the price of lead has tripled, suggesting that recovery rates might be pushed even higher. In this case, the role of legislation and government will become even more important. More regulation will be needed for the protection of the environment and human health. In particular, the management of waste from the lead recovery processes will need to be restricted, especially disposal in surface or sewage water or land of the liquid content of the lead-acid batteries. The primitive family-run recycling plants should be closed. Moreover, the construction of a lead-acid batteries recycling plant needs, with the following priority, consideration of:

· prior to all, organization of a collection scheme to secure the supplies.
· use of modern technology such as pyrometallurgical method securing environmental protection.

5. DISCUSSION

The battery industry is the largest consumer of lead and will become a larger consumer as the worldwide demand for automobiles increases and substitutes for lead in other products are found [27]. The demand for lead is expected to increase disproportionately in developing countries, including China, because of several factors [3]: environmentally preferable technologies including solar and wind energy are reliant on lead batteries for backup power; in China, 75% of all solar installations are linked to lead batteries; lead batteries are widely used in nearly every electric bicycle.

Poor manufacturing quality and tropical climates in many developing countries especially China result in a shorter average cycle life of lead-acid batteries and more frequent recycling. Used batteries are broken apart and the metal plates are removed and melted down, often in small fires on the side of a road or in crude smelters, to sell for scrap metal. In this final disposition system, the waste lead is discharged on the ground without any environmental or health control system. Because of the poor quality of the material produced by these rudimentary recycling processes, the lead must be melted a second time to remove impurities before it can be used to manufacture new lead-acid batteries.

Fortunately, in some lead recycling companies located in east China, advanced technology has already been utilized to enhance the recovery rate. However, generally speaking, there are still many problems to be solved. The following efforts for recycling of lead-acid batteries have been proposed and should be considered further [22]:
a) the processes in the industry should be more tightly regulated
b) a nation-wide recycling scheme should be developed
c) the number and size of lead-acid battery companies should be regulated carefully through registration
d) shared responsibility systems should be set up, with high mandatory collection targets.

Technological, economic and legislative factors all interact to complicate recycling. The cost efficiency of recycling spent batteries is perhaps the greatest challenge to managing the environmental burden of batteries.

6. CONCLUSION

Lead-acid battery recycling could benefit both lead pollution control and resource recovery. Great efforts have been taken in China and some developing countries to improve lead recovery from waste lead-acid battery treatment. However, systematic management of the collection, transportation, storage, and recycling processes need to be implemented to further improve the recovery.

References


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