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Recycling and Treatment of Waste Batteries

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Abstract. Various types of batteries are widely used in daily life, and a large number of waste batteries will eventually be produced. Waste batteries will cause serious environmental pollution. At present, the main treatment methods of waste batteries are incineration and landfill, solidification treatment, manual sorting, wet recovery technology, dry recovery technology and bio-metallurgical technology. In this paper, several disposal methods of waste batteries in recent years are illustrated.

1. Introduction

There are many kinds of batteries, which can be roughly divided into primary batteries, secondary batteries and fuel cells. Primary batteries refer to batteries that can not be recharged after discharge. They can also be called dry batteries, such as ordinary zinc-manganese batteries and alkaline zinc-manganese batteries. Secondary batteries refer to batteries that can be recharged and recovered after discharge and can be used many times. They can also be called storage batteries and rechargeable batteries, such as lithium batteries and lead-acid batteries. Fuel cell is a device that directly converts chemical energy in fuel into electric energy, and it can also be called electrochemical generator.

Table 1 Effects of various components of lithium-ion batteries on the environment and human beings

Material Types	Substances	Chemical Properties	Impacts
Cathode Material	$LiCoO_2$, $LiMnO_4$, $LiFePO_4$, etc.	It can react with acid and base to produce heavy metals.	Heavy metal pollution increases the pH value of the environment.
Anode Material	Graphite, etc.	Combustion can produce CO and so on, and also can cause dust pollution.	CO and solid dust particles produced by combustion can pollute the air.
Electrolyte Solute	$LiPF_6$, $LiBF_4$, $LiCIO_4$, etc.	Strong corrosiveness, toxic gases can be produced when exposed to water or high temperature.	Producing toxic gases, polluting the air and stimulating the human body through skin and breathing contact.
Electrolyte Solvent	EC, EMC, DMC, PC, etc.	Combustion produces CO.	Contamination of alcohol and other organic substances through skin and respiratory contact can cause irritation to the human body.
Other Materials	PVDF	It can react with fluorine, concentrated sulfuric acid, strong alkali and alkali metals.	HF produced by thermal decomposition and fluorine pollution.

Batteries are indispensable thing in people's life. Batteries are used in everything from clocks and watches, remote controllers, toys to cars. Hu [1] and others have carried out questionnaires and interviews with 160 residents, college students and middle school students. Among them, 33.7% of them will put waste batteries at home, 13.4% will collect waste batteries and put them in recycling bins, while 27.1% will throw them away together with domestic waste. In China, 10,000 tons of waste batteries are produced each year [2]. It is predicted that by 2020, there will be 25 billion lithium-ion batteries in China alone with a total weight of 500,000 tons [3,4]. The total amount of waste batteries is more, and it inevitably pollutes the environment. Among them, cadmium, mercury, zinc, lead and chromium are hazardous wastes. These heavy metals will enter the soil, change the soil acidity and alkalinity, affect the growth of crops, and accumulate in the body of crops. Heavy metals will also enter the water body, endangering the survival of aquatic organisms. Some heavy metals will also volatilize into the atmosphere, polluting the atmosphere. For example, nickel powder and smoke are toxic to human respiratory tract, nose and pharyngeal conjunctiva [5]. $LiPF_6$, organic carbonate, copper and other chemical substances contained in lithium iron phosphate batteries are listed in the national hazardous waste list [6]. Lead is mostly used in automobiles, and its recycling methods are constantly improving [7,8]. It is not only our living environment, but also the accumulation of heavy metals in the human body through the food chain, which has a negative impact on the human nervous system, digestive system and so on.

Liu summarized the impact of waste lithium batteries on the environment and human beings as Table 1[9].

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2. Recycling Technology of Waste Batteries

2.1. Incineration and Landfill

Some batteries will be burned after they are discarded, but this will produce a lot of dust or tiny particles to pollute the atmosphere. Some batteries are buried in the soil together with municipal solid waste, but this requires high impervious measures, otherwise, it is very easy to cause serious pollution to the soil.

2.2. Curing Treatment Method

The solidification disposal method refers to the mixing of waste primary batteries with concrete ingredients in a certain proportion after crushing, and then the mixed concrete is used for paving roads or mixing with other building materials. This method has three advantages, one is to save the raw materials of concrete, the other is to improve the quality of concrete by using waste batteries, and the third is to reduce the pollution of waste batteries to the environment due to the characteristics of concrete[10]. Although this method can deal with a large number of waste batteries in a short time, it does not solve the fundamental problem [11].

2.3. Wet Recovery Technology

Wet recovery technology is mainly to break the batteries after full discharge, then leach them with acid to produce soluble salt solution, and then electrolytically separate and purify the recovered metal. It is a commonly used waste battery treatment technology, such as chemical precipitation, solvent extraction, direct leaching and roasting leaching [12]. The latter is more suitable for evaporating low boiling point metals such as mercury and cadmium. Typical processes of wet leaching process include alkali leaching of spent batteries to alkali leaching residue, acid dissolution and extraction after purification; acid leaching of spent batteries to adjust the pH value of solution to separate aluminium and other metals, and then separation of cobalt, nickel and lithium by ion exchange resin; immersion of spent batteries in NMP, separation of aluminium, copper foil and active materials, and filtration of graphite and cathode materials by acid leaching after sieving [13]. The filtrate is precipitated with alkali solution. Electrolysis is also often used in the final metal purification. Wet recovery is prone to secondary pollution.

2.3.1. Chemical Precipitation Method. Chemical precipitation method is to add precipitating agent to the solution to cause precipitation reaction. Hu et al. dissolve $LiCoO_2$ electrodes in waste lithium ion batteries with NaOH solution, so that aluminium enters the solution in the form of $NaAlO_2$ [14]. The concentration of NaOH solution is 10%, which can dissolve aluminium quickly, and separate $LiCoO_2$ from aluminium, and remain in the alkali leaching residue. The solution can be neutralized in H_2SO_4 solution to obtain $Al\ (OH)_3$. Alkali leaching residue is leached by sulfuric acid-hydrogen peroxide system, so that cobalt in $LiCoO_2$ enters the solution in the form of Co^{2+} to form complex ion $[Co(H_2O)_6]^{2+}$, and acetylene black and organic binder remain in the leaching residue. Then $(NH_4)_2C_2O_4$ saturated solution was added to the purified filtrate to precipitate cobalt. The final product $CoC_2O_4{\cdot}2H_2O$ was obtained by drying and sieving precipitation.

The reaction principle is as follows:

$$2Al + 2NaOH + 2H_2O = 2\ NaAlO_2 + 3H_2\uparrow$$
$$4NaOH + 2\ NaAlO_2 + 3H_2SO_4 = 2\ Al(OH)_3\downarrow + 3Na_2SO_4 + 2H_2O$$
$$2LiCoO_2 + 3H_2SO_4 + H_2O_2 = 2CoSO_4 + O_2 + Li_2SO_4 + 4H_2O \quad (1)$$
$$[Co(H_2O)_6]^{2+} + (NH_4)_2C_2O_4 = CoC_2O_4\downarrow + 2NH_4^+ + 6H_2O$$

Kejbalee et al. prepared cobalt-nickel compounds by chemical precipitation and roasting[15].

2.3.2. Solvent Extraction. Solvent extraction uses specific organic solvents to form stable complexes with metal ions, thus selectively separating valuable metal ions [16]. Nan [17] and Kang [18] all used Cyanex 272 (2,4,4-trimethylpentyl) to extract cobalt from leaching solution, and the separation effect was quite good. Swain is also extracted[19].

Nan et al. first pretreated the waste lithium-ion batteries. The batteries were discharged completely by short circuit between positive and negative electrodes of single batteries. The iron shell was selected by magnetic separation with special mechanical equipment, and the core of alkali-leached batteries was used to recover aluminium. In order to improve the extraction rate of cobalt and copper in subsequent operation, the alkali leaching residue was treated with $n(H_2SO_4):n(H_2O_2)= 3:1$ solution. The solid-liquid ratio was 1:10, and the leaching rate of cobalt could reach 92% after 2 hours of treatment.

$$LiPF_6 + H_2O = LiF + POF_3 + 2HF$$
$$HF + NaOH = NaF + H_2O$$
$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2\uparrow$$
$$2NaAlO_2 + H_2SO_4 + 2H_2O = 2Al(OH)_3\downarrow + Na_2SO_4$$
$$2MCoO_2 + 3H_2SO_4 + H_2O_2 = M_2SO_4 + 2CoSO_4 + O_2\uparrow$$

Among them, M^+ is Li^+ and partly replaces Li^+ in alkali leaching process.

At present, the main metal ions in the solution are Cu^{2+}, Co^{2+}, Li^+. Acorga M 5640 is used as extractant to recover copper[20]. The results showed that the concentration of extractant was 10%, the pH value of extractant was 1.0, the ratio of oil to water was 1:1, the extraction time was 10 minutes, and then eluted twice with 2 mol/L sulfuric acid at room temperature. The equilibrium time was 1 minute. Under this condition, the recovery rate of copper could reach 98%.

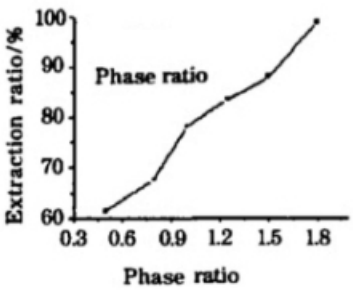

Figure 1. Effect of Comparisons on Cobalt Extraction Rate.

Then, Cyanex 272 with 10% saponification rate treated with 10% NaOH at 1 mol/L was adjusted to pH = 5.0 and shocked for 1 minute. At room temperature, 2 mol/L H_2SO_4 solution was eluted twice according to the ratio of organic phase to water phase 1:1. After 1 minute of oscillation, the following results were obtained. It can be seen that with the increase of the ratio, the extraction rate increased. When the ratio was 1:1, the extraction rate was very high, but it was not conducive to cost savings (Figure 1).

Kang et al. used 0.4 mol/L 50% kerosene saponification rate Cyanex 272. By adjusting the solution pH = 6, the separation coefficients of Co/Li and Co/Ni reached 750. When the organic phase is 2:1 compared with the aqueous phase, the extraction rate of cobalt could reach 99.9% by two-stage countercurrent extraction.

2.3.3. Ultrasound-Assisted Leaching Technology. Because of the mechanical effect, cavitation effect, thermal effect and chemical effect of ultrasound, high temperature and high pressure can be produced in very short time and very small space, and the temperature change rate is as high as 109 K/s. In this special physical environment, chemical bonds (376.8-418.6 kJ/mol) with strong binding force can even be opened[21].

Zhang et al. [22], Zhao et al. [23] used ultrasound to improve the leaching rate of cobalt. According to the orthogonal test of Zhao et al, the optimum leaching conditions were ultrasonic time 20 min, volume ratio of sulfuric acid to hydrogen peroxide 5:1, leaching temperature 80 ^{o}C, and the leaching rate of cobalt could reach 99%.

2.4. Dry Recovery Technology

Dry recovery technology mainly uses physical methods to break the battery after full discharge, roast at high temperature, and get the final product through a series of oxidation-reduction reaction and decomposition reaction, such as pyrometallurgy, mechanical separation, vacuum metallurgy, mechanical grinding method [24]. The mechanical grinding method is to mix the separated electrode materials with abrasives and then grind them mechanically so that the positive active material can be converted into metal salts. Yang also mentioned that reduction furnace technology is used to separate and recover cobalt, nickel and manganese from spent lithium ion batteries, that is, high temperature reduction smelting with carbon reductant by using metal oxides or oxide materials[25]. Rabah et al. recovered nickel and cobalt and other valuable metals by mechanical, pyrometallurgical and wet processes[26]. Mukunoki [27] used atmospheric pressure pyrometallurgical technology to recover ferronickel alloy, while Muller and others [28] used this method to recover nickel-cobalt alloy. Lyakov et al. [29] and Yanakieva et al. [30] mentioned high temperature smelting, the primary task of this method is desulfurization. Dry method has high requirements for equipment, high energy consumption, easy to produce toxic gases and other environmental pollution.

2.4.1. Fire method. Kim et al. [31] recovered waste lithium iron phosphate batteries by pyrometallurgical reduction roasting method. The electrode material was treated in nitrogen flow at 400, 500, 600, 400, 500 and 600^{o}C for 30 minutes. The new battery was reconstituted by adding binder styrene-butadiene rubber (SBR) and sodium carboxymethyl cellulose (CMC). The discharge capacity was tested. The experimental results showed that the effect was the best at 500 ^{o}C.

The process is simple, but the energy consumption is high. It is easy to produce harmful substances such as phosphorus pentoxide to pollute the atmosphere.

2.4.2. Mechanical Separation Method. There are two kinds of mechanical separation methods, one is to remove the battery shell, and then break up, screening, separation; the other is to directly break up the whole battery screening separation.

Zhang et al. used the second method, first discharged waste lithium ion batteries in NaCl solution with 5% mass fraction, then used shear crusher, impact crusher, drying screening, and then analyzed different particles[32].

Zhang et al. separated four kinds of particles with different particle sizes after shearing, impact and drying screening[33]. As shown in the following figure, aluminium shell and diaphragm are separated by blast, copper, aluminium and diaphragm are separated by electrostatic separation, $LiCoO_2$ and graphite are surface modified and flotation with particle size less than 0.075 mm, and grinding and drying screening with particle size less than 0.5 + 0.075 mm can be further divided into two or three types (Figure 2).

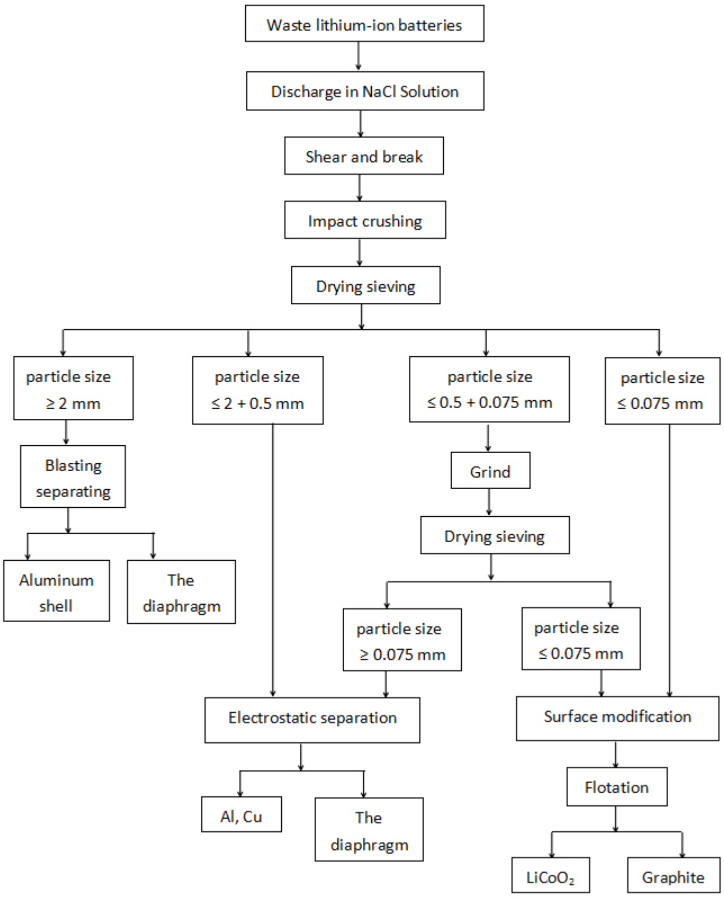

Figure 2. Flow chart of mechanical separation process.

2.5. Biological Method

Biometallurgy can be divided into bioleaching, biooxidation, biosorption and bioaccumulation. At present, bioleaching is the main method[34]. Metal components are usually separated and extracted by bacterial oxidation or biological oxidation, or by bacterial metabolites, such as the treatment of spent nickel-hydrogen batteries with acidophiles and their metabolites [35].

Mishra et al. leached metals from spent lithium-ion batteries with Thiobacillus ferrooxidans. Thiobacillus ferrooxidans utilizes elemental sulfur and ferrous ions as energy sources to produce sulfuric acid and iron ions by a series of redox reactions. It is found that ferrous ions can promote the growth and reproduction of Thiobacillus ferrooxidans, while iron ions can inhibit the activity of Thiobacillus ferrooxidans[36].

Xin et al. [37] and Wu et al. [38] inoculated and treated electrode materials and strains (thiobacillus ferrooxidans and thiobacillus thiooxidans) of dismantled waste batteries, cultured for a period of time, and treated $LiCoO_2$ with sulfuric acid produced by bacterial metabolism to form an extract containing Co^{2+}.

Although the metal extraction from waste batteries by biological method is relatively less polluted and environmentally friendly, it has obvious disadvantages, such as long leaching time, low leaching rate and low efficiency[39]. Moreover, it can only deal with the solution with low metal concentration, and the excessive metal concentration will affect the survival of microorganisms.

3. Conclusion

There are many kinds of batteries, and each kind of batteries has its own way of recovery and treatment. Even if it is the same kind of batteries, there may be many ways of treatment. People are also trying to make more reasonable ways to improve the recovery and utilization of metal components in waste batteries, and reduce the pollution of waste batteries to the environment.

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