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Study on the environmental risk assessment of lead-acid batteries

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Abstract

Lead-acid batteries were widely used as important power supply devices that include automotive, uninterruptible power supply (UPS), telecommunication systems and various traction duties. According to statistics, approximately 3 million tons waste batteries are generated every year and the production of lead-acid batteries will continue to rise even more sharply with sustained and rapid development of economy. Lead-acid batteries were consisted of electrolyte, lead and lead alloy grid, lead paste, and organics and plastics, which include lots of toxic, hazardous, flammable, explosive substances that can easily create potential risk sources. The materials contained in lead-acid batteries may bring about lots of pollution accidents such as fires, explosions, poisoning and leaks, contaminating environment and damaging ecosystem. The environmental risk assessment was required to be studied further in view of the diversity, emergency, and the serious consequences of the environmental accidents that may caused by lead-acid batteries. The environment risk assessment was presented in this paper particularly, the framework of environmental risk assessment on lead-acid batteries was established and methods for analyzing and forecasting the environmental risk of lead-acid batteries were selected. The work procedure included identifying accident, analyzing risk, pollution forecast and defensive measures. By analysing the environmental risk assessment of lead-acid batteries, the study supplied direction for the preventive measures according to the forecast results of lead-acid batteries. The basic theories were provided for the safe use of lead-acid batteries.

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Keywords: lead-acid battery; environmental risk; safe use;

1.Introduction

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Lead-acid batteries have been used for more than 130 years in many different applications that include automotive, uninterruptible power supply (UPS), telecommunication systems and various traction duties. They are the workhorse of the rechargeable battery systems for its reliability, low cost, and good operational life. Predictably, approximately 3 million tons waste batteries are generated every year[1] in China and the production of lead-acid batteries will continue to rise even more sharply with sustained and rapid development of economy. The lead-acid battery is a complex industrial product, constituted by several different materials[2], the consequence was very serious which often caused much property loss, casualties and environment pollution once accidents happen. Therefore, it was necessary for the study on the environment risk assessment(ERA)[3] of lead-acid batteries.

Environmental risk assessment is the process of identifying, evaluating, selecting, and implementing actions to reduce risk to human health and ecosystems[4], which provides important information about the nature, magnitude, and likelihood of possible environmental risks to inform decisions. It is occurrence prediction and quantitative and qualitative analysis of potential dangers considering sensitivity or vulnerability of a surrounding environment[5]. ERA has rapidly become not only a scientific framework for analysing problems of environmental protection and remediation but also a tool for setting standards and formulating guidelines in modern environmental policies [6,7]. The ERA of lead-acid batteries was presented in this paper particularly, the framework of environmental risk assessment on lead-acid batteries was established and methods for analysing and forecasting the environmental risk of lead-acid batteries was selected.

2. Environmental Risk Assessment of Lead-acid Batteries

Based on “Technical Guidelines for Environmental Risk Assessment on Projects”（HJ/T169-2004）and in consideration of the characteristics of the chemical compositions and contents，a framework of environmental risk assessment framework on lead-acid batteries was established in this paper. The work procedure included risk identification, sources analysis, pollution forecast, and defensive measures. The environmental risk assessment system was shown as Fig.1. By analysing the environmental risk assessment of lead-acid batteries, the study supplied direction both for the preventive measures and safe use according to the forecast results of lead-acid batteries.

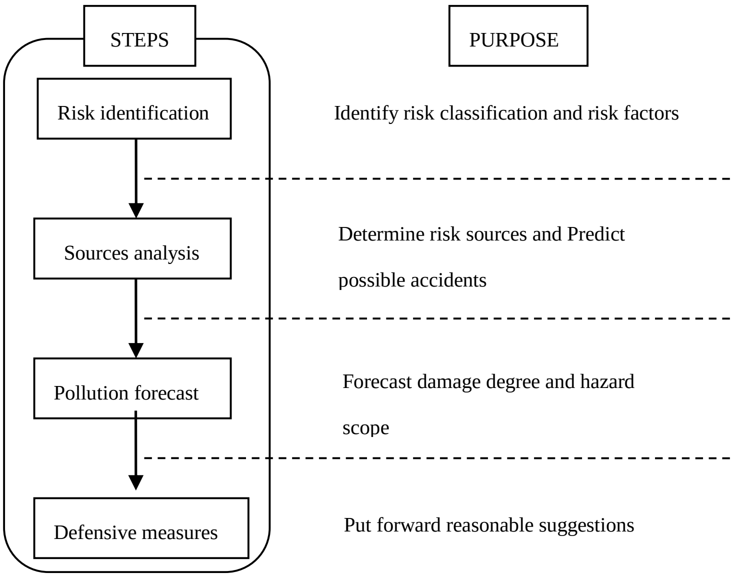

Fig. 1 The Environmental risk assessment system

2.1 Risk identification of Lead-acid Batteries

Lead-acid batteries generally consist of four parts, which are electrolyte, lead and lead alloy grid, lead paste, and organics and plastics[8], which included lots of toxic, hazardous, flammable, explosive substances that can easily create potential risk sources. The materials contained in lead-acid batteries may bring about lots of pollution accidents such as fires, explosions, poisoning and leaks, contaminating environment and damaging ecosystem. The main chemical compositions and contents of spent lead-acid batteries were listed in Table 1.

Table 1 The main chemical compositions and contents of spent lead-acid batteries

Compositions	Contents (wt.%)
Electrolyte	11–30%
Lead and lead alloy grid	24–30%
Lead paste	30–40%
Organics and plastics	22–30%

The recognition scope of lead-acid batteries mainly focused on the pollutants involved in the process of centralized recovery, storage areas and transport. Based on “Technical Guidelines for Environmental Risk Assessment on Projects” and “Identification of hazard installations for dangerous chemicals”（GB18218-2009）, hazard installations were defined when dangerous chemicals were under production, processing, transportation, use or storage both in long term and short term, as well as when the quantity of hazardous substances were above the functional unit of the critical quantity.

According to “Hazardous chemicals directory 2015”, the pollutants and its risk in the process of centralized recovery, storage areas and transport were listed in Table 2.

Table 2 The pollutants and its risk of lead-acid batteries

Materials	Risk	Physical state	Source
Lead and lead compounds	toxicity	solid	electrode and grid
Antimony	toxicity	solid	plates
Sulfuric acid	corrosion	liquid	electrolyte
Hydrogen	explosiveness	gas	water electrolysis

Lead and its compounds and antimony are toxic that have certain hazards both to humans and the environment, however they are the internal structure of the battery whose main existing form is solid, which did not form the conditions of exposure and diffusion in recovery, storage and transportation. The electrolyte exists as the form of liquid and the leakage would be caused due to the collision and the aging of battery tray. Thus this project focused on the consideration of the leakage of electrolyte and the leakage was the main environmental risk of lead-acid batteries in the process of production, processing, transportation, use or storage when risk accidents caused by natural disasters were out of consideration.

2.2 Sources analysis of Lead-acid Batteries

The electrolyte was mainly sulfuric acid of a certain concentration, the main chemical compositions and contents of electrolyte were as Table 3.

Table 3 The main chemical compositions and contents of electrolyte

Composition	Mass fraction	Density (kg/L)	Concentration (mol/L)
H_2SO_4	29-32%	1.2-1.3	4.2-5

Sulfuric acid[9] is a highly corrosive strong mineral acid with the molecular formula H_2SO_4. It is a pungent-ethereal, colourless to slightly yellow viscous liquid which is soluble in water at all concentrations. Sometimes, it is dyed dark brown during production to alert people to its hazards[10]. Sulfuric acid is a diprotic acid and shows different properties depending upon its concentration. Its corrosiveness on other materials, like metals, living tissues or even stones, can be mainly ascribed to its strong acidic nature and, if concentrated, strong dehydrating and oxidizing properties. Sulfuric acid at a high concentration can cause very serious damage upon contact, since not only does it cause chemical burns via hydrolysis, but also secondary thermal burnsthrough dehydration. It can lead to permanent blindness if splashed onto eyes and irreversible damage if swallowed. Accordingly, safety precautions should be strictly observed when handling it. Moreover, it is hygroscopic, readily absorbing water vapour from the air. Physical and chemical properties of sulfuric acid were listed in Table 4.

Table 4 Physical and chemical properties of sulfuric acid

Contents	Properties
Product Name	Sulfuric acid
Molecular Weight	98.08 g/mole
CAS.NO	7664-93-9
Catalog Codes	SLS2539, SLS1741, SLS3166, SLS2371,SLS3793
Synonym	Oil of Vitriol
Flammability of the Product	Non-flammable.
Flash Points	Not applicable.
Flammable Limits	Not applicable.
Toxicological Data on Ingredients	ORAL (LD50): Acute: 2140 mg/kg [Rat.]. VAPOR (LC50): Acute: 510 mg/m^2 hours [Rat]. 320 mg/m 2 hours [Mouse].

Sulfuric acid was under environmental risk assessment since this project focused on the leakage of electrolyte and the electrolyte was mainly sulfuric acid of a certain concentration which is highly corrosive strong mineral acid. Major hazard determination and evaluation level were shown in Table 5.

Table 5 Major hazard determination and evaluation level

Hazardous Chemicals	Threshold quantity （t）	Are major sources of pollution	Risk	Rank
Sulfuric acid	200	no	corrosion	second

2.3 Pollution forecast on the leakage of electrolyte

The sulfuric acid leak was the main environmental risk, the main reason causing leak was that the storage and transportation facilities were lack of maintenance. Suppose the leakage area was $0.025m^2$, and the leakage was handled by spraying foam to cover the material and prevent sulfuric acid from volatilizing in 10 minutes[11]. The sulfuric acid that leaked was taken effective measures and collected to spare tanks as well.

In this article, the leakage amount[12] (Q_L)were calculated by the equation(1) listed as follows:

$$Q_L = C_d A\rho\sqrt{\frac{2(P-P_0)}{\rho}+2gh} \tag{1}$$

Where Q_L is the sulfuric acid leakage rate, kg/s; C_d is the coefficient of leakage between 0.6-0.64, in this article C_d is 0.62; A is the the leakage area, 0.05×0.05=0.0025m^2; P is the medium pressure inside the container, 108000Pa; P_0 is the environmental pressure,1.013×10^{5}Pa; g is the acceleration of gravity， 9.8m/s^2; h is the liquid level above the gap, 0.1m; ρ is the density, 1.2g/mL.

The sulfuric acid leakage rate was calculated to be 0.190kg/s, and the leakage amount in 10 minutes were about 114kg. The concentrated sulfuric acid density is 1.2 t/m^3, the liquid thickness of sulfuric acid formed on the surface is 0.005m, so the leak area of sulfuric acid[13] on the surface of the formation can be calculated to be 19m^2.

Leakage of the liquid mainly consists of flash evaporation, thermal evaporation, and quality evaporation[14]. Since the boiling point of sulfuric acid is 330℃ at atmospheric pressure, flash evaporation and thermal evaporation won't happen and were not considered when the storage and ambient temperatures are below 40℃. The evaporation rate[15] (Q_3)were calculated by the equation listed as follows:

$$Q_3 = a\times p\times M/(R\times T_0)\times u^{(2-n)/(2+n)}\times r^{(4+n)/(2+n)} \tag{2}$$

Where Q_3 is the evaporation rate, kg/s; a, n represent atmospheric stability coefficients， it was shown in Table 6; P is the vapor pressure on the liquid surface, 1300Pa; R is gas constant, 8.31J/mol·k; T_0 is ambient temperature, 282.8K; u is wind speed, m/s; r represents radius of liquid pool, which is calculated to be 2.46m; M is molar mass, 0.064kg/mol.

Table 6 parameters of evaporation model for liquid pool

Stability condition	n	a
Unstable（A、B）	0.2	3.846×10^{-3}
Neutral（D）	0.25	4.685×10^{-3}
Stable（E、F）	0.3	5.285×10^{-3}

The wind speed was determined to be 1m/s and E was chosen as the stability condition in this study due to the fact that the lead-acid batteries were e in a relatively stable state in most case. According to the formula, the evaporation rate of the leakage liquid was Q_3=0.617g/s.

2.4 Calculations of influence scope

Smoky group diffusion model was chosen to calculate and predict the diffusion of pollutants based on "Technical Guidelines for Environmental Risk Assessment on Projects". The formula[16,17] was as follows:

$$C(x,y,o)=\frac{2Q}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z}exp\left[-\frac{(x-x_o)^2}{2\sigma_x^2}\right]exp\left[-\frac{(y-y_o)^2}{2\sigma_y^2}\right]exp\left[-\frac{z_o^2}{2\sigma_z^2}\right] \tag{3}$$

Where C $(x.y.o)$ is the concentration of pollutants at (x, y) over the downwind ground, (mg • m^{-3}); x_o, y_o, z_o represent the center coordinate of the puff; Q is the emissions of the puff during the accident; ; σ_X、、σ_y、σ_z are diffusion parameters in X, Y, Z directions, $\sigma_X = \sigma_y$ usually.

Combined with the risk evaluation index system based on statistical data in Table 7, the concentration of sulfuric acid at different distance was calculated and shown in Table 8 after the accident happened for 10 minutes. Concentrations at different distances were shown in Fig.2.

Table 7 Coefficient of the risk evaluation index

Materials	Short-term exposure limits（mg/m^3）
H_2SO_4	2

Table 8 The concentration of sulfuric acid at different distance

Wind speed (m/s)	Stability condition	Ground maximum concentration /(mg/m^3)	Maximum distance /m	Allowable distance for short-term exposure limits /m
1	E	268.49	2.8	12.7

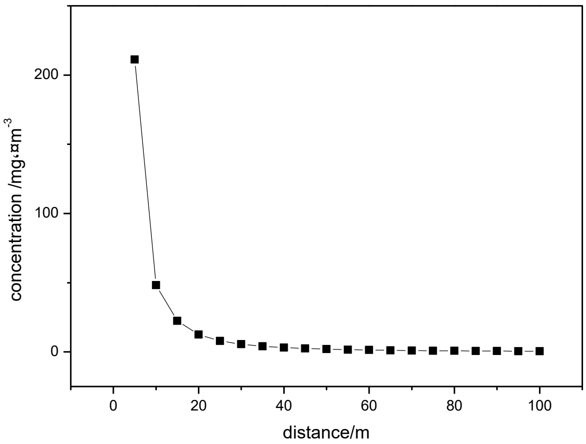

Fig. 2 Concentrations at different distances

Results showed that when the wind speed was 1m/s and the stability condition was E, the ground maximum concentration of sulfuric acid over the downwind ground was 268.49mg/m^3 when the distance was 2.8m, the influence scope of the leakage was 12.7m. Beyond this distance, the impact of the sulfuric acid is without considering which will gradually disappear through atmospheric diffusion and dilution.

2.5 Defensive measures

According to the forecast results, the preventive measures should be put forward. In case of insufficient ventilation, wear suitable respiratory equipment and avoid contact with skin and eyes. In situation of small leak, dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container. Neutralize the residue with a dilute solution of sodium carbonate if necessary. In situation of large leak, stop leak if without risk. Absorb with dry earth, sand or other non-combustible material. Do not get water inside container. Do not touch spilled material. Use water spray curtain to divert vapor drift. Use water spray to reduce vapors. Neutralize the residue with a dilute solution of sodium carbonate.

3.Conclusions

The framework of environmental risk assessment framework on lead-acid batteries was established in this paper, including risk identification, analysing risk, pollution forecast, and defensive measures. This project focused on the consideration of the leakage of electrolyte, which was mainly sulfuric acid of a certain concentration. The leakage of sulfuric acid was the main environmental risk of lead-acid batteries in the process of production, processing, transportation, use or storage. According to the project scale the sulfuric acid leakage rate was calculated to be 0.190kg/s, and the leakage amount in 10 minutes was about 114kg. Results showed that when the wind speed was 1m/s and the stability condition was E, the ground maximum concentration of sulfuric acid over the downwind ground was 268.49mg/m^3 when the distance was 2.8m, the influence scope of the leakage was 12.7m. Beyond this distance, the impact of the sulfuric acid was without considering since it would gradually disappear through atmospheric diffusion and dilution. According to the forecast results, preventive measures have been put forward.

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