Analysis and Identification of the Toxicity of the Solid Waste in Chemical Industry

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Abstract: Through a series tests of corrosion behavior, acute toxicity and leaching toxicity for chemical industry solid waste in a chemical plant in Chongqing, China, a corresponding method of sample collection, preparation and toxicity analysis were established in the laboratory. The cyanide compound and pH value of the solid waste were determined by using this method. The results show that those cyanide waste can be defined as hazardous and corrosive waste according to China standard GB5085.1~GB5085.3-2007. By the discussion on the changes of these indicators, the researches of this paper provide a basis for cyanide slag disposal and utilization, and can be used as the guideline.

Key words: cyanide compound; acute toxicity test; leaching toxicity test; hazardous waste

0. Introduction

The chemical industry solid waste which generated in the production process by the chemical industry, is a toxic, flammable, corrosive, infectious, chemical reactions of chemical residue. Such substances generally have a flammable, explosive, easy-poisoning hazard. Along with hazardous chemicals production, use, storage, so a large number of safety issues are likely to arise and lead to major and serious accidents occur in hidden and have been subject to people's attention [1]. "The directory on comprehensive utilization of resources " (China, 2003), which State Economic and Trade Commission released, described chemical industrial waste residue as: pyrite slag, calcine slag, sulfuric acid residue, sulfur gypsum, phosphogypsum, calcined phosphate slag , cyanide residue, phosphate slag, sulfur residue, barium-containing slag, chromium slag, salt mud, total solvent residue, phosphorus slag, citric acid residue, sugar residue, desulfurized gypsum, fluorine gypsum, waste gypsum molds, etc [2]. In particular, the one referred to cyanide slag, which contains hydrogen cyanide and potassium cyanide, is a toxic waste residue and harmful substances to human and animal. They can enter the body through a variety of ways, such as skin absorption, invasive wound, respiratory inhalation, etc. Moreover, the passive absorption of humans and other organisms is impossible to defend. According to related data, oral lethal dose of sodium cyanide for human is the 100mg, or 120mg as for potassium cyanide. In other words, the average of hydrocyanic acid and cyanide lethal dose is 50~60mg, and the quantity may be smaller for other animals or livestock [3].

According to Ministry of Environmental Protection of China, "The Guide to Solid Waste Discharge Registration", and "National Catalogue of Hazardous Wastes" requirement, hydrocyanic acid and potassium cyanide are HW33 inorganic cyanide waste class. To implement the “law of the People’s Republic of China on Prevention of Environmental Pollution Caused by Solid Waste”, we carried out a lot of experimental study on chemical industry solid waste, and build up a set of methods about sample collection, preparation and toxicity analysis. Through these methods large amounts of scientific and accurate data are provided for the treatment and disposal of those solid wastes in the chemical industry.

1. Collection and treatment of samples

Fine Chemical Industrial Ltd., a company in Chongqing, China, produces large number of cyanide residue annually in the production

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process. To the end of 2007, the accumulated solid waste reached to 28710 t, covered an area of 2000 m^2, in which the main components are cyanide and its derivatives. Those wastes have polluted the surrounding environment of the factory.

1.1 Collection of samples

In order to accurately and objectively reflect the solid waste' nature, composition and total volume, the sample of the residue field is systematic and representatively collected according to HJ/T20-1998 "Technical specifications on sampling and sample preparation from industry solid waste" and HJ/T 298-2007 "Technical Specifications on Identification of Hazardous Wastes".

The appearance of residue field is quadrilateral. A method is adopted that combine simple random sampling and stratified sampling to realize the sampling of the residue field. The residue field is divided into 35 equal size grids, sequentially numbered. Then, 7 grids are sampled by using random number table method described in HJ/T20-1998. Drilling in the enter of each grid sampling in each three layers until there is few mud in the bottom of the sample, a total of 21 samples were got with each sampling is 2 Kg at least. Those samples are made to dry basis for later use. The sampling results shown in Table 1.

Table 1 Sampling results

Code	Sampling method	Sampling depth	Sample number
1	Drilling	150 ㎝, 360 ㎝, 550 ㎝	3
2	Drilling	150 ㎝, 320 ㎝, 450 ㎝	3
3	Drilling	200 ㎝, 400 ㎝, 600 ㎝	3
4	Drilling	200 ㎝, 400 ㎝, 600 ㎝	3
5	Drilling	230 ㎝, 420 ㎝, 600 ㎝	3
6	Drilling	200 ㎝, 400 ㎝, 600 ㎝	3
7	Drilling	200 ㎝, 400 ㎝, 800 ㎝	3

No.5 grid is selected to do the profile analysis, which is most representative. The sampling depths of three samples of No.5 grid are 0-2.3cm, 2.3-4.2cm, 4.2- 6.0cm. The samples of No.1, No. 4, and No.7 are mixed as a large sample in order to do leachate toxicity test and acute toxicity test later.

1.2 Sample preparation

By natural drying at room temperature (25 ± 5℃) , the moisture is less than 5% in the residue samples, and the size of particles are less than 5mm (the particle should be broken when more than 5mm) so all of them will pass through 5mm sieve pore. The samples were mixed well, and collected into the high-density polyethylene containers using sample quartering.

In order to the accuracy of the experimental data, the water capacity should be take into account in the calculation process. Moisture test was carried out for a weight of 20g of a sample under the conditions of the temperature of 105 ℃ and the weight error of 1mg. Then calculated the water content [4]:

$$\text{water content}(\%) = \frac{\text{sample weight} - \text{dry sample weight}}{\text{sample weigh}} \times 100\% \quad (1)$$

1.2.1 Preparation for toxic leaching lixivium

100 g of samples (dry basis, particle size less than 5mm) were put into a polyethylene plastic bottle of 2L, which were added to 1000ml of distilled water (including the sample water content). And the solid-liquid ratio of the mixture is maintained at 1:10 and pH is between 6.0 ~ 6.5. After the plastic bottle was sealed, it was vertically fixed on the oscillator at the oscillation frequency of 120 t/m, and amplitude at 40mm. The mixture was shaken continuously for 4h at room temperature(25±5 ℃) and the undissolved materials from the mixture were removed by 0.45μm membrane

after 18h[5].

1.2.2 Preparation for acute toxicity lixivium

Similarly, 100 g of samples (dry basis, particle size less than 5mm) were put into wide mouth bottle, which was added to 100ml of distilled water and the mixture was stirred uniformly in an incubator at 54℃ for 24 h. At last, the mixture was filtered by medium speed quantitative filter paper, leaving the leachate for the studies.

2 Test Method

According to "law of the People's Republic of China on Prevention of Environmental Pollution Caused by Solid Waste", hazardous waste means waste that is dangerous and included in the national list of hazardous waste or identified as such according to the criteria and methods of identification for hazardous waste as prescribed by the State. The main criteria of identification are corrosive, acute toxicity and leaching toxicity [6].Table 2 shows the hazardous waste identification system of China.

Table 2 Identification Systems of Hazardous Waste

Identification standard for hazardous wastes	Experimental method	Leaching（sampling/preparing）methods
GB5085.2-2007 Screening test for acute toxicity	GB5085.2-2007 Screening test for acute toxicity appendix A	GB5085.2-2007 Screening test for acute toxicity appendix A HJ/T20-1998 Technical specifications on sampling and sample preparation from industry solid waste
GB5085.3-2007 Leaching characteristic identification	GB/T15555.1~15555.11-1995 Test method for leaching toxicity of solid waste	GB5086.1～5086.2-1997 Test method for leaching toxicity of solid waste HJ/T20-1998 Technical specifications on sampling and sample preparation from industry solid waste

2.1 Leaching Toxicity test

Leaching toxicity is not only one of the most important characteristics to identify hazardous wastes, but also the key factor to evaluate which disposal technologies should be applied to deal with the solid wastes. Vast majority of the identification of hazardous wastes are based on the standard. By imitating leaching procedure, the concentrations of dangerous solid waste were detected. Any one in excess of the concentration limits means that the solid wastes are of leaching toxicity. Solid waste and weak acid water mixed in a certain solid-to-liquid ratio (1:10) and the leachate was got by filtering the undissolved materials. The waste is identified whether it is of leaching toxicity by analyze the lixivium.

2.2 Acute toxicity testing

Weighing 18 ~ 22g with the kinds of clean grade of Kunming mice were selected as the experimental animals. Before the test, those mice should be observed three days, with no food for 12-hour but no restrictions on drinking water. The weights of mice were no significant difference. Each sample was used for a group of mice, which is of 20 mice (male and female of 10). Each sample tests 1 group of animals, 20 in each group, half male and female, which respectively has its corresponding control group. Each group of mice were given a dose of 20ml/kg.bw lixivium samples, and the corresponding control group be given the same capacity of distilled water. The weight of the test mice were measured separately 3 times, namely before the test, at the test and the time before the mice were executed. When the test is over, weight gain in mice were recorded statistically. And physical condition of the mice should be carefully observed and the survival statuses of mice within 48h were recorded in detail.

3 Results and discussion

3.1 Acute toxicity screening results

During the test, no abnormal situation was presented. At the end of the test, we dissected the survival of all animals and finding no ab-

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normal tissues or organs. All tested sample mice do not die, except a small number of mice eat less food and lose weight in 14 days observation (test results are in Table 3). According to GB5085.2-2007 "Identification standard for hazardous wastes-Screening test for acute toxicity", the residue field does not belong to that acute toxicity of hazardous wastes.

Table 3 Test results of the acute toxicity

Gender	Group	Mice（No.）	Before（g）	After（g）			Death
				1st week	2nd week	3rd week	
Female	Control group	10	21.3±1.3	32.2±2.3	36.7±3.2	15.4±3.2	Alive
	Experimental group	10	20.9±1.4	32.0±1.7	35.8±2.3	14.9±2.6	
Male	Control group	10	20.1±1.7	28.1±1.4	30.4±1.8	10.3±2.4	Alive
	Experimental group	10	20.5±1.5	27.8±1.9	29.7±1.4	9.2±1.4	

3.2 leaching toxicity test results

From Figure 1, the pH value of leachate in the residue ranges from 9.21 to 13.09, with an average of 10.864, standard deviation of 1.553, coefficient of variation of 14.3%. Cyanide concentration ranges from 0.15 to 0.60, with the average of 0.429, standard deviation of 0.195, variation coefficient of 45.5%. The results show that cyanide content of samples is extremely uneven. It should be carefully treated in the post-treatment.

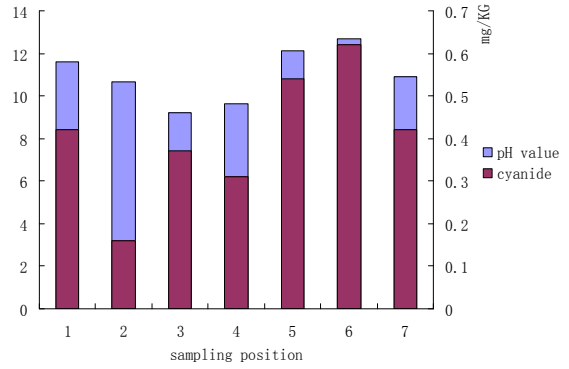

Fig. 1, The experiment results of pH value and cyanide

In this test, the pH value of all samples leachate is greater than 7. That is because the alkali metals in the cyanide are soluble in water and appear to be alkaline after hydrolysis. Among them, according to the standard GB5085.1-2007, the pH value of point no.7 and point no.5 (0-2.3mm) are greater than 12, which show that the dregs are corrosive hazardous waste.

According to the standard GB5085.3-2007, the limit of the cyanide in leachate (CN-) is 5 mg / L. The cyanide contents of all samples in Figure 1 are less than this limit. Therefore, the conclusion can be drawn that the solid dregs in the residue field do not belong to the hazardous waste with the characteristics of leachate hazardous toxicity. This is because the main form of cyanide is hydrogen cyanide, which is volatile. This feature leads to the decrease of the cyanide content of solid waste.

4 Conclusions

Chemical residues are in open-air storage for long time, in which the toxic ingredients go into air by sublimating and weathering, or infiltrate into the groundwater by rain and snow, which result in long time security risks and consequences [9]. So the corresponding treatments must be taken to discharge the toxic materials in the waste. Even if the toxicity of chemical residues in this test is lower than the given toxicity standard, the chronic risk of pollution will be accumulated gradually with the migration of chemicals. Because the toxicity of hazardous waste is not possible to be completely eliminated regardless of what kind of treatment, the toxicity of these wastes will be a potential threat to human health and the environment even though it is up to the standard [5].

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