

Discussion on Management and Disposal Technology of Corrosive Hazardous Waste

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Abstract. Hazardous waste is an important part of the ecological system and the environmental community. Corrosive hazardous waste accounts for a large proportion of hazardous wastes. In addition to waste acid(HW34) and alkali(HW35), it also involves 8 other types and 13 subcodes. Corrosive hazardous waste has various physical states, involves thousands of chemical substances, and can have all kinds of hazardous properties such as toxicity, flammability, oxidation, reactivity, and explosive. The classification, detection, identification, transportation, storage and disposal technologies of corrosive hazardous waste are discussed for hazardous waste generating units, disposal units and regulatory authorities.

Hazardous waste refers to solid or liquid waste with at least one characteristic of toxicity, corrosiveness, flammability, reactivity and infectiousness. The scientific management and effective governance of hazardous wastes have become a major issue faced by all countries in the world today. Corrosive hazardous waste(CHW) accounts for a large proportion of hazardous waste, which is sometimes referred to as corrosive waste. At present, there are many domestic and foreign literatures on the disposal of various waste acids and waste alkalis, but there is no literature on the subject of corrosive hazardous waste[1] in China.

Keywords: Hazardous Waste; Corrosive; Disposal Technology; Neutralization.

1. Classification of corrosive hazardous waste

1.1 Administrative classification

Corrosives mean substances or wastes which will cause severe damage by chemical reaction when in contact with living tissue or damage other goods or transportation or cause other hazards in the case of leakage. According to Annex1 of Basel Convention, Corrosives hazardous waste involves categories of Y34(Acidic solutions or acids in solid form) and Y35(basic solutions or bases in solid form). According to the "Chinese National Hazardous Waste Catalogue (2021 Edition)", corrosive hazardous waste is not only HW34 (waste acid) and HW35 (waste alkali), but also involves 8 other major categories and accounting for 22% of the 46 categories of hazardous waste, 9.0%, of the 467 subcodes in all. Other hazardous wastes identified as having corrosive properties shall be managed according to the subcode 900-000-XX (XX is the category code).

1.2 Technical classification

According to its physical state, corrosive hazardous waste can be divided into liquid (solution), solid (slag), semi-solid (sludge) and gas in the cylinder.

According to the chemical nature, corrosive hazardous waste can be divided into inorganic acid, inorganic base, organic acid, organic base and others. The inorganic acids include HCl, H₂SO₄, HNO₃, H₃PO₄, HF, HClO₄, as well as AlCl₃, SiCl₄, TiCl₄, SO₃, CrO₃, BF₃, NaHSO₄, NH₄HF₂, etc. The inorganic bases mainly include NaOH, Ca(OH)₂, NH₄OH CaO Na₂O₂ etc. Typical organic acids include formic acid, acetic acid, halo-substituted acids, anhydrides, acyl chlorides, and the like. Inorganic bases include amines, piperazines, sodium alkoxides and the like. Other corrosive substances include bromine, mercury, formaldehyde solution, hydrazine hydrate, phenol, cresol, anthracene, fluoranthene, etc[2].

According to the hazardous Characteristics, corrosive hazardous wastes can be divided into 2 categories, with only corrosive Characteristics, and with other hazardous Characteristics. Concentrated inorganic acids can generally volatilize irritating and toxic acid mist, and organic acids volatilize odorous and flammable vapors, and the concentration increases with the increase of temperature. Acetic acid, propionic acid and acetic anhydride are Class B flammable liquids with a flash point below 60°C. Nitric acid, concentrated sulfuric acid, perchloric acid, and peracetic acid are strong oxidants, which have combustion-supporting effects, and can cause combustion and explosion in case of flammable substances. Among them, perchloric acid and peracetic acid can explode directly under sensitive conditions such as temperature and collision.

2. Identification and detection

According to National standard of China "GB5085.1 Corrosive Hazardous Waste Identification", solid waste that meets one of the two following conditions is classified as hazardous waste. The first condition is $\text{PH} \leq 2$ or ≥ 12.5 . The second is that the corrosion rate of 20# steel $\leq 6.35\text{mm/a}$ at 55°C. This standard can be summarized as "strong acid, strong alkali, strong corrosion". The corresponding American RCRA D002 standard is expressed as an aqueous solution with $\text{PH} \leq 2$ or ≥ 12.5 , or a liquid with a corrosion rate of $\geq 6.35\text{mm/a}$ measured. Therefore, the difference is that It United States it's not required to prepare the leachate, but directly measures the pH of the aqueous solution of suspected hazardous waste. Because the leachate method in GBT15555.12(Glass Electrode Method for Determination of Corrosivity of Solid Wastes) includes a dilution step to disperse 100g of sample in 1L of water which restrict the maximum concentration of leachate to 10% at most, so the identification standard of hazardous waste in the United States is stricter. The disadvantage of the American method is that it can only measure solutions with at least 20% water and other liquids with water content less than 20%, but cannot measure solid acid sludge or alkali residue, which leads to the different corrosive identification of solid hazardous waste in various states.

PH testing is often required in the process of receiving and disposing of corrosive hazardous wastes. Use extensive/precision PH strips for quick determinations, or use a pH meter for precise determinations. Since the measurement range of a pH meter is usually between 0 and 14, a negative number (acid) or an error (error) will be displayed outside this range. For too concentrated acid, it can be diluted 10 to 1000 times and tested again.

3. Transfer and storage

The transportation of hazardous wastes shall comply with the regulations on the administration of the transportation of dangerous goods. In the case of road transport, except for containers that meet relevant standards, the tank volume of tank-type special vehicles for transporting highly corrosive dangerous goods shall not exceed 20m³, and the approved weight of non-tank special-purpose vehicles shall not exceed 10 ton. It is not allowed to use tank-type special vehicles or special vehicles for transporting corrosive dangerous goods to transport ordinary goods. Hazardous waste transportation vehicles can transfer multiple types of hazardous wastes per trip. For the transportation of corrosive hazardous waste, attention should be paid to the compatibility and leakproofness of the container, and consideration should be given to the cross-influence of acid liquid or acid mist leakage on personnel, vehicles, transportation and other hazardous wastes. Unstable acids shall not be transported without treatment, including chloronitric acid(aqua regia), mixed acid of nitric acid and sulfuric acid, perchloric acid($\geq 72\%$ or any non-aqueous mixture). Incompatible hazardous wastes need to be isolated and evaluated before they can be transported. The incompatible substances for alkalis include acids and water, and the incompatible substances for acids include alkalis, organic solvents, metals, oxidizing agents. and cyanide, sulfide, fluoride (producing toxic gases). Compatible substances of non-oxidizing acids include HW03 waste

medicine, HW04 pesticide waste, HW08 waste mineral oil, HW09 emulsion, HW12 dye paint waste, etc.

The partition, anti-seepage and anti-corrosion measures should be taken for the storage of corrosive hazardous waste. Waste acid should be stored in a closed container to prevent acid mist from escaping. Gas collection devices should be installed in corrosive hazardous waste warehouses, and lead to gas purification facilities. Hazardous waste warehouses are often designed as "UV photolysis + activated carbon adsorption + chimney" to purify VOCs and other gases. Activated carbon varieties with high adsorption capacity for acid mist can be selected or a soda lime adsorbent module can be added to reduce acid gas emissions. Accident alkali pools[3] which are generally equipped in factories involving chlorine should be considered for neutralization in case of acid leakage. The chlorine arrester is a fire extinguisher cylinder equipped with chlorine removing agent—calcium hydroxide, sodium hydroxide and additives. It is an emergency equipment driven by nitrogen, and can also be used for HCl, HF, H₂S and other acid mist neutralization and removal.

4. Disposal of corrosive hazardous waste

The disposal goal of corrosive hazardous waste is to eliminate the corrosivity, generally through neutralization, but also through utilization and incineration.

4.1 Corrosive gases

Common corrosive gases include fluorine gas, chlorine gas, ammonia, hydrogen sulfide, sulfur oxides, nitrogen oxides, various acid mists, etc. Many kinds of corrosive gases including HF, BF₃, SiF₄, are commonly used in electronics and semiconductor industries, and hazardous wastes are generated correspondingly. Corrosive gases are stored in cylinders, and if the cylinder valve fails, the cylinder can be secured in a custom-made sealed container, drilled to relieve pressure, and neutralized in the container. If the gas cylinder can be opened, introduce the corrosive gas into alkali solution to neutralize or water to absorb it. Ammonia can be used as a reducing agent for flue gas denitrification in hazardous waste incineration systems. Titanium tetrachloride is a smoke agent, and HCl gas is continuously generated with water vapor in the air. Hydrolysis TiCl₄ in a sealed container produces polytitanium chloride as intermediate products, which can replace polyaluminum chloride (PAC) for sewage treatment[4]. Sulfur hexafluoride is widely used in electrical equipment, and its manufacturing purification or arc extinguishing applications will produce highly corrosive substances including SOF₂ and SO₂F₂, which can be hydrolyzed into sulfur oxides and HF—the similar reaction of the Hydrolysis of SO₂Cl₂.

4.2 Corrosive solids

Typical corrosive solids include acid salts such as, ZnCl₂, NH₄HF₂, bases such as NaOH, CaO, basic salts such as Na₂S, NaAlO₃ etc. Waste alkali can generally be utilized for neutralizing other waste acid. Organic corrosive solids such as tetramethylammonium hydroxide are easily disposed of by incineration. Aqueous solutions of sodium potassium sulfide and sodium hydrogen sulfide are corrosive, whose dry powder absorb moisture easily, release heat and ignite spontaneously, and it can also lead to dust explosion. Its sulfur element content is high, and it can be disposed of by mutual precipitation with heavy metals, preferably mercury, lead, cadmium, or nickel-containing wastewater or ferrous sulfate, a commonly used water treatment agent. Sodium tetrachloroaluminate hazardous waste is commonly found in pesticide companies, and its properties are similar to anhydrous aluminum trichloride. It generates heat and HCl when it encounters water. Zhou Shuguang et al.[5] proposed a method for treating sodium tetrachloroaluminate solid slag. After mixing with water, alkali is added to carry out the polymerization reaction, and the liquid product of PAC is obtained after concentrating and aging. This method is superior compared to CN201510697507.1 method in which a large amount of organic solution is added to dissociation the NaAlCl₄, as well as the CN202010543498.1 method in which hydrogen chloride or concentrated

hydrochloric acid is introduced as a separating agent, and the CN202010430609.8 method in which more steps need to be taken and more secondary wastes are produced. Acid salts and other solid acids can be neutralized by converting them into corrosive liquids after being dissolved in water.

4.3 Corrosive liquids

Corrosive liquids are a major part of corrosive hazardous waste. Due to the huge output of waste acid, bulk waste acid should be recycled or degraded to other usage. For example, titanium dioxide waste acid and battery waste acid should be concentrated and recycled. Acid could be recycled from high halogen waste by falling film absorption. The main ways to downgrade are cleaning, derusting, mineral processing and hydrometallurgy. Unusable corrosive solutions are generally neutralized by physicochemical acid and alkali, and then treated as wastewater. Hydrofluoric acid is weakly acidic and volatile, and highly corrosive to metals, organisms, and silicate materials (refractory materials for hazardous waste incinerators and kilns). Yang Sihui et al. [6] designed a safe and environmentally friendly treatment device for hydrofluoric acid in the laboratory. The core is to use a plastic feeding device and a plastic reaction vessel to avoid the corrosion of hydrofluoric acid to the equipment. If glove box is used, the exposure to hydrofluoric acid can be avoided, and the equipment has gone from professional to public during the covid-19 epidemic. Perchloric acid has strong oxidizing properties, and the neutralized perchlorate wastewater needs to be further chemically reduced, or degraded by domesticated perchlorate-reducing bacteria. In practice, there are a large number of corrosive non-aqueous hazardous wastes, such as the concentrated sulfuric acid catalyst from alkylation process of petrochemical industry, sulfonate surfactant from the daily chemical production, pyridine sulfur trioxide from pharmaceutical industry. If the acid and solvent cannot be recovered, the separation of organic phase and inorganic phase can be implemented by adding alkali. Neutralization is not a necessary pretreatment process, It is not suitable to neutralize with sodium alkali to avoid coking of sodium salt when incineration.

5. Conclusion

Corrosive hazardous waste is an important category of hazardous waste. Corrosive hazardous wastes are found in various physical states, involving various chemical substances, with various hazardous characteristics such as toxicity, flammability, oxidation, and reactivity. The detection of corrosive hazardous waste is easier, but the identification criteria may be tightened in specific country when the standard is updated. The stability and compatibility of the acid, and the leakproofness against the acid liquid and acid mist of the container should be considered for the transportation of the corrosive hazardous waste. The measures should be taken into account for the safe storage of corrosive hazardous include partition, anti-seepage, anti-corrosion, gas purification and emergency facilities. The disposal of corrosive hazardous waste is mainly neutralization, comprehensive utilization and incineration, all of which require high corrosion resistance of equipment, and an online corrosion monitoring system[7] can be set up to monitor the corrosion of important equipment in situ.

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