

Heavy Metal Sludge Treatment Technology and Resource Management

Yanan Li^{1, 2, 3}, Jianglong Shen^{1, 2, 3}

¹Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an, 710075, China

²Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an, 710075, China

³Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources, Xi'an, 710075, China

Abstract

Heavy metal sludge is classified as hazardous waste as the sediment after chemical treatment of heavy metal wastewater. With economic development, a large number of industries are bound to produce more heavy metal sludge. This article reviews the morphological distribution and characteristics of heavy metal sludge, and introduces the current technology, advantages and disadvantages of the harmless disposal and resource utilization of heavy metal sludge in my country. Finally, the heavy metal sludge treatment technology and application are prospected.

Keywords

Heavy metal sludge; Recycling; Harmless.

1. Introduction

Heavy metal sludge is the sediment after chemical treatment of heavy metal-containing wastewater, which is mainly composed of bacterial micelles formed by a variety of microorganisms and organic and inorganic substances adsorbed by the bacterial micelles in the sewage treatment process. Contains a variety of heavy metals such as copper, nickel, zinc, chromium, mercury, lead, etc., with complex components and belongs to hazardous waste. With the current economic development, industries that produce large amounts of heavy metal sludge, such as electroplating, electronics, hardware, chemicals, smelting, and many other enterprises and production departments, are bound to produce more heavy metal wastewater. When the chemical method is used to treat wastewater, the biggest disadvantage is that a large amount of chemical sludge, namely heavy metal sludge, will be produced. Although the total amount of sludge is much smaller than that of wastewater, various chemicals such as NaClO, NaOH, chemical salts, surfactants, and organics are added in the treatment of heavy metal wastewater, which makes the composition of heavy metal sludge very complicated. Therefore, heavy metal sludge is more harmful to the environment than heavy metal wastewater. The pollution and damage caused by heavy metals in the surplus sludge to the environment is particularly obvious. Through research, it is found that only part of the sludge in my country's urban sewage treatment plants has taken targeted prevention measures such as sanitary landfill, incineration, and building materials utilization, while most of the other sludge has not undergone standardized treatment. Most of the heavy metal substances contained in it cannot be absorbed by the soil through effective degradation. If the pollution control personnel cannot take scientific treatment measures, dumping or burying the remaining sludge at will, or piling up, it will result in groundwater quality or soil. Very serious damage has occurred, affecting public health and health. Common harmless treatment technologies for heavy metals in sludge include: bioremediation, electric remediation, complex leaching, solidification-stabilization,

and steam extraction. The stabilization of heavy metals refers to the conversion of harmful heavy metals into low-solubility, low-toxicity, and low-migration substances, in order to reduce harmful technologies and technologies that have the potential of heavy metals to pollute the environment. It mainly includes PH value control technology, adsorption technology, oxidation/reduction potential control, precipitation technology and composting technology.

2. Current Status of Heavy Metal Sludge Treatment

At present, the domestic stable and harmless treatment technology for sludge mainly focuses on the solidification and stabilization of heavy metals. Compared with other remediation technologies, solidification-stabilization is not only simple in operation and low in cost, but also improves the mechanical strength of sludge while reducing the concentration of heavy metals. The solidification technology of heavy metals in sludge refers to the process of wrapping heavy metals with inert materials to bind them. It can be used to treat many toxic pollutants such as electroplating sludge, chromium and mercury slag. The specific operation is to add common curing agents such as cement, asphalt, lime, glass, plastic, etc., so that the sludge is fully mixed with it, so that the harmful substances in the sludge are enclosed in the solidified body and are not leached out, so as to achieve harmlessness. The purpose of chemical and stabilization. The solidification-stabilization technology can reduce the fluidity of the sludge, improve the mechanical strength of the sludge, and stabilize the heavy metals and other pollutants in the sludge. The conversion of sludge into soil materials for resource reuse is a cheap and feasible sludge treatment technology. At this stage, there are still some problems such as: poor volume stability, which can not achieve the purpose of volume reduction; microscopic models and mechanism explanations are less, and they cannot explain the percolation behavior of heavy metals from the mechanism. For the future research of this technology, the difficulty to be solved is to simultaneously realize the three aspects of low heavy metal infiltration concentration of the treated sludge solid block, high mechanical strength and good volume reduction effect. In recent years, the United States, Japan and some European countries have generally adopted solidification disposal technology for toxic solid wastes, and believe that this is a final disposal method that converts hazardous materials into non-hazardous materials. The solidified materials used include cement, lime, and glass. And plastic etc. In terms of feasibility, the use of cement as a solidifying material to solidify sludge is the most promising, and it has been used in the treatment of electroplating sludge, mercury slag, and chromium slag. Not only the process and equipment are simple, the equipment and operating costs are low, but the cement raw materials and additives are cheap and easy to obtain. The waste with less water content can be directly solidified. The operation can be carried out at room temperature. The solidified product can effectively reduce pollution through asphalt coating. The strength, heat resistance, and durability of the solidified body is better due to the leaching of the solidified body. Its resource utilization lies in the fact that some products can be used as roadbed or building basic materials, that is, the solidification method can be used to make ecological cement, improved plastics, molten materials and molten micro Crystal glass. The disadvantage is that the leaching rate of the cement solidified body is high, and the solidified body has a large compatibilization.

3. Resource Utilization

Although most of the harmless treatment technologies of heavy metal sludge are relatively mature and widely used, the precious heavy metals in the sludge are not recovered, which makes the heavy metal resources not effectively used. Therefore, the economic and comprehensive benefits are general and can only be localized. Use within the scope. For the sludge with high metal content, there are huge economic benefits. Generally speaking, the

nickel content in nickel ore reaches 2% to meet the mining conditions, while the electroplating sludge generally contains 2%-4% nickel. The content of nickel in the mud reached 5%-10%, showing a moving mine of electroplating sludge. Recycling heavy metals is the best way to treat heavy metal sludge. It not only recovers precious metals, reduces the content of heavy metals in the sludge, but also reduces the difficulty of subsequent treatment and safe disposal, simplifies the process, and reduces disposal. Therefore, it is the most economical, promising and reasonable method to treat heavy metal sludge by recycling it as a resource and then performing effective and safe treatment, which can bring economic and environmental effects.

3.1. Fire Recovery Technology

Traditional methods, including high-temperature melting (dry recovery), roasting, and incineration, are already quite mature for ore metallurgy. When the heavy metal sludge contains high metal content and is classified as sludge, the fire method can be used to recover metals, such as copper sludge smelting copper and chromium sludge smelting stainless steel. The fire method can not only recover metals, but also destroy all organic substances in a short time, quickly and minimize the volume of sludge. After the fire method incineration, the volume reduction of the sludge can reach more than 90%, which makes certain The toxicity of highly toxic components is rapidly reduced, and the sludge disposal speed is fast, without storage and long-term transportation. The disadvantage is that it is difficult to directly recover the metal in the face of mixed sludge with complex composition; the technical core of the fire method is the smelting furnace. Generally, smelting furnaces have serious lining corrosion, short service life, low metal recovery rate, and high processing costs. At the same time, some metals will be discharged with flue gas during the high-temperature pyrometallurgical smelting process. Therefore, incineration flue gas treatment devices must be considered for metal recovery. , Such as the combination of bag dust removal and wet dust removal; also consider the treatment of slag. Consider combining with other treatment methods such as wet method. And it can be considered to use a combined process to treat heavy metal sludge to recover heavy metals, so as to improve the metal recovery rate and purity, so as to facilitate promotion.

3.2. Wet Recovery Technology

The process of extracting and separating metals in electroplating sludge with the help of a series of chemical reactions using certain solvents. Common separation methods include solvent extraction, chemical precipitation, electrolysis, hydrogen reduction, adsorption and analysis, etc. The wet process generally consists of processes such as leaching-leachate purification and enrichment-extraction of metals or compounds. It can recover heavy metal resources such as copper, nickel, and zinc from multi-component electroplating sludge. The recovery level is relatively high and the treatment effect is stable. The recovery of metal ions in the leachate can be achieved through chemical precipitation, solvent extraction, electrolysis/electrodeposition, hydrogen reduction and other methods to realize the resource utilization of valuable metals. Compared with fire recovery technology, its advantages are: 1. Strong selectivity, that is, different elements can be effectively selectively separated by controlling appropriate conditions in the solution; 2. It is conducive to the comprehensive recovery of various valuable elements; 3. It is easy to control various parameters in the aqueous solution, so it is suitable to control the physical properties of the product according to different requirements; 4. It is directly combined with the production process of metals or other compounds, with low cost and simple equipment.

3.3. Ferrite Treatment Technology

Ferrite generally refers to a composite oxide of iron family elements and one or more appropriate metal elements. It is a semiconductor material that is mainly used as a magnetic medium in application and is also an important industrial catalyst. Hydrothermal synthesis of

ferrite is an effective way to realize the resource utilization and self-purification of electroplating sludge. In the method, the hydroxide produced by the precipitation agent and the corresponding soluble metal salt is used as the precursor, and water is used as the solvent, and the composite ferrite is crystallized under a certain pressure in a closed kettle to generate a hydrothermal synthesis reaction. Research status: Domestic use of chromium-containing sludge has made MX-400 medium wave antenna magnetic rod, a manganese-zinc ferrite. Shanghai University uses electroplating sludge as raw material to synthesize ferrite by hydrothermally adding high iron chloride and precipitating agent to solidify and stabilize the Zn, Fe, Cr, and Ni in the sludge in the ferrite lattice. The obtained ferrite has strong magnetic properties, good dispersibility and uniform particle size distribution. Because of its stable crystal structure, it has achieved the purpose of eliminating secondary pollution. Therefore, ferrite is also one of the curing methods in a broad sense. The difference is that the ferrite material has a wide range of uses.

3.4. Materialization Technology

Tanning agent, a large number of tanning agents are used in the leather industry because it can react with cortical collagen molecules and undergo qualitative changes, turning the leather into leather. Chromium-containing sludge can be used to make tanning agents. This is because the chromium-containing sludge contains chromium hydroxide precipitation, which can reduce chromium plating wastewater, waste chromium solution, sodium chromate regeneration solution, etc. with reducing agents such as sulfite, sulfur dioxide, etc. And the precipitation is obtained by neutralization.

Polishing paste, chromium-containing sludge obtained by reduction methods such as sodium bisulfite contains little iron and can be used to make green polishing paste; chromium-containing sludge obtained by ferrous sulfate method and electrolysis method contains more iron, which is used for Make red polishing paste.

The chromium-containing sludge obtained by the electrolysis method is used to make iron chrome red pigments, and then to prepare iron red primer. The iron red primer contains a certain amount of iron trioxide, which can increase the hardness of the paint film. Manufacturing building materials, such as adding electroplating sludge to cement is also an ideal solution, but it is still in the experimental stage. There are currently cases where electroplating sludge is used in the manufacture of red bricks, but determining whether the leaching toxicity in the bricks meets the standard is the key to further popularizing this method.

4. Research Progress

4.1. Microbial Leaching Technology of Heterotrophic Bacteria

In biological leaching technology, inorganic autotrophic bacteria such as *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* are important leaching strains. However, solid waste containing heavy metals generally does not contain energy substances that can be used by autotrophic microorganisms. Therefore, if *Thiobacillus* is used for leaching it, additional energy substances are required, and the low-molecular-weight water-soluble organic substances in the polluted medium are harmful to autotrophic bacteria. Toxicity limits the promotion of biological leaching technology. Through research, it is found that the use of heterotrophic bacteria can solve this problem. Heterotrophic microorganisms can use the dissolved organic matter in the sludge medium as a source of carbon and nitrogen for growth, and provide a good environment for the growth of autotrophic bacteria. The acidic metabolites produced by heterotrophic microorganisms can be reduced, coordinated, and acidified to dissolve insoluble heavy metals from the solid phase into the liquid phase to become soluble metal ions. In addition, Peng et al. studied the combination of biological leaching and electrokinetic

technology to remove heavy metals from sludge. During the biological leaching process, the organic sulfide copper and the carbonate-bound and organic sulfide zinc are transformed into In the form of soluble ions, in the electrokinetic process, these ions can easily migrate to the electrode area and accumulate there. Finally, these heavy metals can be easily recovered or processed.

4.2. Composting Technology

Through the action of microorganisms, the conversion of heavy metal sludge into magnetic composite materials belongs to the materialized resource utilization technology. Electroplating sludge contains heavy metals needed for plant growth. Through composting research, organic matter is converted into humus and the metal components needed for plant growth are retained. This is also a new way for electroplating sludge treatment and disposal. Regarding the problem of heavy metal pollution caused by composting, chelating agents can be used to activate heavy metals in the soil. The main principle is that the chelating agent combines with heavy metal ions in the soil solution to reduce the metal concentration in the soil liquid phase and promote heavy metals in the soil. It accumulates in the upper part of plants and has a strong ability to activate heavy metals such as zinc, cadmium, and nickel.

4.3. Incineration Technology

When the Thermal Engineering Institute of Zhejiang University used a tube furnace to simulate the incinerator to study the heat treatment characteristics of electroplating sludge, it analyzed the migration characteristics of multiple heavy metals such as chromium, zinc, lead, and copper. The moisture, organic matter and volatile matter in the sludge can be well removed, and the high temperature can effectively inhibit the leaching of heavy metals in the sludge. However, this suppression has different effects on various heavy metals. For example, nickel is a non-volatile heavy metal. Heavy metals are recovered from the incineration ash, and the residual rate in the incineration ash is 100%, and the residual rate of chromium in the ash is 100%. It is also as high as 97%, and the precipitation rate of zinc, lead, and copper varies with the increase of the incineration temperature.

5. Summary and Outlook

Referencmy country's vast land, diversified sewage treatment processes and sludge sources have led to large differences in the content, types and forms of heavy metals in the sludge. When dealing with heavy metal sludge, it is necessary to find suitable treatment technologies to deal with sludge in different situations. At present, some treatment technologies for heavy metals in sludge are still in the laboratory stage, and more attention should be paid to the practical research of the technology in the future. Whether it is a single or combined treatment technology, there are inevitably some shortcomings. In the future, it is necessary to continue to find a simple, efficient, cheap, and green urban sludge heavy metal treatment process. When disposing of sludge, it is necessary not only to consider the issue of treatment technology, but also to choose the treatment method based on the local geographical and economic conditions. The best way is to turn waste into treasure, turn waste sludge into resources, and reuse them. , This will be the main direction of sludge treatment in the future.

References

- [1] Cao Zhanping, Zhang Jingli, The effect and technology of biological leaching to remove heavy metals in agricultural sludge[J]. Transactions of the Chinese Society of Agricultural Engineering, 2009, 25(2): 177-182;
- [2] Xiang Changyou, Wang Juan. Discussion on the harmless disposal of electroplating sludge resources[J]. Environmental Science and Technology, 2005, 28(3): 35-36;

- [3] Hao Hanzhou, Chen Tongbin, Jin Menggui, et al. Research progress of heavy metal contaminated soil stabilization/solidification remediation technology [J]. Chinese Journal of Applied Ecology, 2011, (3): 816-824;
- [4] Chen Xian, Cheng Jiehong, Zhou Quanfa. Fire-wet combined process to recover copper from electroplating sludge [J]. Environmental Engineering, 2012, 30 (2): 68-72;
- [5] Chen Dan, Zhu Huajun, Qian Guangren, et al. Experimental study on hydrothermal synthesis of composite ferrite from electroplating sludge and copper recovery [J]. Acta Scientiae Circumstantiae, 2007, (5): 873-879;
- [6] Fu Jiang, Cheng Jiehong, Zhou Quanfa. Technology and prospects for wet recycling of heavy metals from electroplating sludge [J]. Resource Recycling, 2009, (6): 47-49;
- [7] Ye Weimeng. Research methods and progress of heavy metals in municipal sludge[J]. Guangdong Chemical Industry, 2011, 38(7): 116-117;
- [8] Peng G Q, G M, Liu J Z, et al. Removal of heavy metals from sewage sludge with a combination of bioleaching and electrokinetic remediation technology [J]. Desalination, 2011,271(1-3) :100-104.