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Toxicological Analysis of Oily Sludge: A Comprehensive Experiment for the Determination of Cyanide Content in Leaching Solution

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Abstract

Oily sludge is a hazardous waste of oil and gas production, crude oil gathering and transportation, and refining processes. The total cyanide content in oily sludge leachates is an index used for the determination of the hazardous properties of oily sludges and their different treatment degrees. The most common methods used in the laboratory are silver nitrate titration and isonicotinic acid-pyrazolone colorimetry. In this study, we used the silver nitrate titration method to determine the total cyanide content in oily sludge. The weighing and pretreatment of the oily sludge samples, preparation of the leach liquor, and determination of the total cyanide content are sufficiently presented to carry out repeated experiments. The concentration of the calibration reagent and addition can be determined experimentally. In the case of a high value of total cyanide, an increase in the amount of NaOH solution can improve the analysis results. This experiment is exploratory and can be helpful to some extent for students majoring in environmental engineering in understanding the dangerous properties of oily sludge, the methodology of toxicological analysis, and the protection theory of the leaching liquid. Furthermore, it can help students improve their experimental, analytical, and innovation abilities.

Keywords

Oily sludge; Leach liquor; Total cyanide; Measurement and analysis.

1. Introduction

Hazardous waste refers to waste with hazardous characteristics that is included in the National Hazardous Waste List or identified according to the identification standards and methods for hazardous waste stipulated by each state. Oily sludge formed during oil and gas production, crude oil gathering and transportation, and refining and chemical processes, is listed in the National Hazardous Waste List under the code name HW08. The toxicological analysis of tailings after the treatment of oily sludge with different technologies and at varying degrees, such as hot washing, pyrolysis, incineration, and high-temperature thermal oxidation, can be performed in accordance with Hazardous Waste Identification Standard GB5085.3 to determine the degree of harm-free disposal; this is crucial for the harmless disposal of oily sludge [1,2].

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Hazardous Waste Identification Standard GB5085.3 stipulates 43 test contents, including test items, implementation standards (restrictions), and test methods, among which is the determination of the cyanide content in the leach solution. A state environmental protection standard of the People's Republic of China on the water quality of surface water, as well as sewage and industrial wastewater (Determination of cyanide, volumetric method and spectrophotometry, HJ 484-2009), accepts the determination methods of cyanide silver nitrate titration and isonicotinic acid–pyrazolone, isonicotinic acid–barbituric acid, and pyridine barbituric acid spectrophotometry. According to the standard for the Identification for extraction toxicity "GB5085.3-2007," the standard limit value of cyanide compounds in the leaching liquid is less than 5 mg/L. Silver nitrate titration was used for the determination of cyanide in the leaching solution of the oily sludge and tailings of different treatment degrees [3–5].

The total cyanide content in water is an index showing if the water is polluted. Total cyanide refers to alkali-metal cyanide in the water and alkaline earth-metal cyanide as well as cyanide and ammonia complexes (including iron cyanide, ferrocyanide, copper cyanide, nickel cyanide, and zinc cyanide); however, total cyanide excludes cobalt cyanide. Furthermore, cyanide produces deadly toxic effects by inhibiting ferric cytochrome oxidase and causing suffocation or death. Thus, cyanide is a very toxic pollutant and can be divided into two types, namely, complex and simple. Total cyanide includes simple cyanide and most complex cyanides, but it does not include cobalt-cyanide complexes. The main sources of cyanide are organic synthesis, electroplating, mineral processing, as well as chemical and other industrial wastewaters. Cyanide has always been an important basis for monitoring wastewater and the environment [6–8].

At present, the main monitoring methods in China include colorimetry, an electrode method, and silver nitrate titration [9,10]. Silver nitrate titration is used to determine the content of cyanide in water, and environmental engineering students must grasp this concept. Specifically, environmental engineering students majoring on petroleum must learn about the treatment and disposal of oily sludges as well as poison rational analysis, by determining the cyanide content in the oily sludge and the leaching liquid. Thus, students will understand the dangers of oil and gas fields, the properties of oily sludge, the concept of hazardous waste, and identification methods. Hence, students will correctly treat oily sludges and other hazardous waste in their future work, avoiding the unnecessary loss of units. Simultaneously, students are required to combine theoretical knowledge with practice to cultivate their analyzing, experimental data-processing, literature-review, problem-solving, and cooperation abilities [11]. The purpose of higher education in engineering is to cultivate skills and accomplish the innovations required by society. In recent years, a new experimental teaching model has become a development trend of the teaching reform, aiming to cultivate the scientific research and innovation abilities of the students [12–14].

The teaching and research sector has long engaged in the theory and research of oil and gas fields, as well as in the development of applicable technologies for environmental protection with respect to the treatment of wastewater that contains oil and gas, oily sludges, and drilling mud waste. Furthermore, this sector has focused on reservoir protection in areas at the national, provincial, and municipal levels, and it has more than 100 cooperation projects concerning the research and development of stability in the quality of oily sewage water, treatment technologies for high-sulfur-containing wastewater, flocculation—excluding boron integration technology, technologies for the adjustment of the size distribution of oily sludge grains, low-temperature catalytic pyrolysis of oily sludge, and high-temperature thermal-oxidation technologies [15–17]. Combining scientific research achievements, establishing a grid connection between scientific research achievements and teaching practices, and continuously integrating the scientific research achievements into teaching are conducive to improving the

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abilities of the students to apply theoretical knowledge and nurturing learning enthusiasm. Through the determination of the total cyanide content, the students understand the poison rational analysis and the concept of hazardous waste, as well as identification methods; the experimental teaching entails established research content. We designed a method for the determination of the total cyanide content in the leaching liquid of the oily sludge that requires 4 hours to complete. This method will help students realize the benign interaction of scientific research and teaching aiming to enhance teaching activities. This experiment is not only in line with the students' knowledge of oily sludge and hazardous waste, but it also improves their experimental abilities. Furthermore, it helps students decipher scientific research and develop innovative thinking, as well as cultivate awareness of environmental protection in their future work.

2. Experimental Design

2.1. Experimental Purpose

(1) Understand the concept and identification methods of hazardous waste and the dangerous properties of oily sludge, as well as strengthen the standard concept.

(2) Master the method of using silver nitrate titration to determine cyanide in an oily sludge leachate solution.

(3) Learn to obtain accurate measurement results through data processing, analysis, and calculation of relevant parameters.

2.2. Scope of Application

This method is suitable for contaminated surface water, domestic sewage water, industrial wastewater, and solid waste leachate.

The detection limit of this method is 0.25 mg/L, the lower limit is 1.00 mg/L, and the upper limit is 100 mg/L.

2.3. Experimental Principle

Pure water is used as the leaching agent to simulate the harmful effects of the solid waste leachate in surface water or groundwater on specific occasions, that is, the leaching of components into the environment.

The experimental principle for the determination of cyanide is that cyanide can be separated by distillation after heating in a phosphoric acid and EDTA medium with a pH of less than 2. In this experiment, cyanide is distilled in the form of hydrogen cyanide, absorbed by a sodium hydroxide solution, and the cyanide content is calculated.

2.4. Reference Standards

(1) For the identification of the hazardous properties of oily sludge and tailings of different treatment degrees, please refer to the Identification Standard of Hazardous Waste for the Identification for Extraction Toxicity GB5085.3-2007.

(2) For the leaching toxicity method of the oily sludge and tailings of different treatment degrees refer to Solid Waste Leaching Toxicity Method, Horizontal Oscillation HJ 557-2009.

(3) For the determination of the total cyanide content in the leaching solution of the oily sludge and tail slagging of different treatment degrees, refer to "Water Quality—Determination of Cyanide–Volumetric Method and Spectrophotometric Method HJ 484-2009."

2.5. Reagents and Materials

(1) Leaching agent: water, GB/T 6682, level II

(2) Phosphoric acid: The density of 1.69 g/mL

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(3) 1% (m/V) sodium hydroxide solution
(4) 10% (m/V) Na2-EDTA solution
(5) 1: 5 sulfuric acid solution
(6) 1.26% (m/V) sodium sulfite solution
(7) Sulfamic acid
(8) 4% (m/V) sodium hydroxide solution
(9) Silver nitrate standard solution

2.6. Instruments and Equipment

(1) Oscillation device: reciprocating horizontal oscillation device with adjustable frequency.

(2) Extraction bottle: 2 L wide-mouth bottle with screw cap and inner lid, made of inert materials (e.g., glass or polyethylene) that cannot leach or adsorb the components contained in the sample.

(3) Filters.

(4) Filter device: pressure or vacuum filter device; a centrifugal separation device can also be used for waste that is difficult to filter.

(5) Filtration membrane: 0.45 m microporous membrane.

(6) Balance: accuracy of not less than ±0.01 g.

(7) Sieve: sieve coated with Teflon with an aperture of 3 mm.

(8) Distillation bottles.

(9) Cyanide receiving vessel.

(10) Adjustable electric furnace.

2.7. Experimental Steps

2.7.1. Sampling of Oily Sludge and Preparation of Leaching Solution

(1) Depending on the water content of solid waste, 20–100 g samples are weighed to ± 0.01 g and dried in a pre-dried container with a constant weight at 105 ℃, and the moisture content of the samples is calculated.

Note 1: The material of the container must not react with the waste.

(2) When the sample contains the initial liquid phase, it shall be filtered by pressure, and the moisture content of the filter residue shall be determined. Refer to 2.7.1 (1) for the determination steps. The moisture content and dry solid percentage of the sample are calculated based on the total sample amount (sum of initial liquid phase and filtrate weights).

Note 2: Samples determined by moisture content shall not be used for the leaching toxicity test.

(3) When the sample contains the initial liquid phase, it is filtered using a pressure filter and a 0.45 m filter. If the percentage of dry solid is less than or equal to 9%, the initial liquid phase obtained is the leachate, and the analysis is performed directly. If the percentage of dry solid is more than 9%, the filter residue is leached according to 2.7.1 (4), and the initial liquid phase is mixed with all leachates for analysis.

(4) A sample of 100 g dry weight is placed in a 2 L extract in a bottle, depending on the moisture content of the sample, at a liquid–solid ratio of 10:1 (L/kg) to calculate the volume of the leaching agent. Tightly capped bottle caps are vertically fixed in the horizontal oscillation device, which operates at an oscillation frequency of 110 ± 10 times/min and amplitude of 40 mm. The oscillation proceeds for 8 h at 10-30℃ under the extraction bottle, and then it is left for 16 h. The extraction bottle should be opened regularly in the fume hood to release the excessive pressure due to gas produced during the oscillation.

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(5) Install the filter film on the pressure filter, collect the filtered leachate, and store it in accordance with the requirements of the analysis method for each subject to be measured.

(6) Unless digestion causes the loss of the metal to be tested, the leaching solution used for the metal analysis shall be dissolved in accordance with the requirements of the analytical method.

2.7.2. Absorption and Release of Hydrogen Cyanide

(1) Take precisely 100.0 mL sample (if the cyanide content is high, take less), transfer it to a 500 mL distillation flask, dilute it with water to 200 mL, and add several glass beads.

(2) Add 10.0 mL 1% sodium hydroxide solution into the cyanide container as the absorption solution.

(3) Connect the distillate pipe to the outlet of the condensing pipe at the top and insert the bottom into the absorption liquid of the receiving vessel to check the connection part and tighten it.

(4) Add 10.0 mL Na2-EDTA solution into the distillation flask.

(5) Add 10 mL of phosphoric acid quickly. If the alkalinity of the sample is high, add phosphoric acid appropriately and adjust the pH to 2. Cork the bottle at once. Turn on the condensed water, adjust the electric furnace, gradually increase from the low grade, and conduct heating distillation at a distillate speed of 2–4 mL/min.

(6) When the volume of the solution in the receiving bottle approaches 100 mL, stop the distillation, wash the distillate tube with a small amount of distilled water, take out the receiving bottle, and dilute the solution with water until the line. The alkaline distillate (C) is used for the determination of total cyanide.

2.7.3. Blank Test

The blank test distillate (D) is obtained by replacing the sample with experimental water and following steps 2.7.2 (1)–(6) for the determination of total cyanide.

2.7.4. Determination of Cyanide

Take 100 mL distillate A (if the cyanide content in the sample is high, take a smaller amount and dilute it with water to 100 mL), and place it in a conical flask. Add 0.2 mL of testing silver indicator solution and shake well. Titrate the solution to be tested with a standard solution of silver nitrate. When the solution changes from yellow to orange-red, take the reading (Va). Another 100 mL of blank experimental distillate B was taken, titrated in a conical flask depending on the sample determination, and the reading (Vb) was recorded.

3. Data Processing

The cyanide content is calculated using the following formula:

$$Cyanide\quad content = \frac{c * (Va - Vb) \times 52.04 \times 1000 \times \frac{Vm}{Vn}}{V},$$

Where C – Concentration of silver nitrate standard solution (Mo/L)

Va – Amount of silver nitrate standard solution (mL) in the determination of the sample

Vb – Silver nitrate standard solution (mL) of blank test

V – Sample volume (mL)

Vm – Volume (mL) of sample (distillate A)

Vn – Volume (mL) of sample (distilled liquid A taken during the determination)

52.04 – Cyanogen (2CN-) molar mass (g/mol)

4. Matters Requiring Attention

Before titrating the sample to be tested with a silver nitrate standard solution, the pH value of the solution to be tested should be measured with a pH paper. If necessary, a sodium hydroxide solution should be added to adjust the pH to 11.

5. Questions and Exercises

(1) Can all cyanide waste liquid be poured directly into the sewer without detoxification treatment or should the collection be returned to the specialized departments?

(2) Can the operator continue with exposed parts (such as arms and hands)?

(3) A small amount of oil does not affect the determination. Does neutral or acidic oil have any effect on the determination? How can we eliminate this interference?

(4) Cyanide is highly toxic. When handling cyanide and its solution, special care should be taken to prevent cyanide from coming in contact with the skin and eyes, which can absorb the solution.

6. Conclusion

Cyanide is a highly toxic substance, and its toxicity to the human body is mainly due to its inhibition of ferric cytochrome oxidase, which loses the function of oxygen transmission, causing tissue hypoxia and asphyxia. In addition, HCN molecules are highly toxic to aquatic organisms. Therefore, it is greatly significant to accurately detect the content of cyanide in water. This experiment applies knowledge of organic and oil-field chemistry, and the determination of total cyanide in oily sludge via toxicological analysis is described with reference to relevant standards.

In the experiment, oily sludge and its leaching liquid were used as experimental objects to measure the total cyanide content, which could not only train the ability of students to operate extraction equipment but also improve their understanding of the hazardous waste properties of oily sludge produced in oil and gas production. By using silver nitrate titration to measure the total cyanide content, students can master the basic procedures of the experiment as well as improve their ability to subsequently process the experimental data. This experiment is carried out in groups, which is conducive to improving the students' cooperation ability and team spirit.

7. Conflict of Interest

There are no conflicts of interest to declare.

8. Ethical Approval

This article does not contain any studies with humans or animals subjects performed by any of the authors.

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