YS

NONFERROUS METAL INDUSTRY STANDARD

OF THE PEOPLE'S REPUBLIC OF CHINA

ICS 77.150.99

CCS H 62

YS/T 1460-2021

Crude nickel cobalt hydroxide

粗氢氧化镍钴

Issued on: December 02, 2021 **Implemented on: April 01, 2022**

Issued by: Ministry of Industry and Information Technology of PRC

Table of Contents

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1 Scope

This document specifies the technical requirements, test methods, inspection rules, markings, packaging, transportation, storage, accompanying documents and order forms for crude nickel cobalt hydroxide.

This document is applicable to crude nickel cobalt hydroxide products, which are obtained by wet enrichment processes such as pretreatment, leaching, impurity removal, and precipitation of lithium-ion battery waste containing nickel and cobalt elements. It can be used as raw materials for the production of nickel, cobalt, manganese three-element composite hydroxides, nickel cobalt manganese oxide, nickel or cobalt chemical salts and other related materials.

2 Normative references

The contents of the following documents constitute the essential terms of this document through normative references in the text. Among them, for referenced documents with dates, only the version corresponding to that date applies to this document; for referenced documents without dates, the latest version (including all amendments) applies to this document.

GB/T 6682 Water for analytical laboratory use - Specification and test methods

GB/T 8170 Rules of rounding off for numerical values and expression and judgement of limiting values

YS/T 1157.2 Methods for chemical analysis of crude cobalt hydroxide - Part 2: Determination of nickel, copper, iron, manganese, zinc, lead, arsenic and cadmium contents - Inductively coupled plasma atomic emission spectrometry

YS/T 1229.2 Methods for chemical analysis of crude nicked hydroxide - Part 2: Determination of cobalt content - Flame atomic absorption spectrometric method

YS/T 1229.3 Methods for chemical analysis of crude nickel hydroxide - Part 3: Determination of copper, cobalt, manganese calcium, magnesium, zinc, iron, aluminum, lead, arsenic and cadmium contents - Inductively coupled plasma atomic emission spectrometry

YS/T 1342.1 Methods for chemical analysis of waste secondary battery - Part 1: Determination of nickel content - Dimethylglyoxime gravimetric method and flame

5.2 Moisture

The moisture content of the product shall not exceed 60%.

5.3 Appearance quality

The product is in the form of wet block or dry mud or powder; it shall not be mixed with inclusions. The color of the same batch of products shall be consistent. Due to the oxidation of the surface, a certain difference in color between the surface and the inside is allowed.

5.4 Others

If the buyer has other requirements for the product, it shall be determined by negotiation between the supplier and the buyer and indicated in the order.

6 Test method

6.1 When the nickel content in the product is less than 1.00%, it shall be determined according to the provisions of YS/T 1157.2; when the nickel content is not less than 1.00%, it shall be determined according to the provisions of YS/T 1342.1.

6.2 When the cobalt content in the product is less than 1.00%, it shall be determined according to the provisions of YS/T 1229.2; when the cobalt content is not less than 1.00%, it shall be determined according to the provisions of YS/T 1342.2.

6.3 When the manganese content in the product is less than 0.10%, it shall be determined according to the provisions of YS/T 1229.3; when the manganese content is not less than 0.10%, it shall be determined according to the provisions of YS/T 1342.3.

6.4 The lithium content in the product shall be determined according to the provisions of YS/T 1342.4.

6.5 The copper, aluminum, arsenic, cadmium, lead contents in the product shall be determined according to the provisions of YS/T 1229.3.

6.6 The phosphorus and chromium contents in the product shall be determined according to the provisions of Appendix A or the method agreed upon by the supplier and the buyer.

6.7 The hydrochloric acid insoluble matter content in the product shall be determined according to the provisions of Appendix B or the method agreed upon by the supplier and the buyer.

6.8 The fluorine content in the product shall be determined in accordance with the provisions of Appendix C or the method agreed upon by the supplier and the buyer.

6.9 The moisture content in the product shall be determined in accordance with the provisions of Appendix D or the method agreed upon by the supplier and the buyer.

6.10 The appearance quality of the product shall be inspected by visual inspection.

7 Inspection rules

7.1 Inspection and acceptance

7.1.1 The product shall be inspected by the supplier or a third-party inspection department. The supplier shall ensure that the product quality complies with the provisions of this document and the order form.

7.1.2 The buyer may inspect the received products in accordance with the provisions of this document. If the inspection results do not comply with the provisions of this document or the order form, the buyer shall submit the matter to the supplier within 30 days, from the date of receipt of the product; the supplier and the buyer shall negotiate to resolve the issue. If arbitration is required, the supplier and the buyer shall jointly sample or negotiate at the buyer's place.

7.2 Group-batching

The products shall be submitted for inspection in batches; each batch shall consist of products of the same grade. One batch shall be formed by products of the same mixture.

7.3 Inspection items

Each batch of products shall be inspected for chemical composition, moisture content, appearance quality.

7.4 Sampling and specimen preparation

7.4.1 Randomly sample at least 50% of the packaging quantity of each batch of products. When the packaging quantity is less than 10 bags, each bag shall be sampled; the sampling volume of each bag shall not be less than 0.4%.

7.4.2 The sampling points of each bag shall be evenly distributed at the top, middle, and bottom points according to any diagonal line on the side of the packaging bag. The sample rod shall penetrate both sides of the packaging bag; rotate the sample rod 180° and pull it out; the sample rod shall be full. When the material is not easy to sample, a hand hammer can be used to assist the sample rod to do sampling. Each sample shall be put into a plastic bag and sealed in time.

7.4.3 The whole batch of samples shall be put into a woven bag and sealed. All samples of each batch shall be fully mixed and divided into samples of about 4.0 kg by the grid method.

Appendix A

(Normative)

Determination of phosphorus and chromium content in crude nickel cobalt hydroxide - Inductively coupled plasma atomic emission spectrometry

A.1 Method summary

Dissolve the sample in hydrochloric acid; determine the phosphorus content by the working curve method and the chromium content by the standard addition method on an inductively coupled plasma atomic emission spectrometer.

A.2 Reagents and materials

Unless otherwise specified, the reagents used in this Appendix are all high-purity reagents; the water used meets the first-grade water specified in GB/T 6682.

A.2.1 Hydrochloric acid (ρ = 1.19 g/mL).

A.2.2 Hydrochloric acid (1 + 1).

A.2.3 Phosphorus standard stock solution: Weigh 0.4390 g of potassium dihydrogen phosphate ($w_{KH_2PO_4} \geq 99.99\%$) in a 100 mL beaker; dissolve it with water; transfer it to a 100 mL volumetric flask; dilute it to the mark with water; mix it. 1 mL of this solution contains 1 mg phosphorus.

A.2.4 Chromium standard stock solution: Weigh 0.2829 g of potassium dichromate ($w_{K_2Cr_2O_7} \geq 99.99\%$) in a 100 mL beaker; dissolve it with water; transfer it to a 100 mL volumetric flask; dilute it to the mark with water; mix it. 1 mL of this solution contains 1 mg chromium.

A.2.5 Phosphorus standard solution: Pipette 20.00 mL of phosphorus standard stock solution (A.2.3) into a 100 mL volumetric flask; add 10 mL of hydrochloric acid (A.2.2); dilute to the mark with water; mix it. 1 mL of this solution contains 200 μg of phosphorus.

A.2.6 Chromium standard solution A: Pipette 10.00 mL of chromium standard stock solution (A.2.4) into a 200 mL volumetric flask; add 20 mL of hydrochloric acid (A.2.2); dilute to the mark with water; mix it. 1 mL of this solution contains 50 μg of chromium.

A.2.7 Chromium standard solution B: Pipette 10.00 mL of chromium standard solution A (A.2.6) into a 100 mL volumetric flask; add 10 mL of hydrochloric acid (A.2.2); dilute to the mark with water; mix it. 1 mL of this solution contains 5 μg of chromium.

A.3 Instruments

excitation intensity of phosphorus in the blank test solution (A.4.3) and the test solution (A.4.4) at the wavelength recommended in Table A.1; obtain the mass concentration of phosphorus in the blank test solution and the test solution from the working curve.

A.4.5.2 Determination of chromium content

Take 25.00 mL of test solution (A.4.4) and place them in a group of 50 mL volumetric flasks. Add 0 mL, 1.00 mL, 2.00 mL, 3.00 mL, 4.00 mL of chromium standard solution [select chromium standard solution B (A.2.7) when the chromium content is ≤ 0.0050%; select chromium standard solution A (A.2.6) when the chromium content is > 0.0050%] in sequence; add 5mL of hydrochloric acid (A.2.2) to each; dilute to the scale with water; mix well.

On an inductively coupled plasma atomic emission spectrometer, measure the excitation intensity of chromium in the above solution series from low to high, according to the wavelength recommended in Table A.1. Draw a calibration curve for chromium with the mass concentration of chromium added to the test solution as the abscissa and the corresponding excitation intensity as the ordinate. The correlation coefficient of the calibration curve shall be greater than 0.995. The reverse extension line of the calibration curve intersects with the abscissa, the intersection is the mass concentration of chromium in the test solution.

A.4.6 Drawing of phosphorus working curve

Pipette 0 mL, 0.50 mL, 1.00 mL, 2.50 mL, 5.00 mL, 10.00 mL of phosphorus standard solution (A.2.5) into a set of 100 mL volumetric flasks; add 10 mL of hydrochloric acid (A.2.2) to each; dilute to the scale with water; mix well. On the inductively coupled plasma atomic emission spectrometer, measure the excitation intensity of phosphorus in the standard solution series from low to high, according to the wavelength recommended in Table A.1. Draw the phosphorus working curve with the mass concentration of phosphorus as the abscissa and the corresponding excitation intensity as the ordinate. The correlation coefficient of the working curve shall be greater than 0.999.

A.5 Test data processing

A.5.1 Phosphorus test data processing

Phosphorus content is calculated as the mass fraction w_P of phosphorus according to formula (A.1):

$$w_P = \frac{(\rho_2 - \rho_1) V_1 \times 10^{-6}}{m_1} \times 100\% \qquad \cdots\cdots (A.1)$$

Where:

ρ_2 - Mass concentration of phosphorus in the test solution obtained from the

Appendix B

(Normative)

Determination of the content of hydrochloric acid insoluble matter in crude nickel cobalt hydroxide - Gravimetric method

B.1 Method summary

The sample is dissolved in hydrochloric acid, filtered using a glass sand core crucible, washed with water, placed in an electric constant temperature drying oven at 105 °C ± 2 °C, dried to constant weight. The content of hydrochloric acid insoluble matter is calculated.

B.2 Reagents

Unless otherwise specified, the reagents used in this Appendix are analytical grade or higher; the water used is grade 3 water or higher in accordance with GB/T 6682.

B.2.1 Hydrochloric acid (ρ = 1.19 g/mL).

B.2.2 Hydrochloric acid (1 + 1).

B.2.3 Silver nitrate solution: 10 g/L.

B.3 Instruments and equipment

B.3.1 Electric constant temperature drying oven: Temperature can be controlled at 105 °C ± 2 °C.

B.3.2 Glass sand core crucible: Filter plate pore size 5 μm ~ 15 μm.

B.4 Test steps

B.4.1 Sample

Weigh 10.0 g of specimen (7.4.5), accurate to 0.0001 g.

B.4.2 Parallel test

Perform two tests in parallel; take the average value.

B.4.3 Determination

Place the sample (B.4.1) in a 500 mL beaker; moisten it with a small amount of water; add 60 mL of hydrochloric acid (B.2.2); boil it at low temperature for 5 min ~ 10 min. Filter it while it is hot with a glass crucible (B.3.2) that has reached a constant weight; wash it with hot water until there is no chloride ion (check with silver nitrate solution).

Appendix C

(Normative)

Determination of fluorine content in crude nickel cobalt hydroxide - Ion selective electrode method

C.1 Method summary

The sample is melted with sodium hydroxide; the melt is leached with water; sodium citrate is used as the total ionic strength regulator; the working curve method is used to determine the fluorine content with a fluoride ion selective electrode.

C.2 Reagents

Unless otherwise specified, the reagents used in this Appendix are reagents of analytical purity or above; the water used meets the requirements of grade 3 or above purity water specified in GB/T 6682.

C.2.1 Sodium hydroxide, high-grade pure.

C.2.2 Sodium fluoride, high-grade pure.

C.2.3 Nitric acid (ρ = 1.42 g/mL).

C.2.4 Nitric acid (1 + 4).

C.2.5 Sodium citrate solution: Weigh 294 g of sodium citrate; place in a 500 mL beaker; add water to dissolve; transfer to a 1000 mL volumetric flask; use water to dilute to the mark; mix well.

C.2.6 Fluorine standard storage solution: Weigh 2.2110 g of sodium fluoride (C.2.2) dried at 120 °C for 2 h; dissolve in water; transfer to a 1000 mL volumetric flask; use water to dilute it to the mark; mix well; store in a plastic bottle. 1 mL of this solution contains 1 mg fluorine.

C.2.7 Fluorine standard solution A: Pipette 10.00 mL of fluorine standard stock solution (C.2.6) into a 100 mL volumetric flask; use water to dilute it to the mark; mix well; store in a plastic bottle. 1 mL of this solution contains 100 μg of fluorine.

C.2.8 Fluorine standard solution B: Pipette 20.00 mL of fluorine standard solution A (C.2.7) into a 100 mL volumetric flask; use water to dilute it to the mark; mix well; store in a plastic bottle. 1 mL of this solution contains 20 μg of fluorine.

C.2.9 Phenol red indicator (2 g/L): Weigh 0.2 g of phenol red; add 12 mL of sodium hydroxide solution (2 g/L); transfer to a 100 mL volumetric flask; use water to dilute it to the mark; mix well.

C.3 Instruments and equipment

C.3.1 Nickel crucible (30 mL).

C.3.2 High temperature furnace: Temperature can be controlled at 600 °C ± 2 °C.

C.3.3 Fluoride ion selective electrode.

C.3.4 Saturated calomel electrode.

C.3.5 Electromagnetic stirrer.

C.3.6 Potentiometer: Accuracy is 0.1 mV.

C.4 Test steps

C.4.1 Sample

Weigh 0.50 g of specimen (7.4.5), accurate to 0.0001 g.

C.4.2 Parallel test

Perform two tests in parallel; take the average value.

C.4.3 Blank test

Perform a blank test with the sample.

C.4.4 Determination

C.4.4.1 Place the sample (C.4.1) in a nickel crucible (C.3.1); add 4 g of sodium hydroxide (C.2.1); heat and melt on an electric furnace; mix well. Place in a high-temperature furnace (C.3.2) that has been heated to 600 °C and melt for 20 minutes; take out; shake the melt evenly on the inner wall of the crucible; cool slightly.

C.4.4.2 Place the crucible and the melt in a 250 mL beaker filled with 100 mL hot water; cover with a watch glass; heat and soak the melt; wash out the crucible with water; cool to room temperature; transfer to a 250 mL volumetric flask; use water to dilute it to the mark; mix well; dry filter with a quick qualitative filter paper.

C.4.4.3 Take 10.00 mL of the test solution (C.4.4.2); place it in a 100 mL volumetric flask. Add 20 mL of sodium citrate solution (C.2.5) and 2 drops of phenol red indicator (C.2.9). Use nitric acid (C.2.4) to adjust the solution to just turn yellow. Use water to dilute it to the mark; mix well.

C.4.4.4 Pour all the test solution into a dry 250 mL beaker; add a stirrer; insert a fluoride ion selective electrode (C.3.3) and a saturated calomel electrode (C.3.4); place it on an electromagnetic stirrer (C.3.5) and stir it. Measure the equilibrium potential value of

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