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# New technology for recycling materials from oily cold rolling mill sludge

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**Abstract:** Oily cold rolling mill (CRM) sludge is one of metallurgical industry solid wastes. The recycle of these wastes can not only protect the environment but also permit their reutilization. In this research, a new process of "hydrometallurgical treatment + hydrothermal synthesis" was investigated for the combined recovery of iron and organic materials from oily CRM sludge. Hydrometallurgical treatment, mainly including acid leaching, centrifugal separation, neutralization reaction, oxidizing, and preparation of hydrothermal reaction precursor, was first utilized for processing the sludge. Then, micaceous iron oxide (MIO) pigment powders were prepared through hydrothermal reaction of the obtained precursor in alkaline media. The separated organic materials can be used for fuel or chemical feedstock. The quality of the prepared MIO pigments is in accordance with the standards of MIO pigments for paints (ISO 10601-2007). This clean, effective, and economical technology offers a new way to recycle oily CRM sludge.

**Keywords:** cold rolling mills; sludge disposal; hydrometallurgy; hydrothermal synthesis; recycling, waste utilization

## 1. Introduction

Oily cold rolling mill (CRM) sludge, a kind of steel making by-product generated in cold rolling processes, is a mixture of metal particles, cooling fluids, lubricants, etc. In China, according to incomplete statistics, about more than one hundred thousand tons of oily CRM sludge are produced each year. These residues occupy precious land, and the construction and maintenance of oily CRM sludge disposal sites also increase the production cost of steelmaking plants. In addition, high content of organic materials and fine metal powders can cause a serious threat to the environment. At the same time, iron content of oily CRM sludge is high, and the processing of oily CRM sludge as a secondary resource rather than waste has become a more attractive route for sustainable production on account of the depletion of iron ores and rapid rise of metal prices [1-5]. The concerns over oily CRM sludge are not exclusively environmental but economic as well.

Nowadays, oily CRM sludge is mainly reutilized as raw materials in the secondary smelt furnaces [6-8], which can lead to some problems, such as environmental pollution, equipment problems, low value-added utilization of secondary resources, etc. The high content (7wt%-20wt%) of organic materials in oily CRM sludge can not only result in increased emission of volatile organic compounds including dioxins but also lead to problems in waste gas purification systems, e.g., glow fires in electrostatic precipitators. Landfill and incineration are the most commonly used methods to remove oil of oily CRM sludge because of low cost and simple process. However, this can create a risk of contamination, particularly of the ground water and air, thus causing adverse health effects. Recently, some new routes have also been developed to remove organic materials from solid wastes, including supercritical extraction [9-10], aqueous surfactant washing [11-12], biological treatment [13], distillation technology [14-16], etc. Compared with landfill and incineration, these ways have advantages in environmental protection, however, there are some obvious shortcomings, such as high cost, long processing time, poor treatment effect. Therefore, environment-friendly, high-effective, and high value-added reutilization technologies of oily CRM sludge are in great demand.

Micaceous iron oxide (MIO) pigment is widely used in construction materials, paints, coatings, and other fields, thanks to its advantages, such as nontoxicity, chemical stability, high tinting strength, hiding power, long durability, and low cost [17-21]. Today, the demand of MIO pigment

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is continuously increasing. However, there are only few reports concerning the preparation of MIO pigment using oily CRM sludge. In this paper, a new process of "hydrometallurgical treatment + hydrothermal synthesis" was presented for the combined recovery of iron and organic materials from oily CRM sludge. The experimental conditions were carefully studied in order to obtain the optimal ones. Moreover, different methods, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM), were applied to characterize the structure and morphology of the prepared MIO pigment powders.

## 2. Experimental

### 2.1. Recycling process

A new process was put forward in this study, including acid leaching, centrifugal separation, preparation of the ferric hydroxide precursor, and hydro-thermal reaction. The experimental flow chart is given in Fig. 1. At first, the oily CRM sludge was leached by sulfuric acid ($H_2SO_4$) solution and separated into the organic part and the liquid part. The organic component was separated out by centrifugal force and reused. At the same time, a mixture solution of ferrous and ferric sulfate was gained. Ammonia ($NH_3{\cdot}H_2O$) was added to the mixture solution as a precipitant, and the obtained precipitates were oxidized by bubbling air into the mixture solution. The resulting red brown solid product was then used as a hydrothermal reaction precursor for the preparation of MIO pigments. Finally, MIO pigments were obtained when these precursors were subjected to a hydrothermal process.

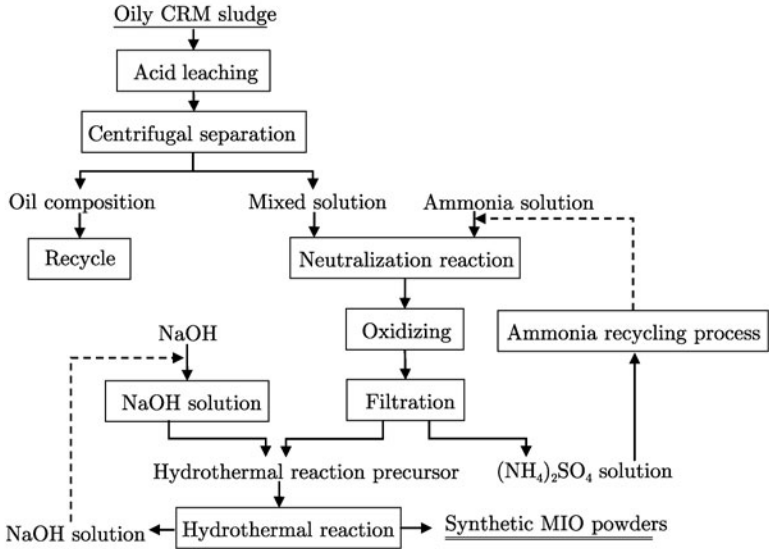

**Fig. 1. Flow chart of MIO synthesized from the oily CRM sludge.**

### 2.2. Materials and reagents

All reagents used in this study were of analytical grade and locally procured. The oily CRM sludge used in the experiment was obtained from the Shanghai Baosteel Group Corporation. Table 1 shows the chemical composition of the oily CRM sludge sample dried at 600°C under vacuum. The content of moisture and oil in oily CRM is about 18.2 wt%.

**Table 1. Chemical composition of the oily CRM sludge dried at 600°C under vacuum wt%**

| $Fe_2O_3$ | $Na_2O_3$ | MnO | $SiO_2$ | $SO_3$ | $Cr_2O_3$ | BaO | NiO |
|---|---|---|---|---|---|---|---|
| 90.57 | 5.37 | 0.72 | 0.71 | 0.62 | 0.46 | 0.40 | 0.28 |
| CuO | $P_2O_5$ | $Al_2O_3$ | MgO | CaO | $TiO_2$ | ZnO | $K_2O$ |
| 0.27 | 0.20 | 0.13 | 0.08 | 0.06 | 0.05 | 0.05 | 0.03 |

### 2.3. Acid leaching and separation of organic component

First, CRM sludge was leached in sulfuric acid ($H_2SO_4$) solution with magnetic stirring, until complete dissolution. After leaching, the mixtures were separated into the organic part and the liquid part in a centrifugal separator. The separated organic part was reused. The liquid part was a mixture solution of ferrous and ferric sulfate and was used as raw material to prepare the MIO pigment. The reaction processes are listed as follows:

$$\mathrm{Fe} + \mathrm{H_2SO_4} \rightarrow \mathrm{FeSO_4} + \mathrm{H_2}\uparrow \tag{1}$$

$$\mathrm{FeO} + \mathrm{H_2SO_4} \rightarrow \mathrm{FeSO_4} + \mathrm{H_2O} \tag{2}$$

$$\mathrm{Fe_2O_3} + 3\mathrm{H_2SO_4} \rightarrow \mathrm{Fe_2(SO_4)_3} + 3\mathrm{H_2O} \tag{3}$$

### 2.4. Preparation of ferric hydroxide precursor

At room temperature, 25% $NH_3{\cdot}H_2O$ solution used as a precipitant was added dropwise to the mixed solution obtained by leaching the oily CRM sludge at constant stirring until the pH value of the reaction solution reached about 10. The aqueous suspensions were stirred gently for 15 min to achieve good homogeneity and to attain a stable pH conditions. Then, air was bubbled into the mixture for 5 h at 0.4 L/min flow rate. The resulting red brown precipitate was obtained. The reaction processes are given as follows:

$$2NH_4OH + FeSO_4 \rightarrow Fe(OH)_2 \downarrow + (NH_4)_2SO_4 \quad (4)$$

$$6NH_4OH + Fe_2(SO_4)_3 \rightarrow 2Fe(OH)_3 \downarrow + 3(NH_4)_2SO_4 \quad (5)$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \downarrow \quad (6)$$

$$2NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_2O \quad (7)$$

After filtration, the obtained ferric hydroxide precipitate was mixed into sodium hydroxide solution of a certain concentration; the obtained $(NH_4)_2SO_4$ solution was used to prepare ammonia by ammonia recycling process.

### 2.5. Preparation of MIO pigment

The obtained ferric hydroxide precipitate was mixed into sodium hydroxide solution of a certain concentration. After a period of mechanical stirring, a homogeneous mixture of ferric hydroxide and hydrated alkali was obtained. The mixture was then poured into a 100-mL Teflon lined reaction kettle at a certain temperature for a certain time. After allowing the reactor to cool down to room temperature, the obtained MIO was separated from the suspension by centrifugation, washed with deionized water, and dried at 80°C overnight. The filtrate contained a large amount of sodium hydroxide, so it can be reused.

### 2.6. Analytical methods

The chemical compositions of the oily CRM sludge sample were evaluated by X-ray fluorescence (XRF) in Shimadzu XRF-1800 equipment. X-ray diffraction (XRD) analyses were performed using a Philips APD-10 X-ray diffractometer with Cu $K_\alpha$ radiation, 40 kV voltage, and 150 mA current at 10°/min scanning rate from 10° to 100°. The morphology and mean particle size were observed in a scanning electron microscope (Zeiss EVO-18, Germany). In order to know the composition of the separated oil, the types of functional groups present in distillation oils were determined by FT-IR analysis using a Nicolet Nexus-470 Fourier transform infrared spectroscope. Chemical analysis of the liquids was performed to examine the ferrous and ferric ion concentration according to GB/T 1863–2008 (China Industrial Standard). The results were the mean values of two experiments using the same sample. The oil absorption of hydrothermal products was measured according to GB 1864-2008 (China Industrial Standard).

## 3. Results and discussion

### 3.1. Acid leaching and separation of organic component

In order to find the optimum leaching conditions in the course of acid leaching of the oily CRM sludge, four important factors were selected including sulfuric acid concentration, acid leaching temperature, acid leaching time and sludge-to-acid ratio, and orthogonal experiment as shown in Table 2 was conducted. From Table 2, it is obvious that the optimum factors of acid leaching of the oily CRM sludge are as follows: the sulfuric acid concentration is 6 mol/L; the acid leaching temperature is 85°C; the acid leaching time is 4 h; the sludge-to-acid ratio is 1:5. Under these conditions, the iron leaching rate is 99.4%.

**Table 2. Orthogonal experiment of the oily CRM sludge leached by sulfuric acid**

| No. | Sulfuric acid concentration / $(mol \cdot L^{-1})$ | Acid leaching temperature / °C | Acid leaching time / h | Sludge-to-acid ratio |
|---|---|---|---|---|
| 1 | 4 | 25 | 2 | 1:4 |
| 2 | 4 | 55 | 3 | 1:5 |
| 3 | 4 | 85 | 4 | 1:6 |
| 4 | 5 | 55 | 4 | 1:4 |
| 5 | 5 | 85 | 2 | 1:5 |
| 6 | 5 | 25 | 3 | 1:6 |
| 7 | 6 | 85 | 3 | 1:4 |
| 8 | 6 | 25 | 4 | 1:5 |
| 9 | 6 | 55 | 2 | 1:6 |
| $\bar{K}_1$ | 90.6 | 93.2 | 94.2 | 93.5 |
| $\bar{K}_2$ | 93.7 | 94.5 | 94.4 | 95.0 |
| $\bar{K}_3$ | 99.4 | 95.7 | 94.8 | 94.8 |

Note: $\bar{K}_m (m = 1, 2, 3)$ is the corresponding average value of iron leaching rate at the $m$ level.

After leaching, the organic part was separated from the liquid part in a centrifugal separator. In order to know the composition of the separated organic materials, the types of functional groups present in the separated organic materials were determined by FT-IR analysis (Fig. 2). Band assignments of the separated organic materials are shown in Table 3. The spectra of the separated organic materials contained a large peak between 3500 $cm^{-1}$ and 3300 $cm^{-1}$, associated with O–H stretches in either alcohols or phenols. The two peaks between 3000 $cm^{-1}$ and 2800 $cm^{-1}$ can be associated with methylene groups. The absence of the absorbance peak between

1725 $cm^{-1}$ and 1700 $cm^{-1}$ may indicate the presence of aromatic carboxylic acids or α/β unsaturated carboxylic acids. The peaks between 1650 $cm^{-1}$ and 1420 $cm^{-1}$ can be associated with aromatic C=C stretches, and the peaks appearing at 966 $cm^{-1}$ and 721$cm^{-1}$ are associated with C–H out-of-plane deformation vibrations in benzene rings. The bands between 1390 $cm^{-1}$ and 1220 $cm^{-1}$ are always present when phenols are analyzed, although they can also be associated with other functional groups.

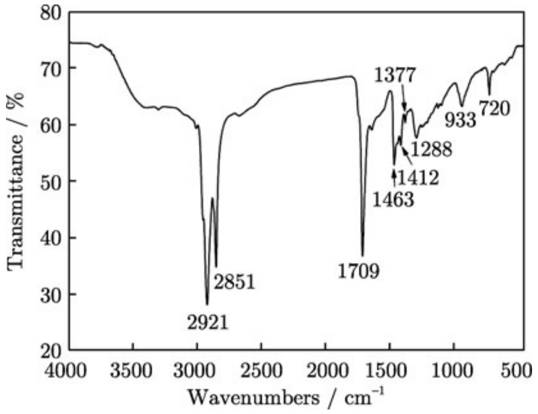

**Fig. 2. FT-IR spectrum of the organic component separated from the oily CRM sludge.**

The FT-IR analysis results indicate that most of separated organic materials consist of saturated aliphatic carboxylic acid and substituted phenols. Therefore, the separated organic materials can be used as fuel or chemical feedstock for further processing.

**Table 3. FT-IR spectrum band assignments**

| Band number / $cm^{-1}$ | Assignment |
|---|---|
| 2921, 2851 | $\nu$(C–H) vibration in methylene groups |
| 1709 | $\nu$(C=O) vibration in saturated aliphatic carboxylic acid |
| 1463, 1412 | $\nu$(C=C) vibration in aromatics groups |
| 1377, 1288 | $\nu$(O–H) vibration in phenols or phenol derivatives |
| 933, 720 | $\nu$(C–H) vibration in aromatic groups |

## 3.2. Preparation of MIO pigment

Among processing parameters, which affect the quality of MIO synthesized by hydrothermal method, NaOH concentration, reaction temperature, reaction time, and total iron concentration in the hydrothermal system are of primary importance. The influence of these processing parameters on the properties of MIO has been studied by various researchers [20-22]. In order to study the effect of the processing parameters, most of the researchers follow the traditional way, i.e., by varying one parameter and keeping others constant. However, this way does not account for the interaction between the processing parameters. Considering the above facts, the orthogonal experimental method was adopted to determine the process parameters for the optimal properties of MIO pigment. The factor levels of orthogonal experimental design are shown in Table 4.

Tables 5 and 6 show the orthogonal experimental results and range analysis, respectively. As shown in Table 6, the effect significance sequences of factors on the $Fe_2O_3$ content and oil absorption are BACD and ABDC,

**Table 4. Factor levels of orthogonal experimental design**

| Parameter | Factor | Level 1 | Level 2 | Level 4 |
|---|---|---|---|---|
| NaOH concentration / (mol·$L^{-1}$) | A | 4 | 8 | 12 |
| Reaction temperature / °C | B | 160 | 200 | 240 |
| Reaction time / h | C | 1.0 | 2.0 | 3.0 |
| Total iron concentration / (mol·$L^{-1}$) | D | 1.25 | 1.87 | 2.49 |

**Table 5. Orthogonal experimental results**

| No. | Factors | | | | Experimental results | |
|---|---|---|---|---|---|---|
| | A, NaOH concentration / (mol·$L^{-1}$ ) | B, Reaction temperature / °C | C, Reaction time / h | D, Total iron concentration / (mol·$L^{-1}$) | $Fe_2O_3$ content / % | Oil absorption / % |
| 1 | 4 | 160 | 1.0 | 1.25 | 76.8 | 38.1 |
| 2 | 4 | 200 | 2.0 | 1.87 | 86.2 | 31.2 |
| 3 | 4 | 240 | 3.0 | 2.49 | 88.6 | 35.4 |
| 4 | 8 | 160 | 2.0 | 2.49 | 82.2 | 32.6 |
| 5 | 8 | 200 | 3.0 | 1.25 | 98.8 | 19.8 |
| 6 | 8 | 240 | 1.0 | 1.87 | 91.2 | 18.7 |
| 7 | 12 | 160 | 3.0 | 1.87 | 87.3 | 21.2 |
| 8 | 12 | 200 | 1.0 | 2.49 | 90.6 | 24.8 |
| 9 | 12 | 240 | 2.0 | 1.25 | 98.4 | 18.0 |

**Table 6. Range analysis results of orthogonal experiment**

| Factors | Extreme difference analysis results | A | B | C | D |
|---|---|---|---|---|---|
| $Fe_2O_3$ content | $K_1$ | 251.6 | 246.3 | 258.6 | 274 |
| | $K_2$ | 272.2 | 275.6 | 266.8 | 264.7 |
| | $K_3$ | 276.3 | 278.2 | 274.7 | 261.4 |
| | $\bar{K}_1$ | 83.9 | 82.1 | 86.2 | 91.3 |
| | $\bar{K}_2$ | 90.7 | 91.9 | 88.9 | 88.2 |
| | $\bar{K}_3$ | 92.1 | 92.7 | 91.6 | 87.1 |
| | Range | 8.2 | 10.6 | 5.4 | 4.2 |
| | Optimized combination | $A_3B_3C_3D_1$ | | | |
| Oil absorption | $K_1$ | 104.7 | 91.9 | 81.6 | 75.9 |
| | $K_2$ | 71.1 | 75.8 | 81.8 | 71.1 |
| | $K_3$ | 64 | 72.1 | 76.4 | 92.8 |
| | $\bar{K}_1$ | 34.9 | 30.6 | 27.2 | 25.3 |
| | $\bar{K}_2$ | 23.7 | 25.3 | 27.3 | 23.7 |
| | $\bar{K}_3$ | 21.3 | 24.0 | 25.5 | 30.9 |
| | Range | 13.6 | 6.6 | 1.7 | 5.6 |
| | Optimized combination | $A_3B_3C_3D_2$ | | | |

Note: $K_m$ ($m$ = 1, 2, 3) represents the sum of corresponding iron leaching rate at the $m$ level.

respectively. The better level combination for the $Fe_2O_3$ content is $A_3B_3C_3D_1$, while the better level combination for the oil absorption is $A_3B_3C_3D_2$. The experiment was carried out according to the results of orthogonal experimental analysis, and the results obtained were compared with the ninth experimental result of orthogonal experiment.

The results of better experimental combinations and the ninth experiment of orthogonal experiment were shown in Table 7. The combination $A_3B_3C_3D_1$ and $A_3B_3C_3D_2$ achieves a higher content of $Fe_2O_3$ (99.4%) and a better oil absorption (17.5%), respectively. From orthogonal experiment, it can be concluded that NaOH concentration (factor A) and reaction temperature (factor B) are the leading factors influencing the results. According to our previous studies, the iron hydroxide precursors were first generated goethite by hydrothermal reaction, and then, the phase transformation from goethite to hematite occurred through the dissolution/recrystallization mechanism, which coincided with many research results [23-25]. High NaOH concentration can increase the solubility of goethite, thus promoting the transformation from goethite to hematite. Besides, high reaction temperature can also accelerate the transformation from ferric hydroxide precursor to hematite.

**Table 7. Results of better experimental combinations**

| Experimental combination | $Fe_2O_3$ content / % | Oil absorption / % |
|---|---|---|
| $A_3B_3C_3D_1$ | 99.4 | 18.6 |
| $A_3B_3C_3D_2$ | 99.1 | 17.5 |
| $A_3B_3C_2D_1$ | 98.4 | 18.0 |

Taking into account all these results discussed above and economic factors, the optimal parameters of MIO synthesized from the oily CRM sludge are 12 mol/L sodium hydroxide concentration, 240°C reaction temperature, 3 h reaction time, and 1.87 mol/L total iron concentration.

### 3.3. Properties of the synthesized MIO

Fig. 3 shows the XRD pattern of the product obtained at the optimal parameters. In Fig. 3, it can be observed that the diffraction peaks match the standard $\alpha$-$Fe_2O_3$ sample perfectly (JCPDS No. 85-0599), indicating that the product synthesized at the optimal parameters is $\alpha$-$Fe_2O_3$.

Fig. 4 shows the morphology of hydrothermal products

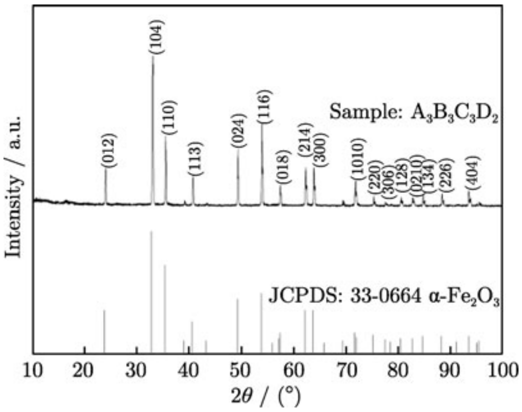

**Fig. 3. XRD pattern of products obtained at the optimal parameters.**

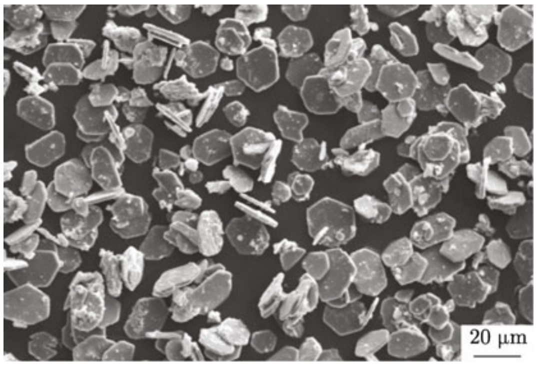

**Fig. 4. SEM image of products obtained at the optimal parameters.**

prepared at the optimal experimental parameters. It can be seen in Fig. 4 that the synthesized powders are in the shape of hexagonal flakes with a particle size of about 12 μm.

MIO pigments powders prepared at the optimal parameters were evaluated according to the international standard ISO 10601-2007, and the results are shown in Table 8. In Table 8, it can be seen that the synthesized MIO powders meet the required characteristics of micaceous iron oxide pigments for paints and the international standard ISO 10601-2007.

**Table 8. Quality of MIO synthesized from the oily CRM sludge under the optimal conditions**

| Characteristic | ISO 10601-2007 (Grade A) | Synthesized sample |
|---|---|---|
| Thin-flake content / wt% | 65 | >65 |
| Iron content, expressed as $Fe_2O_3$ / wt% | 85 | 99.1 |
| Oil absorption value / wt% | 13-19 | 17.5 |
| Matter solubility in water / wt% | $\leqslant 0.5$ | 0.32 |
| Matter volatility at 105°C / wt% | $\leqslant 0.5$ | 0.38 |
| pH value of aqueous suspension | 6-8 | 7.37 |
| Residue on sieve / wt% | $\leqslant 5$(63 μm); $\leqslant 0.1$(105 μm) | 0 |

## 4. Conclusions

In this paper, a new process of "hydrometallurgical treatment + hydrothermal synthesis" has been developed to process the oily CRM sludge. The conclusions are summarized as follows.

(1) The optimum factors of acid leaching of the oily CRM sludge are given as follows: the sulfuric acid concentration is 6 mol/L, the acid leaching temperature is 85°C, the acid leaching time is 4 h, and the sludge-to-acid ratio is 1:5. Under these conditions, the iron leaching rate is 99.4%. After acid leaching, organic materials in the oily CRM sludge are separated by centrifugation. The separated organic materials can be used as fuel or chemical feedstock for further processing.

(2) Four experimental conditions were carefully investigated and optimized by orthogonal experiment. Under optimized conditions, we have the following results: NaOH concentration 12 mol/L, hydrothermal reaction temperature 240°C, reaction time 3 h, total iron concentration 1.87 mol/L, and the resulting MIO pigment has excellent performance with the high purity about 99.1% and the good oil absorption about 17.5%. Furthermore, the pigment is metallic gray with uniform flake shape, and its particle size is about 12 μm.

(3) Quality test, according to the international standard ISO 10601-2007, indicates that the synthesized MIO pigment meets the required characteristics of micaceous iron oxide pigments for paints.

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