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Preparation of nanometer-sized black iron oxide pigment by recycling of blast furnace flue dust

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ABSTRACT

Blast furnace (BF) flue dust is one of pollutants emitted by iron and steel plants. The recycling of BF flue dust can not only reduce pollution but also bring social and environmental benefits. In this study, leaching technique was employed to the treatment of BF flue dust at first. A mixed solution of ferrous and ferric sulfate was obtained and used as raw material to prepare nanometer-sized black iron oxide pigment (Fe_3O_4, magnetite) with NaOH as precipitant. The optimal technological conditions including total iron ion concentration, Fe^{3+}/Fe^{2+} mole ratio, precipitant concentration and reaction temperature were studied and discussed carefully. The spectral reflectance and oil absorption were used as major parameters to evaluate performance of pigment. Furthermore, Fe_3O_4 particles were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Under optimized conditions obtained pigment has low average spectral reflectance (<4%), good oil absorption (~23%), high black intensity, and narrow size distribution 60–70 nm.

1. Introduction

Everyday significant quantities of solid waste materials such as blast furnace (BF) flue dust, slag and sludge are generated from iron and steel plants during steel production. The recycling of these wastes can not only reduce pollution and protect environment but also permit their reutilization. Since generally they contain some useful resources, such as iron, calcium, zinc, etc. How to utilize these secondary resources is still a major problem that bothers experts who work for iron and steel industries or environmental protection societies. Nowadays, the wastes from iron and steel industries are mainly recycled as sinter, blast furnace and basic oxygen furnaces feed [1,2], red ceramic [3], ceramic glass [4,5], iron oxide [6,7], etc.

The BF flue dust from Tianjin Iron and Steel Trade Co. Ltd. studied in this paper has high iron content mainly in the form of Fe_2O_3 and FeO. However, most of dust was used as building materials such as bricks, cement, etc., which has caused a great waste of iron resources. In order to make full use of iron, a simple method is developed to prepare nanometer-sized black iron oxide pigment (Fe_3O_4, magnetite), which can potentially benefit environment and society. Black iron oxide pigment is exploited in a variety of applications such as construction materials, paints, coatings, magnetic recording materials, etc., thanks to its advantages, such as nontoxicity, chemical stability, high tinting strength, hiding power, long durability and low cost. Today the demand of black iron oxide pigments is continuously increasing. However, there are only few reports concerning the preparation of black iron oxide pigment by BF flue dust at home.

In this study the BF flue dust was firstly leached with sulfuric acid, by which a mixed solution of ferrous and ferric sulfate was obtained and used as raw material to prepare Fe_3O_4 pigment. The factors influencing color, particle size and crystalline perfection of Fe_3O_4 pigment were discussed. The experimental conditions were carefully studied in order to obtain optimal ones. Moreover, different methods such as XRD and TEM were applied to characterize structure, morphology and size distribution of Fe_3O_4 pigment particles.

2. Experimental

2.1. The BF flue dust material

The BF flue dust used in the experiment was obtained from Tianjin Iron and Steel Trade Co. Ltd. in Tianjin City, China. Table 1 reports that the chemical compositions of the BF flue dust sample contains predominantly of Fe_2O_3 (45.05%), FeO (18.70%), C (16.25%) and alkalis (13.38%) with small amounts of S, P and other metal oxides. Fig. 1 shows the particle size distribution of dust sample.

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Table 1
Chemical composition of the BF flue dust.

Component	%
Fe_2O_3	43.38
FeO	20.37
C	16.25
Alkalis	13.38
S	0.37
P	0.02
CaO	2.06
MgO	0.26
Si_2O	2.82
Al_2O_3	0.68
K_2O	0.04
Na_2O	0.14

2.2. Treatment of the BF flue dust

At first, BF flue dust was soaked in distilled water with stirring for 15 min in order to remove water-soluble inorganic components (mainly alkalis). Then, the insoluble dust was leached by sulfuric acid at 80 °C and separated into solid and liquid parts. Carbon and other metal oxides precipitates were filtered out and a mixed solution of ferrous and ferric sulfate with Fe^{3+}/Fe^{2+} mole ratio (about 2.1) was gained. This mixed solution was used as raw material to prepare the black iron oxide pigment. The C and metal oxides were used to prepare activated carbon and leach valuable metals.

2.3. Preparation of black iron oxide pigment

Iron chips were added to the raw material obtained by leaching dust with stirring in order to adjust initial Fe^{3+}/Fe^{2+} mole ratio in the range of 1.0–1.4 before preparation. At room temperature, sodium hydroxide (NaOH) used as precipitant was added rapidly to raw material at constant stirring until the pH value of the reaction solution reached about 7.0. Consequently, the Fe^{3+} ions and Fe^{2+} ions were precipitated in the form of FeOOH and $Fe(OH)_2$ respectively. Then, the reaction solution was heated up to 80–95 °C. The pH was kept ~7.0 by the drop-wise addition of sodium hydroxide. The temperature and pH were maintained for about 4 h with continuous stirring. The pH was then adjusted to 9–10 with addition of NaOH. The solution was stirred for 30 min under the same temperature, followed by filtering and washing precipitate. Finally the precipitate was dried at 70 °C and black iron oxide pigment was obtained.

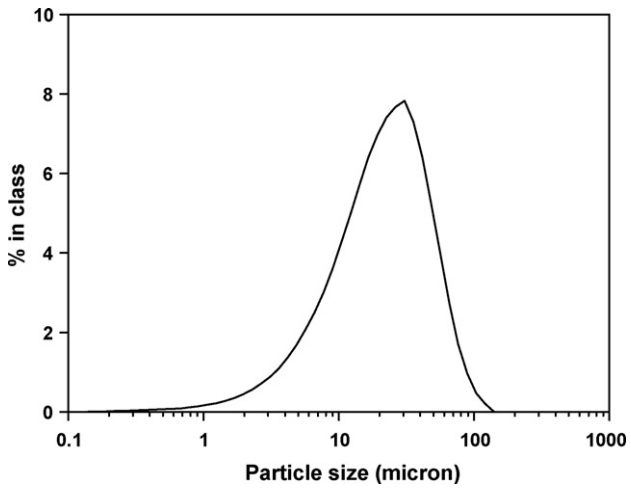

Fig. 1. Size distribution of the BF flue dust.

2.4. Analysis method

The chemical compositions of BF flue dust sample were evaluated by X-ray fluorescence (XRF) in a Rigaku 3070E equipment. Particle size distribution of BF flue dust sample was determined using laser particle size analyzer (LS 230). 1,10-phenanthroline spectrophotometric analysis method was used for Fe^{2+} ions concentration determination by spectrophotometer (721) in this study [8]. In the medium of pH 2–9, the red complex of Fe^{2+} irons reacted with 1,10-phenanthroline was formed with a maximum absorption at 510 nm. Based on using hydroxylamine hydrochloride as a reduction agent, CuCl as the catalyst, Fe^{3+} ions could be reduced rapidly to Fe^{2+} ions. It was suitable for the measurement of total iron ion concentration. Then the Fe^{3+}/Fe^{2+} mole ratio could be determined.

The spectral reflectance and oil absorption are used as major parameters to evaluate the performance of black iron oxide pigment. The average reflectance shows the degree of blackness of the pigment. The lower the average reflectance, and the more black the pigment. Color measurement instrument (JFY-AB_1) was used to obtain the spectral reflectance of Fe_3O_4 pigment. The oil absorption is relevant to the particle size and the space between pigment particles [9–11]. If the space is larger, more quantity of oil is needed in order to fill it completely. The relation between oil absorption and the particle size is complicated. In fact, oil absorption decreases with the particle size decreasing firstly, then increases with the further decrease of the particle size. Therefore, there is a suitable particle size corresponding to optimal oil absorption. Oil absorption (X) was calculated with the formula $X = \frac{m_1}{m} \times 100\%$, where m_1 is mass of sample, m is mass of oil used in measurement. Usually the black pigment is considered to have pronounced performance when the average spectral reflectance is lower than 4% and oil absorption is between 15% and 25% [10].

TEM images were taken with a JEOL 100CX-II transmission electron microscopy to estimate morphology, nature of agglomerates and particle size distribution in the resultant pigment particles. The phase analysis of the pigment particles was carried out by BDX-3300 X-ray diffractometer to obtain X-ray diffraction (XRD) patterns.

3. Results and discussion

3.1. Treatment of the BF flue dust

The factors affecting the leaching rate of iron in the BF flue dust were examined. This paper shows four important factors including temperature, reaction time, sulfuric acid concentration and ratio of dust to sulfuric acid in Table 2. It is clear that the optimum conditions are suggested as follows: temperature 80 °C, reaction time 4 h, sulfuric acid concentration 3 mol/L (lower cost than 5 mol/L) and ratio of dust to sulfuric acid 1:4. Under such conditions the leaching rate of iron reaches 98%.

3.2. Preparation of black iron oxide pigment

As mentioned above different experimental conditions, such as total iron ion concentration as well as Fe^{3+}/Fe^{2+} mole ratio in raw material, precipitant concentration, reaction temperature, etc., can affect the performance and structure of magnetite pigment. Therefore, it is necessary to carry out experiments to optimize these technological conditions in order to obtain high-quality products. In this paper all these four experimental conditions are optimized one by one by keeping the three other conditions constant at once. The color change, average reflectance and oil absorption of Fe_3O_4 pigment prepared on different experimental conditions are given in Table 3.

Table 2
Iron leaching rate in the BF flue dust under different conditions.

Factors	Iron leaching rate (%)
Sulfuric acid concentration (mol/L)	
5	98.5
3	98.3
1	92.7
Temperature (°C)	
20	91.2
50	95.0
80	98.8
Ratio of dust to sulfuric acid (g/mL)	
1:2	87.9
1:3	93.1
1:4	98.2
Reaction time (h)	
2	92.5
3	95.2
4	98.6

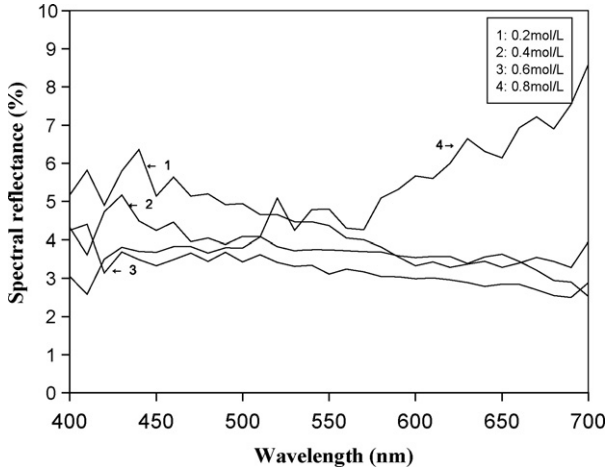

Fig. 2. Spectral reflectance curves of Fe_3O_4 pigment obtained at different total iron ion concentrations.

3.2.1. Total iron ion concentration in raw material

To study the influence of total iron ion concentration in raw material, a series of experiments were performed with the concentration ranging from 0.2 to 0.8 mol/L. According to Table 3, it is observed that the color of pigment turns from brownish black to black with the increase of total iron ion concentration in range of 0.2–0.6 mol/L. However, when total iron ion concentration reaches 0.8 mol/L, the color becomes reddish black. The color change of pigment obtained at different total iron ion concentrations can be explained by the spectral reflectance curves as shown in Fig. 2 and the XRD patterns as shown in Fig. 4.

The spectral reflectance is recorded with the wavelength ranging from 400 to 700 nm in Fig. 2. In order to better understand the relationship between the color of pigment and the average reflectance, the spectral reflectance of several colors is shown in Fig. 3, it can be observed that the pigment with reflectance lower than 4% is pure black. From Fig. 2, the reflectance of pigment prepared at 0.2 mol/L is a little higher than 4% at low wavelength region of 400–580 nm, with the help of Fig. 3, it can be predicted that the pigment is mainly black with somewhat russet, which is in consistence with the results in Table 3. The reflectance of pigment obtained at 0.6 mol/L is lower than 4% in the full wavelength range; moreover, it varies very slightly. It indicates that the blackness of pigment obtained at 0.6 mol/L is high. The pigment obtained at 0.8 mol/L has a higher reflectance (5–9%) in wavelength range of 600–700 nm. Therefore, the pigment is sort of reddish black.

The XRD patterns illustrated in Fig. 4 all have obvious diffraction peaks and match well with the standard Fe_3O_4 reflections. The diffraction peak intensity enhances with concentration increasing between 0.2 and 0.6 mol/L whereas weakens at 0.8 mol/L. Because it is easy for air to enter reaction solution at lower total iron ion concentration, Fe(II) is oxidized to Fe(III) easily by rich air, which leads to over-oxidation of magnetite pigment due to production of excess hematite (Fe_2O_3). As a result, the color of pigment is brownish black. So the weak diffraction peak intensity of spectrum 1 (corresponding to 0.2 mol/L) indicates Fe_3O_4 phase is less than spectra 2 and 3. When the total iron ion concentration is too high, it is not favorable for homogenous distribution of air in reaction solution, and induces heterogeneous nucleation of the precipitate due to partial over-oxidation or partial light oxidation. Consequently, pigment prepared at 0.8 mol/L (spectrum 4) is reddish black and less Fe_3O_4 phase with lower diffraction peak intensity.

Table 3
Characteristic parameters of Fe_3O_4 pigment obtained under different conditions.

Factors	Color	Average reflectance (%)	Oil absorption (%)
Total iron ion concentration (mol/L)			
0.2	Brownish black	4.29	31.8
0.4	Black	3.78	26.4
0.6	Black	3.25	23.5
0.8	Reddish black	4.98	38.2
Mole ratio of Fe^{3+}/Fe^{2+}			
1.92	Brownish black	14.09	38.3
1.81	Brownish black	10.28	36.0
1.64	Brownish black	8.21	32.5
1.36	Black	3.90	22.8
1.16	Black	3.66	23.9
1.01	Black	3.50	24.3
0.91	Black	3.90	24.7
0.33	Black	4.32	23.6
Precipitant concentration (mol/L)			
7.50	Reddish black	9.32	36.6
5.00	Brownish black	6.63	32.8
3.75	Brownish black	4.87	30.3
2.50	Black	3.66	23.6
1.25	Black	2.89	23.9
Reaction temperature (°C)			
20	Reddish brown	9.50	37.1
40	Yellowish brown	6.41	30.7
60	Brownish black	5.19	25.5
75	Black	3.91	23.9
85	Black	3.53	23.4
95	Black	3.50	22.8

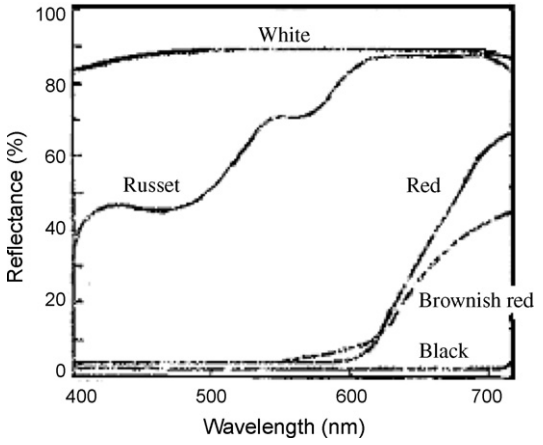

Fig. 3. The spectral reflectance curves of various colors.

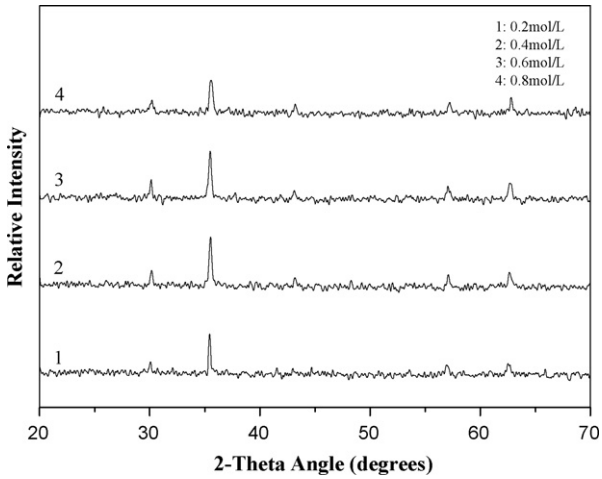

Fig. 4. XRD patterns of Fe_3O_4 pigment obtained at different total iron ion concentrations.

Furthermore, the pigment particle size varies with reaction solution concentration, which reflects, in fact, the relation between the nucleation rate and the growth rate of nucleus for the formation of crystalline precipitate [12,13]. When the concentration of reaction solution is low, the nucleus growth rate is higher than the nucleation rate. Therefore, there is enough time for nuclei to grow and form perfect crystalline shape but too big particle size. On the contrary, at high concentration of reaction solution, the supersaturation degree increases, which favors formation of nuclei of the crystal. Consequently, nucleation rate of nucleus is faster than the growth rate. Thereby, the size of pigment particles is very small but in imperfect crystalline shape [14]. As shown in Fig. 5a, the pigment particles obtained at 0.8 mol/L are very fine (about 25–35 nm) but in imperfect crystalline form. Moreover, according to Scherrer's formula [15], the half peak width (width of the most intense diffraction peak at half-height) is inversely proportional to the particle size. From Fig. 4, half peak width of pigment prepared at 0.8 mol/L is wider than the others. And half peak width decreases with decreasing total iron ion concentration. Fig. 5b shows the pigment particles prepared at 0.6 mol/L are about 60–70 nm with perfect crystalline form. It agrees well with the XRD analysis result showing the highest diffraction peak intensity and medium half peak width.

Table 3 also shows the pigment obtained at 0.6 mol/L have low average reflectance (<4%) and good oil absorption (23.5%). Taking into accounts all these results discussed above, the optimum total iron ion concentration is 0.6 mol/L. Under this condition, the particle size is nanometer (60–70 nm) with good crystalline form.

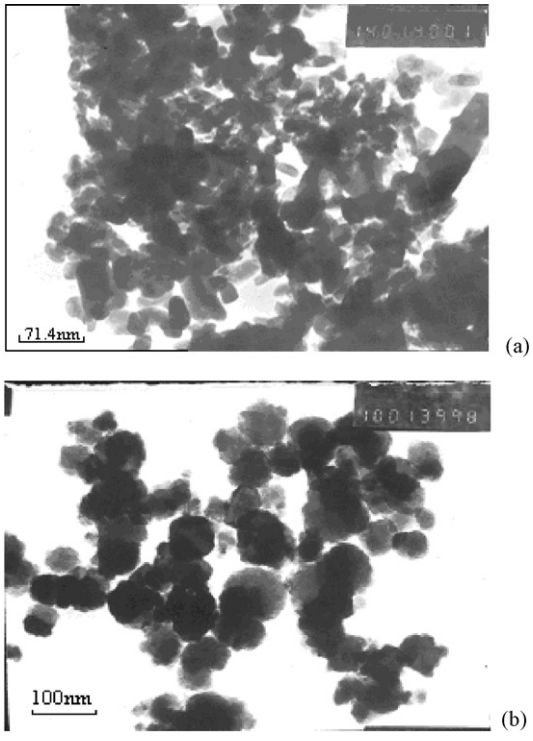

Fig. 5. TEM images of Fe_3O_4 pigment particles obtained at the total iron ion concentrations of 0.8 mol/L (a) and 0.6 mol/L (b).

3.2.2. *Mole ratio of Fe^{3+} to Fe^{2+}*

The black iron oxide pigment is composed of Fe(III)–Fe(II) oxides of magnetite structure (molecular formula: Fe_3O_4 or $Fe_2O_3{\cdot}FeO$). In this study, the raw material is a mixed solution of ferric and ferrous sulfate, it is necessary to optimize Fe^{3+}/Fe^{2+} mole ratio. Eight mole ratios in the range of 0.33–1.92 are studied. The corresponding characteristic parameters are summarized in Table 3, which shows the pigment is black when the mole ratio is lower than 1.36, but it is brownish black when the mole ratio is higher than 1.36. It is clear that Fe^{3+}/Fe^{2+} mole ratio in raw material has an obvious effect on the color of pigment.

At high mole ratio, not only there is a large quantity of Fe^{3+} ions in reaction solution, but also some $Fe(OH)_2$ precipitate will be oxidized to FeOOH precipitate during reaction. These two factors lead to an excess of FeOOH precipitate. Thus, the obtained pigment contains relatively more Fe(III) than Fe(II) and has partly reddish brown. The color of Fe_3O_4 pigment changes into black with the decrease of Fe^{3+}/Fe^{2+} mole ratio. The average reflectance decreases with the mole ratio decreasing shown in Table 3, it is consistent with the color change. Table 3 also shows oil absorption decreases with the decrease of mole ratio. When Fe^{3+}/Fe^{2+} mole ratio in raw material is lower than 1.36, the obtained pigments show good performance with the average reflectance lower than 4% and oil absorption between 22 and 25%. Fig. 6 shows the XRD pattern of the pigment prepared at Fe^{3+}/Fe^{2+} mole ratio of 1.16. The XRD pattern matches well with the standard Fe_3O_4 reflections. It has obvious diffraction maximum, indicating that it has highly crystal structure and pure Fe_3O_4 phase.

According to Fig. 7, the reaction time strongly depends on the Fe^{3+}/Fe^{2+} mole ratio in raw material. The higher the mole ratio of Fe^{3+}/Fe^{2+}, the shorter the reaction time. Short reaction time will get very fine particles but in imperfect crystalline shape at high Fe^{3+}/Fe^{2+} mole ratio. When the ratio is lower than 1.0, the reaction

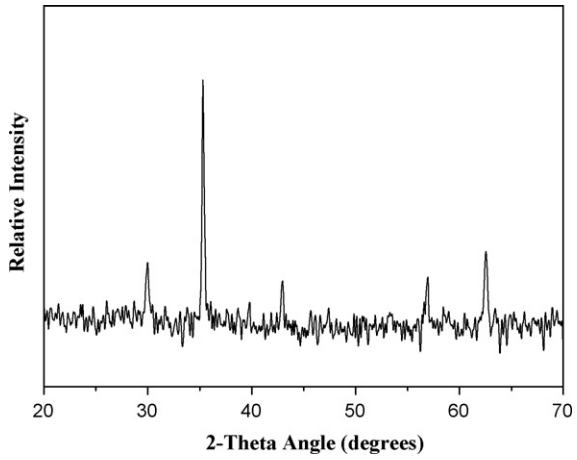

Fig. 6. XRD pattern of Fe_3O_4 pigment obtained at Fe^{3+}/Fe^{2+} mole ratio of 1.16.

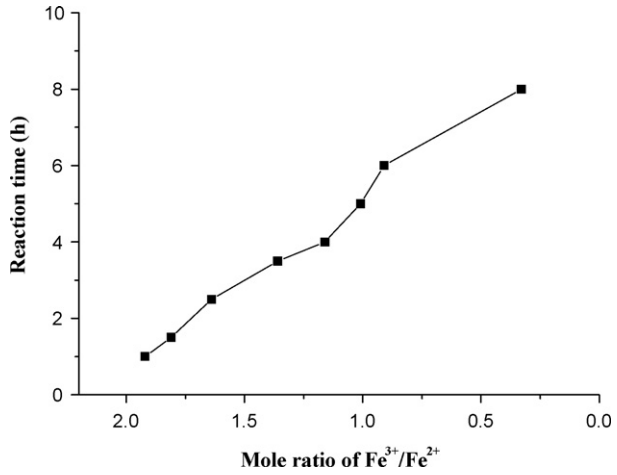

Fig. 7. Reaction time change with Fe^{3+}/Fe^{2+} mole ratio.

time is more than 6 h. In practice, such a long reaction time can make pigment particles have good crystalline shape but very large particle size and often lead to color fade of the pigment. Therefore, reaction time should be taken into account for the choice of the optimal mole ratio. Considering the cost, 3–5 h for reaction time is better in this study.

Taking into accounts all these parameters including average reflectance, oil absorption, the color, reaction time, the optimum Fe^{3+}/Fe^{2+} mole ratio in raw material is 1.0–1.36. In this range the obtained Fe_3O_4 pigment nanoparticles have saturated blackness (average reflectance <4%) and pure Fe_3O_4 phase.

3.2.3. Precipitant concentration

Precipitant concentration is another important condition that has influence on the performance of the pigment as shown in Table 3. It can be seen that with the precipitant concentration lower than 3.75 mol/L, the obtained pigments are black owing to average reflectance lower than 4% and the oil absorptions are ~23%. However, the pigment obtained at precipitant concentration higher than 3.75 mol/L is reddish black or brownish black with average reflectance higher than 4% and oil absorption higher than 25%.

The XRD patterns of Fe_3O_4 pigment obtained at five different precipitant concentrations shown in Fig. 8 all have obvious diffraction maximum. It matches well with the standard Fe_3O_4 reflections. Among them, diffraction peak intensity of pigment prepared at the highest precipitant concentration 7.5 mol/L (spectrum 1) shows apparent weak than the others. And its half peak width is the widest. It indicates the pigment has less Fe_3O_4 phase and imperfect crystalline shape with small particle size. Thus, this sample has the highest oil absorption and the highest average reflectance with a reddish black color. The reason is that high precipitant concentration is in favor of forming large amount of precipitate nuclei. The nucleation rate is higher than nucleus growth rate so that the excess $Fe(OH)_2$ precipitate will be produced in that it cannot be converted to FeOOH precipitate timely. The excess $Fe(OH)_2$ precipitate turns to FeO after drying, further to be oxidized to Fe_2O_3 owing to oxidizability of FeO in the air and gives the pigment a reddish black color. Moreover, when precipitant concentration is too high, the growth of crystal is limited due to the rapid nucleation rate. Therefore, the pigment particles obtained at higher precipitant concentration than 3.75 mol/L are impure and have imperfect magnetite structure.

With precipitant concentration decreasing, the diffraction peak intensity increases, while the half peak width, average reflectance as well as oil absorption reduces. The Fe_3O_4 pigment has pronounced magnetite structure according to strong diffraction peak in XRD pattern and shows high black color intensity and nanometer size thanks to its low average reflectance (3.66%) and good oil absorption (23.6%), when the precipitant concentration is 2.50 mol/L. Although the diffraction peak intensity of pigment prepared at 1.25 mol/L is higher than that of pigment prepared at 2.50 mol/L, more reaction time is needed, which prefers to the growing of nucleus and contributes to big particle size in sample based on the smaller half peak width. Therefore, 2.50 mol/L is chosen as the optimal precipitant concentration.

3.2.4. Reaction temperature

To study the effect of reaction temperature, a series of experiments were performed at different temperatures ranging from 20 to 95 °C under the optimal conditions for the other three experimental conditions: the total iron ion concentration in raw material 0.6 mol/L, the mole ratio of Fe^{3+}/Fe^{2+} 1.16, and the precipitant concentration 2.50 mol/L. According to Table 3, reaction temperature is also an important factor since it can affect color, luster and performance of magnetite pigment. It can be observed that the color of pigment is red or yellow at the reaction temperature lower than 70 °C, while the color of pigment changes into black at the reaction temperature higher than 70 °C. The color change of pigment can be explained by the spectral reflectance (Fig. 9) and diffraction peak intensity (Fig. 10).

Fig. 9 shows samples 1, 2 and 3 prepared at lower temperature all have high spectral reflectance with wavelength ranging

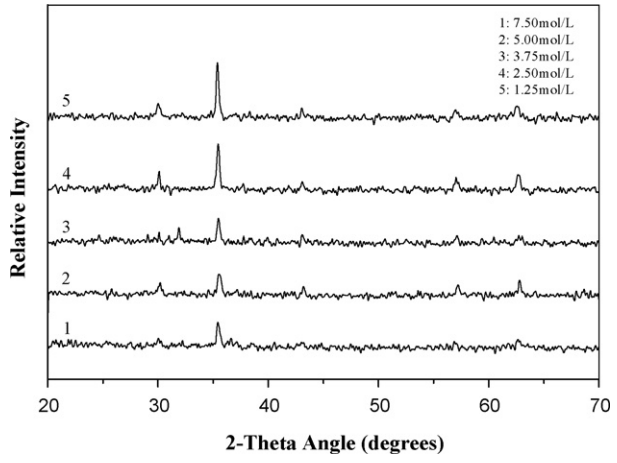

Fig. 8. XRD pattern of Fe_3O_4 pigment obtained at different precipitant concentrations.

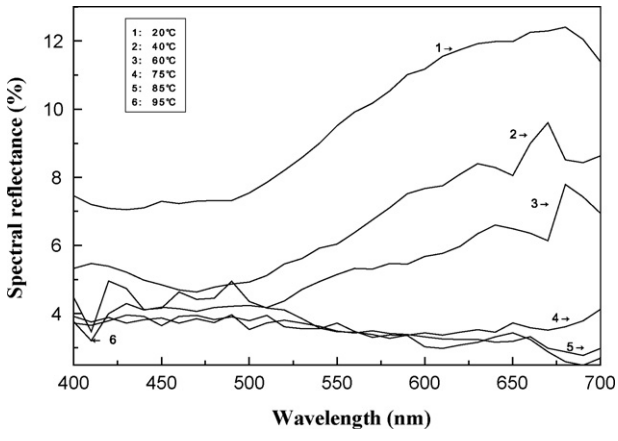

Fig. 9. Spectral reflectance curves of Fe_3O_4 pigment obtained at different reaction temperatures.

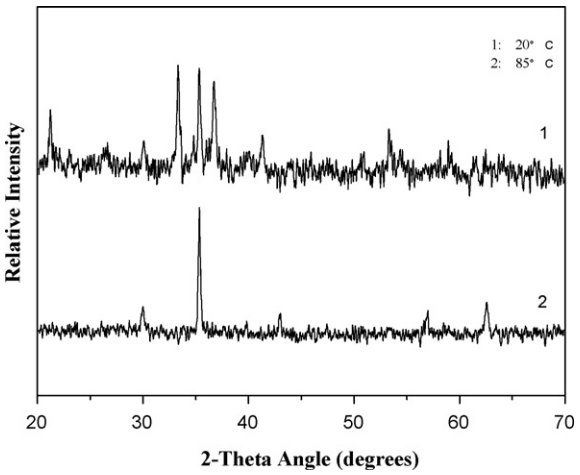

Fig. 10. XRD patterns of Fe_3O_4 pigment obtained at different reaction temperatures.

from 500 to 700 nm, while samples 4, 5 and 6 obtained at higher temperature keep low average reflectance in range of 400–700 nm. According to Fig. 10, the XRD pattern of sample prepared at 85 °C matches well with the standard Fe_3O_4 reflections, while diffraction peak intensity of sample obtained at 20 °C is weak and part peaks can be assigned to Fe_2O_3 and FeOOH phase. It can be inferred high reaction temperature is benefit to prepare Fe_3O_4 pigment. A similar opinion was reported by Misawa et al. [16] who considered $Fe(OH)_2$ is oxidized to intermediates green rusts firstly, then green rusts are converted into Fe_3O_4 at high temperature, but converted into α-FeOOH or γ-FeOOH at low temperature.

Table 3 also indicates oil absorption decreases with increasing reaction temperature. Therefore, the optimal reaction temperature is chosen in the range of 80–95 °C. In this temperature range, the pigment has perfect magnetite structure owing to its strong diffraction peak, low average reflectance and good oil absorption ~23%.

4. Conclusions

In this paper a simple method for recycling of the BF flue dust has been developed to produce nanometer-sized black iron oxide pigment. The chemical analysis of the dust sample has shown that it is a ready source of iron due to its sufficiently high iron content for the production of Fe_3O_4 pigment. Firstly, the BF flue dust was pretreated. Carbon, alkalis and other metal oxides were removed and a mixed solution of ferrous and ferric sulfate with Fe^{3+}/Fe^{2+} mole ratio ~2.1 was obtained.

Four experimental conditions were carefully studied and optimized. Under optimized conditions giving as follows: the total iron ion concentration in raw material at 0.6 mol/L with Fe^{3+}/Fe^{2+} mole ratio in the range of 1.0–1.4, the precipitant concentration at 2.50 mol/L and the reaction temperature between 80 and 95 °C, the resulting Fe_3O_4 pigment has excellent performance with average spectral reflectance lower than 4% and good oil absorption about 23%. Furthermore, the pigment has high blackness degree, nanometric size with narrow size distribution range (60–70 nm) and pronounced magnetite structure.

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