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Preparation and formation mechanism of nano-iron oxide black pigment from blast furnace flue dust

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Abstract

A mixed solution of ferrous and ferric sulfate leached from blast furnace (BF) flue dust was used to prepare nanometer-sized iron oxide black pigment (Fe_3O_4, magnetite) by the co-precipitation method. The pH value played a very important role in affecting the color and particle size of Fe_3O_4 and the evolution of green rust in to Fe_3O_4 or FeOOH. The experimental conditions including the solution pH, the way of adding precipitant, volume of air and reaction time for the formation of nano-iron oxide black pigment were investigated carefully in order to determine the optimal ones. The color, morphology and particle size of as-prepared Fe_3O_4 pigment were characterized by means of a color measurement instrument, X-ray diffraction (XRD) and transmission electron microscopy (TEM) respectively. The results showed that the obtained pigment had low average spectral reflectance ($<4\%$), good oil absorption ($\sim 23\%$), high black intensity and narrow size distribution of 60–70 nm. Furthermore, the formation mechanism of Fe_3O_4 from the mixed solution of ferrous and ferric sulfate was discussed.

Keywords: Nano-iron oxide black; Pigment; Formation mechanism; BF flue dust

1. Introduction

Iron oxide black pigment is widely used in construction materials, paints, coatings, magnetic recording materials and other fields [1–6], thanks to its advantages, such as nontoxicity, chemical stability, high tinting strength, hiding power, long durability and low cost. This paper proposed a simple co-precipitation method to prepare nanometer-sized iron oxide black pigment using a mixed solution of ferrous and ferric sulfate obtained by leaching the BF flue dust with sulfuric acid. This method opened up a new way for the preparation of iron oxide black pigment. One reason is that, the raw material used is BF flue dust, from solid waste materials, generated from iron and steel plants rather than $FeCl_2$ or other chemical reagents. The wastes became the secondary resources, which not only improved efficiency of resource utilization but also reduced environmental pollution. In our previous paper [7], the chemical composition, the particle size distribution and the treatment of BF flue dust have been described in detail. On the other hand, compared with the traditional preparation methods by using either Fe(III) hydrolytic reactions or Fe(II) oxidative precipitations, the method using a mixed solution of Fe(II) and Fe(III) in this paper is more simple and efficient.

In the present work, the experimental conditions including solution pH, the way of adding precipitant, reaction time and volume of air were carefully studied in order to obtain optimal ones. These factors have a great effect on the chemical composition, color, particle size, morphological characteristics and other properties of the resultant products. The formation mechanism of Fe_3O_4 from this mixed solution of Fe(II) and Fe(III) was further explored. Temperature and pH are the two most important factors controlling the structure and composition of final products transformed from green rust. The results showed that nano-Fe_3O_4 pigment could be prepared by using BF flue dust.

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2. Experimental

2.1. Characterization

The spectral reflectance of Fe_3O_4 pigment was carried out by a color measurement instrument (JFY-AB_1). The spectral reflectance can reflect the blackness degree and color uniformity of pigment. It is a main index to evaluate the performance of Fe_3O_4 pigment. Taking black and white as the reference standard, the spectral reflectance ratio of the standard sample to the tested sample is the spectral reflectance. Measurement range is from 400 nm to 700 nm and the interval of wavelength is 10 nm. The spectral reflectance curve was obtained with spectral reflectance (R) as ordinate and wavelength (λ (nm)) as abscissa. The hiding power and tinting strength of pigment are related to oil absorption, and so the oil absorption is another important indicator to measure the performance of Fe_3O_4 pigment. Determination of oil absorption is as follows [8]: a certain quantity of the pigment sample is placed on a glass plate, and linseed oil is dropped into the pigment. Oil absorption (X) can be calculated with the formula $X = m_1/m \times 100\%$, where m_1 is the mass of pigment, and m is the mass of oil used in measurement. When oil absorption is lower than 25%, moderate size and fine crystallization degree of Fe_3O_4 particles can be obtained. The morphology, size, uniformity and nature of agglomerates of iron oxide black nanoparticles were observed by a JEOL100CX-H transmission electron microscope (TEM). X-ray diffraction (XRD) patterns were measured on a BDX-3300 diffractometer using CuKα radiation (wavelength, $\lambda = 1.5406$ Å) with variable slits at 45 kV/40 mA. The XRD technique was used to characterize the size of nano-Fe_3O_4 particles.

2.2. Preparation of Fe_3O_4 pigment

Magnetite pigment nanoparticles were synthesized by using a mixed solution of Fe(III) and Fe(II) with mole ratio in the range 1.0–1.4 with NaOH as precipitant. The NaOH solution was added rapidly in the mixed solution to raise the pH to 7.0–8.0 at room temperature or below 40 °C. The reaction solution was heated up to 80–95 °C by using water bath. At the same time, the NaOH solution was added by dropping it to the reaction solution to keep the pH at 7.0. When the reaction was close to the end, the pH was adjusted to 9.0–10.0 to make Fe^{2+} ions precipitate completely. Crystals were allowed to grow for 30 min with continuous stirring. The black precipitates were then washed several times with distilled water until the pH was neutral. Lastly, the black precipitates were air dried at 60 °C for 24 h to obtain the iron oxide black pigment.

3. Results and discussion

Under the optimal experimental conditions [7], the total iron ions concentration in raw material was 0.6 mol/L, the mole ratio of Fe^{3+}/Fe^{2+} was 1.16, precipitant concentration was 2.50 mol/L and reaction temperature was 85 °C; the other four experimental conditions including solution pH value, the way of adding precipitant, reaction time and ventilation time were studied and the optimum parameters were determined in this paper. The influences of these four experimental conditions on the color change, spectral reflectance and oil absorption of Fe_3O_4 pigment are summarized in Table 1. Furthermore, the formation mechanism of Fe_3O_4 pigment precursor was discussed.

3.1. Solution pH

To study the effect of solution pH, a series of experiments was performed at different reaction pH and final pH was ranging from 4 to 11. According to Table 1, it can be seen that the pigment is black with average reflectance lower than 4% and oil absorption lower than 25% when the reaction pH and final pH are both more than 7, while the pigment is brown or brownish black owing to average reflectance higher than 4% and oil absorption higher than 25% when the reaction pH and final pH are less than 7. The color change of pigment can be explained by the spectral reflectance curves as shown in Fig. 1.

From Fig. 1a, the reflectance of pigment prepared at reaction pH and final pH 4 (spectrum 1) is significantly higher than 4% in the whole wavelength range, which shows that the obtained pigment may be Fe_2O_3 or FeOOH with yellowish brown color. Thus, this sample has the highest oil absorption, which is consistent with the higher oil absorption of Fe_2O_3 and FeOOH than that of Fe_3O_4. From Fig. 1b, when the reaction pH and final pH are both 6, the reflectance of pigment is slightly higher than 4% in the whole wavelength range. It indicates that the pigment has impure Fe_3O_4 phase with brownish black color and slightly higher oil absorption. The other samples obtained at both reaction pH and final pH higher than 7 are mainly of Fe_3O_4 phase with most reflectance lower than 4% in the wavelength range 400–700 nm and oil absorption lower than 25%.

Both the reaction pH and final pH of solution have a significant effect on the performance of product. The reaction pH of solution affects the structure and chemical composition of sample. It has been reported [9] that $Fe(OH)_2$ is easily oxidized to FeOOH at a pH lower than 4.9. The reaction is expressed by the following reaction equation:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad (1)$$

$$Fe(OH)_2 + O_2 \rightarrow 4FeOOH + 2H_2O \qquad (2)$$

In fact, the solution pH of 7 is a benefit for forming Fe_3O_4 during the preparation process. In this process, the consumption of NaOH results in a decrease of solution pH value. In order to get pure magnetite pigment, it is necessary to keep the solution pH of 7 by adding NaOH continuously to prevent the reaction equation (2).

The final pH value has a great effect on the purity of product. The reason is that it is easy for residual Fe^{2+} ions

Table 1
Characteristic parameters of Fe_3O_4 pigment obtained under different conditions.

Factors		Color	Average reflectance (%)	Oil absorption (%)
Reaction pH	Final pH			
4	4	Yellowish brown	10.34	40.3
6	6	Brownish black	4.36	27.4
7	7	Black	3.83	25.8
7	8	Black	3.50	22.5
7	9	Black	2.89	21.4
7	10	Black	3.53	23.3
7	11	Black blue	3.66	23.7
Adding way of the precipitant[a]				
Method 1		Reddish black	6.33	38.3
Method 2		Brownish black	4.66	30.5
Method 3		Brownish black	4.28	27.2
Method 4		Black	3.25	23.6
Method 5		Black	2.89	22.8
Reaction time (h)				
1.5		Brownish black	5.52	34.8
2		Brownish black	4.80	30.1
3		Black	3.64	22.8
4		Black	3.53	22.5
5		Black	3.66	23.4
6		Black	4.31	27.3
7		Brownish black	5.08	29.7
Ventilation time (min)				
0		Black	3.25	23.5
10		Black	3.66	24.1
30		Black	4.08	25.8
60		Brownish black	5.54	30.3
Continuous ventilation		Reddish brown	7.34	36.2

[a] Method 1: raising temperature to 80 °C before adjusting pH to 9–10 quickly with NaOH; Method 2: raising temperature to 80 °C after adjusting pH to 7 by dropping NaOH; Method 3: simultaneous raising temperature and dropping NaOH; Method 4: raising temperature to 80 °C after adjusting pH to 7 quickly with NaOH, then dropping NaOH to keep pH 7; Method 5: raising temperature to 40 °C before adjusting pH to 7 quickly, then simultaneous raising temperature and dropping NaOH to keep pH 7.

to go into the crystal lattice of Fe_3O_4 to influence the purity of pigments. Therefore, the final pH should be controlled more than 8.95 to ensure the complete precipitation of Fe^{2+} ions according to the solubility constant of $Fe(OH)_2$. In addition, the reaction solution will produce bubbles and overflow at a final pH higher than 11. And, when the final pH is more than 12 or more NaOH is left, it is also favorable for forming FeOOH [10]. Therefore, the optimum reaction pH is 7 and final pH value is 9–10.

3.2. Way of adding precipitant

The way of adding the precipitant is an important condition that has influence on the performance of Fe_3O_4 pigment, because different ways of adding cause different reaction pH. The properties of prepared products are highly dependent on pH and temperature during the precipitation process. The spectral reflectance and oil absorption of pigment samples obtained by varying the way of adding the precipitant and with other experimental conditions fixed are given in Table 1 and Fig. 2. According to Fig. 2, it is found that the pigment obtained by method 1 (spectrum 1) has a higher reflectance (5–9.5%) in the wavelength range 400–700 nm. It can be predicted that the color of pigment is reddish black. The pigments prepared by methods 2 and 3 (spectra 2 and 3) are brownish black with average reflectance higher than 4% and oil absorption higher than 25%. The latter two spectra show that the reflectance is lower than 4% and oil absorption is lower than 25%.

In the first method, the mixed solution of $Fe_2(SO_4)_3$ and $FeSO_4$ was heated to 80 °C firstly, and then NaOH was added into the solution once to adjust pH to 9–10 at this temperature. The Fe^{2+} and Fe^{3+} ions were precipitated immediately. These precipitates will be transformed into Fe_3O_4 rapidly at 80 °C. Therefore, Fe(II) will enter the resulting products in which it cannot be oxidized to Fe(III) timely. During drying, the surplus Fe(II) will be changed to FeO, further to be oxidized to Fe_2O_3, which leads to the impure Fe_3O_4 with reddish black color. According to the

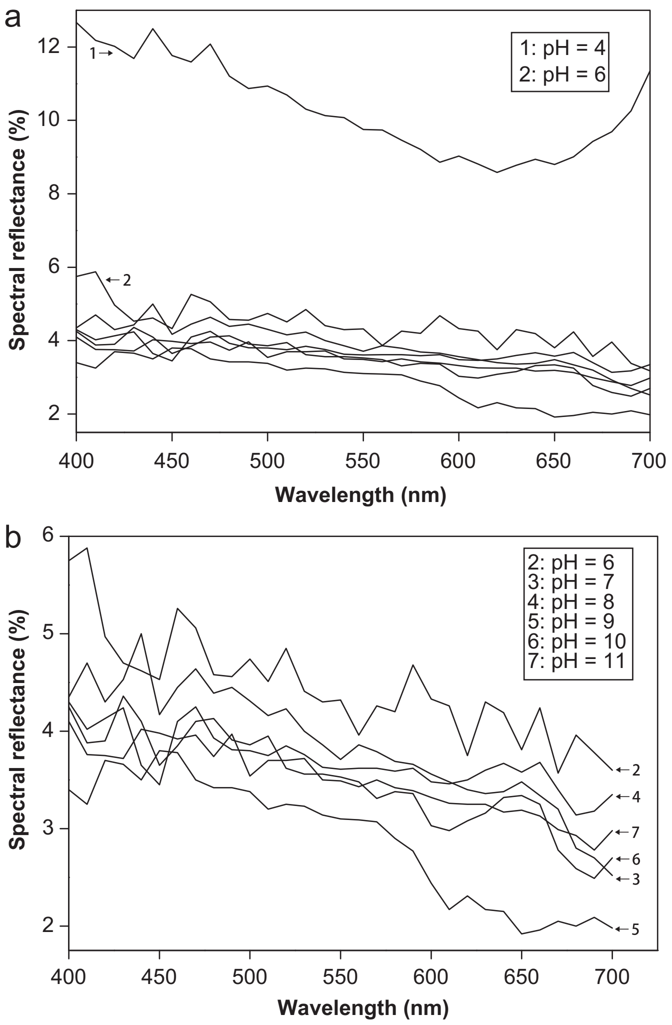

Fig. 1. Spectral reflectance curves of Fe_3O_4 pigment obtained at different pH (a); (b) is an expanded view of (a).

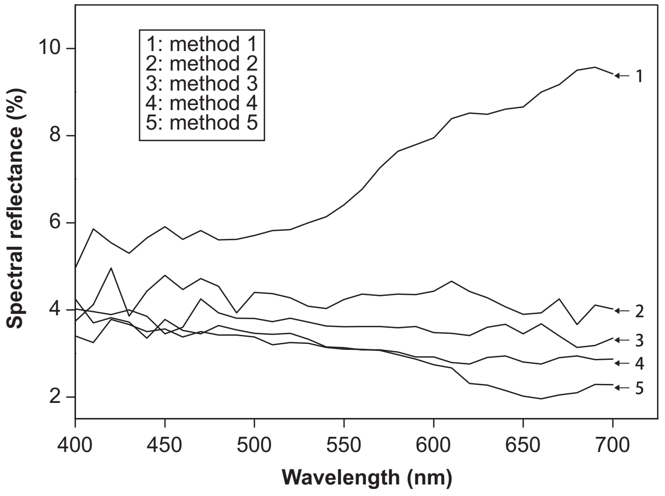

Fig. 2. Spectral reflectance curves of Fe_3O_4 pigment obtained by different way of adding precipitant.

crystal growth process [11], the great supersaturation degree produces a large amount of nuclei; these nuclei do not have enough time to grow, and the nucleation rate is higher than the nucleus growth rate, which results in very small particle size of pigment with imperfect crystalline shape. Because of this, pigment obtained by method 1 has high oil absorption of 38.3% and average reflectance of 6.33% as illustrated in Table 1.

As for methods 2 and 3, due to the addition of NaOH by dropping, solution pH value increases slowly. At pH lower than 5 and temperature lower than 40 °C, Fe(II) is easily oxidized to FeOOH, which leads to impure pigment with some brown color. Once the solution pH is adjusted above 5, Fe_3O_4 can be obtained easily. Due to the slow addition of NaOH, it takes a long time for the precipitation and oxidation of Fe(II). The particles generated initially have enough time to grow and form perfect crystalline shape with big particle size, while the particles formed later do not have time to grow and produce very small ones with imperfect crystalline shape. A wide size distribution of pigment particles with higher oil absorption and average reflectance is obtained. The SEM image of pigment particles obtained by method 2 is shown in Fig. 3a.

In the last two methods, the only difference is that the reaction solution is heated to 40 °C before adding NaOH in method 5. This is the reason the properties of pigment prepared by method 5 are better than those of pigment prepared by method 4. At 40 °C and pH 7, it is favorable for preventing the formation of FeOOH and favorable for forming Fe_3O_4. These conditions are beneficial to the evolution from Fe(II) to Fe(III) as well and no more Fe(II) are left in solution. All Fe_3O_4 particles are produced almost at the same time, and the particles are regular and uniform with moderate size (50–70 nm) as shown in Fig. 3b, which suggests that the pigment will show a quality hiding power and high tinting strength. Therefore, the ideal adding way of the precipitant is method 4 or 5.

3.3. Reaction time

To study the effect of reaction time, a series of experiments was performed in different time durations ranging from 1.5 h to 7 h under the optimal experimental conditions: the total iron ion concentration in raw material was 0.6 mol/L, mole ratio of Fe^{3+}/Fe^{2+} was 1.16, NaOH concentration was 2.5 mol/L and temperature was 80 °C. The corresponding characteristic parameters are summarized in Table 1. It can be observed that the pigment is black in the time range from 3 to 6 h, but it is brownish black when reaction time is less than 3 h or more than 6 h. The average reflectance and oil absorption decrease with the increase of reaction time first, while increase when the time is longer than 5 h. The color change of pigment obtained with different time durations can be explained by the spectral reflectance curves as shown in Fig. 4 and the XRD patterns as shown in Fig. 5.

The mole ratio of Fe^{3+}/Fe^{2+} is 1.16:1 in raw material indicates that there is a large quantity of Fe^{2+} ions which should be oxidized to Fe^{3+} to reach the ratio 2:1 of Fe_3O_4. Obviously, the longer oxidation time will produce Fe_2O_3,

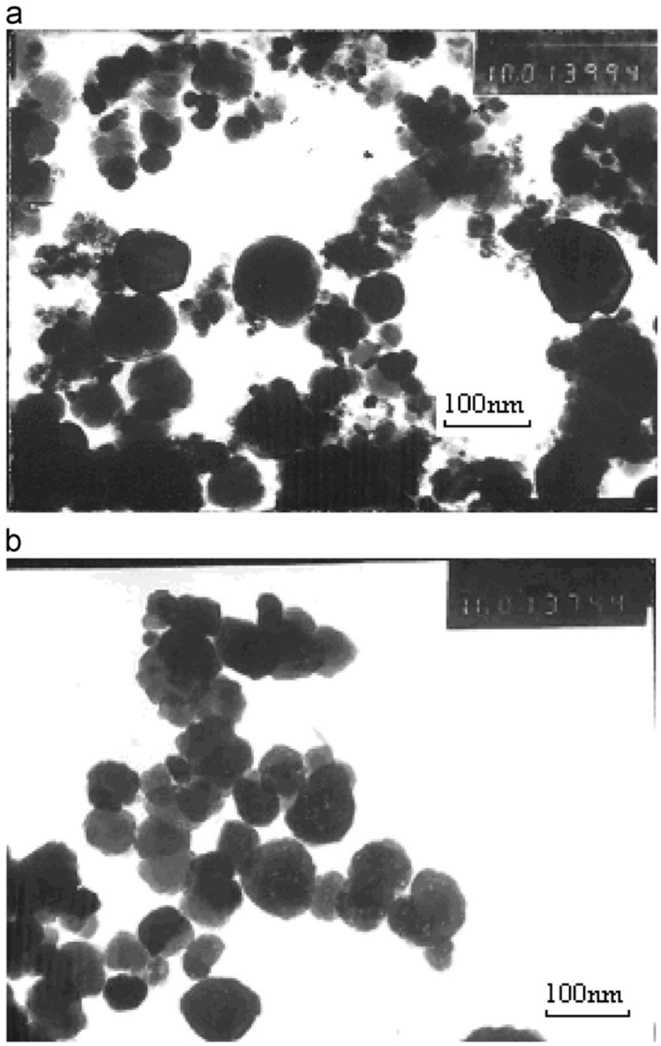

Fig. 3. TEM images of Fe_3O_4 pigment particles obtained by method 2 (a) and method 5 (b).

while short oxidation time cannot make Fe^{3+}/Fe^{2+} ratio meet the requirement of Fe_3O_4 formula. When the reaction time is shorter than 3 h, it does not have enough time for the oxidation of Fe(II) and so Fe(II) will exist in the final products. After drying, Fe(II) turns into FeO and then is oxidized to Fe_2O_3, which makes the pigment impure and shows a brownish black color. With the increase of reaction time, more Fe(II) can be oxidized to Fe(III), which makes the mole ratio of Fe^{3+}/Fe^{2+} in the product increase. When this ratio is about 2.0, the blackness of pigment is high with a low average reflectance and oil absorption. However, reaction time is too long to bring over-oxidation of Fe(II) and more Fe(III) in the product. As a result, the pigment shows the brownish black color.

The XRD patterns illustrated in Fig. 5 all have obvious diffraction peaks and match well with the standard Fe_3O_4 reflections. Fig. 5 shows the change of the intensity of diffraction peak and the half peak width of pigments obtained with different reaction times. Peak intensity decreases after showing a trend of increase first, and the half peak width decreases with the increase of reaction time. X-ray diffraction peak intensity reflects the degree of crystalline particles. The stronger the intensity of diffraction peak, the better the crystallization of particles. The half peak width reflects the size of the particles. The half peak width increases with particle size decrease. According to Fig. 5, when the reaction time is 2 h, the diffraction peak intensity is slightly weaker and the half peak width is slightly larger than 0.32. There is no time to grow for nuclei due to the short reaction time. Therefore, the particles formed are very fine with poor crystalline shape. And some Fe(II) were brought into products to lead to impure pigment with brownish black color. When the reaction time is 4 h, the diffraction peak intensity is the highest and the half peak width is 0.28 (spectrum 3) lower than spectra 1 and 2 (corresponding to 2 h and 3 h respectively), which indicates that the pigment is pure

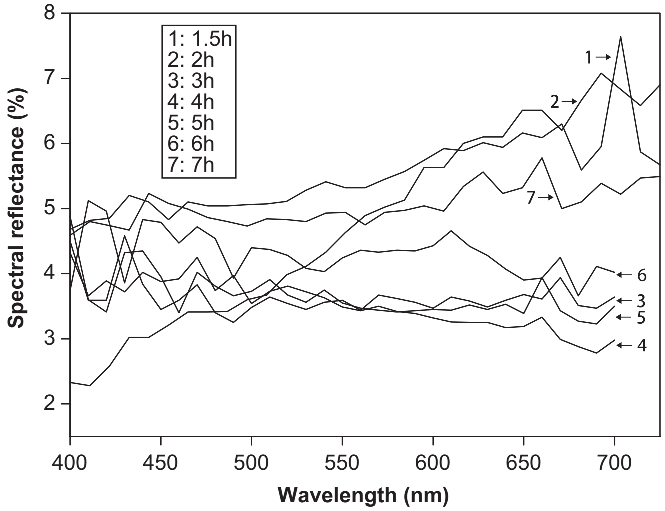

Fig. 4. Spectral reflectance curves of Fe_3O_4 pigment obtained in different reaction times.

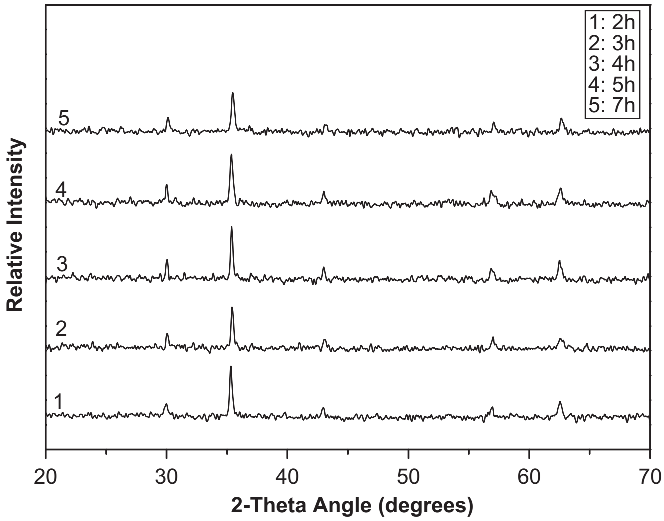

Fig. 5. XRD patterns of Fe_3O_4 pigments obtained in different reaction times.

Fe_3O_4 phase with better degree of crystallization and moderate particle size. When the reaction time is 6 h, the diffraction peak intensity is weaker than spectrum c and the half peak width is the smallest of 0.26. The reaction time of 6 h is favorable for the growth of grains with good crystalline shape but very large particle size and often causes color fade of the pigment owing to over-oxidation.

From Table 1, the oil absorption decreases with the reaction time increase firstly due to the increase of particle size, and then increases with the further increase of the reaction time due to the increase of space along with particle size increase. Taking into account all these parameters including average reflectance, oil absorption and the color, the optimum reaction time is 3–5 h. The Fe_3O_4 pigments obtained in this period of time have saturated blackness (average reflectance $<4\%$) and pure Fe_3O_4 phase.

3.4. Volume of air

The volume of air is another important condition which has significant effect on the composition and performance of the pigment as shown in Table 1. It can be observed that the average reflectance and oil absorption increase with the increase in ventilation time (ventilation rate 0.05 m^3/min). The ventilation time of 0 min indicates that air enters reaction solution naturally. The others need additional ventilation through the pump on the basis of natural air. The color of Fe_3O_4 pigment changes gradually from black to brownish black with the increase of ventilation time. The Fe_3O_4 pigments show the saturated black color when the ventilation time is 10 or 0 min. The spectral reflectance curves of the samples are given in Fig. 6.

From Fig. 6, the reflectance of spectra 4 and 5 is higher than 4% at low wavelength region of 400–580 nm, and it can be predicted that the pigments are a sort of russet black. Meanwhile, there is a higher reflectance of spectrum 5 at 600–700 nm, indicating that the pigment also has a little red color. The reflectance of spectrum 3 is slightly higher than 4% in the full wavelength range, and the pigment is mainly black with somewhat russet. The reflectance of spectra 1 and 2 is lower than 4% in the full wavelength range. Therefore, the pigment is pure with saturated blackness.

There are a lot of Fe^{3+} ions in raw material, which correspond to a part oxidation of Fe^{2+} ions, and the mole ratio of Fe^{3+}/Fe^{2+} can reach the ratio 2:1 of Fe_3O_4 within a short time. Less air is beneficial to the oxidation of Fe(II) and cannot cause over-oxidation of Fe(II). With the increase of ventilation time, the speed of oxygen transport increases and the oxidation rate of Fe(II) accelerates. This will lead to over-oxidation of Fe(II) and more Fe(III) in the products with some brown color. Therefore, in the reaction process, the Fe_3O_4 pigment prepared by a small amount of air is pure with low average reflectance and good oil absorption.

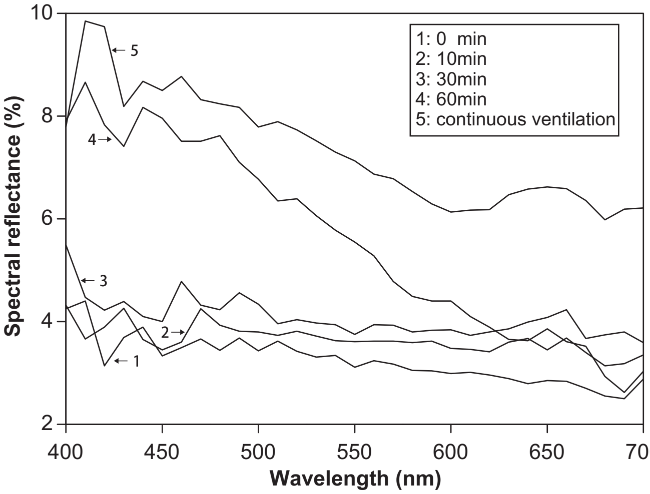

Fig. 6. Spectral reflectance curves of Fe_3O_4 pigment obtained by different ventilation times.

3.5. Formation mechanism of Fe_3O_4

The preparation of Fe_3O_4 could be largely affected by the technological conditions or the environment, because different products, including α-FeOOH, γ-FeOOH, Fe_3O_4, etc., would be obtained at different preparation conditions. The mechanism of evolution from $Fe(OH)_2$ to Fe_3O_4 had been described in previous papers [12–14]. On the basis of these studies, the mechanism of evolution from a mixed solution of ferrous and ferric sulfate to Fe_3O_4 with NaOH as precipitant was investigated in this paper.

When the precipitant was added to the mixed solution containing ferrous and ferric ions, the $Fe(OH)_3$ and $Fe(OH)_2$ precipitates were generated rapidly. $Fe(OH)_2$ precipitates could be easily and quickly oxidized to $Fe(OH)_3$ in the air; then the solution turned to green color, which was an intermediate amorphous form (known as green rust in alkaline solution) combined by the Fe^{2+}, Fe^{3+}, OH^- and SO_4^{2-} ions and this period was considered to be the formation and growth of seeds stage. In the amorphous aggregates, Fe^{2+} and Fe^{3+} ions were in the octahedron or tetrahedron coordinated by OH^- and SO_4^{2-} ions. These ions were not been fixed in the crystal lattice but in a semi-free state, and the substitution between ions was easy. When more alkaline solution was added, the increase of OH^- ions decreased the free Fe^{2+} and Fe^{3+} ions since OH^- ions could gather more Fe^{2+} and Fe^{3+} ions around them to convert into more amorphous aggregates. When all of the free Fe^{2+} and Fe^{3+} ions in solution were transformed into aggregates, OH^- ions added later would gradually replace the SO_4^{2-} ions in aggregates. The amorphous aggregates were very unstable and quickly changed into green rust. It was proven that the amorphous aggregate colloids formed were not $Fe(OH)_3$ and $Fe(OH)_2$ precipitates but their hydrates by means of modern analyzing and testing technology. Moreover, Fe_3O_4 particles were prepared not by reaction of $Fe(OH)_3$ and $Fe(OH)_2$, which could not be detected in the whole reaction process, but by conversion from green rust [15]. Molecular formula of green rust was not yet a unified conclusion. It was found that it was difficult to generate Fe_3O_4 from the mixture of $Fe(OH)_3$ and $Fe(OH)_2$ obtained in advance. With the change of reaction conditions, the green rust might be transformed into FeOOH or Fe_3O_4 or their mixture. The structure and composition of final products transformed from green rust were determined by many factors, such as temperature, concentration of solution, pH value, volume of air, impurities, etc. For instance, Fe(II) was easily oxidized into Fe(III), which would produce more FeOOH in dilute solution or in rich air.

Temperature and pH are the two most important ones among these factors. Under the condition of constant pH, further oxidation of green rust formed was governed by the temperature. At low temperature, Fe(II) could be oxidized to Fe(III) easily due to the low diffusion rate of Fe(II), so that the products were mainly FeOOH and $Fe(OH)_3$ precipitates. With the increase of temperature, the diffusion rate of Fe(II) increased gradually. When it reached a certain temperature, part of Fe(II) entered the lattice to produce some Fe_3O_4 phase owing to the faster diffusion rate of Fe(II). With the temperature increase, Fe_3O_4 content increased and FeOOH content decreased, and eventually the pure Fe_3O_4 pigment was formed at high temperature. At constant temperature, the diffusion of Fe(II) was slow due to the low concentration of Fe(II) precipitate in acidic solution, and it was beneficial to the oxidation of Fe(II) and the formation of FeOOH. Therefore, FeOOH and $Fe(OH)_3$ precipitates were the main products. The concentration of Fe(II) precipitate increased with the increase of solution pH. In alkaline solution, the diffusion rate of Fe(II) was high, partial Fe(II) ions had no time for oxidation and then entered the lattice to form Fe_3O_4. Overall, at pH value of above 9, green rust was converted into Fe_3O_4 at high temperature, and into α-FeOOH at low temperature [16]. Green rust would be converted into Fe_3O_4 at high temperature, and γ-FeOOH at low temperature in neutral solution. In this experiment, pH value of Fe^{2+} ions precipitated initially is 6.70 and pH value of Fe^{2+} ions precipitated completely is 8.95 when using the mole ratio of Fe^{3+}/Fe^{2+} 1.0:1. Hence, a high temperature of more than 50 °C and initial pH above 7 were favorable for the formation of Fe_3O_4. When the ratio was close to 2:1, it was necessary for solution pH to reach 9 by adding alkali once. Although a pH of 9 was helpful for the generation of Fe_3O_4, however it was helpful to prevent FeOOH generation due to the oxidation of Fe(II) [17].

The transformation process from amorphous aggregate to Fe_3O_4 could be analyzed from their structure. The amorphous aggregate was easily converted with aerial oxidation into green rust possessing the stacking of both hexagonal and cubic layer of oxygen. Along with the development of the reaction, the component of hexagonal close packing structure decreased and the component of cubic close packing structure increased until all green rust converted to cubic close packing structure. The nano-Fe_3O_4 has an inverse spinel structure, in which the oxygen atoms are also in cubic close packing. The same structure made green rust change to Fe_3O_4 successfully. Therefore, Fe_3O_4 nanoparticles could be prepared from BF flue dust.

4. Conclusions

The nano-Fe_3O_4 pigment was successfully prepared using a mixed solution of Fe(II) and Fe(III) ions obtained by leaching BF flue dust with sulfuric acid. The optimum technological parameters are as follows: reaction pH is 7, final pH is 9–10, the precipitant is added quickly to adjust pH to 7 after raising temperature to 40 °C, then to raise temperature to 80 °C and drop NaOH to keep pH 7 simultaneously, reaction time is 3–5 h, a small amount of air is better. The as-prepared iron oxide black pigment has a high blackness degree and pronounced magnetite structure and shows an average spectral reflectance lower than 4%, oil absorption lower than 25%, and narrow particle size distribution of 60–70 nm. The formation mechanism of Fe_3O_4 from a mixed solution of ferrous and ferric sulfate is explored and discussed. The temperature and pH play important roles in the structure and composition of final products transformed from green rust.

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