Production of Hematite Micro- and Nanoparticles in a Fluidized Bed Process—Mechanism Study†

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Abstract

A continuous, compact and simple process was developed to synthesize micro- and nanoparticles of iron oxide. The process combines the spraying (pulverization) of an aqueous solution of iron nitrate in a fluidized bed reactor containing coarse and hot glass beads (T = 200 °C) for the production of solids and a transported bed reactor for calcination (T = 490 °C). The intermediate product formed in the fluidized bed reactor is 2-line ferrihydrite, while the calcination reactor allows the production of hematite micro- and nanoparticles. These particles are characterized by a narrow size distribution, a mean size of 0.5 μm, a specific surface area of 24 m²g⁻¹ and a density of 4499 kg m⁻³. Particles are made up of small clusters of crystallites having an average size of 47 nm and a low internal porosity (0.12).

The reaction mechanism was studied using a muffle furnace and a lab convective dryer. It was found that several steps are involved leading first to the production of iron nitrate dihydrate after the removal of the solution water, as well as two and then five molecules of water of hydration. After that, the elimination of nitrate leads to the production of ferrihydrite. Finally, ferrihydrite is transformed into hematite due to the removal of residual nitrate and water of hydroxylation.

Keywords: hematite nanoparticles, ferrihydrite, fluidized bed, properties, mechanisms

1. Introduction

The production of nanometric particles is of great interest for various industrial sectors since they have attractive properties. In particular, magnetite, hematite and maghemite nanoparticles present interesting magnetic, electrical and optical properties. They are used for wastewater treatment, biomedical and catalytic applications, or as pigments for painting. Moreover, they are intensively investigated for applications in gas sensors, lithium batteries and cosmetic products.

Conventional processes for the synthesis of hematite nanoparticles, such as chemical precipitation (Lunin A.V. et al., 2019), hydrothermal synthesis (Zhu M. et al., 2012), forced hydrolysis (Wang W. et al., 2008), sol-gel (Pawar M.J. and Khajone A.D., 2012) and microemulsion (Housaindokht M.R. and Pour A.N., 2011), comprise numerous steps: precipitation and crystallization, filtration, washing, drying and dry grinding. All these operations need numerous devices which may lead to a high cost of production and may affect the reproducibility of the product properties. Other methods such as thermal decomposition (Glasgow W. et al., 2016) or spray pyrolysis (Ozcelik B.K. and Ergun C., 2015) were proposed as a continuous process. However, the production capability of some of them is limited.

In previous studies carried out in our laboratory (Pont V. et al., 2001; Hemati M. et al., 2003), fine particles were produced using a hot fluidized bed reactor containing coarse and hydrophobic beads with a diameter of over 500 μm. Aqueous solutions containing organic or inorganic salts were pulverized within the reactor. The solution was then dried at the contact of the hot beads, leading to the formation of nano- and microparticles which were then removed from the beads’ surface due to a strong mixing of the fluidized medium under the effect of the fluidizing gas. This operation led to the production of particles having a nature identical to that of the products in solution.

In the study presented here, we propose to add a step which allows transformation of the particles leaving the fluidized bed. For this purpose, we implemented calcination after the particles’ production in the fluidized bed, in order to produce hematite particles using a precursor solution of iron nitrate nonahydrate dissolved in water.

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The objectives are to characterize the products formed in the process, and to understand and analyze the various phenomena occurring in the generation and calcination reactors. The manner in which the particles are formed in the process is also explained. Finally, a mechanism is proposed, defining the different reaction steps appearing during the transformation of the iron nitrate solution.

2. Experimental

2.1 Equipment and procedures

2.1.1 Fluidized bed process

The process used in this study is presented in Fig. 1. The fluidized bed reactor is a vertical stainless steel column with an inner diameter of 0.1 m and a height of 0.5 m, filled up to half its capacity with 1.5 kg of glass beads (diameter = 1.4–1.6 mm) and topped by a conical freeboard section. This conical section is closed by a lid equipped with a guide tube for the introduction of a spraying system and an exit for evacuating gas and particles. The column is provided at its base with a vine box permitting air homogenization. The fluidization gas distribution is ensured by a distributor made up of a perforated stainless steel plate with a porosity of 2 %, under which a metallic grid of low opening is fixed, whose role is to prevent the fine particles from passing through the distributor. Before entering the bed, the fluidizing air flow rate is measured by means of rotameters and the air is preheated by an electrical heater (4 kW). The precursor solution (aqueous solution of iron nitrate nonahydrate) is stored in a reservoir placed on a balance in order to control the flow rate of the solution. It is drawn up by a volumetric pump from the reservoir to an internal mixing two-fluid spray nozzle (Spray System Co.). The atomizing gas (air) flow rate is controlled by a middle valve and measured by a rotameter. The atomizer is a downward facing nozzle and is located in the bed. The bed temperature is controlled by means of a PID regulator. Monitoring of temperature and pressure drop is achieved during operation.

A cyclone (0.09 m in diameter and 0.15 m in height), with a cut diameter of around 10 μm for the operating conditions used in this study, is placed at the fluidized bed reactor outlet. It allows recovering particles larger than its cut diameter (large solid particles or broken beads), while fine particles are entrained in the gas current towards the end of the process.

Then, the gas-particle suspension supplies a second reactor (calcinator). This reactor, made up of a heat resistant stainless steel tube (0.1 m in diameter and 1.7 m in length), is heated externally by an electrical furnace (8 kW). Prior to filtration, the suspension at the outlet of the calcinator is cooled at 150 °C by a cold air current to avoid any degradation of the filter. The filtration is carried out by a vibrated metallic sleeve filter containing four compartments, each of them including one cartridge. Iron oxide particles are recovered at the filter bottom. This filter was preferred to a cyclone because of its greater efficiency to arrest fine particles ($d_p > 0.3 \mu m$).

The experimental protocol is as follows. The fluidized bed reactor is charged with the glass beads and then closed. The bed is fluidized with preheated air, to reach the set point temperature. The second reactor is also heated and in parallel the cooling air is fed to its outlet side. In order to reduce the thermal disturbance caused by the liquid atomization, pure solvent (distilled water) is initially sprayed into the fluidized bed reactor at the same flow rate as the precursor solution. When the bed temperature returns to the set value, the distilled water is switched with the iron nitrate solution, and 1.5 kg of solution is
Partially dried into the reactor. Particles are recovered at the bottom of the cyclone and the filter and are maintained in a desiccator at ambient temperature before being analyzed.

The experiment was repeated 5 times with the same operating conditions in order to verify the synthesis reproducibility.

2.1.2 Muffle furnace

In parallel, solution samples (2 g with the same concentration as the solution used in the fluidized bed process) were placed in glass cups and heated for one hour in a muffle furnace kept at different temperatures (30, 50, 80, 100, 120, 130, 140, 150, 200, 250, 300, 400, and 500 °C).

After the treatment, the samples were removed from the furnace and weighed. Photos were taken and the products were immediately analyzed.

2.1.3 Lab convective dryer

For a better understanding of phenomena occurring at low temperatures, a lab convective dryer was used to dry solution samples at several fixed air temperatures up to 80 °C, which is the maximum temperature in this device.

Hot air flowed parallel to the surface of a sample holder having a disc shape covered by cotton, on which 7 g of solution with the same concentration as indicated above were deposited. The sample holder was placed on a sample port pipe. It was connected to a scale (Metler Toledo France, AT261, precision +/– 0.1 mg) in order to continuously register the sample mass, while an infrared pyrometer (Kheller, Cellatemp PQ13AF1, Germany) placed above the sample allowed the temperature of the sample surface to be measured in parallel.

A preliminary study showed that the air flow velocity has a significant effect on the drying kinetics for values lower than 0.5 m/s while the effect can be neglected for higher values. Thus, this parameter was fixed at 0.8 m/s.

2.2 Material characterization

The particles’ composition was characterized using Fourier transform infrared spectroscopy (FTIR TENSOR 27, Bruker Optic) and Raman spectroscopy (RAMAN D8 ADVANCE, Bruker). The crystalline structure was identified by X-ray powder diffractometry (D8 ADVANCE, Bruker). The average crystallite size of the samples, \( d_{X-ray} \), was calculated from X-ray diagrams according to the Debye-Scherrer equation:

\[
d_{X-ray} = \frac{k \lambda}{\beta \cdot \cos \theta}
\]

where \( \lambda \) is the X-ray wavelength (\( \lambda = 1.5418 \ \text{Å} \) in this study), \( \theta \), the diffraction angle for the (104) peak, \( \beta \), the peak width at mid-height and \( k \), the Scherrer constant, equal to 0.9.

The size distribution of the particles was measured by means of a dry laser granulometer MALVERN Mastersizer 2000 equipped with a Scirocco. Data were treated with the Mie theory in order to minimize artefacts at very small sizes. The particles were also observed using a scanning electron microscope (SEM-FEG JSM 7100F TTLS, JEOL). The particles’ real (skeleton) density was determined using a helium pycnometer (Micromeritics Accupyc 1330TC). Finally, the Brunauer-Emmett-Teller (BET) surface area, pore size distribution, pore volume and average pore diameter were measured using a multigas porosimeter ASAP 2010 M Micromeritics.

Analyses were repeated 3 times to control the reproducibility of the properties.

2.3 Precursor solution

The precursor used in this study was iron nitrate nonahydrate, \( \text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \), purchased from Sigma Aldrich France (purity ≥ 98 %, impurities: chloride, sulfate). The properties of this precursor are the following: mean diameter = 150 μm, molecular weight = 404 g mol⁻¹, solubility at 20 °C = 300 g/100 g water, melting point = 47.2 °C, boiling point = 125 °C and real density = 1684 kg m⁻³.

The precursor was dissolved in water to form a solution having a concentration equal to 66.7 wt%, i.e. 2 kg of iron nitrate nonahydrate per kg of distilled water, which is 89 % of the saturation concentration at 20 °C. The porosity and the density of this solution at 20 °C are \( 7.6 \times 10^{-3} \) Pa s and 1360 kg m⁻³, respectively.

3. Characterization of the materials produced in the process

3.1 Operating conditions

The operating conditions of the process were fixed as follows.

Concerning the fluidized bed and the calcinator temperatures, we analyzed the variation of the mass loss of the solution samples in the muffle furnace (Fig. 2).

Taking into account the slope changes, four steps can be defined:

- between ambient temperature and 80 °C, with a mass loss of 54.4 wt.%,
- between 80 °C and 130 °C, with a mass loss of 10.1 wt.%.
- between 130 °C and 150 °C, with a mass loss of 19.3 wt.%,
- between 150 °C and 500 °C, with a mass loss of 3.2 wt.%.
The zones correspond to different reactions that will be described later.

In order to ensure that the reactions of the three first steps occurred in the fluidized bed reactor, while the last step took place in the calcinator since it needs a high temperature, the fluidized bed and the calcinator temperatures were set at 200 °C and 490 °C respectively. After different attempts, the temperature of the generation reactor was fixed at 200 °C, i.e. a little above 150 °C, to be sure that the third reaction step was achieved before the particles left this reactor, since the residence time in the fluidized bed is shorter than in the muffle furnace. Thus, the first apparatus is the particle generation reactor where an intermediate material is produced, while the second one is the transformation reactor that the final material leaves.

The fluidization air flow rate was equal to 40 m$^3$/h at 200 °C, the corresponding velocity being equal to 1.6 times the minimum fluidization velocity of the beads which was determined at 0.84 m/s. The spraying air flow rate, fixed at 1.6 m$^3$/h at ambient temperature, was high enough in order to obtain a good dispersion of solution droplets within the fluidized bed. Finally, the mass flow rate of the solution was equal to 0.3 kg h$^{-1}$.

### 3.2 Intermediate material

The intermediate material is produced in the solid-generation reactor. Given the configuration of this reactor, particles cannot be directly sampled in the fluidized bed during experiment. Consequently we analyzed the product recovered at the cyclone bottom. Furthermore, to be sure that the product recovered at the cyclone bottom is representative of the product in the reactor, at the end of the experiment glass beads were removed from the reactor after the process was stopped, and the powder adhered to the beads was collected.

#### 3.2.1 Composition of the product

The intermediate powder, recovered at the cyclone bottom, was characterized by infrared spectroscopy, as well as the precursor (Fig. 3a).

Concerning the precursor, one can observe different absorption bands characteristic of nitrate at 825, 1384 and 1764 cm$^{-1}$, of OH stretching vibration at 3400 cm$^{-1}$, of H-O-H bending stretching vibration at 1635 cm$^{-1}$ and of atmospheric CO$_2$ at 2360 cm$^{-1}$.

![FTIR spectra](image)

**Fig. 2** Mass variation of the solution heated at different temperatures in the muffle furnace.

![Raman spectra](image)

**Fig. 3** Analyses of the products.  
- a) FTIR spectra  
- b) Raman spectra  
- c) X-ray diagrams
As for the product recovered at the cyclone bottom, similar bands are observed. However, the characteristic nitrate band at 1384 cm\(^{-1}\) is narrower than that on the spectrum of iron nitrate nonahydrate. In addition, three bands appear between 800 and 400 cm\(^{-1}\), respectively at 700, 570 and 460 cm\(^{-1}\), which are not present on the iron nitrate nonahydrate spectrum. These bands suggest that the product is ferrihydrite (Mazzetti L. and Thistlethwaite P.J., 2002). The product was also analyzed by Raman spectroscopy (Fig. 3b) and the spectrum confirms the nature of the intermediate product. Two forms of this product are mainly proposed in the literature: 2-line and 6-line ferrihydrites. They have similar FTIR and Raman spectra (Mazzetti L. and Thistlethwaite P.J., 2002) but different X-ray diffraction patterns (Majzlan J. et al., 2004). The first one shows two broad XRD peaks and the second one six XRD peaks. The intermediate product was also analyzed by X-ray diffraction (Fig. 3c). Two broad peaks are clearly observed at 34.7° and 62.4°, indicating that it is 2-line ferrihydrite that is produced in the generation reactor.

Finally, some powder fixed on the surface of the glass beads directly sampled in the generation reactor at the end of the experiment was analyzed by infrared spectroscopy and X-ray diffraction. The results confirm that 2-line ferrihydrite was also synthesized within the dry fluidized bed reactor and consequently did not undergo any transformation in the cyclone.

### 3.2.2 Structure and morphology

The powder collected at the cyclone bottom was analyzed with a laser granulometer and a scanning electron microscope. The particle size distribution of the powder is between 0.2 and 550 μm with a mean diameter (d\(_{50}\)) of 31.4 μm (Fig. 4). SEM micrograph of Fig. 5 shows that the powder is made up of:

- Large fragments with a size of several micrometers, on which small particles are agglomerated. These fragments constitute the population with sizes higher than the cut diameter of the cyclone (10 μm).
- Smaller particles with a size lower than the cut diameter of the cyclone. This population contains small microfragments and nanoparticles, and should not be stopped by the cyclone. Their presence in the sample taken at the cyclone bottom is due to a partial desagglomeration of small particles stuck on large fragments under the effect of the particles’ movements within the cyclone. These ephemeral agglomerates were formed according to Van der Waals or electrostatic forces.

These different particles populations are formed at the surface of glass beads during solid generation. SEM micrographs of a bead surface are presented in Fig. 6. One can observe particles with a size lower than 1 μm stuck on a compact deposit which is cracked.

To explain the presence of both small particles and solid film on these photos, Fig. 7 shows different schemes explaining the progressive behavior of the precursor solution pulverized on the beads.

During the generation step, the precursor solution is pulverized in the bed of coarse glass beads fluidized by hot air. When the beads pass under the spraying jet, a liquid film is formed around them (a). This thin film is then dried and decomposed, which leads to the formation of nanoparticles of intermediate product on the beads (b). Some of the particles are removed from the bead surface under a friction effect, either in an individual form or in the form of small agglomerates, and they leave the reactor with the air current (c). However, some particles remain adhered to the beads’ surface. Prolonged spraying of the precursor solution leads to a liquid deposition on the small particles remaining on the beads’ surface or between them (d). The transformation of the solution thus deposited leads on the one hand to a progressive filling of the interstitial spaces between the particles by other nanoparticles, and on the other hand to an increase of...
their size. These repeated phenomena allow the production of a solid film with a low porosity around the glass beads, and nanoparticles are deposited on this solid film, as it can be seen in Fig. 6. If all these steps are repeated throughout the experiment, the thickness of the solid film is increased (g). Under precursor transformations (drying and decomposition), the film is subjected to cracking, and collisions between beads weaken the solid phase which can be broken and form fragments.

Besides these explanations, one can also think that the residual moisture and the sticky nature of the intermediate solid phase deposited on the beads’ surface generate, during collisions, an instantaneous bonding between the beads at their contact points (solid bridge formation). The resistance of the bridges between the beads depends on the deformability of the solid film. Under the effect of the bed agitation created by fluidization, these contacts are broken, extracting a part of the solid bridges and thus forming large fragments. However, if bonding strengths exceed those of breakage imposed by the fluidized medium, the beads will stick to each other, the bed will form a block and fluidization will stop.

In this study, the production of nano- or microparticles in the fluidized bed reactor may be due to:
— Attrition caused by friction between the beads. This mechanism leads to the formation of nanometric particles that are removed from the film surface. These particles cannot be retained by the cyclone because of their small size and feed the calcination reactor;
— Partial removal of the solid deposit formed by bonding forces between glass beads. The solid bridges between the beads may be broken under the effect of the intense movement of the fluidized bed, causing a detachment of large fragments whose size is sufficient for them to be stopped by the cyclone;
— Cracking and fragmentation of the solid film deposited around the beads, due to collisions between them. Under a drying effect, the film can crack, which is observed in Fig. 6a, and fragments larger and more angular than fine particles can be released. Nanoparticles can stick on these fragments, most of them ranging in size from a few micrometers to several tens of micrometers. These fragments,

Fig. 6  SEM photos of a glass bead covered with powder at 4000× (a) and 25000× (b).

Fig. 7  Formation of a solid film and particles on the beads’ surface.
An example of which is shown in Fig. 5, are stopped by the cyclone.

In the generation zone of the process, four types of particles are formed: elementary spheroidal grains, small agglomerates of these grains, large and angular fragments, as well as these large fragments on which elementary grains are stuck. These two last populations of particles are mainly stopped by the cyclone, while the two first are essentially carried by the air flow towards the calcination reactor. Note that the size of the fragments can be modified by fragmentation or agglomeration caused by their interactions with the fluidized medium that can act as a ball mill.

3.2.3 Surface properties

The real density of the synthesized ferrihydrite was determined using helium pycnometry. It is equal to 3730 kg m\(^{-3}\) and is close to the value reported by Cornell R.M. and Schwertmann U. (2003) which is 3960 kg m\(^{-3}\).

Fig. 8a shows adsorption-desorption isotherms of the synthesized ferrihydrite. This product exhibits an isotherm of type II with a hysteresis, characteristic of a micro and mesoporous product. From this data, the surface area was determined at 83 m\(^2\) g\(^{-1}\). According to other works, the specific surface area of ferrihydrite depends on the synthesis method and ranges from 50 to 400 m\(^2\) g\(^{-1}\) (Cornell R.M. and Schwertmann U., 2003; Waychunas G.A. et al., 2005; Qi P. and Pichler T., 2014). The value for our product is in the lowest range. The pore size distribution of the particles is presented in Fig. 8b. Pore diameters vary between 3.3 and 20 nm with a mean diameter equal to 6 nm. Moreover, the pore volume is equal to 0.03 cm\(^3\) g\(^{-1}\). This latter value corresponds to a low internal porosity of 0.1. These results suggest that particles of the synthesized ferrihydrite are mesoporous.

3.3 Final material

3.3.1 Composition of the product

Fig. 3a shows not only the FTIR spectra of the precursor and the intermediate product, but also the spectrum of the final product, while its Raman spectrum is presented in Fig. 3b. These two spectra are those of hematite (\(\alpha\)-Fe\(_2\)O\(_3\)). In addition, the final product was analyzed by X-ray diffraction (Fig. 3c). All peaks are indexed to a rhombohedral crystalline phase of hematite (JCPDS card 33-0664). The average crystal size of the hematite nanoparticles was calculated from the dominant peak (104) at 2θ equal to 33.2\(^\circ\), using the Debye-Scherrer equation, and is equal to 47 nm. Zhu M. et al. (2012) synthesized hematite nanoparticles having a crystallite mean size of 51.4 nm by a hydrothermal method. As for Gurmen S. and Ebin B. (2010), they applied ultrasonic spray pyrolysis for the production of hematite particles. The crystallite size of their nanoparticles was between 18 and 33 nm, depending on the operating conditions.

3.3.2 Structure and morphology

The particles recovered at the process outlet were analyzed with a laser granulometer. Fig. 9 shows a narrow particle size distribution, between 200 nm and 2.1 \(\mu\)m, with a mean diameter \((d_{50})\) of 0.5 \(\mu\)m. Chin S.M. et al.
produced hematite particles through an auto-
combustion synthesis. The size distribution of their parti-
cles was multimodal, ranging between 0.6 and 450 μm.
The particles were made up of large agglomerates of
nanoparticles with a size from 60 to 140 nm. These au-
thors indicate that drying and dry grinding do not allow
individualizing nanoparticles. Ozcelik B.K. and Ergun C.
(2015) produced spherical α-Fe₂O₃ particles via spray py-
rolysis. Agglomerates of elementary particles were ob-
served with an average diameter between 315 nm and
1.16 μm, depending on operating conditions. The average
diameter of their elementary particles was between 70
and 320 nm. Tan W.-F. et al. (2014) obtained monodis-
persed hematite nanoparticles through chemical precipita-
tion. It was possible to control the morphology of the
α-Fe₂O₃ samples by the synthesis conditions, which
yielded spherical particles (diameter 50–80 nm) or elliptic
particles (diameter of 50–80 nm and length of 250–
300 nm).
A SEM micrograph of particles recovered at the filter
bottom is presented in Fig. 10a. They are made up of
spherical nanoparticles mostly individual or weakly ag-
glomerated, since the agglomeration tendency is low, un-
der the effect of interparticle forces. The smaller
elementary spherical particles are rather compact and
their surface is smooth, while the larger ones are nano-
structured. Concerning the small particles, one may sug-
gest that they are the result of fine droplets of spray
drying in the air before reaching the beads’ surface. As
for the nanostructured particles, the plastic character of
the precursor during its transformation is at the origin of
their formation.
The size distribution of the elementary particles was
determined using SEM images treatment, by analyzing
about 1000 particles (Fig. 10b). Half of the elements have
a size lower than 100 nm, which can be related to the ave-
rage crystal size (47 nm) calculated from X-ray diffraction
data in Section 3.3.1. As for the elements having a size
higher than 100 nm, one can consider that they corres-
dpond to the large nanostructured elements.

3.3.3 Surface properties
Helium pycnometry analysis was used to determine the
real density of the synthesized powder which is equal to
4499 kg m⁻³.
BET results (Fig. 11) show that:

- The adsorption-desorption isotherms curves are of type III, which is characteristic of a crystalline product with a low specific surface area. This one was determined from these data and equal to 24 m² g⁻¹.
- The total pore volume is equal to 0.03 cm³ g⁻¹.
- The pore size diameters are between 1.8 and 10 nm with a mean pore diameter of 6.5 nm.

From these results, an internal porosity, \( \chi \), of the formulated product equal to 0.12 was calculated using the equation:

\[
\chi = \frac{V_{\text{pore}}}{\frac{1}{\rho} + V_{\text{pore}}}
\]

(2)

where \( \rho \) is the real density of Fe₂O₃ nanoparticles and \( V_{\text{pore}} \) the specific total pore volume.

Taking into account this porosity and assuming that the agglomerates consist of spherical nanoparticles, the mean diameter of the nanoparticles was calculated by:

\[
d_p = \frac{6 (1 - \chi)}{S_{\text{BET}} \rho}
\]

(3)

This mean diameter is estimated at 47 nm and is similar to the crystal size determined in section 3.3.1.

These results suggest that the particles are agglomerates of crystallites. The low value of the internal porosity indicates that a particle can be considered as a consolidated granular medium whose pore network is the space between the crystallites. Indeed, the change in the physical state and the mechanical and thermal stresses exerted by the fluidized bed on the precursor during its transformation may be at the origin of the formation of spherical solid particles.

Housaindokht M.R. and Pour A.N. (2011), applying a microemulsion method, obtained a mean pore diameter in the range of 7.1–29.1 nm and a total pore volume of between 0.16 and 0.21 cm³ g⁻¹, depending on the operating parameters used in their study. Ahmad B. et al. (2013), using a biosynthesis method, found a lower pore size distribution, comprised between 3 and 15 nm with a total pore volume of 0.03 cm³ g⁻¹.

In the dry fluidized bed process used in this study, significant forces are imposed, which lead to the synthesis of spherical solid particles. These particles are constituted of agglomerates of crystallites held together by bonding forces. These agglomerates are rigid and ordered under the effect of external forces.

Regarding the production efficiency, it is equal to the ratio between the mass of the powder recovered at the filter bottom and the mass expected from conversion of the precursor injected into the process. For the operating conditions fixed in this study, it is about 75%. Indeed, a small amount remains in the fluidized bed (on the beads’ surface) while the main lost powder is stopped by the cyclone. This efficiency depends, on the one hand, on the surface properties of the glass beads, and, on the other hand, on the fluidized bed movement which is strongly impacted by the operating conditions. In particular, a higher fluidization velocity enhances the mixing of the beads in the fluidized bed, leading to a decrease of the solid film thickness around the beads and of the size of the fragments removed from the beads’ surface. This will be analyzed in detail in a further study.

4. Reaction mechanisms

To our knowledge, no study is presented in the literature on the reaction mechanism of the thermal decomposition of an iron nitrate solution. Few works based on thermogravimetric and differential thermal analyses were done on the mechanism of thermal decomposition of iron nitrate nonahydrate powder into hematite. However, the authors do not agree on the nature and the number of molecules removed during the first reactions, or on the intermediate material formed:

- Removal of 9 molecules of water to form anhydrous iron nitrate (Keely W.M. and Maynor H.W., 1963; Mu J. and Perlmutter D.D., 1982; Pereira Da Silva C. et al., 2018); 7 molecules of water (Gadalla A.M. and Yu H.F., 1990; Elmasry M.A.A. et al., 1998; Melnikov P. et al., 2014); 6 molecules of water and 1 molecule of nitric acid (Erri P. et al., 2004; Wieczorek-Ciurowa K. and Kozak A.J., 1999; Tong G. et al., 2010);
- Intermediate material: Fe₂O₃·3H₂O (Gadalla A.M. and Yu H.F., 1990), Fe(OH)₃ (Elmasry M.A.A. et al., 1998; Melnikov P. et al., 2014); 7 molecules of water (Gadalla A.M. and Yu H.F., 1990); FeOOH (Elmasry M.A.A. et al., 1998) or FeOOH (Erri P. et al., 2004; Wieczorek-Ciurowa K. and Kozak A.J., 1999; Tong G. et al., 2010).

Other authors suggested ferrihydrite as the intermediate material but they did not propose any reaction mechanism (Bødker F. et al., 2000; Oliveira A.C. et al., 2003; Rzepa G. et al., 2016). The reason may be that the ferrihydrite formula is not well defined.

The thermal decomposition of the solution of iron nitrate nonahydrate involves various reactions in four steps, as seen in Fig. 2. The study on the reaction mechanism is presented below.

The process configuration does not allow taking samples over time and at different temperatures within the solid generation reactor. In addition, setting the temperature of the fluidized bed at a value lower than 100 °C leads to a risk of caking of the bed due to a too slow drying of
the solution and creation of solid bridges between the beads. Consequently, it was decided to carry out the study using the muffle furnace. This work was completed by experiments carried out in the lab convective dryer described in Section 2, in order to define more precisely the phenomena occurring at temperatures lower than 100 °C.

4.1 Results obtained with the muffle furnace

The 13 samples heated in the muffle furnace at different temperatures were all analyzed by FTIR spectroscopy. Some spectra are presented in Fig. 12. The product obtained after the third step and the final product were also analyzed by X-ray diffraction (no diagram presented) to control that they are ferrihydrite and hematite, respectively. Moreover, some photos of the samples are shown in Fig. 13.

Studying the first step of the mechanism between ambient temperature and 80 °C, one can say from the two first photos and the two first FTIR spectra that the solution dries progressively as the temperature increases and its color changes. A solid film is formed at the sample surface. Since the two FTIR spectra are similar, no reaction occurs. Thus the mass loss of 54.4 wt.% of the initial solution sample is only due to the removal of water. This mass loss corresponds to the elimination of the water added to the precursor powder to make the solution, and of seven molecules of water of hydration of iron nitrate nonahydrate (dehydration). Consequently, after this step, the sample is made up of iron nitrate dihydrate.

Concerning the second step of the mechanism between 80 and 130 °C, the samples become pasty and brown. On the FTIR spectra, the width of the nitrate peak at 1384 cm⁻¹ is reduced, while three bands with a low intensity appear between 800 and 400 cm⁻¹. The calculated mass loss of 10.1 wt.% of the initial solution sample corresponds to the elimination of one molecule of nitrate.

As for the third step between 130 and 150 °C, with a mass loss of 19.3 wt.% of the initial solution sample, the nitrate peak on the FTIR spectrum becomes narrower, indicating that nitrate is still eliminated, and the bands between 800 and 400 cm⁻¹ continue to evolve, to come close to those of ferrihydrite. The samples are dark brown and under a powder form.

Finally, the fourth step ranges between 150 and 500 °C, with a mass loss of 3.2 wt.% of the initial solution sample. The powder color changes from dark brown to red. The nitrate peak has totally disappeared and the bands between 800 and 400 cm⁻¹ have significantly changed to match those of hematite. Thus the residual nitrate is removed, as well as the two last molecules of water, called hydroxylation water. During this step, ferrihydrite is transformed into hematite.

4.2 Results obtained with the convective dryer

During the first step in the muffle furnace, more than half of the solution mass is lost. In order to understand how the molecules of water are removed, the lab convective dryer described in Section 2 was used to dry the solution between 40 and 80 °C.

4.2.1 Water drying

A first series of experiments was performed with distilled water in order to have a reference. Fig. 14 shows the variation with time of the water mass, the temperature of

![Fig. 12 FTIR spectra of samples heated in the furnace.](image)

![Fig. 13 Photos of samples heated in the furnace.](image)
the water surface and the drying rate for an air temperature fixed at 80 °C.

Three zones are observed on the figure:

— Prior to 380 seconds, the water sample is heated by hot air, and its temperature increases rapidly. This leads to an increase in equilibrium vapor pressure (i.e. saturating vapor pressure). This first zone is called initiation period.

— Between 380 and 3000 seconds, the water temperature is constant and equal to 48.8 °C, the mass decreases linearly and the drying rate is constant. Water is evaporated, and the water molecules have a low binding energy. The evaporation enthalpy of water is due to the energy supplied by hot air. The partial pressure of water vapor at the surface of the wet cotton (equilibrium pressure) is that of the saturating vapor of water at the sample temperature. This second zone is called drying period at constant rate.

— Above 3000 seconds, when almost all the weakly bound water is eliminated, the cotton temperature increases rapidly to reach the set point value fixed at 80 °C. An increase in binding forces between the last water molecules and cotton, as well as a combination of convective transport and resistance of water transfer from the cotton inside to the surface lead to a decrease of the water partial pressure at the surface (equilibrium pressure), and consequently to a slowdown of the evaporation rate. The supplied heat is higher than that necessary for evaporation, and thus the temperature of the cotton surface increases to reach a new equilibrium state at which the cotton temperature becomes equal to that of the hot air. This third zone is called drying period at decreasing rate.

For other experiments on water drying, the air temperature was fixed at 40 and 53 °C. Similar curves were obtained, with a temperature of the cotton surface in the second zone at 27.8 and 34.8 °C respectively, i.e. the sample temperature increases with air temperature. Furthermore, when increasing this parameter, the drying rate is increased and the evaporation time is reduced.

4.2.2 Solution drying

The precursor solution was then dried at different air temperatures in the convective dryer. Fig. 15 shows the influence of this parameter on the mass and the temperature of the sample surface during drying.

Different points are added on the curves, defining the mass loss corresponding to the removal of the solution water, of the solution water + 2 molecules of water of hydration in iron nitrate nonahydrate, of solution water + 4 molecules of water of hydration, and of solution water + 7 molecules of water of hydration. This last point is present only for the two highest temperatures since it was not possible to reach this level at 40 and 53 °C.

Based on these results and on the evolution of the drying rates (curves not presented), it was possible to delimit...
5. Conclusions

Hematite nanoparticles were synthesized in a compact and simple process where a solution of iron nitrate nonahydrate was pulverized, dried and transformed in a fluidized bed reactor containing glass beads to produce particles that were then submitted to calcination in an entrained bed reactor. Different analytical techniques have made it possible to characterize the produced materials, to determine their properties and to propose a reaction mechanism.

An intermediate product called ferrihydrite is produced in the fluidized bed reactor. The product leaves the reactor in different forms: on the one hand a solid film which coats the beads is cracked during drying and is fragmented under the effect of high stresses caused by the movement of the fluidized bed, to generate micron-sized particles that are retained by the cyclone, and on the other hand nanoparticles that are removed from the glass beads’ surface to be entrained in the calcination reactor where they are transformed into hematite (α-Fe2O3). These particles are individual or hardly agglomerated. Their size distribution is narrow and monomodal (between 0.2 and 2.1 μm). The particles produced are small agglomerates of crystallites whose size is about 47 nm. They can be considered as a consolidated porous granular medium because of the low internal porosity (0.12).

The heat treatment of the solution of iron nitrate nonahydrate in a muffle furnace and in a lab convective dryer has allowed the proposal of a reaction mechanism defined in different steps. First, the water added to make the solution is lost as well as two molecules of water initially contained in the precursor. This elimination is rapid and leads to Fe(NO₃)₃·7H₂O. Then, five other molecules of precursor water are removed slowly to form iron nitrate dihydrate. These two steps occur below 80 °C. Between 100 and 200 °C, iron nitrate dihydrate is decomposed into ferrihydrite with the elimination of nitric acid and nitrate. These different steps take place in the fluidized bed reactor from which ferrihydrite particles are entrained by the
Fluidizing air. Finally, above 200 °C, ferrihydrite is transformed into hematite in the calcination reactor, with a removal of the residual nitrate and of hydroxylation water.

### Nomenclature

- $d_p$: Particle mean diameter (m)
- $d_{X-ray}$: Average crystallite size (m)
- $k$: Scherrer constant (–)
- $S_{BET}$: Specific surface area ($m^2 g^{-1}$)
- $V_{pore}$: Total specific pore volume ($m^3 g^{-1}$)
- $\beta$: Peak width at mid-height (m)
- $\theta$: Diffraction angle (°)
- $\lambda$: X-ray wavelength (Å)
- $\rho$: Real density (kg m$^{-3}$)
- $\chi$: Internal porosity (–)

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