

Extraction of Nanosized α -Fe₂O₃ Particles from Hematite Ore

Nagy M. Khalil¹⁺, Elhadi E. Saad¹ and M. M. S. Wahsh²

¹ Chemistry Department, Faculty of Science, Sebha University, Sebha, Libya.

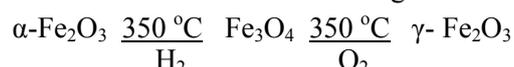
² Refractories, Ceramics and Building Materials Department, National Research Centre, Dokki, Cairo, Egypt

Abstract. This work aims at the extraction of nanosized α -Fe₂O₃ particles from hematite raw material widespread in south Libya using simple classical wet chemical method. The extracted iron oxide and the insoluble residue were investigated using XRD technique. Scherrer's equation was used to calculate the grain size of the extracted particles using the XRD data. The morphology of the extracted iron oxide was tested using SEM. About 96.80 % of the total iron oxide present in the raw sample could be extracted in the form of α -Fe₂O₃. The average particles size of the extracted α -Fe₂O₃ were less than 100 nm. The extracted nanosized α -Fe₂O₃ particles are considered as a promised material with great technological importance in the field of ceramic humidity sensors, catalysts, pigments, ferrofluid, recording systems...etc.

Keywords: Hematite, Composition, XRD, Nano- α -Fe₂O₃.

1. Introduction

In recent years the synthesis of nanosized α -Fe₂O₃ (hematite) is a matter of great interest of several research works [1-14] because of the use of this material as ceramic humidity sensors, [15-17] catalysts, [18, 19] pigments, [20] and as the raw material for the synthesis of γ -Fe₂O₃ (maghemite). This latter material has great technological importance as a ferrofluid and for its use in magnetic recording systems and magnetic pigments. [21-25] It is well known [19, 26] that maghemite is commonly synthesized through two consecutive steps of reduction and oxidation of hematite according to the following reactions:



According to a scientific research report carried in the Libyan Industrial Research Centre, [27] huge deposits of hematite ores are widespread throughout Libya especially in the south area (Sebha and surroundings e.g., Wadi Elshatti ...etc.), According to the recommendations of the Libyan Industrial Research Centre, these raw materials at these areas needs further research studies to evaluate their suitability for various possible industries.

This research work aims at studying the extraction of nano-iron oxide particles from local hematite ore using simple chemical method.

2. Materials and Experimentals

2.1. Materials

A hematite rock (about 5 kg) was selected from Wadi El-shatti area, South Libya for this investigation. Some laboratory chemicals namely dilute hydrochloric acid, and ammonia solutions were used for iron oxide extraction process.

2.2. Processing and Investigation of the Raw Hematite

⁺ Corresponding author. Tel.: +(00218925340147); fax: +(0021871627939).

E-mail address: saad_196410@yahoo.com

The selected hematite ore batch was processed through crushing in a jaw crusher, then ground in a porcelain ball mill with porcelain balls as grinding medium until they completely passed through a 75-micron standard sieve. To obtain representative samples, the batch was thoroughly hand mixed then divided into four equal portions; two of them from the opposite sides were removed while the two other portions were taken, hand mixed and quartered repeatedly until we finally obtained 50 g of the hematite ore batch. The representative sample was investigated for its mineralogical compositions using Infrared (IR) and X-ray diffraction (XRD) technique. IR spectra were recorded on a Perkin Elmer Model 337 Grating Spectrophotometer using KBr as the matrix. A Phillips PW1710 diffractometer with Ni filtered Cu-K α radiation operating at 30 mA and 40 kV was used for XRD testing. The chemical composition of the hematite ore batch was investigated through X-ray fluorescence technique using a BRUKER XRF 3400 instrument. The thermal behavior including thermogravimetric (TG) and differential thermogravimetry (DTG) of such sampl was also investigated using a thermogravimetric analyzer (Brand: Mettler Toledo, model: TGA/SDTA 851e), over a range of temperatures from room temperature up to \approx 1000°C.

2.3. The Iron Oxide Extraction Process

To 10 gm of the representative hematite ore sample about 100 ml of dilute HCl (1:9) were added with quiet stirring and gently heating for 30 minutes. The solution was filtered, washed several time with distilled water. The insoluble residue was fired at 700 oC for 1hr and investigated using XRD technique. To the filtrate 1:1 ammonia solution was added until the PH reaches 7 at which a brown precipitate is obtained. The precipitate was left aside to settle down then filtred, washed and fired at 700 oC for 1hr and investigated also using XRD technique. The extraction process is summarized in Fig 1. [28] The grain size was calculated from the broadening of the XRD peaks using Scherrer's equation:

$$D = (k \cdot \lambda) / (\beta \cdot \cos \theta)$$

Here β is the full width at half maxima of the XRD peak in radiant, θ is the reflection angle of the peak, k is a constant nearly equal 0.90, and λ is the wavelength of the diffracted X-rays.

The morphology of the extracted particles was tested using scanning electron microscope (SEM) (A Philips XL30 scanning electron microscope attached with an EDX unit with accelerating voltage 30 kv and magnification up to 20.000 x). The polished surfaces were then cleaned under water by ultrasonic before coating under vacuum with thin layer of gold for SEM investigation.

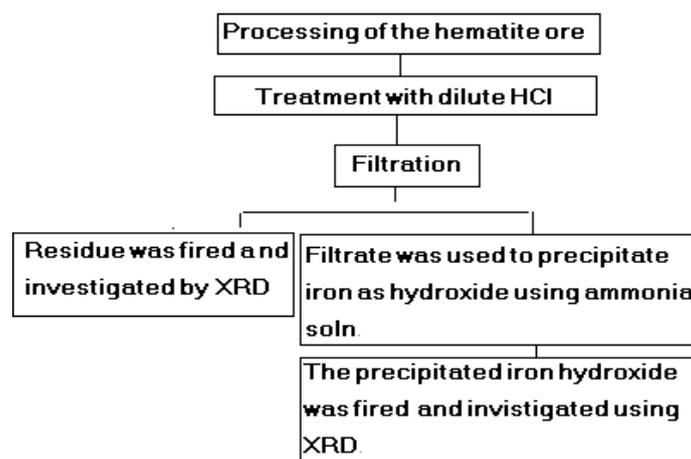


Fig. 1: Flowchart of the iron oxide extraction process

3. Results and Discussion

3.1. Mineralogical and Chemical Compositions of the Starting Raw Material

The mineralogical and chemical investigations of the selected hematite sample was studied in details in a previous work , it was concludes; the hematite ore present in Wadi El-shatti, South Libya is composed mainly of hematite mineral with some impurities of quart and kaolin. Nano-sized α -Fe $_2$ O $_3$ could be extracted from this hematite ore using simple chemical method, the efficiency of extraction was 96.80 %.

The extracted nano-sized $\alpha\text{-Fe}_2\text{O}_3$ is considered as a promised material in the field of nano-technological applications.

3.2. Chemical Detection of Ferric Ion in Solution

Table 1 indicates the classical chemical tests for qualitative detection of ferric ions in the filtrate resulting from dissolving the raw sample in dilute HCl and separation of the insoluble residue. All tests give were positive detection for ferric ions.

Table 1: Detection of Ferric Ions in Solution

Detection	Result
Filtrate + Sodium hydroxide.	Red precipitate
Filtrate + Pottasium ferrocyanide.	Dark blue Prussian color
Filtrate + Pottasium ferricyanide.	No precipitate, but green color with dilute soln. and black color with concentrated one.
Filtrate + Potassium thiocyanate.	Bloody red color soln.

The positive detections are explained by the following chemical reactions. [18]

- $\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe}(\text{OH})_3$
- $4\text{Fe}^{3+} + 3[\text{Fe}(\text{CN})_6]^{4-} \rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
- $\text{Fe}^{3+} + [\text{Fe}(\text{CN})_6]^{3-} \rightarrow \text{Fe}[\text{Fe}(\text{CN})_6]$
- $\text{Fe}^{3+} + 3\text{SCN}^- \rightarrow \text{Fe}(\text{SCN})_3$

3.3. Solid Phase Compositions of the Insoluble Residue and the Extracted Material

Fig 2 shows the insoluble residue XRD pattern in which only the main peaks characterizing quartz mineral could be detected while the peaks characterizing hematite mineral have disappeared, the reverse is true in Fig 3 showing the XRD pattern of the extracted material in which all peaks characterizing $\alpha\text{-Fe}_2\text{O}_3$ could be detected i.e., no peaks characterizing quartz or any other impurities could be detected which indicate the complete extraction of pure iron oxide ($\alpha\text{-Fe}_2\text{O}_3$ form). The percent of the extracted iron oxide was 45.60 wt. %, taking in consideration the its total percent in the raw sample (47.25 wt. %), the efficiency of $\alpha\text{-Fe}_2\text{O}_3$ extraction reaches 96.80 %.

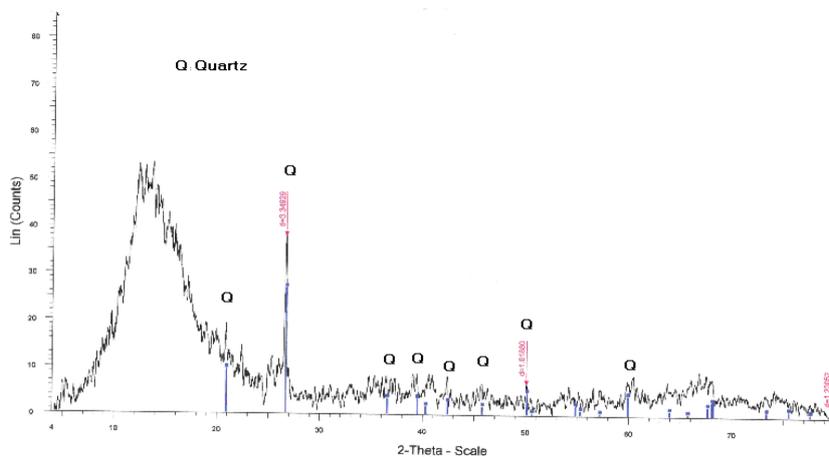


Fig. 2: XRD pattern of the insoluble material.

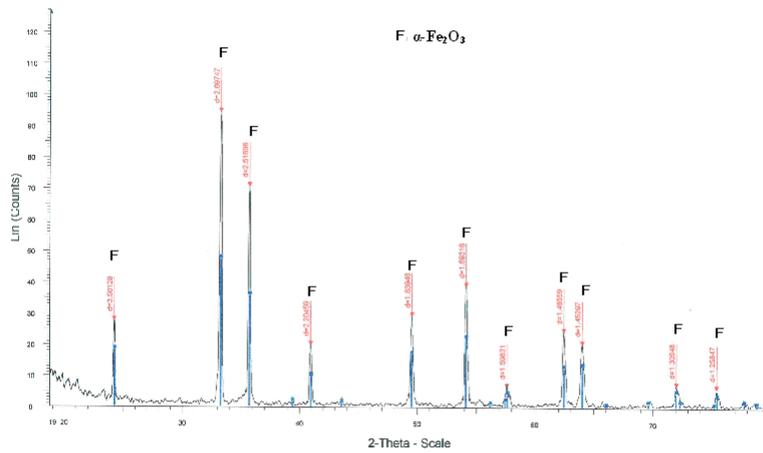


Fig. 3: XRD pattern of the extracted material.

3.4. Grain Size of the Extracted Ferric Oxide

Table 4 indicates the crystal size data of different particles of the separated α -Fe₂O₃. The average crystal size does exceed 100 nm which means that the extracted α -Fe₂O₃ particles belong to the field of nano-materials. Fig 4 shows the very small crystals of α -Fe₂O₃ that crystallize in the hexagonal form. Individual particles coalesced as a result of an increased area of contact between the particles. Pores between the particles diminished in size, and some of the pores completely disappeared as the region of contact between the particles enclosing a pore grew on heating. [29]

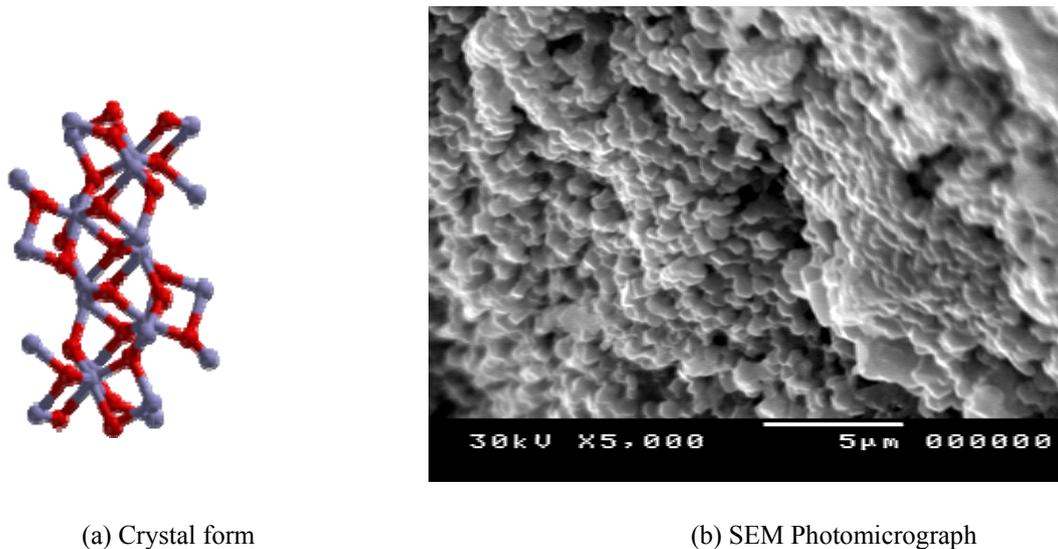


Fig. 4: Crystallography and SEM photomicrograph of the extracted α -Fe₂O₃.

4. Summary and Conclusion

Nano-sized α -Fe₂O₃ could be extracted from this hematite ore using simple chemical method, the efficiency of extraction was 96.80 %. The extracted nano-sized α -Fe₂O₃ is considered as a promised material in the field of nano-technological applications.

5. References

- [1] M. Žic, M. Ristić and S. Musić. The effect of temperature on the crystallization of α -Fe₂O₃ particles from dense β -FeOOH suspensions, *Mater. Chem. and Phys.* 2010, **120**: 160-166.
- [2] A.S. Madden, V.E. Hamilton, M.E. Elwood Madden, P.R. Larson, M.A. Miller. *Earth and Plan. Sc. Lett.* 2010,

298: 377-384.

- [3] M. Žic, M. Ristić and S. Musić. Effect of phosphate on the morphology and size of α -Fe₂O₃ particles crystallized from dense β -FeOOH suspensions. *J. Alloys Compd.* 2008, **466**: 498-506.
- [4] Sanc, S. Music, K. Nomura and S. Popovic. Microstructural properties of Fe-oxide powders obtained by precipitation from FeCl₃ solutions. *Mater. Sci. Eng.* 1998, **56**: 43-52.
- [5] S. Music, I. Czako-Nagy, I. Salaj-Obelić, N. Ljubeš. ⁵⁷Fe Mössbauer, FT-IR and TEM investigations of Fe-oxide powders obtained from concentrated FeCl₃ solutions. *Mater. Lett.* 1997, **32**: 301-305.
- [6] M. Žic, M. Ristić and S. Musić. ⁵⁷Fe Mössbauer, FT-IR and FE SEM investigation of the formation of hematite and goethite at high pH values. *J. Mol. Str.* 2009, **924-926**: 235-242.
- [7] S. Krehula, S. Musić. The influence of a Cr-dopant on the properties of α -FeOOH particles precipitated in highly alkaline media. *J. Alloys Compd.* 2009, **469**: 336-342.
- [8] M. Žic, M. Ristić and S. Musić. Microstructural changes in particles detected during the transformation from β -FeOOH to α -Fe₂O₃ in dense aqueous suspensions. *J. Alloys Compd.* 2008, **464**: 81-88.
- [9] S. Krehula, S. Musić. Influence of aging in an alkaline medium on the microstructural properties of α -FeOOH. *J. Crys. Grow.* 2008, **310**: 513-520.
- [10] S. Musić, S. Krehula, S. Popović. Thermal decomposition of β -FeOOH. *Mater. Lett.* 2004, **58**: 444-448.
- [11] C. Janzen, P. Roth. Formation and characteristics of Fe₂O₃ nano-particles in doped low pressure H₂/O₂/Ar flames. *Comb. Flame.* 2001, **125**: 1150-1161.
- [12] S. Musić, I. Czako-Nagy, I. Salaj-Obelić, N. Ljubešić. Formation of α -Fe₂O₃ particles in aqueous medium and their properties. *Mater. Lett.* 1997, **32**: 301-305.
- [13] S. Musić, S. Krehula, S. Popović; Z. Skoko. Some factors influencing forced hydrolysis of FeCl₃ solutions. *Mater. Lett.* 2003, **57**: 1096-1102.
- [14] S. Krehula and S. Musić. Influence of aging in an alkaline medium on the microstructural properties of α -FeOOH. *Journal of Cry. Grow.* 2008, **310**: 513-520.
- [15] L. A. Pe´rez-Maqueda, J. M. Criado, C. Real, J.S. ubrtb, J. Boha´cˇekb. Study of thermal evolution of porous hematite by emanation thermal analysis. *J. of Eur. Cer. Soc.* 1999, **22**: 2277-2281.
- [16] S. Gupta, D. French, R. Sakurovs, M. Grigore, H. Sun, T. Cham, T. Hilding, M. Hallin, B. Lindblom, V. Sahajwalla, Minerals and iron-making reactions in blast furnaces. *Prog. in En. & Comb. Sc.* 2008, **34**: 155-197.
- [17] M. Pelino, C. Colella, C. Cantalini, M. Faccio, G. Ferri and A. D'Amico. Microstructure and electrical properties of an α -hematite ceramic humidity sensor. *Sen. & Act. B: Cheml.* 1992, **7**: 464-469.
- [18] K.S. Tanwar, C. S. Lo, P. J. Eng, J. G. Catalano, D. A. Walko, G. E. Brown Jr., G. A. Waychunas, A. M. Chaka and T. P. Trainor. Surface diffraction study of the hydrated hematite($1\bar{1}02$) surface. *Surf. Sc.* 2007, **106**: 460-474.
- [19] H. Randall, R. Doepper, A. Renken. Modeling the dynamics of the N₂O reduction on Iron Oxide, *Catalysis Today.* 1997, **38**: 13-22.
- [20] C. Scherer and A. M. Figueiredo. Neto, Ferrofluids: properties and applications. *Brazilian Journal of Physics,* 2005, **35**: 718-727.
- [21] C. Sestier, M. F. Dasilva, D. Sabolovic, J. Roger, J. N. Pons. Surface modification of superparamagneticnanoparticles (Ferrofluid) studied with particle electrophoresis: application to the specific targeting of cells. *Electrophoresis* 1998, **19**: 1220-1226.
- [22] F. Gazeau, J. C. Bacri, F. Gendron, R. Perzynsky, Y. L. Raikher, V. I. Stepanov, E. Dubois. Factors Influencing the Texture and Stability of Maghemite Obtained from the Thermal Decomposition of Lepidocrocit. *J. Magn. Mater.* 1998, **186**: 157.
- [23] J. L. Dorman, D. Fiorani. Magnetic properties of fine particles, North Holland, Amsterdam, 1992.
- [24] M. P. Sharrok, R. E. Bodnar. An analysis of time dependent magnetization and coercivity and of their relationship to print through in recording tapes, *J. Appl. Phys.* 1985, **57**: 3919.
- [25] Y. Maeda, E.C.L. *Techn. Publ.* 1978, **179**: 1.

- [26] C. Cannas , A. Musinu , G. Navarra and G. Piccaluga. Structural investigation of Fe₂O₃-SiO₂ nanocomposites through radial distribution functions analysis. *Phys. Chem. Chem. Phys.* 2004, 6: 3530-3534.
- [27] E. Ebaid, S. Turkey. Geol. Report, *Industrial Research Centre.Tripoli. Libya.* 2004.
- [28] W. R. Fisher, U. Schwertmann. The formation of hematite from amorphous iron(III) hydroxide. *Clays and Clay Min.* 1975, 23: 33-37.
- [29] M. Usman, K. Hanna, M. Abdelmoula, A. Zegeye, P. Faure and C. Ruby, Formation of green rust via mineralogical transformation of ferric oxides (ferrihydrite, goethite and hematite). *Ap. Clay Sc., In Press, Corrected Proof, Available online 30 November.* 2011