Synthesis of Maghemite Pigment (γ-Fe_2O_3) from Lathe Waste Using Precipitation-Calcination Route

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Abstract. Lathe waste from iron craft industry encompassed high iron that potential to be ferric precursor to synthesize maghemite pigment. In this research work, maghemite pigment was synthesized by the precipitation-calcination method using the variation of temperature: 300, 350, 400 and 450oC. The XRD data indicated the formation of magnetite at precipitation stage and then transformed into maghemite after calcination. X-ray diffraction data showed that maghemite has a tetragonal structure with space group P43212. The result showed that the particle size of maghemite increase with increasing temperature. Based on the color parameter, maghemite synthesized at 350oC has the highest lightness. From the SEM-EDS data shows that maghemite has the distribution of particle size was not a uniform and still have impurities, such as carbon and Manganese.

Keywords: Maghemite; Pigment; Lathe Waste; Precipitation-Calcination Route

1 Introduction

Lathe waste is solid waste that generated from iron craft industries. Every day the quantity of 3-4 kg of lathe waste per industry was resulted [1]. The lathe waste has 97.11% iron content that contribute to environmental pollution [2]. One of the process to reduce these waste with treatment efficiency, low cost, and improve added value of waste is the synthesis of maghemite.

Maghemite (γ-Fe_2O_3) is a brown iron oxide with cubic or tetragonal structure [3][4] that rarely used to be pigment [5]. Maghemite pigment is a widely useful used in coating, construction materials [6][7] and other application, because have advantage including chemical stability, biocompatible, nontoxic, biodegradable, stable, and resistance at high temperature [2][8]. Many methods have been developed in synthesizing maghemite, such as hydrothermal [9], microwave-assisted reduction [10], ferrihydrite reduction [11], reduction-precipitation method [12], co-precipitation [13,14] precipitation-calcination [7][15], thermal decomposition [16], and sintering treatment [17]. Precipitation-calcination method is reproducible, simple, low cost, and large yield quantity of product [13][14]. In the calcination route, the structure, phase, particle size, and morphology of iron oxide depend on temperature [18][19][20][21].

In this work, maghemite was synthesized using the precipitation-calcination method using the variation in calcination temperature, in order to establish the composition of iron oxide pigment. The products are well characterized by various characterization techniques such as

ICONQUHAS 2018, October 02-04, Bandung, Indonesia

DOI 10.4108/eai.2-10-2018.2295571

the X-Ray Diffraction (XRD), color reader, and Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS).

2 Materials and Methods

2.1 Materials

All reagents used to synthesis were analytical grade and without further purification. Sulfuric acid (H_2SO_4), nitric acid (HNO_3), ammonium hydroxide (NH_4OH), and sodium hydroxide (NaOH) were purchased from Merck, Germany. Iron lathe waste used to synthesize were from Malang, Indonesia.

2.2 Methods

Ferrous (Fe2+) and Ferric (Fe3+) Precursors Preparation

In ferrous precursor (Fe^{2+}) preparation, 30 gr of a sample was mixed with 150 mL of dilute sulfuric acid for 24 hours. The greyish white slurry heated until dry.

The ferric precursor (Fe^{3+}) prepared by mixing 30 gr of sample with 300 mL of dilute nitric acid for 24 hours. The deep brown slurry heated until dry.

Synthesis of Maghemite Pigment (γ-Fe2O3) with Calcination Temperature Variations.

The synthesis was prepared by precipitation of ferrous and ferric precursors. Ferrous and ferric precursors (60 gr:30 gr) were dissolved into 540 mL of distilled water by stirring. After the pH ± 11 by adding NH_4OH, the reaction system kept 60°C for 90 minutes under vigorous stirring. After 24 hours, the black precipitates were separated and washed until the ammonia odor disappeared. The relevant chemical reaction below:

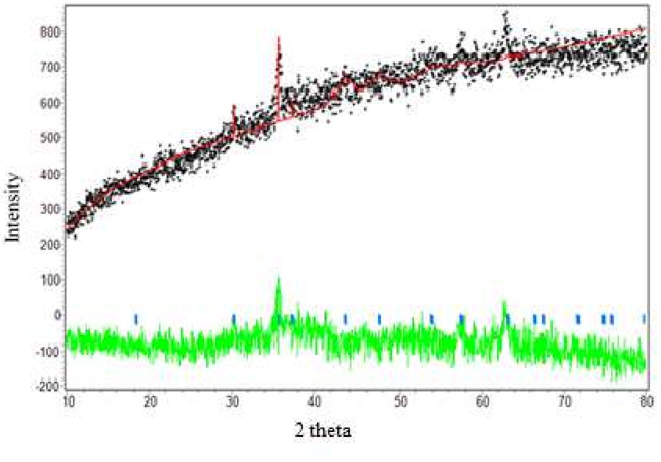


Fig. 2. XRD pattern of magnetite and maghemite

(1)

Then, the black precipitate was oxidized to maghemite in the furnace at 300, 350, 400 and 450°C for 3 hours. The reaction of maghemite formation was:

$$2Fe_3O_{4(s)} + \tfrac{1}{2} O_{2(g)} \qquad 3\gamma\text{-}Fe_2O_{3(s)} \tag{2}$$

2. 3 Characterizations

The X-rays diffraction (XRD) analysis were performed using a Cu Kα (1,5418 Å) source (40 kV, 40 mA) from Philip X-Pert to know structure and phase of the product. Crystallite size determines by Scherer formula. Color characteristics were analyzed using white Xenon lamp with D65 illuminate from Minolta CR-10. The Lightness (L*), green-red (a*) and blue-yellow (b*) parameters were analyzed using a color reader. Chroma (C*) and hue (H°) data calculated from a* and b*. The morphology of particle and composition product at an optimum temperature in this research was analyzed by the EVO® MA 10 BRUKER scanning electron microscope-energy dispersive x-ray.

3 Results and Discussion

3.1 A. X-ray diffraction

Figure 1 shows the XRD pattern of magnetite that obtained at precipitation stage. They matched well with the standard patterns of magnetite (*ICSD* 158505). The reflection of magnetite can be indexed in agreement with the expected cubic crystal with space group FD-3M has unit parameter cell a= 8.310964 (Å) with cell volume 574.055847 $Å^3$.

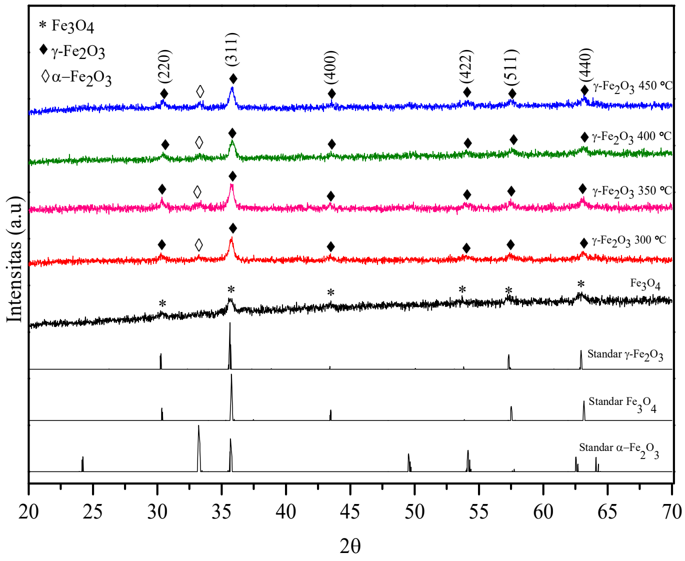


Figure 1. XRD pattern of maghemite (Fe_3O_4) obtained at precipitation stage

Magnetite transformed into maghemite after calcination (Fig. 2). Maghemite was successfully synthesized using this method and was highly crystalline. This result in accordance with reference [22] that magnetite can be transformed into maghemite after calcination 300°C. The reflections of all the variation temperature have an agreement with the standard pattern of maghemite (*ICSD* 87121). The reflection of maghemite revealed with tetragonal structure with space group $P4_32_12$ as predominant phase.

In addition, the differentiation between magnetite and maghemite were showed by crystal lattice data (Table 1). Magnetite has the lower lattice than maghemite. The lattice of magnetite has similar to magnetite's result on reference [23] that magnetite has a spinel structure. Based on refinement data by Le Bail refinement method, the increased temperature caused the lattice crystal decreased. Maghemite at 350°C has Rp, Rwp and x^2 (<4%) value lower than others, that indicated maghemite using calcination 350 °C the most similar with the standard.

Table 1. Difference Between Magnetite And Maghemite

Product	Crystal lattice (Å)		
	A	b	c
Magnetite	8.3109	8.3109	8.3109
Maghemite 300 °C	8.3453	8.3453	25.009
Maghemite 350 °C	8.3393	8.3393	24.977
Maghemite 400 °C	8.3241	8.3241	25.036
Maghemite 450 °C	8.3338	8.3338	25.033

Magnetite and maghemite have similar peaks position at 2θ with reflection peaks at 220, 311, 400, 422, 511 and 440. The most intense peaks were observed at 220, 311 and 440, which were compared with ICSD values. At the maghemite sample, there was a peak appears at 2θ (33) that correspond to hematite phase, that indicated using calcination with high temperature can affect nucleation of hematite. Hematite phase established is affected possible thermodynamically less stable due to the higher surface energy of the particle.

Table 2 shows the average crystallite size that evaluated by Scherrer's equations at the highest intensity peak (311 planes). Increasing temperature caused the increased crystal size, in contrast to crystal lattice was decreased. Increasing temperature causes the loss of grain boundaries when nucleating so that the crystallite size increases.

Table 2. Crystallite Size Of Products

Products	*kl*	rystallite size (nm)
Magnetite	11	4.94
Maghemite 300 °C	11	7.72
Maghemite 350 °C	11	1.20
Maghemite 400 °C	11	9.92
Maghemite 450 °C	11	1.20

Fig. 5. Value of a* and b* color space of

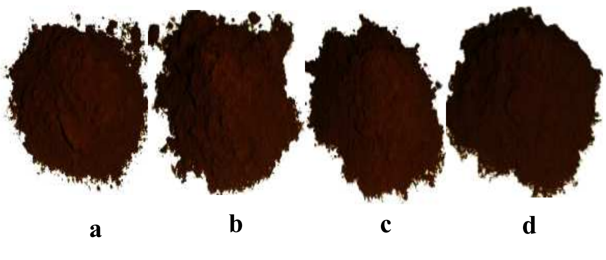
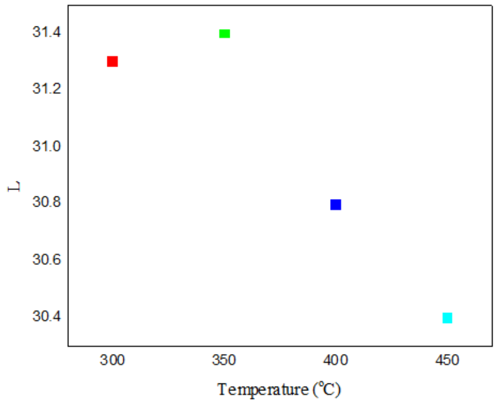


Figure 3. Visual aspect of Maghemite obtained at

3.2 Color Parameter

The visual aspect of maghemite has dark brown colored. The color parameter of maghemite in Fig. 4 have high positive of lightness. Maghemite synthesized at 350°C has the highest lightness level which occurs due to the highest particle size. The particle size decreases as increase the lightness (L*) level. The* (green-red) and b* (blueness-yellow) of maghemite have a positive value that shows maghemite have red and yellow composition. Fig. 5 shows maghemite obtained at 350°C has highest b*.

Figure. 4. Parameter of lightness of Maghemite



The chroma of maghemite at 350 and 400°C overly identically, due to the narrow differentiation of temperature. Based on hue (Fig. 6), maghemite products were not hue range of standard, but on hematite range, which occur due to hematite phase present, influenced by acid type at a formation of precursors process, and increased of temperature at calcination.

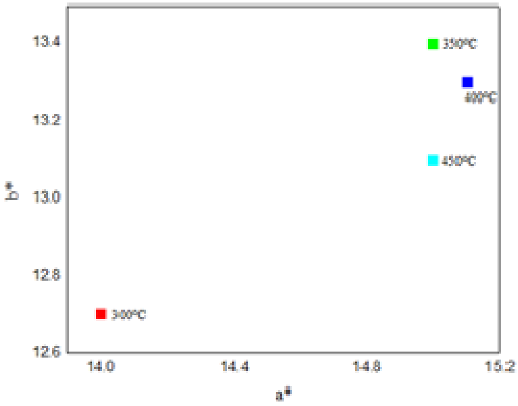


Figure 5. Value of a* and b* color space of Maghemite

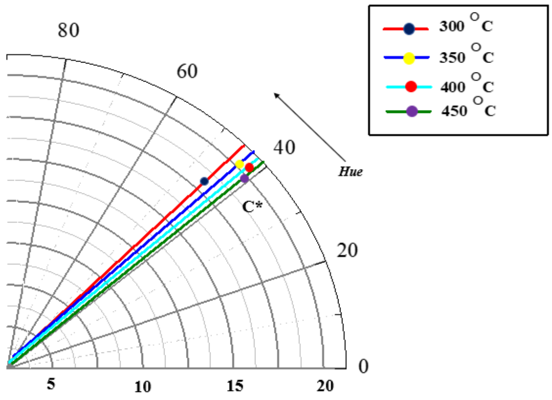


Figure 6. Color parameter (Chroma and Hue) of Maghemite

3.3 SEM-EDX

The shape and particle size distribution of maghemite were analyzed by scanning electron microscopy (SEM) as shown in Fig. 6. It is clearly observed maghemite particle have shape and size were not uniform. There are few large particles which are found to be aggregated, which may due long-range magnetic dipole-dipole interaction between particles.

The composition of maghemite was observed using EDS. The EDS data presented (Table 3) that maghemite from lathe waste has high iron and oxygen content. These results indicate the purity of the synthesis product. Although, there are impurities such carbon and manganese.

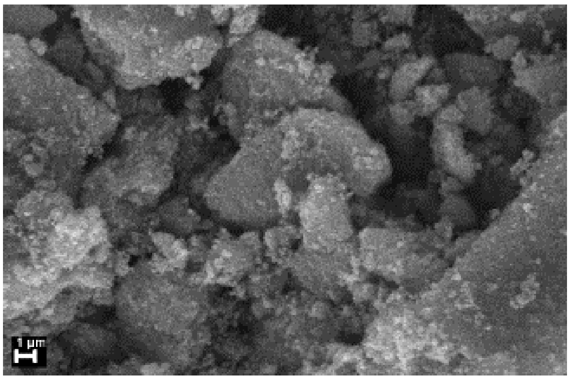


Figure 7. SEM Micrograph of Maghemite 350°C

Table 3. Composition of Maghemite 350°c

Element	Content (wt%)

Fe	74.5
C	3.06
Mn	1.19
O	21.16

4 Conclusion

Maghemite was synthesized from lathe waste using precipitation-calcination route have a tetrahedral structure with space group $p4_32_12$. Maghemite has identically brown color and the highest lightness achieved at 350°C. The morphology of maghemite was not uniform and there were impurities such as carbon and manganese.

Acknowledgements. We thank to iron oxide team. The sponsor of this research is PKM of Faculty of Science and Technology, UIN Maulana Malik Ibrahim Malang. This paper in conjuction with the 1st International Conference On Islam, Science, And Technology (ICONIST) 2018, Malang, East Java

References

[1] A. H. Abbas, "Management of steel solid waste generated from," *European Journal of Scientific Research,* vol. 50, no. 4, pp. 481-485, 2011.

[2] D. J. Pooja Shrivastava, "Reuse of lathe waste steel scrap in concrete pavements," *Pooja Shrivastava Int. Journal of Engineering Research and Applications ,* vol. 4, issue 12, pp. pp.45-54, 2014.

[3] D. J. Pooja Shrivastava, "Reuse of lathe waste steel scrap in concrete pavements," *Pooja Shrivastava Int. Journal of Engineering Research and Applications ,* vol. 4, issue 12, pp. pp.45-54, 2014.

[4] A. I. M. A. O. A. D. L. S. V. L. L. F. A. B. D. Juan Adrián Ramos Guivar, "Structural and magnetic properties of monophasic maghemite (γ-Fe_2O_3) nanocrystalline powder," *Advances in Nanoparticles,* vol. 3, pp. 114-121, 2014.

[5] Y. S. e. Y. e. Y. D. D. Y. Derya Aksu Demirezen, "Green synthesis and characterization of iron oxide nanoparticles using," *Journal of Bioscience and Bioengineering,* vol. xx no. xx, pp. 1-5, 2018.

[6] J. C. V. F. Q. M. D. M. Z. L. F. G. H. F. J. A. Marcelo Müller, "Synthesis and characterization of iron oxide pigments through the method of the forced hydrolysis of inorganic salts," *Dyes and Pigments,* vol. 120, pp. 271-278, 2015.

[7] S.-g. Z. D.-a. P. C.-c. C. Bo Liua, "Synthesis and characterization of micaceous iron oxide pigment from oily cold rolling mill sludge," *Procedia Environmental Sciences,* vol. 3, p. 653 – 661, 2016.

[8] M. L. R. J. K. B. B. S. S. A. a. A. J. M. T. N. Md. Saiful Quddus, "Synthesis and characterization of pigment grade red iron oxide from mill scale," *International Research Journal of Pure & Applied Chemistry,* vol. 16(4), pp. 1-9, 2018.

[9] A. S. S. B. P. N. S. M. K. a. R. T Saragi, "Synthesis and properties of iron oxide particles prepared by hidrothermal method," in *IOP Conf. Series: Materials Science and Engineering*, Sumedang, 2016.

[10] Z. W. T. Y. C. J. a. W.-S. K. Wei Wu, "Recent progress on magnetic iron oxide nanoparticles:synthesis, surface functional strategies and biomedical applications," *Sci. Technol. Adv. Mater,* vol. 16, 2015.

[11] X. W. a. Z. Z. B. Z. L. Y. X. Y. Genkuan Ren, "Characterization and synthesis of nanometer magnetite black pigment from titanium slag by microwave-assisted reduction method," *Dyes and Pigments,* vol. 147, pp. 24-30, 2017.

[12] Y. Z. Q. L. W. s. L. Y. P. h. W. L. S. Q. L. Y. W. Zheng Chen, "Maghemite (γ-Fe_2O_3) nanoparticles enhance dissimilatory ferrihydrite reduction by Geobacter sulfurreducens: Impacts on iron mineralogical change and bacterial interactions," *Journal Of Environmental Science,* pp. 4-14, 2018.

[13] A. k. D. M. A. A. j. Esmaeel Darezereshki, "Synthesis of magnetite nanoparticles from iron ore tailings using a novel reduction-precipitation method," *Journal of Alloys and Compounds,* vol. 749, pp. 336-343, 2018.

[14] R. a. S. Irwan Nurdin, "Stability of superparamagnetic maghemite nanoparticles suspension,," *Journal of Materials Science and Chemical Engineering,* vol. 4, pp. 35-41, 2016.

[15] V. G.-C. B. M.-M. C. L.-B. L. G.-C. E.M. Múzquiz-Ramosa, "Synthesis and characterization of maghemite nanoparticles for hyperthermia applications," *Ceramic International,* 2014.

[16] N. G. H. M. a. M. M. M. M. Nazari, "Synthesis and characterization of Hydroxyapatite nanopowders by chemical precipitation method," *J. Nanostructure Chem,* vol. 4, no. 2, p. 99, 2014.

[17] N. N. M. M. Aliahmad, "Synthesis of maghemite (g-Fe_2O_3) nanoparticles by thermal-decomposition of magnetite (Fe_3O_4) nanoparticles," *Materials Science-Poland,* vol. 31(2), pp. 264-268, 2013.

[18] I. Kazeminezhad and S. Mosivand, "Phase transition of electrooxidized Fe3O4 to y and a-Fe2O3 nanoparticles using sintering treatment," *Acta Phys. Pol. A,* vol. 125, no. 5, pp. 1210–1214, 2014.

[19] D. M. A. S. a. B. I. Lilik Miftahul Khoiroh, "Synthesis of hematite pigments (α-Fe_2O_3) by thermal transformations of FeOOH," *J.Pure App. Chem. Res. ,* vol. 2 (1), pp. 27-34, 2013.

[20] N. R. R. V. S. R. M. P. Bhavani, "Manipulation over Phase Transformation in iron oxide nanoparticles via calcination temperature and their effect on magnetic and dielectric properties," *IEEE Transactions on Magnetics,* 2017.

[21] K. K. A. Loganathan, "Effects on structural, optical, and magnetic properties of pure and Sr-substituted $MgFe_2O_4$ nanoparticles at different calcination temperatures," *Applied Nanoscience,* vol. Volume 6, no. Issue 5, pp. 629–639, 2016.

[22] K. W. B. M. M. M. D. Filipe Quadros Mariani, "Sustainable innovative method to synthesize different shades of iron oxide pigments," *Dyes and Pigments,* vol. Volume 137, pp. Pages 403-409, 2017.

[23] N. N. M. M. Aliahmad, "Synthesis of maghemite (g-Fe2O3) nanoparticles by thermal-decomposition of magnetite (Fe3O4) nanoparticles," *Materials Science-Poland,* vol. 31(2), pp. pp. 264-268, 2013.

[24] R. M. V. B. J. I. H. J. S. Veena Gopala, "Synthesis and characterization of iron oxide nanoparticles using DMSO as a stabilizer,," *Materials Today: Proceedings,* vol. 2, p. 1051 – 1055, 2015.