# إعداد مركبات أكسيد الألومينوم والحديد بالطريقة الترسيب وهلام التبخر مع توصيف

**\*فهميدا كولشان و\*\*كيوشي أوكادا**

\*قسم هندسة المواد والمعادن، جامعة بنغلاديش للهندسة والتكنولوجيا، دكا، بنغلاديش

\*\*مختبر المواد والهياكل، معهد طوكيو للتكنولوجيا، طوكيو، اليابان

## الخلاصـة

تم إعداد المركبات (Fe2O3-Al2O3) بطريقة الترسيب (CP) وهلام التبخر (GE) مع مكونات الحديد وأكسيد الألومنيوم في درجات حرارة عالية (300ºC-1000ºC). ومراحل البلورية في العينات تم تحديدها بواسطة طريقة (XRD)، والمعلمات الشعيرية لنتائج مراحل البلورية تم تحديدها بواسطة طريقة المربع الأقل. وأيضا تم توصيف الخصائص بواسطة قياسات المغناطيسية. وتشكيل مراحل البلورية (على سبيل المثال، المجماتيت، الهيماتيت)، ودرجة حرارة التحول، والخواص المغناطيسية لأكسيد الحديد كانوا جميعا يتأثرون بنسبة العنصر والمعالجة الحرارية.

# Preparation of alumina-iron oxide compounds by coprecipitation and gel evaporation methods and their characterization

Fahmida Gulshan* and Kiyoshi Okada**

*Materials and Metallurgical Engineering Department*

*Bangladesh University of Engineering and Technology, Dhaka, Bangladesh.*

**Materials and Structures Laboratory*

*AMDII division, Tokyo Institute of Technology, Tokyo, Japan*

*Corresponding author: fahmidagulshan@mme.buet.ac.bd*

## ABSTRACT

$Fe_2O_3$-$Al_2O_3$ compounds were synthesized by coprecipitation (CP) and gel evaporation (GE) method with different Fe/Al compositions and calcined at high temperatures (300°C-1000°C). The crystalline phases in the samples were determined by XRD, the lattice parameters of the resulting crystalline phases were calculated by a least-square method. The properties were also characterized by magnetization measurements. The formation of crystalline phases (e.g., maghemite, hematite), transformation temperature, magnetic properties of iron oxide were all affected by the component ratio and thermal treatment.

**Keywords**: Coprecipitation; $Fe_2O_3$-$Al_2O_3$ compounds; gel evaporation; hematite, maghemite

## INTRODUCTION

The pollution of wastewater and surface water by toxic ions and textile dyes has become a severe environmental problem. There are already some excellent adsorbents like zeolites, layered double hydroxides (LDH) for cations and anions respectively, but sorbents with simultaneous uptake abilities for both cations and anions are preferable for practical applications. Fe and Al hydroxides and oxides are well known to show high uptake abilities for anions and cations because of their amphoteric property. El-Sharkawy *et al*. (2000) prepared $Fe_2O_3$-$Al_2O_3$ compounds by coprecipitation and examined their catalytic activity, reporting that the texture, acidic properties and catalytic activitiy depended on the thermal treatment and $Fe_2O_3/Al_2O_3$ ratios of the compounds. Michel *et al*. (1951) prepared Al-substituted maghemits by oxidation of magnetite. They observed that the temperature in which the transformation to hematite takes place is increased from approximately 300C for the Al-free maghemite to 760C

for a highly substituted sample. The conclusion was that the addition of a foreign cation stabilizes the defective maghemite structure. Wolska & Schwertmann, 1989 also studied Al-maghemites prepared by thermal treatments of coprecipitated Al-Fe hydroxides. The cell parameter was observed to decrease from 0.834 nm to 0.831 nm for the sample with 10 mole% Al. Higher substitution caused no further decrease leading to the conclusion that the solubility limit of Al in $Fe_2O_3$ is close to 10 mole%. Another study of aluminium substituted maghemites was published by Filho *et al.* (1992). Four samples containing between 0 and 11mole% Al were prepared by oxidation of Al-maghemites at 250C in air. The cell parameter decreased from 0.8337 nm (0 mole% Al) to 0.8292 nm (11 mole% Al). Li *et al.* (2007) synthesized $Fe_2O_3$-$Al_2O_3$ compounds by a coprecipitation method and investigated their photocatalytic performance. The highest photocatalytic decomposition rate of bisphenol A molecules was observed at 90 mol% $Fe_2O_3$ composition, demonstrating the effect of Al incorporation. It is therefore of interest to investigate the effect of $Al^{3+}$ substitution for $Fe_2O_3$ in the $Fe_2O_3$-$Al_2O_3$ system on the removal of toxic ions and dyes from water by these compounds. Moreover iron oxide phases have good magnetic properties, suggesting the possibility of combining their adsorption properties with the magnetic separation of harmful components from a polluted system by applying a simple magnetic field. This could replace the common technology of filtration and centrifuge separation, and after magnetic separation, the harmful components could be easily removed from the magnetic particles that could then be reused.

The present investigation was carried on the effect of synthesis procedure, component ratio and thermal treatment conditions on the phase composition and structure, where the samples were prepared by CP and GE methods. The samples prepared were also studied for adsorption of toxic ions and photocatalytic activity in the decomposition of methylene blue: these parts are described in other papers (Gulshan *et al.,*2009; Gulshan *et al.*,2010).

## EXPERIMENTAL

Synthesis procedures of $Fe_2O_3$-$Al_2O_3$ compound by coprecipitation method and gel evaporation method are described in detail in the reference papers (Gulshan *et al.*, 2009; Gulshan & Okada, 2013). Coprecipitated gels were prepared with various ratios of 0.2 M $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ solutions using conc. $NH_4OH$ (25 mass%) as the precipitant. Samples containing 0, 20, 40, 60, 80 and 100 mol% $Fe_2O_3$ were prepared. For gel evaporation method, the starting materials (ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$) and aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$) were dissolved in ethylene glycol at a molar ratio of (total metal nitrates):(ethylene glycol)=1:3 with the addition of a minimum volume of water to dissolve the nitrates. Samples containing 0, 20, 40, 60, 70, 80, 90, 95 and 100 mol% $Fe_2O_3$ were prepared.

After drying, the powders were dry-ground in a planetary ball mill (LAPO-1, Ito Seisakusho Ltd., Japan) using a $Si_3N_4$ pot with 30 $Si_3N_4$ balls (5 mmφ) at 300 rpm for 3 hours with a ball: sample mass ratio of 30:1. After grinding, the samples were calcined at 300°-1000°C in air for 5 hours at a heating rate of 10°C/min.

## Characterization of samples

The crystalline phases in the samples were determined by XRD (XRD-6100, Shimadzu) using monochromated Cu Kα radiation. The lattice parameters of the resulting crystalline phases were calculated by a least-squares method using Si powder as the internal standard. The magnetic properties were examined using vibrating sample magnetization (VSM) equipment (BHV-50H, Riken Electronics).

## RESULTS AND DISCUSSION

The SEM pictures of the 40 mol% $Fe_2O_3$ GE and CP samples calcined at 500°C are shown in Figure 1. The GE sample was much smaller in particle size than the CP sample.
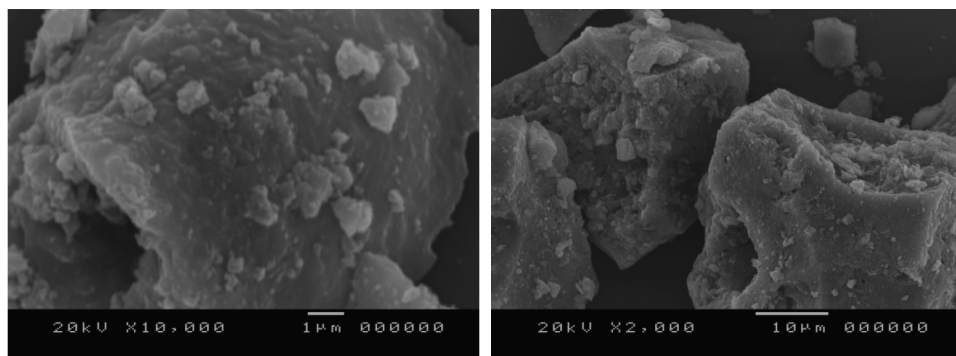


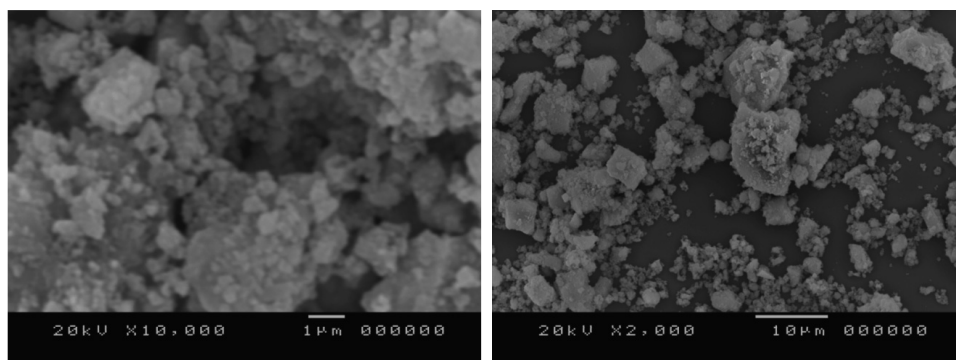**Fig. 1. (a)** SEM pictures of the 40 mol% $Fe_2O_3$ CP sample calcined at 500°C.



**Fig. 1. (b)** SEM pictures of the 40 mol% $Fe_2O_3$ GE sample calcined at 500°C.

## Phases formed by CP and GE method

After calcination at 300-1000°C, the crystalline phases in the calcined samples were identified from the X-ray diffraction patterns using the relevant ICDD data to investigate the structural changes caused by the thermal treatment and by changing the Fe/(Fe+Al) molar ratio. The phases formed at different compositions and heating temperatures are shown in field maps in previous papers (Gulshan *et al.*, 2009; Gulshan & Okada, 2013).

For both CP and GE samples effect of alumina was prominent on the phases formed. For example for CP samples in the Fe-rich region, $\gamma$-$Fe_2O_3$ is formed at 300°C to 600°C while $\alpha$-$Fe_2O_3$ and $AlFeO_3$ appeared >600°C. But In the Al-rich region, $\gamma$-$Al_2O_3$ is formed >500°C and $\alpha$-$Al_2O_3$ >900°C. From the field map of GE samples (Gulshan *et al.*, 2009), it can be seen that the crystallization of $\alpha$-$Fe_2O_3$ shifted gradually to higher temperature by increasing the alumina content, indicating the effect of alumina.

The lattice parameter values of $\gamma$-$Fe_2O_3$ and $\alpha$-$Fe_2O_3$, calculated by the least squares method, showed variation corresponding to the compositions. For CP samples the lattice parameter values (Table 1) of $\gamma$-$Fe_2O_3$ ($a = 0.8347$ nm) of the 100 mol% $Fe_2O_3$ sample calcined at 300°C is in good agreement with the reported value $a = 0.8352$ nm (ICDD card No. 39-1346). Increasing Al content results in a decrease of the lattice parameter values due to the substitution of the smaller $Al^{3+}$ (ionic radius ($r$)=0.0535 nm) for $Fe^{3+}$ (r=0.0645 nm) (Shannon, 1976).

**Table 1. (a)** Lattice constant [nm] of $\gamma$-$Fe_2O_3$

| Temp. [°C] | Fe/(Fe+Al)[mol%] | | | | | | |
|---|---|---|---|---|---|---|---|
| | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| 300 | | | 0.8287(11)* | 0.8311(40) | 0.8311(30) | 0.8336(9) | 0.83465(4) |
| 400 | 0.8280(52) | 0.8299(71) | 0.8302(10) | 0.8309(4) | 0.8327(5) | 0.8330(3) | 0.8358(30) |
| 500 | 0.8246(23) | 0.8299(22) | 0.8301(18) | 0.8311(10) | 0.8312(10) | 0.8329(10) | |
| 600 | 0.8.283(25) | 0.8297(22) | 0.8305(13) | 0.8300(30) | 0.8302(27) | | |

*The numbers in the parentheses represent the standard deviation in the last decimal places.

**Table 1. (b)** Lattice constants [nm] of $\alpha$-$Fe_2O_3$ .

| Temp [°C] | | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|
| | | Fe/(Fe+Al)[mol%] | | | | | | |
| 500 | *a* | | | | | | | 0.5032(2) |
| | *c* | | | | | | | 1.3741(2) |
| 600 | *a* | | | | | | 0.5023(3) | 0.5033(3) |
| | *c* | | | | | | 1.3712(2) | 1.3740(2) |
| 700 | *a* | 0.5019(14)* | 0.5022(4) | 0.5018(7) | 0.5024(9) | 0.5015(3) | 0.5021(4) | 0.5032(3) |
| | *c* | 1.3682(11) | 1.3696(3) | 1.3680(5) | 1.3713(6) | 1.3678(2) | 1.3704(3) | 1.3742(2) |
| 800 | *a* | 0.5011(16) | 0.5022(12) | 0.5004(17) | 0.5012(2) | 0.5008(19) | 0.5016(6) | 0.5028(13) |
| | *c* | 1.3648(12) | 1.3708(9) | 1.3662(7) | 1.3669(2) | 1.3653(6) | 1.3691(4) | 1.3719(10) |
| 1000 | a | 0.4990(13) | 0.5018(12) | 0.5008(9) | 0.5018(44) | 0.4999(9) | 0.5016(5) | 0.5028(13) |
| | c | 1.373(10) | 1.3695(9) | 1.3634(7) | 1.3608(33) | 1.3627(3) | 1.3687(4) | 1.3720(10) |

*The numbers in the parentheses represent the standard deviation in the last decimal places.

For GE samples, the lattice parameters of the Fe-rich samples (Table 2) decreased with decreasing $Fe_2O_3$ content up to 40 mol% $Fe_2O_3$ in samples heated at ≤800°C. The amount of $Al_2O_3$ estimated from the resulting lattice parameters was about 20 mol% in these samples. By contrast, the lattice parameters of the samples heated at 1000°C decreased in samples containing up to 90 mol% but became constant in the samples containing ≤90 mol% $Fe_2O_3$. The limit of $Al_2O_3$ incorporation in these samples is found to be ≤10 mol%, in fair agreement with Pownceby *et al.* (2003). Thus, the resulting data observed at ≤800°C appear to correspond to a transient state that attains equilibrium on heating at ≥1000°C.

The lattice parameters determined for Al-rich samples suggest that 10-20 mol% of $Fe_2O_3$ is incorporated in the $\gamma$-$Al_2O_3$ and $\alpha$-$Al_2O_3$ phases.

**Table 2.** Lattice constants (nm) of α-Fe$_2$O$_3$ in the various samples

| Temp [°C] | | Fe/(Fe + Al) [mol%] | | | | |
|---|---|---|---|---|---|---|
| | | 20 | 40 | 60 | 80 | 100 |
| 500 | a | | 0.4961(8)* | | | 0.50388(9) |
| | c | | 1.3630(62) | | | 1.3768(7) |
| 600 | a | | 0.49941(9) | | 0.50135(4) | 0.50498(30) |
| | c | | 1.3641(6) | | 1.3678(3) | 1.3815(23) |
| 700 | a | | 0.49970(43) | 0.50107(11) | 0.50150(13) | 0.50327(2) |
| | c | | 1.3579(32) | 1.3672(9) | 1.3691(10) | 1.3737(2) |
| 800 | a | 0.50167(15) | 0.50008(12) | 0.50113(22) | 0.50090(14) | 0.50344(1) |
| | c | 1.3702(12) | 1.3642(9) | 1.3675(17) | 1.3667(11) | 1.37360(6) |
| 1000 | a | 0.5009(30) | 0.50177(4) | 0.50237(19) | 0.50172(9) | 0.50368(4) |
| | c | 1.378(23) | 1.3682(3) | 1.3713(15) | 1.36848(7) | 1.3748(3) |

**\*** The numbers in the parentheses represent the standard deviation in the last decimal places
**Reference data** α-Al$_2$O$_3$: a=0.4758, c=1.2991 [ICDD No.10-0173]
α-Fe$_2$O$_3$: a=5.0356, c=13.7489[ICDD No. 33-064]

## Magnetic properties of the samples prepared by CP and GE methods

The saturation magnetization ($M_s$) values obtained for the samples prepared by GE methods with different Fe/(Fe+Al) molar ratios and subjected to different calcination temperatures are shown in reference paper (Gulshan *et al*., 2009).The increase of phase transition temperature (i.e. the stabilization of γ-Fe$_2$O$_3$) causes enhancement of γ-Fe$_2$O$_3$ content in their samples and increased the sample magnetization, thus, the addition of Al$_2$O$_3$ to Fe$_2$O$_3$ influences the magnetic property of these Fe$_2$O$_3$-Al$_2$O$_3$ compounds. The GE samples in the Fe-rich region contain high γ-Fe$_2$O$_3$ contents, showed high $M_s$ values (Maximum 61 emu/g) having the advantage of facilitating magnetic separation of the absorbent from solution at the completion of the adsorption process.

On the other hand, all the CP samples showed very weak saturation magnetization, <1 emu/g. The samples containing α-Fe$_2$O$_3$ solid solutions showed very weak hysteresis loops in the magnetization curves corresponding to the antiferromagnetic property of α-Fe$_2$O$_3$ and the magnetization was insufficient to attract these powders to a domestic magnet.

All these differences indicate that the synthesis procedure significantly affects the phase formation at different calcination temperatures.

## CONCLUSION

The synthesis procedure CP and GE influenced the phase formation at different calcination temperature. Also alumina addition had significant effect on phase formation, lattice parameter and magnetic property of iron oxide.

## REFERENCES

**El-Sharkawy, E.A., El-Hakam, S.A. & Samra, S.E. 2000**. Effect of thermal treatment on the various properties of iron (III) aluminum (ID) coprecipitated hydroxide systems. Materials Letters **42**(5) : 331-338.

**Filho, M.F.D.J., Mussel, W.D.N., Qinjan, Q. & Coey, J.M.D. 1992**. Proc. of the 6th Internt. Conf on Ferrites, Tokyo.**126**.

**Gulshan, F., Kameshima, Y., Nakajima, A. & Okada, K. 2009**. Preparation of alumina-iron oxide compounds by gel evaporation method and its simultaneous uptake properties for $Ni^{2+}$, $NH_4^+$ and $H_2PO_4^-$ . Journal of Hazardous Materials. **169**(1-3): 697-702.

**Gulshan, F., Yanagida, S. Kameshima, Y., Isobe, T., Nakajima, A. & Okada, K. 2010.** Photodecomposition of methylene blue by iron-oxides in an oxalate solution. Journal of water research **44**: 2876-2884.

**Gulshan, F. & Okada, K. 2013**. Preparation of alumina-iron oxide compounds by coprecipitation methods and its characterization. American Journal of Materials Science and Engineering **1** (1): 6-11.

**Li, F.B., Li, X.Z., Liu, C.S. & Liu, T.X. 2007**. Effect of alumina on the photocatalytic activity of iron oxides for bisphenol A degradation. Journal of Hazardous Materials. **149**: 199-207.

**Michel, A., Chaudron, G. & Benard, J. 1951**. Propriétés des composés ferromagnétiques non métalliques Journal of Phys Radium **12**(3):189-201.

**Pownceby, M.I. Constanti-Carey, K.K. & Fisher-White, M.J. 2003.** Subsolidus phase relationships in the system $Fe_2O_3$-$Al_2O_3$ -$Ti_2O_2$ . Journal of American Ceramic Society. **86**(6): 975-980.

**Shannon, R.D. 1976.** Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides Acta Crystallography. A32: 751-767.

**Wolska, E.&Schwertmann, U. 1989**. The vacancy ordering and distribution of aluminium ions in $\gamma$-$(Fe,Al)_2O_3$ .Solid state ionics **32/33**: 214-218.