

Ferrite grade iron oxides from ore rejects

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Abstract. Iron oxyhydroxides and hydroxides were synthesized from chemically beneficiated high $\text{SiO}_2/\text{Al}_2\text{O}_3$ low-grade iron ore (57.49% Fe_2O_3) rejects and heated to get iron oxides of 96–99.73% purity. The infrared band positions, isothermal weight loss and thermogravimetric and chemical analysis established the chemical formulas of iron-oxyhydroxides as $g\text{-FeOOH}\cdot 0.3\text{H}_2\text{O}$; $\alpha\text{-FeOOH}\cdot 0.2\text{H}_2\text{O}$ and amorphous FeOOH . The thermal products of all these were $\alpha\text{-Fe}_2\text{O}_3$ excepting that of $g\text{-FeOOH}\cdot 0.3\text{H}_2\text{O}$ which gave mainly $g\text{-Fe}_2\text{O}_3$ and some admixture of $\alpha\text{-Fe}_2\text{O}_3$. The hydrazinated iron hydroxides and oxyhydroxides, on the other hand, decomposed autocatalytically to mainly $g\text{-Fe}_2\text{O}_3$. Hydrazine method modifies the thermal decomposition path of the hydroxides. The saturation magnetization, J_s , values were found to be in the range 60–71 emu g^{-1} which are close to the reported values for $g\text{-Fe}_2\text{O}_3$. Mechanism of the $g\text{-Fe}_2\text{O}_3$ formation by hydrazine method is discussed.

Keywords. Ore rejects; chemical beneficiation; iron hydroxide; iron oxyhydroxide; ferrite.

1. Introduction

The ferrites, both hard and soft, find technological importance in ever expanding electronic industry and this is evident from the estimated world ferrite production (Ruthner 1989, 1997) of 5,16,000 metric tons per year (MTPY) in 1990 and 15,00,000 MTPY in the year 2005. The ferrite grade iron oxide, $\alpha\text{-Fe}_2\text{O}_3$, required for such a production of ferrites in year 2005 would be of about 10,50,000 MTPY. The ferrites production had been on rise ever since the commercialization of these took place some 60 years ago (Sugimoto 1999) and comparing with the world ferrite producing countries capacity (Ruthner 1989) the Indian contribution was mere 2% in 70s and 80s. And there is no significant improvement in the Indian ferrite production capacity, at present. India can certainly increase its ferrite production capacity, as we have huge iron oxide sources in our country. It is being estimated (Ruthner 1989) that the iron oxide required for such a huge production of ferrites would mostly come from the upgraded hematite ore and we have plenty of that sort of iron oxide sources. But, the Indian iron mine industry caters high-grade ore for the domestic steel industry requirements and export, and the highly mechanized industry discards the low-grade ore and tailings at the mining areas that are creating environmental problems. And, considering deteriorating mineral resources, it is high time that one should look into the low-grade ores to make them value added materials. We (Verenkar 1997; Sawant 1998; Rane *et al* 1999, 2000) have been making a modest effort to make use of these ore rejects to synthe-

size active pure iron oxides and from these ferrites to see the suitability of such iron oxide sources in ferrite industry, after chemical beneficiation.

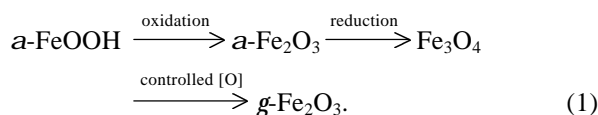
Advantages of chemically synthesized iron oxides are many as one can get (i) impurity free fine particles of high surface area and hence reactive and (ii) oxide of desired crystal structure. The need of high surface area fine particles in solid state reactions is well known and industrial process for achieving this is mechanical grinding. The necessity of desired crystal structure of the raw materials seems also essential in obtaining ferrite of good quality. We (Verenkar 1997; Sawant 1998; Rane *et al* 1999, 2000) observed the formation of low porosity single phase MgFe_2O_4 of uniform saturation magnetization, $4 pM_s \cong 1000\text{--}1150$ Gauss, from synthetic cubic iron oxide, $g\text{-Fe}_2\text{O}_3$ and cubic MgO at 1000°C . On the other hand, a high porosity and low $4 pM_s$ (609 G) mixed phase MgFe_2O_4 containing unreacted $\alpha\text{-Fe}_2\text{O}_3$ was obtained at 1000°C from the usual ferrite raw material of commercial grade hexagonal, corundum $\alpha\text{-Fe}_2\text{O}_3$.

The high reactivity of the synthetic $g\text{-Fe}_2\text{O}_3$ is no doubt due to their fine particles of nanometer size. But, the cubic structure of $g\text{-Fe}_2\text{O}_3$ may also be the reason for it to easily react with cubic MgO to give cubic spinel MgFe_2O_4 , while the hexagonal corundum $\alpha\text{-Fe}_2\text{O}_3$ may not react that easily. Solid state reactions are sluggish and several factors influence the reactivity such as particle size, gas atmosphere, and defect nature of the reactants. As compared to the hexagonal corundum $\alpha\text{-Fe}_2\text{O}_3$, the cubic $g\text{-Fe}_2\text{O}_3$ is a defect spinel with vacancies on the octahedral sites. The unit cell structure of $g\text{-Fe}_2\text{O}_3$ is represented as, $(\text{Fe}_8^{3+})_{\text{tetr.}}[\text{Fe}_{40/3}^{3+} \square_{8/3}]_{\text{oct.}}\text{O}_{32}$ and this defective iron oxide may have superior reactivity. The enhanced reactivity of $g\text{-Fe}_2\text{O}_3$ may also be viewed as due to its phase transfor-

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mation to α -Fe₂O₃ during the heat treatment in ferrite preparation. The g - to α -phase transformation takes place at $\sim 350^\circ\text{C}$. Certain solid state reactions are favoured (Rao and Gopalakrishnan 1997) if they are carried out at the phase transformation of one of the reactants (Hedvall effect); formation of CoAl₂O₄ is easier at the $g \rightarrow \alpha$ transition of Al₂O₃.

The use of g -Fe₂O₃ in the synthesis of ferrites giving superior magnetic properties in systems such as ZnFe₂O₄ (Huhn 1987), NiZn ferrites (Shrotri *et al* 1992), LiMn ferrite (Sano and Tamaura 1999) are in conformity with our own studies on MgFe₂O₄ (Verenkar 1997; Sawant 1998; Rane *et al* 1999, 2000). Having understood the effectiveness of g -Fe₂O₃ in ferrites synthesis we investigated different techniques to prepare the oxide easily, as the commercial manufacture of the oxide is a multi step process,



There are several methods of preparation of active iron oxide, α -Fe₂O₃, from precursors such as hydroxides, oxyhydroxides, carboxylates, etc. g -FeOOH on dehydration yields, g -Fe₂O₃, but the commercial g -Fe₂O₃ is a magnetic recording material of needle shape which is being synthesized from acicular α -FeOOH, as shown in (1). Since our requirement of g -Fe₂O₃ in ferrite synthesis is not of acicular one, any method which gives the oxide in fine size is good enough.

1.1 Hydrazine method

We adopted (Rane *et al* 1981) the decomposition of ferrous oxalate dihydrate precursor in a controlled moisture atmosphere to get g -Fe₂O₃ at $\sim 310^\circ\text{C}$. However, we found (Moye *et al* 1993) that the hydrazine complex of the ferrous oxalate decomposed autocatalytically at an ordinary temperature and pressure when a small portion was ignited with a burning splinter. The decomposition occurred instantaneously yielding mainly g -Fe₂O₃. Several ferrous carboxylato-hydrazinates were also found (Verenkar 1997; Rane *et al* 2001) to decompose autocatalytically to g -Fe₂O₃. Although g -FeOOH dehydrates at $\sim 300^\circ\text{C}$ to g -Fe₂O₃, the hydrazinated iron oxyhydroxide immediately catches fire when exposed to air yielding g -Fe₂O₃ of superior magnetic characteristics (Verenkar 1997) compared to the product of the un-hydrazinated g -FeOOH.

Hydrazine method of preparation of transition to rare earth metal oxides of spinel and perovskite structure is a novel way adopted (Ferrari *et al* 1966; Braibanti *et al* 1969; Sharov *et al* 1977; Patil and Pai Verenkar 1982; Ravindranathan and Patil 1987; Kikkawa *et al* 1995; Patil

et al 1997) to obtain fine nano metre sized reactive substances. We prepared active g -Fe₂O₃, NiZn/MnZn/Mg ferrites (Moye *et al* 1990, 1993; Verenkar 1997; Sawant 1998; Rane *et al* 1999, 2000) by hydrazine method. The MgFe₂O₄ synthesized from synthetic iron oxides (mainly g -Fe₂O₃) from iron ore rejects by the hydrazine method indicated superior magnetic and electrical properties as compared to the ferrite prepared from commercial grade α -Fe₂O₃. Here in this paper we discuss the novel hydrazine method of easy preparation of g -Fe₂O₃ from iron hydroxide and iron oxyhydroxides obtained from iron ore rejects.

2. Experimental

High SiO₂/Al₂O₃ = 2.56 low grade iron ore (57.49% Fe₂O₃) rejects were extracted with acid and precipitated as iron hydroxide and iron oxyhydroxides: g -FeOOH, α -FeOOH and amorphous FeOOH using precipitants (Verenkar 1997; Sawant 1998) such as NH₃, NaOH, NaOH + NH₃, and Na₂CO₃. The thermal products at $\sim 300^\circ\text{C}$ of all these hydroxides yielded 96–98% pure iron oxide, α -Fe₂O₃, excepting g -FeOOH which transformed into mainly g -Fe₂O₃ and partly α -Fe₂O₃. Also a solvent extraction method using methyl iso-butyl ketone (MIBK) was adopted to get 99.73% pure iron oxide. The chemical beneficiation reduced the SiO₂/Al₂O₃ ratio to 0.02.

2.1 Hydrazine method

The iron hydroxide and oxyhydroxides were then equilibrated with hydrazine by storing them on a petri dish over hydrazine hydrate, N₂H₄·H₂O (99%), in a desiccator for 4–5 days. On exposure to ordinary atmosphere they all autocatalytically decomposed to iron oxides, mainly g -Fe₂O₃.

2.2 Analysis

Chemical analysis of iron was done by standard method. Pycnometric density measurements were done in CCl₄. Infrared band positions were detected on Shimadzu FTIR instrument, model 8101A. Isothermal weight loss of the hydroxides and iron oxyhydroxides was established in a muffle furnace. Thermogravimetric analysis was done on Rigaku TAS 1000 instrument in N₂ atmosphere. The X-ray diffraction patterns of all oxide products were obtained on Rigaku DMAX II using Cu and Fe targets. Saturation magnetization values, J_s in emu g⁻¹, of all oxide products were measured using an alternating current high field hysteresis loop tracer (Likhite *et al* 1965) supplied by M/s Arun Electronics, Mumbai, India. Pure nickel (99.9%) was used as a standard. Scanning electron microscopic (SEM) studies done on Cambridge Stereoscan

S 250 MK III were used to find out the particle size distributions in the final oxide products.

3. Results and discussion

3.1 Phase identification

The d_{hkl} values of all oxide products were compared with the JCPDS files: 24–81 and 25–1402. All were found to be mainly $g\text{-Fe}_2\text{O}_3$ as shown in table 1. The X-ray diffraction (XRD) pattern of one representative sample of $g\text{-Fe}_2\text{O}_3$ obtained from autocatalytically decomposed hydrazinated $g\text{-FeOOH}$ and one standard commercial $g\text{-Fe}_2\text{O}_3$ is shown in figure 1. The detailed d_{hkl} values of all other samples are tabulated in table 1. A thermal dehydration of the unhydrazinated $g\text{-FeOOH}$ gives $g\text{-Fe}_2\text{O}_3$ the XRD pattern of which, however, is similar to figure 1, but with few extra peaks (table 1) attributing to the presence of $\alpha\text{-Fe}_2\text{O}_3$ along with the main product $g\text{-Fe}_2\text{O}_3$. $\alpha\text{-FeOOH}$ dehydrates in air to give $\alpha\text{-Fe}_2\text{O}_3$, while the hydrazinated iron oxyhydroxide decomposes to form a mixture of $g\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$.

The hydrazinated amorphous FeOOH autocatalytically decomposes to $g\text{-Fe}_2\text{O}_3$, while the unhydrazinated one dehydrates into $\alpha\text{-Fe}_2\text{O}_3$. Thus the hydrazination method yields easily $g\text{-Fe}_2\text{O}_3$ from iron oxyhydroxides.

3.2 Magnetic characterization

The saturation magnetization values, J_s , for all these oxide products were obtained from the high field hysteresis loops using Ni as a standard and a representative loop of

$g\text{-Fe}_2\text{O}_3$ prepared from the autocatalytic decomposition of hydrazinated $g\text{-FeOOH}$ is shown in figure 2. The figure also shows the detailed J_s values in emu g^{-1} of all the oxide products that fell in the range 2.36–71.65 emu g^{-1} . The saturation magnetization, J_s of 71.65 emu g^{-1} was observed for $g\text{-Fe}_2\text{O}_3$ prepared from the autocatalytically decomposed hydrazinated $g\text{-FeOOH}$ and the value is close to the reported (Khalafalla and Morrish 1972) value of 71–74 emu g^{-1} . The mixture of $g\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ obtained by heating $g\text{-FeOOH}$ in air amounts to lower J_s value of 19.20 emu g^{-1} and this suggests that the hydrazine method produces single phase $g\text{-Fe}_2\text{O}_3$ of better magnetic character.

$\alpha\text{-FeOOH}$ in air decomposed to a non magnetic $\alpha\text{-Fe}_2\text{O}_3$ and it showed J_s value of 2.36 emu g^{-1} , while the mixed products $g\text{-Fe}_2\text{O}_3 + \alpha\text{-Fe}_2\text{O}_3$ obtained from autocatalytically decomposed hydrazinated $\alpha\text{-FeOOH}$ showed an increased J_s of 16.03 emu g^{-1} , suggesting that the hydrazine method modifies the decomposition path of the oxyhydroxide. The thermal product of amorphous FeOOH showed a low J_s of 2.46 emu g^{-1} which means the formed oxide product was $\alpha\text{-Fe}_2\text{O}_3$, but the hydrazine method yielded a product, $g\text{-Fe}_2\text{O}_3$ of high J_s of 60.14 emu g^{-1} . These results are in conformity with the X-ray phase analysis (table 1). The J_s values in the range of 50–74 emu g^{-1} were also observed (Coey and Khalafalla 1972; Khalafalla and Morrish 1972) for $g\text{-Fe}_2\text{O}_3$ synthesized from different techniques and hence our values in the range 60–71 emu g^{-1} for the oxide from $g\text{-FeOOH}$ and amorphous FeOOH by hydrazine method suggest that the hydrazination modifies the thermal decomposition path of these oxyhydroxides.

Table 1. X-ray data of iron oxides obtained by autocatalytic decomposition of hydrazinated iron oxyhydroxides and $g\text{-FeOOH}$ in air.

$g\text{-Fe}_2\text{O}_3^*$	D	–	2.95	2.78	–	2.51	2.09	–	1.70	1.60	1.47	1.27
Tetragonal	I/I_0	–	30	13	–	100	15	–	19	20	40	08
$g\text{-Fe}_2\text{O}_3^*$	D	–	2.95	2.78	–	2.52	2.08	–	1.70	1.61	1.48	1.27
Cubic	I/I_0	–	30	19	–	100	24	–	12	33	53	11
Fe_3O_4^*	D	–	2.97	–	–	2.53	2.09	–	1.71	1.61	1.48	1.28
	I/I_0	–	30	–	–	100	20	–	10	30	40	10
$\alpha\text{-Fe}_2\text{O}_3^*$	D	3.66	–	–	2.69	2.51	2.20	1.84	1.69	–	1.45	–
	I/I_0	25	–	–	100	50	30	40	60	–	35	–
$g\text{-FeOOH}$ (in air)	D	–	2.94	2.78	2.70	2.52	2.08	1.83	1.70	1.60	1.47	–
Decomp.	I/I_0	–	47	58	62	99	30	45	45	34	35	–
$g\text{-FeOOH}$	D	–	2.96	2.78	–	2.52	2.09	–	1.70	1.61	1.48	1.27
Hydrazinate/ autocatalytic	I/I_0	–	53	43	–	100	33	–	27	33	43	17
$\alpha\text{-FeOOH}$	D	–	–	–	2.70	2.52	–	1.83	1.69	1.60	1.48	1.27
Hydrazinate/ autocatalytic	I/I_0	–	–	–	78	100	–	42	42	36	51	23
Amorphous FeOOH	D	–	–	–	–	2.51	2.08	–	–	1.60	1.47	1.27
Hydrazinate/ autocatalytic	I/I_0	–	–	–	–	99	58	–	–	74	81	71

*Reported values from JCPDS files Nos. 6–615; 13–534; 19–629; 24–81 and 25–1402.

3.3 Chemical formula fixation

3.3a *Iron oxyhydroxides*: The total weight loss values, iron contents, density and IR band positions of the iron oxyhydroxides are shown in table 2. From the analytical observations the following chemical formulas have been fixed for the oxyhydroxides

$g\text{-FeOOH}\cdot 0\cdot 3\text{H}_2\text{O}$; $a\text{-FeOOH}\cdot 0\cdot 2\text{H}_2\text{O}$ and amorphous $\text{FeOOH}\cdot 0\cdot 8\text{H}_2\text{O}$.

At high temperatures ($\sim 250^\circ\text{C}$) the simple dehydration of $a\text{-FeOOH}$ yields $a\text{-Fe}_2\text{O}_3$, while $g\text{-FeOOH}$ topotactically transforms (Dasgupta 1961) into $g\text{-Fe}_2\text{O}_3$. An increase in temperature may lead to the phase transformation of $g\text{-Fe}_2\text{O}_3$ to $a\text{-Fe}_2\text{O}_3$.

3.3b *Hydrazination of iron oxyhydroxides*: The reddish orange $g\text{-FeOOH}\cdot 0\cdot 3\text{H}_2\text{O}$ and reddish brown amorphous $\text{FeOOH}\cdot 0\cdot 8\text{H}_2\text{O}$ when equilibrated with hydrazine in a hydrazine hydrate (99%) atmosphere in a desiccator turned black, while yellow $a\text{-FeOOH}\cdot 0\cdot 2\text{H}_2\text{O}$ did not change its colour. On exposure to air all fumed immediately into reddish brown magnetic oxide products. All hydrazinated compounds were unstable in an ordinary atmosphere and hence the hydrazine uptake could not be analyzed to fix plausible formula of the complexes.

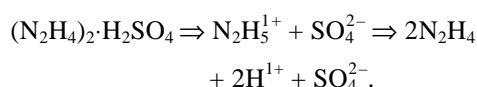
Therefore, a special reactor was built to monitor the hydrazine uptake and analyse titrimetrically by KIO_3 .

3.4 Equilibration with 80 (%) $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$

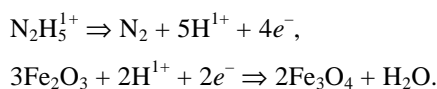
In a special reactor when hydrazine uptake was analyzed the hydrazine contents of 10.4% and 10.8% were observed, respectively, in $g\text{-FeOOH}\cdot 0\cdot 3\text{H}_2\text{O}$ and amorphous $\text{FeOOH}\cdot 0\cdot 8\text{H}_2\text{O}$, while just 1.5% was found in $a\text{-FeOOH}\cdot 0\cdot 2\text{H}_2\text{O}$. Both $g\text{-FeOOH}\cdot 0\cdot 3\text{H}_2\text{O}$ and amorphous $\text{FeOOH}\cdot 0\cdot 8\text{H}_2\text{O}$ turned black and the yellow colour of $a\text{-FeOOH}\cdot 0\cdot 2\text{H}_2\text{O}$ remained unchanged. On estimating the iron contents of the black coloured samples, it was observed that $\sim 41\%$ FeO was present in the product of hydrazinated $g\text{-FeOOH}\cdot 0\cdot 3\text{H}_2\text{O}$, while amorphous FeOOH showed just 1.2% FeO. As the black coloured product of $g\text{-FeOOH}\cdot 0\cdot 3\text{H}_2\text{O}$ contains $\sim 41\%$ FeO, it must be ferrous-ferric oxide of $\text{Fe}_3\text{O}_4 = \text{FeO}\cdot\text{Fe}_2\text{O}_3$ type whose theoretical FeO content is 31.03%. These observations suggest that the black coloured product in 99% hydrazine hydrate equilibration was a ferrous-ferric type oxide which may be the intermediate phase of the final fumed product $g\text{-Fe}_2\text{O}_3$.

3.5 Mechanism of hydrazine method of synthesis of metal oxides

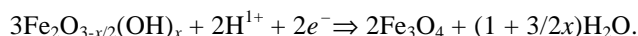
Hydrazine is a reducing agent and the X-ray diffraction done (Tikkanen 1961) on the catalyst, $a\text{-Fe}_2\text{O}_3$, on hydrazine decomposition found the oxide converted into Fe_3O_4 . Hydrazine sulfate decomposition in an alkaline medium on $a\text{-Fe}_2\text{O}_3$ also converts the oxide into magnetite (Fakuda 1957) and here the hydrazine sulfate first dissociates into hydrazine,



The reduction of Fe_2O_3 is then a coupled reaction,



Similarly a hydrous ferric oxide decomposes hydrazine sulfate (Furuichi *et al* 1969) and transforms itself into magnetite



In the present study the formed magnetite type phase in the hydrazinated $g\text{-FeOOH}\cdot 0\cdot 3\text{H}_2\text{O}$ transforms in air into maghemite, $g\text{-Fe}_2\text{O}_3$. The hydrazinated amorphous FeOOH , however, also shows black product consisting of 1.2% FeO which transforms into maghemite. The low per cent

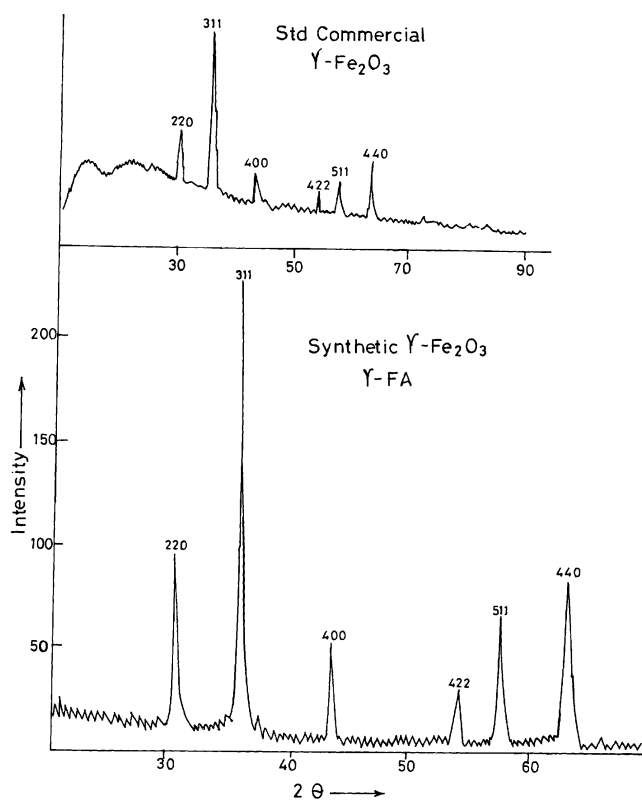


Figure 1. X-ray diffractogram of $g\text{-Fe}_2\text{O}_3$.

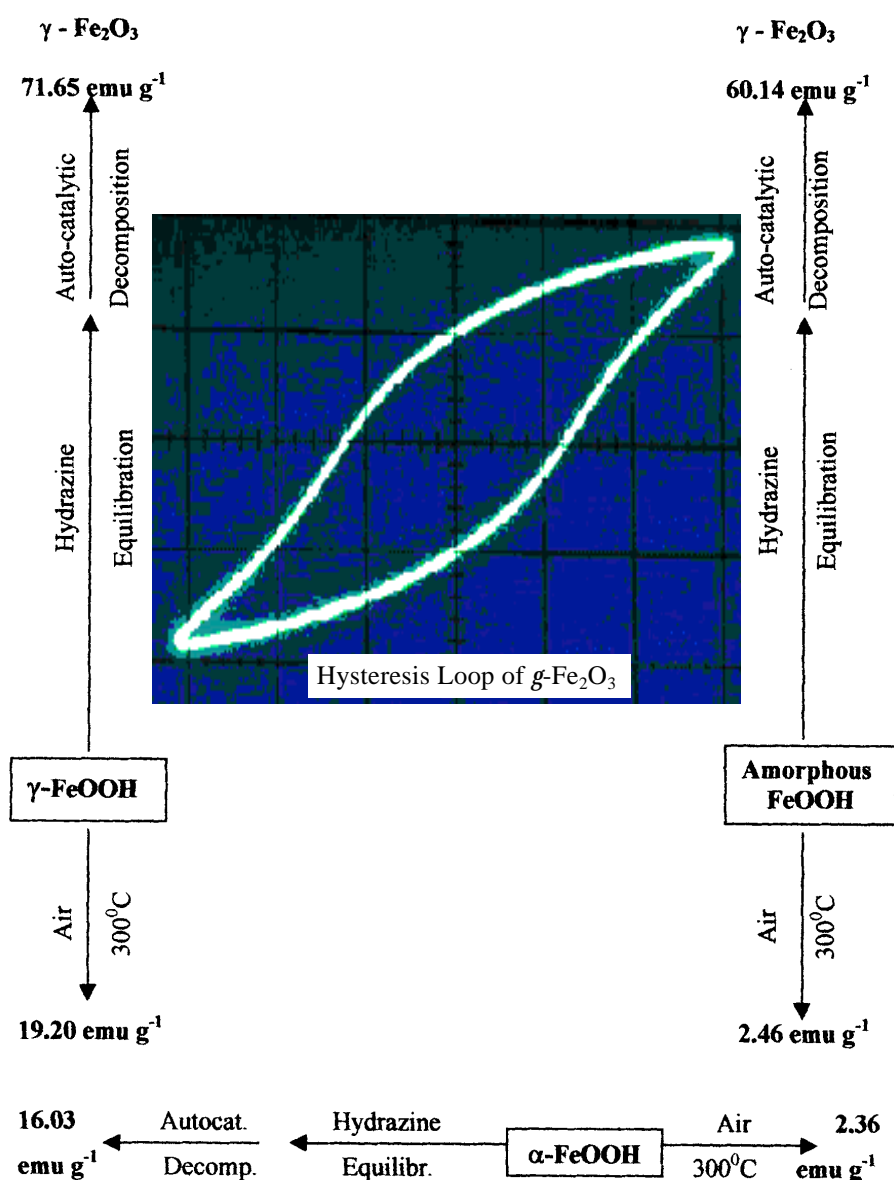


Figure 2. Saturation magnetization, J_s , (emu g⁻¹), values of the thermal products of the iron oxyhydroxides and hydrazinated iron oxyhydroxides. (Inset: A typical hysteresis loop of synthetic g -Fe₂O₃).

Table 2. Chemical analysis, density, IR, total weight loss of iron oxyhydroxides.

Sample	% Fe Obsd. (Calcd.)	Density (g cm ⁻³)	Infrared bands (cm ⁻¹)			Total % weight loss Obsd. (Calcd.)	
			O-H stretch	O-H stretch	Fe-O bend	Air	N ₂
g -FeOOH·0.3H ₂ O	59.00 (59.25)	1.54	2890	1020	747	15.62 (15.28)	15.00
Amorphous FeOOH·0.8H ₂ O	54.00 (54.09)	1.73				22.90 (22.66)	23.00
α -FeOOH·0.2H ₂ O	60.00 (60.41)	2.66	3100	904	774	13.76 (13.63)	15.00

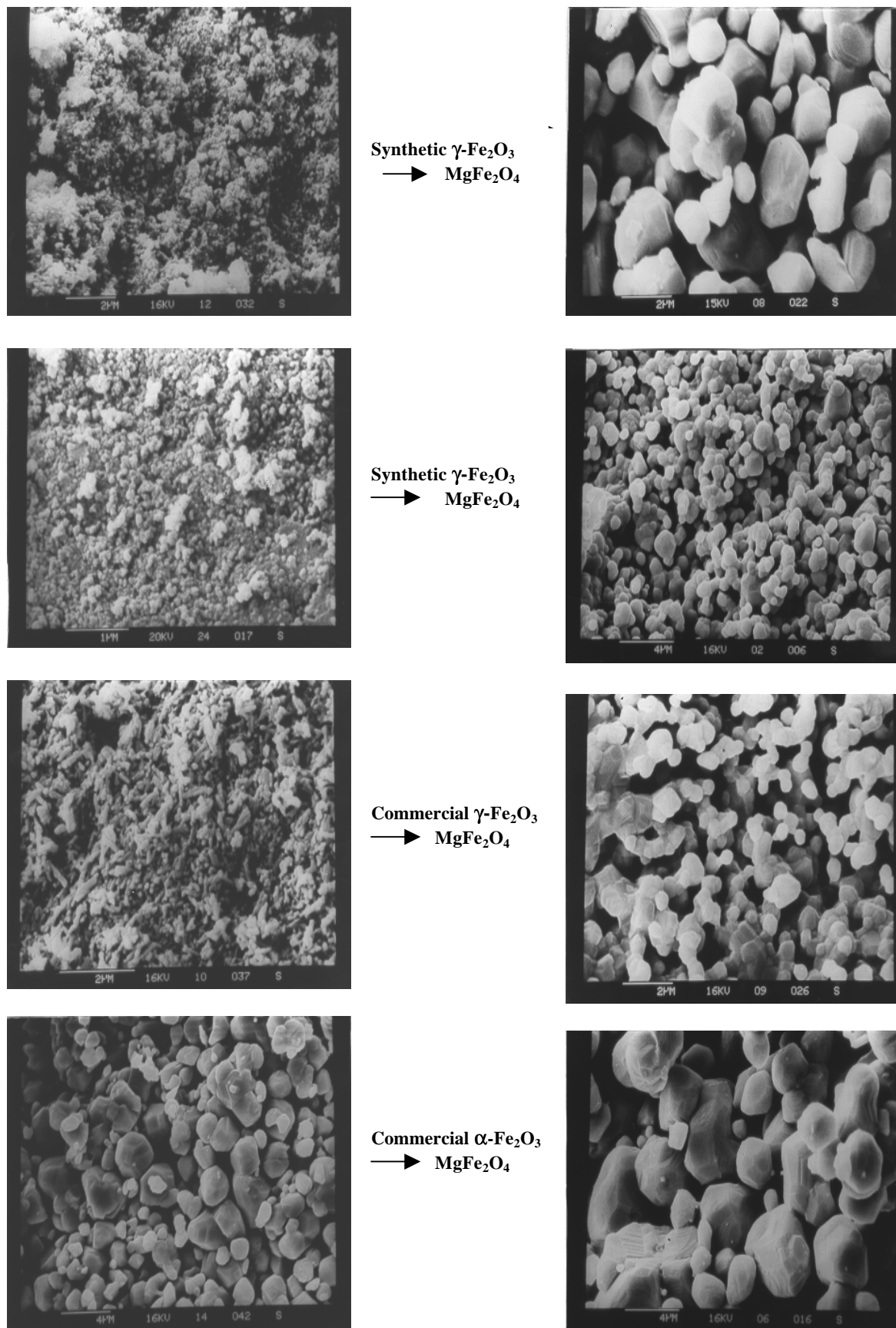
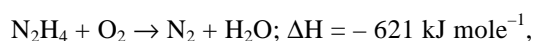


Figure 3. SEM micrographs of synthetic iron oxides and MgFe_2O_4 .

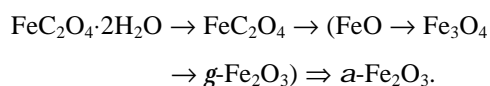
of FeO may be due to the formation of *g*-Fe₂O₃ directly in the hydrazine atmosphere itself. The absence of FeO in the yellow product of the hydrazinated *a*-FeOOH suggests that no intermediate magnetite phase is formed, but the product transforms into *a*-Fe₂O₃. Hydrazination in 99% N₂H₄·H₂O makes the iron oxyhydroxides to fume immediately when exposed to air.

Hydrazine methods are adopted because the hydrazinated complexes, in general, especially carboxylato-hydrazinates, decompose explosively. Metal carboxylates are pyrophoric and the hydrazination further enhances their pyrophoric nature. And we observed (Rane *et al* 1981; Moye *et al* 1993) FeC₂O₄·2H₂O in air decomposes at 300–350°C to *a*-Fe₂O₃, while in an inert atmosphere of N₂ the decomposed product is black magnetic Fe₃O₄, but a controlled atmosphere of moisture at ~ 310°C allows the formation of *g*-Fe₂O₃. In fact, moist ferrous oxalate when heated in muffle furnace shows a bright glow at ~ 310°C (Rao *et al* 1974), which on removal from the furnace and cooling the product indicates magnetic nature due to *g*-Fe₂O₃. The FeC₂O₄·2H₂O on hydrazination (Moye *et al* 1993) forms FeC₂O₄·2N₂H₄ which when brought near a burning splinter catches fire and a glow that forms spreads through the bulk completing the decomposition autocatalytically to *g*-Fe₂O₃. Thus, hydrazinated complexes are pyrophoric which allow the decomposition to take place easily at an ordinary temperature. Similar observations were also made on iron (II) carboxylato-hydrazinates such as ferrous fumarato-, succinato-, maleato-, malato-, malonato- and tartrato-hydrazinate (Verenkar 1997; Rane and Verenkar 2001) which autocatalytically decomposed to *g*-Fe₂O₃. Iron oxyhydroxides also become pyrophoric on hydrazination.

The easy formation of *g*-Fe₂O₃ from hydrazinated ferrous oxalate without controlling the moisture atmosphere, which otherwise is needed for the unhydrazinated complex, indicates that the required partial pressure of water is supplied by the decomposed products (N₂ + H₂O). Thus the hydrazine released from the hydrazinated ferrous oxalate reacts with the atmospheric oxygen liberating enormous energy (Schmidt 1984),



which enables to oxidatively decompose the dehydrazinated complex to *g*-Fe₂O₃. The decomposition of ferrous oxalate in air (Rane *et al* 1981, 1999) leads to,



In inert atmosphere of N₂ the decomposition arrests at Fe₃O₄, while the controlled atmosphere of moisture allows the magnetite to oxidize to *g*-Fe₂O₃ without allowing it to go further to thermodynamically stable phase *a*-Fe₂O₃. Thus, a metastable cubic spinel phase *g*-Fe₂O₃ is the oxida-

tion product of cubic inverse spinel Fe₃O₄ and the stabilization of the *g*-Fe₂O₃ occurs in a controlled atmosphere of moisture. Therefore, the pyrophoric hydrazinated iron oxyhydroxide, *g*-FeOOH, decomposes to Fe₃O₄ and further oxidation to metastable *g*-Fe₂O₃ occurs under the moisture atmosphere, N₂ + H₂O produced due to the oxidation of N₂H₄ in air.

All iron oxyhydroxides and iron hydroxides easily produce mainly *g*-Fe₂O₃ or mixture of *g*-Fe₂O₃ + *a*-Fe₂O₃ by hydrazine method. All show high BET surface area in the range 50–80 m² g⁻¹ and particles distribute in the 0–1 μ size as revealed by SEM. The ferrite, MgFe₂O₄, prepared from these (Rane *et al* 1999, 2000) show superior magnetic and electrical properties as compared to the ferrite synthesized from commercial grade (1–2 μ sizes) *a*-Fe₂O₃ and needle shape *g*-Fe₂O₃. The SEM micrographs of some representative samples of the synthetic *g*-Fe₂O₃ and the ferrite from these are reproduced in figure 3 (Sawant 1998; Rane *et al* 1999, 2000).

In fact, the commercial *g*-Fe₂O₃ particles are acicular (needle shaped) suitable for use as a magnetic tape material. The MgFe₂O₄ prepared from such acicular shaped particle gave a dumb bell shaped porous ferrite (figure 3), while all synthetic submicron size non-acicular *g*-Fe₂O₃ samples from the present studies gave well dense ferrites.

The commercial grade (1–2 μ sizes) *a*-Fe₂O₃ ended up into porous ferrite. Uniform saturation magnetization values (4 pM_s ≅ 1000–1150 Gauss) and Curie temperatures (T_c = 670 ± 30 K) and normal dielectric dispersions observed for low porosity (20–25%) MgFe₂O₄ (Verenkar 1997; Sawant 1998; Rane *et al* 1999, 2001) suggest that iron oxides prepared from iron ore rejects are quite suitable for ferrite preparation. High porosity (40–41%) mixed phase MgFe₂O₄ containing some unreacted *a*-Fe₂O₃ obtained from commercial *a*-Fe₂O₃ showed low 4 pM_s value of 609 G. Thus, iron ore rejects can be efficiently chemically beneficiated to obtain value added iron oxide of ferrite grade.

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