

Purification of Iron Oxides and Application to Magnetic Hard Ferrite

Jeong Seog Kim, Kyoung Ho Chou, Jai-Young Kim* and Chol Woo Kim*

Department of Materials and Chemical Engineering, Hoseo University, Asan, ChungNam 336-795, Korea

*SamYang Industries Co., Ltd., Kumsan, ChungNam 312-940, Korea

(Received July 26, 1996)

Hematite iron ore and waste iron oxide sludge containing about 3-5 wt% SiO₂ were purified by three types of method developed on the basis of the Bayer process which is known as the purification process of bauxite ore. The basic principle of the developed methods lies in the fact that the impurities contained in the iron oxides, such as SiO₂ and Al₂O₃ are soluble in the alkaline reagents. Reaction of the raw materials with KOH was done in pressure vessel, at atmospheric pressure, and by both of these two. By the pressure vessel method SiO₂ content was reduced to below 0.5 wt% in the waste iron oxide sludge, while, in iron ore, SiO₂ remained at 2-3 wt%. The atmospheric pressure reaction rendered the waste iron oxide sludge SiO₂ content below 0.5 wt% when the reaction temperature increased to above 900°C. The combined method of two previous methods was the most effective process and rendered the refined iron oxide about 300-400 ppm of SiO₂. Using some refined iron oxides, Ba-ferrite was produced and magnetic properties were measured. The highest quality of magnetic properties obtained in this study were Br=2.09 G, bHc=1.99 KOe, iHc=4.54 KOe. (BH)_{max}=1.06 MGOe. Effect of sintering condition and chemical composition will be discussed.

Key words : Purification, Waste iron oxide, Hard ferrite

I. Introduction

Recently, the demand for iron oxide as a raw material of magnetic ferrites has increased far beyond the domestic supply due to the steady growth of the electronics industries within the country. Regarding the iron oxide as a raw material for hard ferrite, the total domestic production was about 1,960 tons/month while that of the demand was about 3,400 tons/month in 1995. The imported iron oxide filled up the gap. The shortage of iron oxide for hard ferrite is expected to continue until upcoming several years in Korea. Consequent upon the current situation, the study on developing the iron oxide resources has been carried out. In addition this study of recycling the waste iron oxide as a useful ceramic raw material also has an importance in the aspect of environmental protection.

Major source of the iron oxide is the regeneration plant of hydrochloric acid pickling liquor^{1,2)} in the steel industries. Hot-rolled mill scale³⁾ and refined iron ore⁴⁾ also have been applied for the manufacture of hard ferrite. The impurities in the iron oxide to be refined are mainly SiO₂, CaO and Al₂O₃. The impurities level in the mill scale is low enough for the hard ferrite. Only the iron oxide particle size and oxidation state are the major powder characteristics to be controlled for obtaining the required magnetic properties. On the other hand, iron ore generally contains too high SiO₂ and Al₂O₃ contents to be used as hard ferrite. Mineral dressing methods for refining iron ore include magnetic separation, flotation,

and sedimentation. But the iron oxide refined by the mineral dressing contains relatively high level of SiO₂ and Al₂O₃, which make the oxide unsuitable for hard ferrite manufacturing. However, Narita et al.⁵⁾ have succeeded in producing a relatively high purity iron ore containing less than 0.2 wt% SiO₂ and 0.15 wt% Al₂O₃ by the mineral dressing method. The refining method consisted of primary grinding, classification, and wet magnetic separation and followed by secondary grinding and classification. They obtained the required magnetic properties of Sr-hard ferrite with the refined iron ore by adjusting additives and calcining temperature.

In this study a new type of refining process using alkaline reagent will be reported. And the application results of refined iron oxides to hard ferrite will be also discussed. This method is for refining the iron oxides containing SiO₂ and Al₂O₃ as impurities. As raw materials, two types of iron oxides are adopted, i.e. hematite iron ore and waste iron oxide sludge which is being produced as a by-product in a pigment manufacturing factory by 150 tons/month. These iron oxides contain large amount of SiO₂ which makes them unsuitable for high quality hard ferrite.

The basic principle of the new refining method developed in this study lies in the Bayer process which is a well known process for refining bauxite of aluminous ore⁶⁾. The silica(SiO₂) and Al₂O₃ particles show low solubility in acid and water but are very soluble in alkaline reagent. In a similar manner, a glassy phase containing both SiO₂ and alkaline oxide as major components becomes very soluble

in acid and even in water. It is well known in analytical chemistry that for a chemical composition analysis of silicate materials, such as glass and clay, these materials melt in alkaline reagents, e.g. Na_2CO_3 , NaOH , and K_2CO_3 , at about 900°C as pretreatment process⁶. Then the molten alkaline-silicates become very soluble in water⁷.

II. Experimental Procedure

The refining process of iron oxides in this report is a similar process in nature to the one described the introduction. Figure 1 shows the thermal analysis on the waste iron oxide sludge discharged after filter pressing in the pigment manufacturing factory. The filter-pressed sludge contained non-solid portion less than 20-30% of the total sludge weight. The non-solid portion was composed of water and an organic substance ($\text{C}_6\text{H}_2\text{CH}_3\text{NH}_2\text{ClSO}_2\text{Na}$), which was used as chemical interactant for the pigment manufacturing process. On the TG curve the first sharp drop at near room temperature corresponds to the water evaporation and the second drop at about 280°C to the evaporation of the organic substance ($\text{C}_6\text{H}_2\text{CH}_3\text{NH}_2\text{ClSO}_2\text{Na}$) remained in the filter-pressed and disposed sludge. It appears that, at near room temperature, the thermal analysis instrument used in this experiment was to a degree imprecise in the indicated temperatures with respect to the actual temperature. In Table 1 is shown the chemical composition analysis by EPMA (electron probe microanalysis) on the sludge pre-fired at 800°C for 1 hour in air. The analysis was done on several particles.

The original state of the waste iron oxide sludge was the cast iron scrap powder, which was oxidized during the pigment manufacturing processes. The SiO_2 is in-

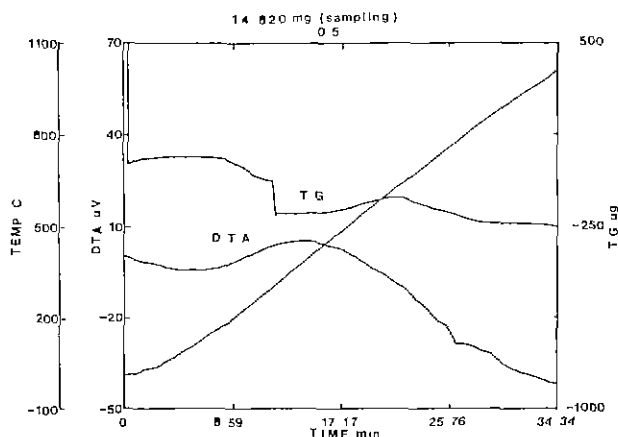


Fig. 1. Thermal analysis of waste iron oxide sludge.

Table 1. Chemical Composition of the Waste Iron Oxide Sludge by EPMA

Components	Fe_2O_3	SiO_2	MnO_2	CaO	Na_2O
wt%	93-95	2-5	0.2-1	0-0.3	0-0.3

herent in the cast iron source and the Na_2O originates from the organic substance used for the pigment manufacturing. The iron oxide sludge fired at 800°C showed a particle size of about $0.62\ \mu\text{m}$ and $2.62\ \text{m}^2/\text{g}$ of BET.

Based on the Bayer process three types of refining process were derived. One of the refining process is shown in Fig. 2 which is the same as the Bayer process. The iron oxide raw material and 10 wt% KOH solution were mixed at 1 : 2 wt. ratio and reacted in a pressure vessel at below 330°C for 2-3 hours. The pressure vessel had a dimension of 100 mm dia. \times 150 mm height and no stirring system. After the reaction remanent alkaline solution was filtered out and the solid matter was rinsed in water. Figure 3 shows the second type of developed refining process. In this process the mixture of the waste sludge and 5-10 wt% KOH was reacted at atmospheric pressure in the temperature range of 100 - 1000°C for 1-12 hours. The reactant was pulverized and leached in hydrochloric or sulfuric acid solution. The purified oxide was then washed in water. The last type of refining process investigated is shown in Fig. 4 which is a combined type of the two previously described methods. Firstly, the mixture of raw material and 5 wt% KOH was reacted at 900°C at atmospheric pressure. Then the reactant was reacted again in a pressure vessel at below 360°C and leached using acid solution.

Using some of the refined oxide samples, Ba-hard ferrites were prepared. The mixtures of BaCO_3 and the refined iron oxides with varying ratio were calcined at 1070°C for 1-2 hours. After adding 1.5 wt% PVA (polyvinyl alcohol) the calcined powder was isotropically compacted to discs. The compacts were then fired at the temperature range of 1180 - 1220°C for 1 hour. Two types of sinter-additives^{8,9} were adopted. In some samples no additive was used.

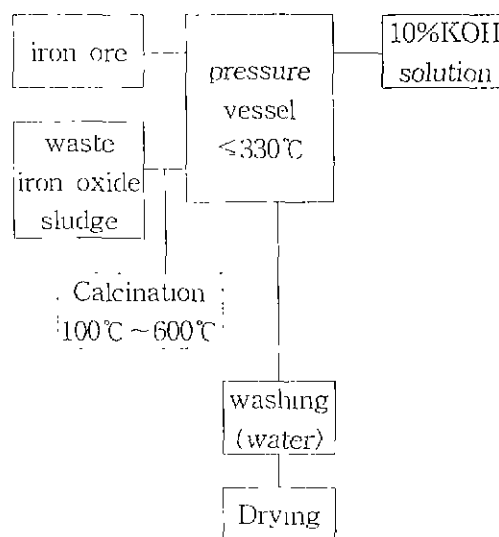


Fig. 2. Purification method by pressure vessel reaction (Bayer process)

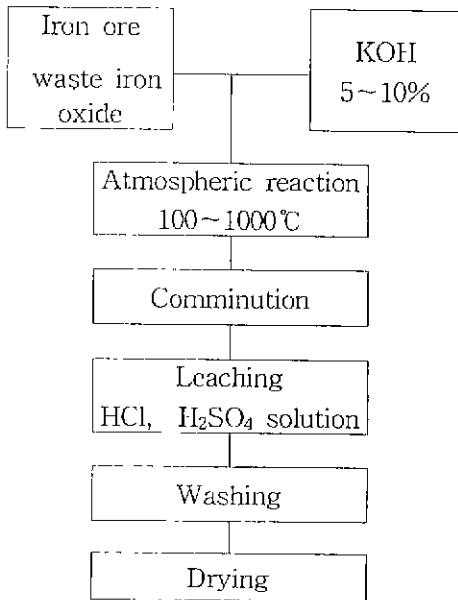


Fig. 3. Purification method by atmospheric pressure reaction.

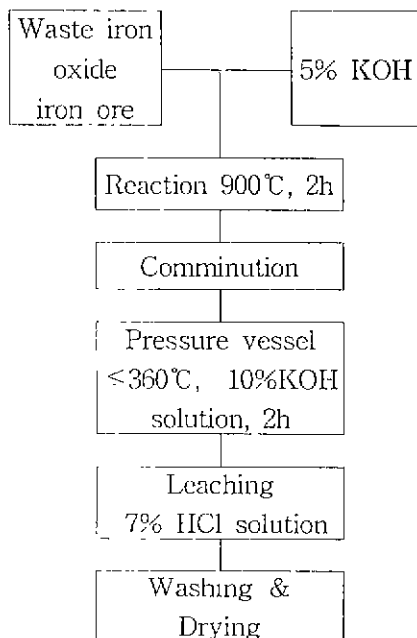


Fig. 4. Combined purification method of pressure vessel and atmospheric pressure reaction.

III. Results and Discussion

1. Refining Process

Figure 5 shows the purification results by the method shown in Fig. 2 (Bayer process). The SiO₂ contents at reaction temperature of 0°C imply the initial state of the raw materials. In this experiment SiO₂ content was measured by a wet chemical method, i.e. after evaporating a concentrated hydrochloric acid dissolved with iron oxide at boiling temperature, the weight of the left-

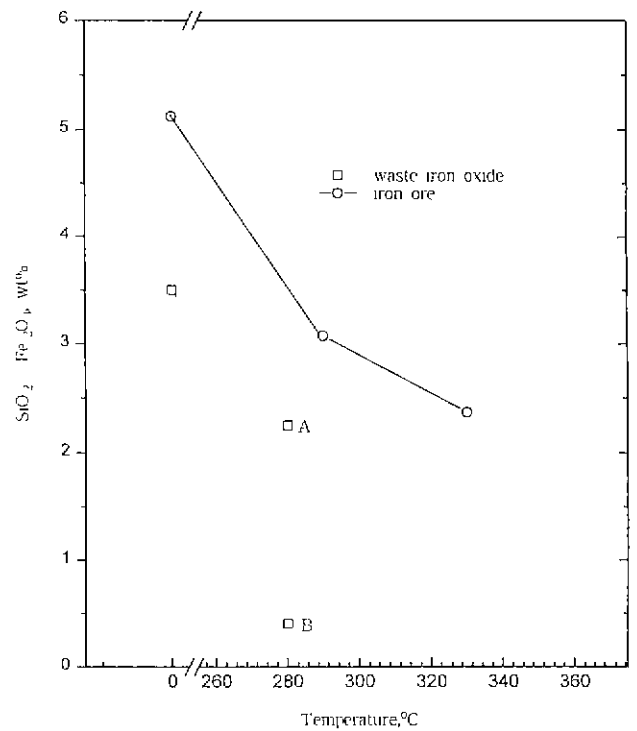


Fig. 5. Variation of SiO₂ contents with reaction conditions following the refining procedure in Fig. 2. (A and B calcined at 100°C and 600°C, respectively)

over (SiO₂) was measured. In the iron ore the silica level decreased by only about 50%, from 5.12 wt% to 2.37-3.08 wt%, regardless of the reaction temperature. On the other hand, the silica content critically depended upon the firing temperature of the waste sludge before the pressure vessel reaction. At calcination temperature of 600°C the silica content reduced to 0.40 wt%, while the calcined sludge at 100°C refined only to about 2.3 wt%. As shown in Fig. 1, the organic substance contained in the waste sludge can fully vaporize above 280°C. When the oxide sludge calcined at 100°C for 12 hours was re-calcined at 600°C for 2 hours in air the weight of the calcined sample reduced by about 3 wt% which corresponds to the organic substance evaporation. The organic substance remained in the waste sludge fired at 100°C appeared to reduce the reactivity of the sample with the alkaline solution.

In Fig 6 are shown the purification results by the second type of refining process of Fig. 3. The silica content in the refined oxide steeply decreased when the reaction temperature increased to about 900°C. Above this temperature the silica content reduced below 0.5 wt%. The type of acid solution for the leaching appeared to have no effect on the purification level. The binary phase diagram of K₂O-SiO₂¹⁰ provides some clues to the rationale of the steep decrease of the silica content only at reaction temperature higher than 900°C. This binary diagram shows that glass phases containing both SiO₂ and K₂O as major components begin to form at above 750°C

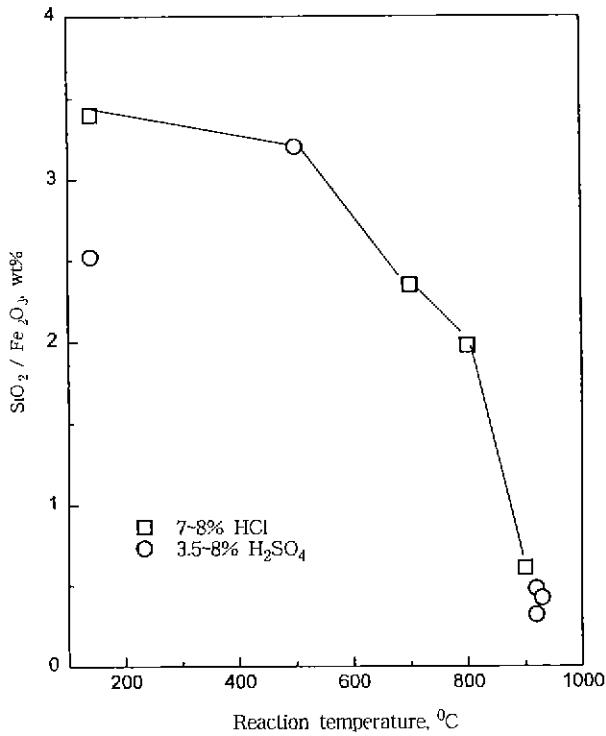


Fig. 6. Effect of reaction temperature on the SiO₂ content following the refining procedure in Fig. 3.

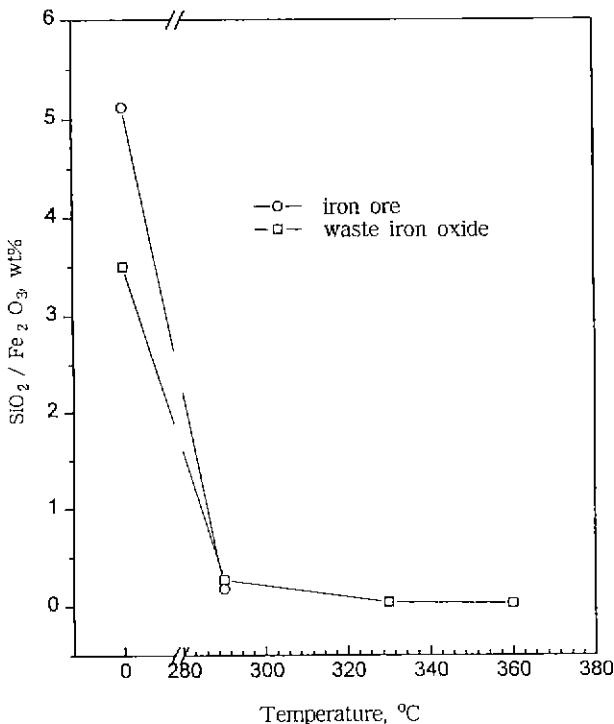


Fig. 7. Effect of pressure vessel reaction temperature on the SiO₂ content following the refining procedure in Fig. 4.

by eutectic reactions. And these glass phases are known to readily dissolve in acid and even in water. Based on the binary diagram, in the mixture of KOH and the waste sludge, KOH is conjectured to form a glass phase

Table 2. ICP(inductively coupled plasma) Analysis of the Refined Iron ore with 0.18% wt% SiO₂ in Fig. 7

components	Si	Na	Ca	Al	K	Mn	Fe
wt% (refined)	0.103	--	0.0265	0.160	--	0.210	99.5
wt% (raw)	5.120	0.589	0.0790	0.938	--	0.110	

*wet chemical analysis.

Table 3. ICP Analysis of the Refined Iron Oxide Sludge with 0.27 wt% SiO₂ in Fig. 7

components	Si	Na	Ca	Al	K	Mn	Fe
wt% (refined)	0.134	--	0.032	0.0056	--	0.810	99.00
wt% (raw)	3.500	0.0202	0.125	0.020	--	0.519	

*wet chemical analysis.

with SiO₂ at about 900°C.

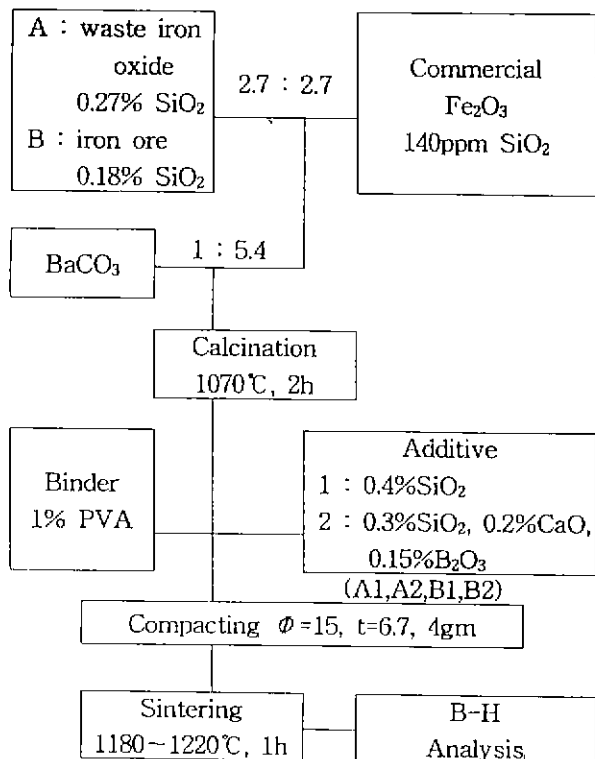
The result of purification by the combined method of Fig. 4 is shown in Fig. 7. The SiO₂ contents at 0°C again imply the initial state of the raw materials. By this combined method both the iron ore and waste sludge were more effectively purified than the previous methods. The silica content was critically affected by the pressure vessel reaction temperature. At the reaction temperature of 290°C, 0.18 wt% and 0.27 wt% of SiO₂ were obtained in iron ore and waste iron oxide sludge, respectively. In the waste iron oxide sludge SiO₂ content drastically decreased to about 300-420 ppms when the reaction temperature increased to above 300°C. However, it is not clear whether the SiO₂ purification level of 300-400 ppms can be attained by only the pressure vessel reaction by increasing the reaction temperature above 300°C without the atmospheric pressure reaction. For the waste iron oxide sludge the reaction temperature higher than 300°C in the pressure vessel was applied only in this combined type process. For the case of iron ore, by combining the atmospheric pressure reaction of 900°C and pressure vessel reaction, the SiO₂ content could be decreased to below 0.2 wt%, while only with the pressure vessel reaction the SiO₂ was not effectively refined, as shown in Fig. 5. Tables 2 and 3 show the ICP(inductively coupled plasma) analyses on the refined iron ore and waste iron oxide sludge at the pressure vessel reaction temperature of 290°C. Other impurities, such as Al₂O₃ and CaO were also reduced to low level as well as SiO₂, as listed in Tables 2 and 3. Alkaline elements such as Na and K were not detectable.

2. Application to Hard Ferrite

There are several factors affecting the magnetic properties of hexagonal ferrites. In an Isotropic hexaferrite (BaOFe₂O₃), high coercivity H_c can be obtained at n=5.3-

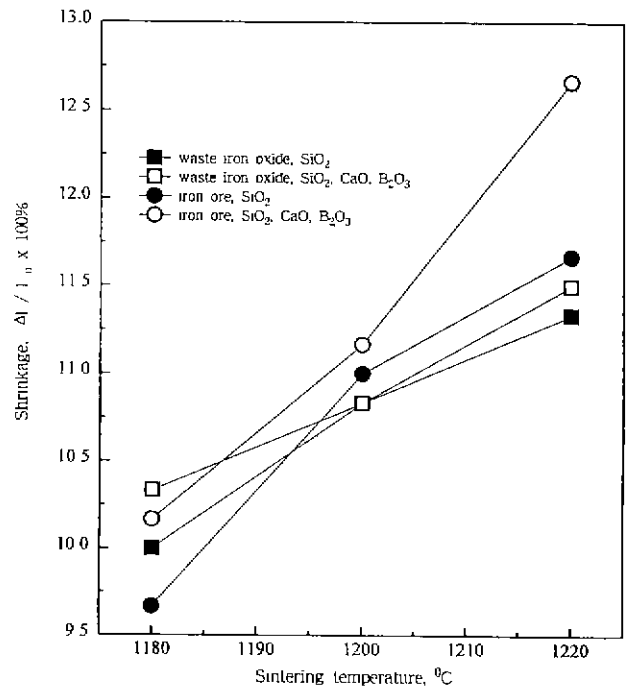
Table 4. Magnetic Properties of Ba-ferrite Produced using the Refined Iron Oxide Sludge with 0.48 wt% SiO₂

property sample	iron oxide APD μm	ferrite APD μm	DP (gm/cm ³)	DF (gm/cm ³)	SH(%)	BH characteristic			
						Br G	bHc Oe	iHc Oe	BH(max) MGOe
Commercial iron oxide	0.65	1.16	3.37	4.99	15.15	2450	1840	3300	11.5
refined waste Fe ₂ O ₃	1.0	1.52	3.68	4.69	11.10	2070	1150	640	0.71

**Fig. 8.** Experimental procedure for the preparation of Ba-ferrite.

5.5, and high remanence Br can be obtained at around $n=5.8$. The coercivity Hc depends on the particle size of a barium hexaferrite powder and generally it shows a maximum at about 1 μm size. The sinter additives, such as SiO₂, CaO, Al₂O₃, B₂O₃, and Bi₂O₃, inhibit the excessive grain growth and give rise to a high sintered density. The powder characteristics (particle size, shape) and chemical composition (especially, impurity contents, such as SiO₂, CaO, Al₂O₃) of the raw materials, and sintering temperature and milling condition are also important factors to be controlled. Since all of the above factors are interactive each other, the parameters mentioned above needs to be properly tuned to obtain optimum magnetic properties for a given condition.^{5,11)}

Firstly, using the iron oxide of 0.48 wt% SiO₂ refined by the atmospheric pressure reaction method, Ba-ferrite with BaO/Fe₂O₃=5.3 mole ratio¹²⁾ was prepared. The calcined powder was isotropically compacted to discs of 20

**Fig. 9.** Effect of sintering temperature on the shrinkage of Ba-ferrite samples.

mm dia. and 17 gm of weight. In this case no additive was used. In Table 4 are summarized the sintering characteristics and magnetic properties of the prepared samples sintered at 1200°C for 1 hour and compared to a commercial product. Magnetic properties of the prepared ferrites were poor compared to the commercial product. Relatively high SiO₂ content of the refined iron oxide powder used for the samples, and the unoptimized sample preparation conditions, such as sinter-additives and milling method, can be considered to attribute to these low magnetic properties.

Secondly, using the refined iron oxides shown in Tables 2 and 3, four types of Ba-ferrite were prepared following the procedure shown in Fig. 8. The BaO/Fe₂O₃=5.4 molar ratio was prepared. The calcined ferrite powder mixed with 1.5% PVA and some additives was isotropically pressed into discs of 4 gm and 15 mm dia. at 1.5 ton. Two types of sinter-additives^{5,9)} were adopted as shown in Fig. 8 to produce four types of Ba-ferrite samples. The dimensional changes and magnetic properties with sintering conditions are summarized in Fig. 9 and

Table 5. The shrinkage is an average value on three samples. Sinter-shrinkage increased continuously with the temperature. Samples with three components additives, e.g. SiO_2 , CaO , and B_2O_3 , showed large shrinkage at low temperature (1180°C). The samples prepared using the refined waste iron oxide were superior to those of iron ore. Remanent magnetic flux density B_r was about 10-20% lower than that of the commercial product. Coercive magnetic field strength values bH_c and iH_c were higher than those of the commercial product. $(BH)_{\max}$ was about 80-90% of the commercial product. To improve the magnetic properties to as the commercial product, more precise experiments need to be carried out. In this experiment, for instance, the calcined powders were only ball-milled instead of attrition milling which is commonly being used for the ferrite production. And the molar ratio of $\text{BaO}/\text{Fe}_2\text{O}_3$ needs to be tuned properly for the refined iron oxides to an optimum value.

IV. Conclusion

Purification methods of iron oxide were developed based on the purification process of bauxite ore, the Bayer process. The basic principle of these methods is to dissolve the impurities, such as SiO_2 and Al_2O_3 , in the alkaline reagents. Pressure vessel reaction of waste iron oxide sludge with KOH solution rendered about 0.5 wt% SiO_2 content, while iron ore was not effectively purified. Atmospheric pressure reaction of the waste iron oxide sludge with 5 wt% KOH also resulted in SiO_2 content below 0.5 wt%. The combined method of two previous types was the most effective method. When the pressure vessel reaction temperature increased higher than 300°C in the combined method, SiO_2 content drastically decreased to 300-400 ppms. However, further work needs to be done to find out whether the pressure vessel reaction method itself can reduce the SiO_2 content to several hundred ppms when the reaction temperature increased higher than 300°C.

Using some refined iron oxides, Ba-ferrites were produced. Ferrite sample showing the highest quality in this study was obtained from the refined iron oxide sludge of 0.27 wt% SiO_2 . The coercive magnetic field strength values, bH_c and iH_c , were higher than those of the high quality commercial product, while B_r and $(BH)_{\max}$ were about 90% of the commercial product. To improve the magnetic pro-

erties further works to optimize the milling condition and chemical composition need to be done.

Acknowledgement

This paper was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation in 1995. The authors thank to Mr. Jijong Park (Chungnam National University) and Mr. Seil Oh (Magnetrio Co) for their assistances analyzing the magnetic properties.

References

1. M. J. Ruthner "The Importance of Hydrochloric Acid Regeneration Process for the Industrial Production of Ferric Oxides and Ferrite Powders," Ferrites: Proceedings of the International Conference, Sept.-Oct., Japan. 64-67 (1980)
2. S. Itoh, I. Endo, K. Maki, and A. Kosaka, "Ferric Oxide Produced by Spray Roasting of HCl Pickling Liquor," *Tetsu to Hagane*(in Jpn), **62**[8], 1035 (1976).
3. Y.-T. Chien, H.-C. Pan, and Y.-C. Ko, "Preparation and Properties of Barium Ferrite Using Hot-Rolled Mill Scale," *J. Am. Ceram. Soc.*, **72**[8], 1328 (1989).
4. Y. Narita, S. Ogasawara, T. Ito, Y. Ikeda, "Refined Iron Ore as a Raw Material of Hard Ferrite," Ferrites: Proceedings of the Sixth International Conference on Ferrites (ICF6), Tokyo and Kyoto, Jap., 143(1992).
5. A. J. Moluson and J. M. Herbert, *Electroceraamics*, pp 212-214, Chapman & Hall, London & NewYork, 1992.
6. Dept. of Inorganic Materials, Tokyo Industrial University. Ceramics Experiment (in Jpn), pp. 1-22, Uchida Rokakuho, Tokyo, 1988.
7. B.-H Kim, *Glass Technology*(in Korean), pp. 19-21, Chongmungak, Seoul, 1922.
8. A. M. Gadalla, H. E. Schutz, and H. W. Henniscke, "Effect of Some Additions on the Sinterability and Magnetic Properties of Barium Hexa-ferrite," *J. Mag. Mag. Mater.*, **1**, 241-250 (1976).
9. R. H. Arendt, "Liquid Phase Sintering of Magnetically Isotropic and Anisotropic Compacts of $\text{BaFe}_{12}\text{O}_{19}$ and $\text{SrFe}_{12}\text{O}_{19}$," *J. Appl. Phys.*, **44**[7], 3300-3305 (1973).
10. E. M. Levin, C. R. Robbins, and H. F. McMurdie, *Phase Diagram for Ceramists*, vol.1, p 87, The Am. Ceram. Soc. Inc., Columbus, 1964.
11. G. Hiraga, K. Okutani, and D. Ogima, *Ferrites* (in Japanese), pp. 135-143, Ganjo Press, Tokyo, 1986.
12. M. Schieber, "Preparation and Magnetic Heat Treatment of Barium-ferrite Permanent Magnet Containing Lead Oxide Addition," *Ceramic Bulletin*, **40**[9], 563 (1961).