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CHARACTERIZATION OF FERRIC OXIDE OBTAINED FROM UPGRADING OF IRON ORES.

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ABSTRACT

Iron ore samples were collected from iron deposits in the north east of Thailand. Samples were assessed both before and after an upgrading process (solvent extraction method). Iron salts contributed approximately 40% of the weight of the original samples, and the main impurities were found to be silica plus acid insolubles. After upgrading, a purity of 99% Fe_2O_3 *(by weight) was obtained. Aluminium, barium, zinc and copper salts were measured in small quantities* ($\langle$ *0.1%), and traces of silicon and antimony were detected. Attention was also given to physical properties of the upgraded* Fe_2O_3 *(which, for instance, showed good crystallinity and fine grain). Both the chemical and physical properties were found to compare favorably with commercial laboratory grade* Fe_2O_3.

INTRODUCTION

Ferrites are one of the best known members of the family of ceramics. Their magnetic properties (in particular) have ensured their widespread use in industrial, engineer and domestic products.

Ferrites are often divided into two groups, the "soft" and "hard" ferrites. Soft ferrites include manganese-zinc, nickel-zinc, and manganese-manganese ferrites. They are found in many products such as radios, television sets, telephones, various recording instruments and computers. Barium and strontium ferrites are examples of hard ferrites. They are employed in electric motors, loud speaker and toys. Both types of ferrites are solid solutions of mixed oxides, in which ferric oxide (Fe_2O_3) contributes at least 50% of the weight. Increasing quantities of the ferrites are needed every year. Therefore, there is an increasing demand for ferric oxide. An estimate of the world ferrite consumption was reported increasing at about 5-18% during the years 1981-1983[1].

In this paper, iron ore deposits which are found in a large area of the north east of Thailand are examined. Solvent extraction methods[2, 3] (ion association complex extraction) were employed for upgrading. These methods are suited to small-scale and large-scale production, and they compare favorably (in terms of selectivity, convenience, speed and cost) with the more conventional wet analysis methods.[4] The resulting upgraded ferric oxide is compared with a commercial product. Assessment of the materials was achieved by optical and electron microscopy, X-ray fluorescence, atomic absorption spectrometry, X-ray and electron diffractometry, and differential thermal analysis.

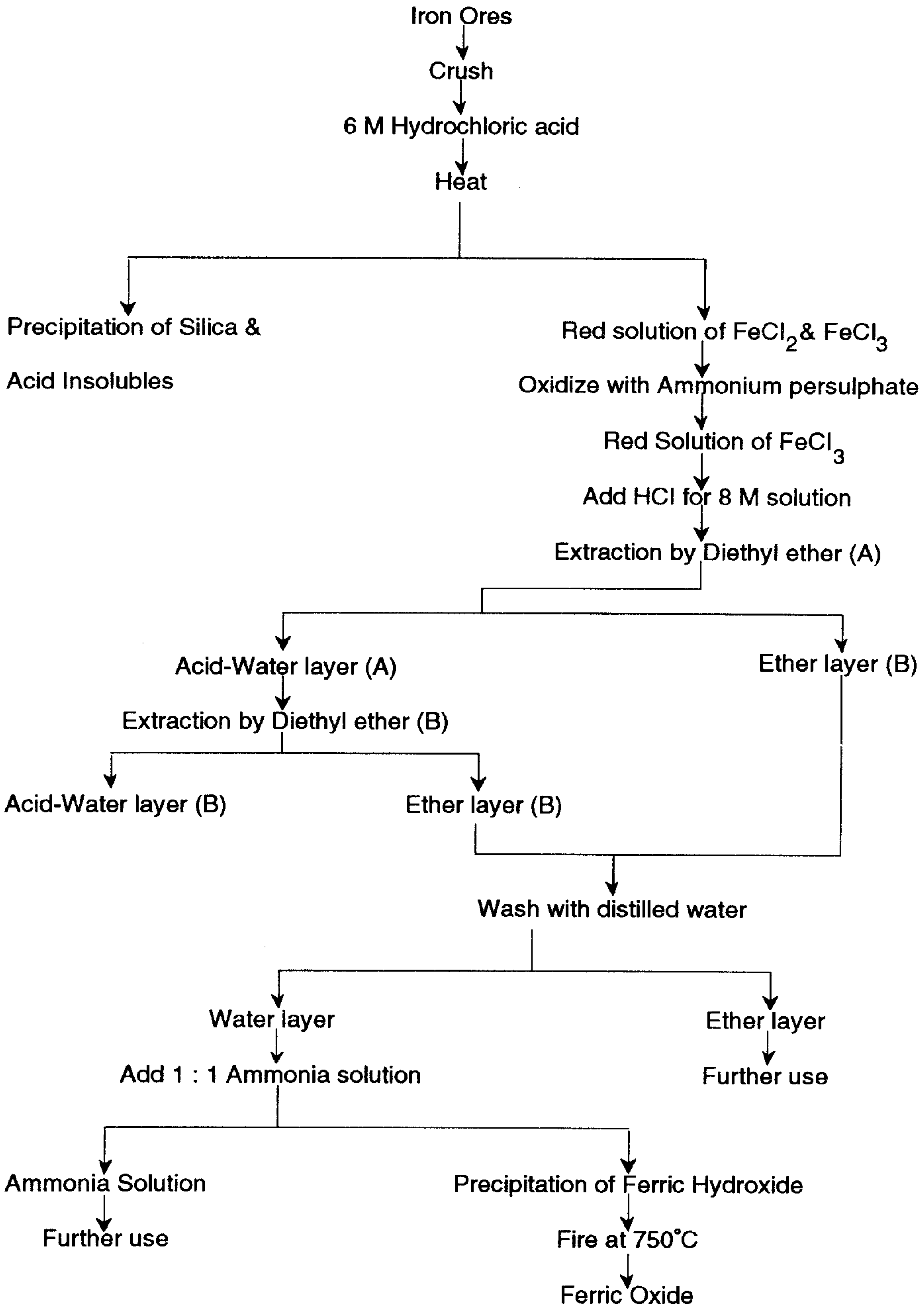

Fig. 1. Upgrading process of iron ores.

This paper describes methods for the assessment and upgrading of iron ore with the aim of application to the production of ferrites. Barium carbonate which is a starting material for production of many hard ferrites can be obtained by upgrading barites.[5, 6]

METHODS AND RESULTS

1) Iron ores geologic setting

Two deposits were intensively surveyed and assessed. Details of the deposits are described elsewhere.[6]

The iron deposits are associated with (either lying beside or embedded in) large barite veins which cross-cut the surrounding (country) rocks. Fractures in the country rocks result in the iron ore extending away from the barite vein to form small veins and stockwork. The country rocks are an interbedded sequence of sandstone, siltstone and shale of Permian age which is intruded by Permo-Triassic granite.

2) Upgrading process

The process of upgrading of the ores is described as follows.

a) Crush and sieve the iron ore (mesh # 100).
b) Dissolve the iron powder in 6 M.HCl and heat to 100°c.
c) Remove the insoluble salts by filtering. The resulting red coloured solution ($FeCl_2$ and $FeCl_3$) is oxidized with ammonium persulphate to yield $FeCl_3$.
d) Increase the concentration to 8 M. by adding further HCl.
e) Extract the iron salt with diethyl ether, using a separating funnel and agitation. The iron salts are extracted into the diethyl ether.
f) Pour out the acid-water layer and collect the ether layer (A) in a closed container. Extract the iron salts in the acid-water part again by adding diethyl ether and agitaling. Most of remaining iron salts should mix in the ether layer part (B).
g) Combine ether layers (A) and (B) then add distilled water. The iron salts will leave the ether layer and mix with the water.
h) Separate the water layer from the ether layer (since the ether can be used again). Add the solution to ammonia solution 1:1 in weight. Ferric hydroxide will precipitate.
i) Fire the precipitate of Ferric Hydroxide at 750°c Ferric axide (Fe_2O_3) is the result.

The processes are summarized diagrmamatically in Fig. 1 where A and B are more clearly defined.

3) Analysis

The yields obtained from this purification were determined and are presented in the Table 1. Iron ore sites and reserved quantities in tons were determined and are presented in Table 2. Specimens of the iron minerals (Fe-minerals) were polished and investigated using an optical microscope Fig. 2 and analysis was carried out according to Spry[7] and Craig.[8] The

TABLE 1. Yields of Ferric oxides

	Weight (gm)	
Iron Ores	F_1	F_2
Iron Ore	31.3404	30.8147
Yield (Ferric Oxide)	12.1236	15.7093
Silica plus acid insolubles	19.2482	15.0450
Percentage (by weight)	38.7	50.9

TABLE 2 Analysis using XRF

Batch number (Iron Ore)	F_1	F_2
Sites	**Namrin, Phrae**	**Phulek, Loei**
Elements found prior to upgrading	Fe, Ba, S, Si, Al, Sr	Fe, Si (sb, Ca traces)
Elements found in upgraded products	Fe (Si, Sb traces)	Fe (Sb, Si traces)
Reserved Quantity (tons)	>100,000	800,000

TABLE 3. Analysis of impurities of Iron Ores and products using A.A.S. (% by weight)

	F_1		F_2		Commercial Fe_2O_3
	P	**A**	**P**	**A**	
Ba	2.99	0.275	1.32	0.15	–
Al	0.40	0.10	0.40	0.10	–
Sr	0.06	0.025	0.40	0.025	–
K	0.39	–	–	–	–
$Sb^{\#}$	/	/	–	–	–
Ca	0.38	0.062	–	–	0.05
$Mn^{\#}$	/	–	–	–	–
Zn	0.30	0.10	–	–	0.05
Cu	0.21	0.10	–	–	0.1
Pb	–	–	–	–	0.05
I	46.96	–	59.56	0.45	1.5
Fe^{*}	48.11	–	38.68	–	–
$Fe_2O_3{}^0$		98.90		99.20	98

P=Prior to upgrading process.
A=After upgrading process.
I=Complex insoluble (in HCl) salts.
Fe^{*}=Iron salts/minerals.
^{0}=Analysis by classical titration with $KMnO_4$
$\#$=Traces, unable to determine (《 0.01%)

N.B. Small experimental errors result in the percentages not adding to 100%.

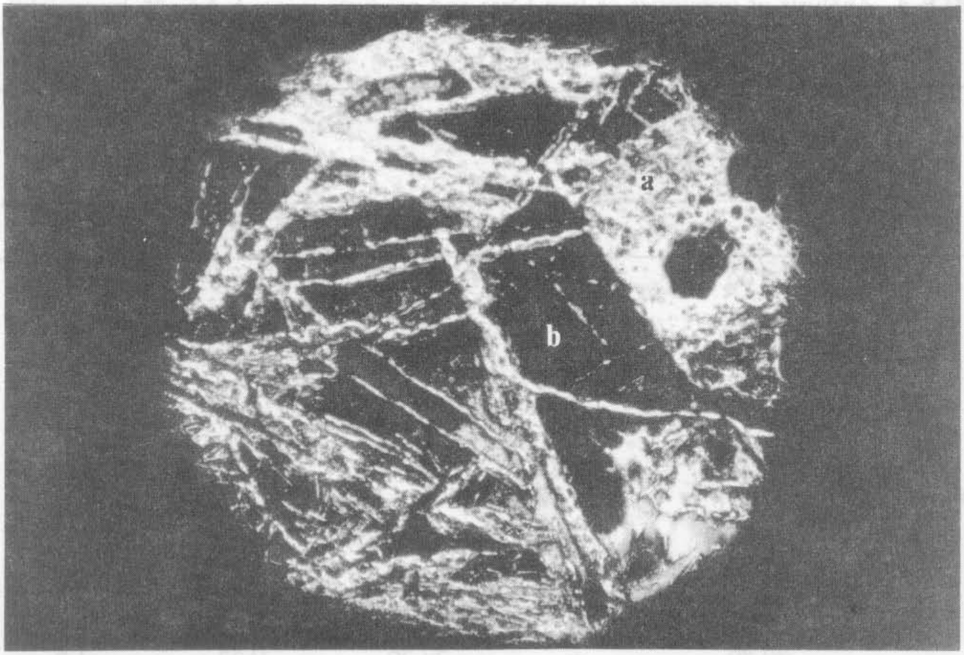

Fig. 2. Image by optical microscope of the Fe-minerals, which were found to be an intergrowth of Haematite (light gray, a) and magnetite (dark gray, b). (× 400).

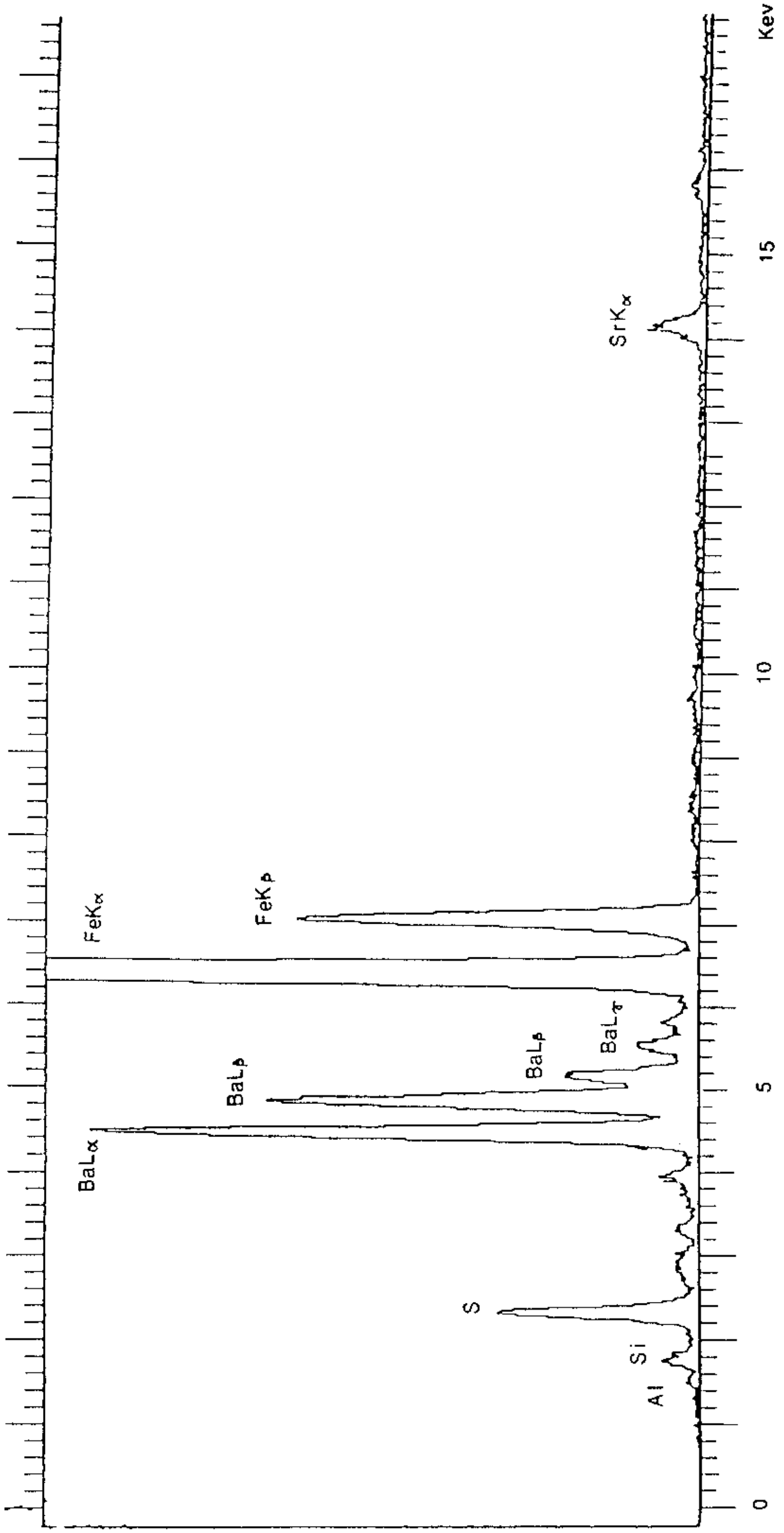

Fig. 3. XRF analysis of iron ore (F_1).

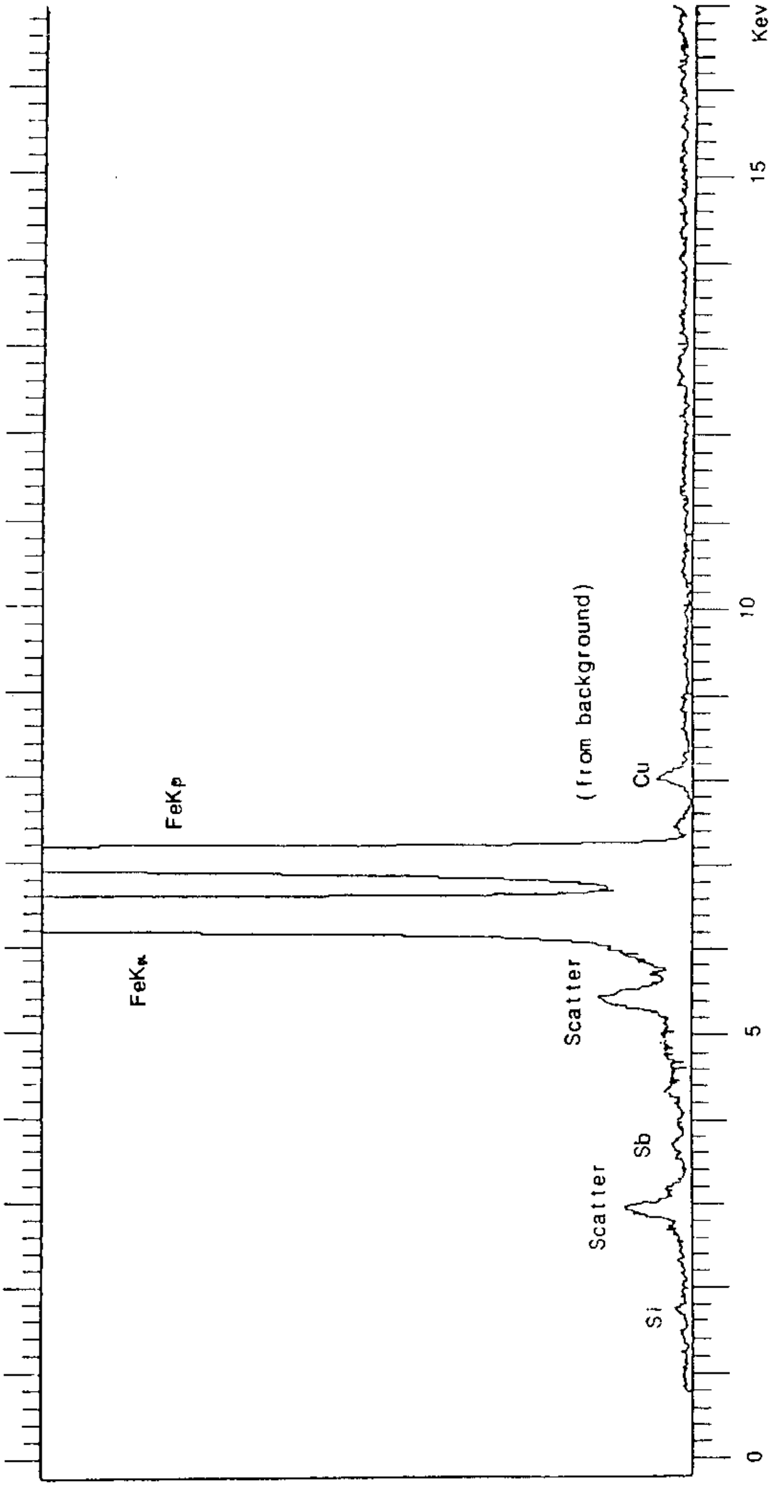

Fig. 4. XRF analysis of Fe_2O_3 obtained from upgraded iron ores (F_1).

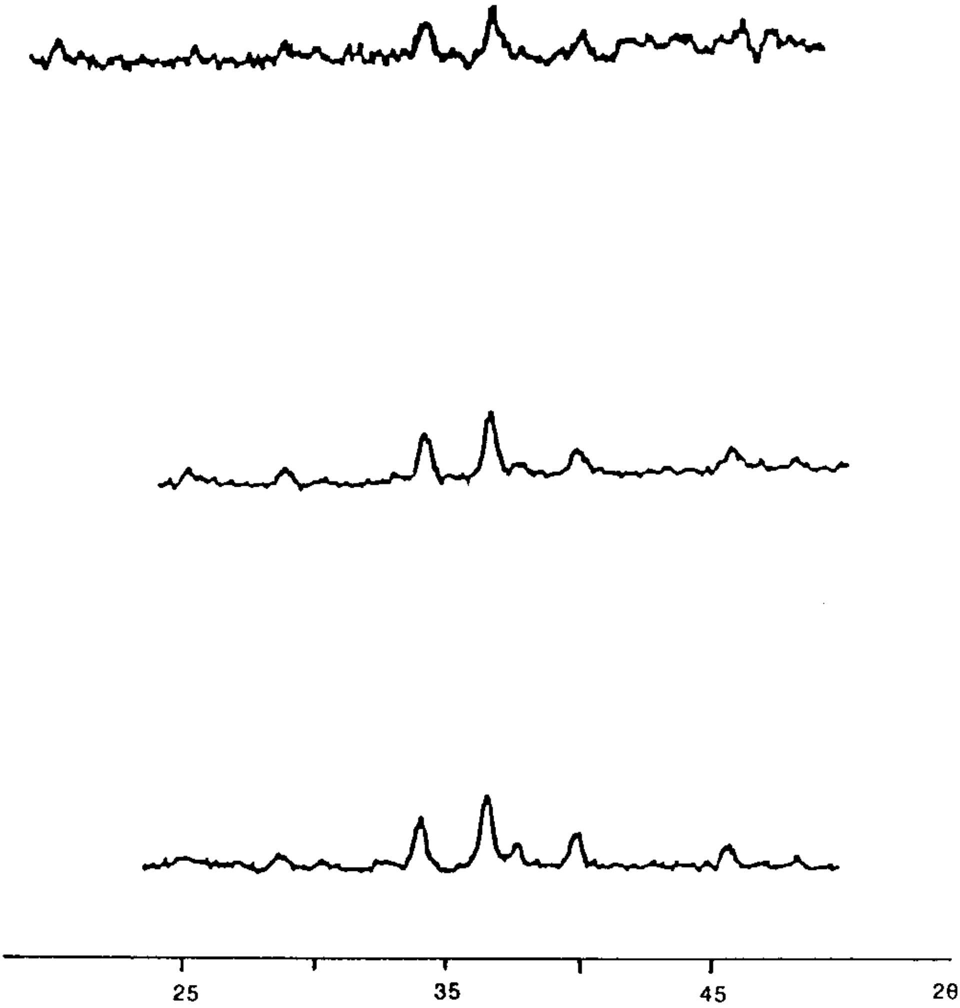

Fig. 5. X-Ray diffractograms of

a) iron ores (from Namrin, Phrae F_1)

b) Fe_2O_3 obtained from upgrading ore (F_1)

c) Fe_2O_3 (commercial).

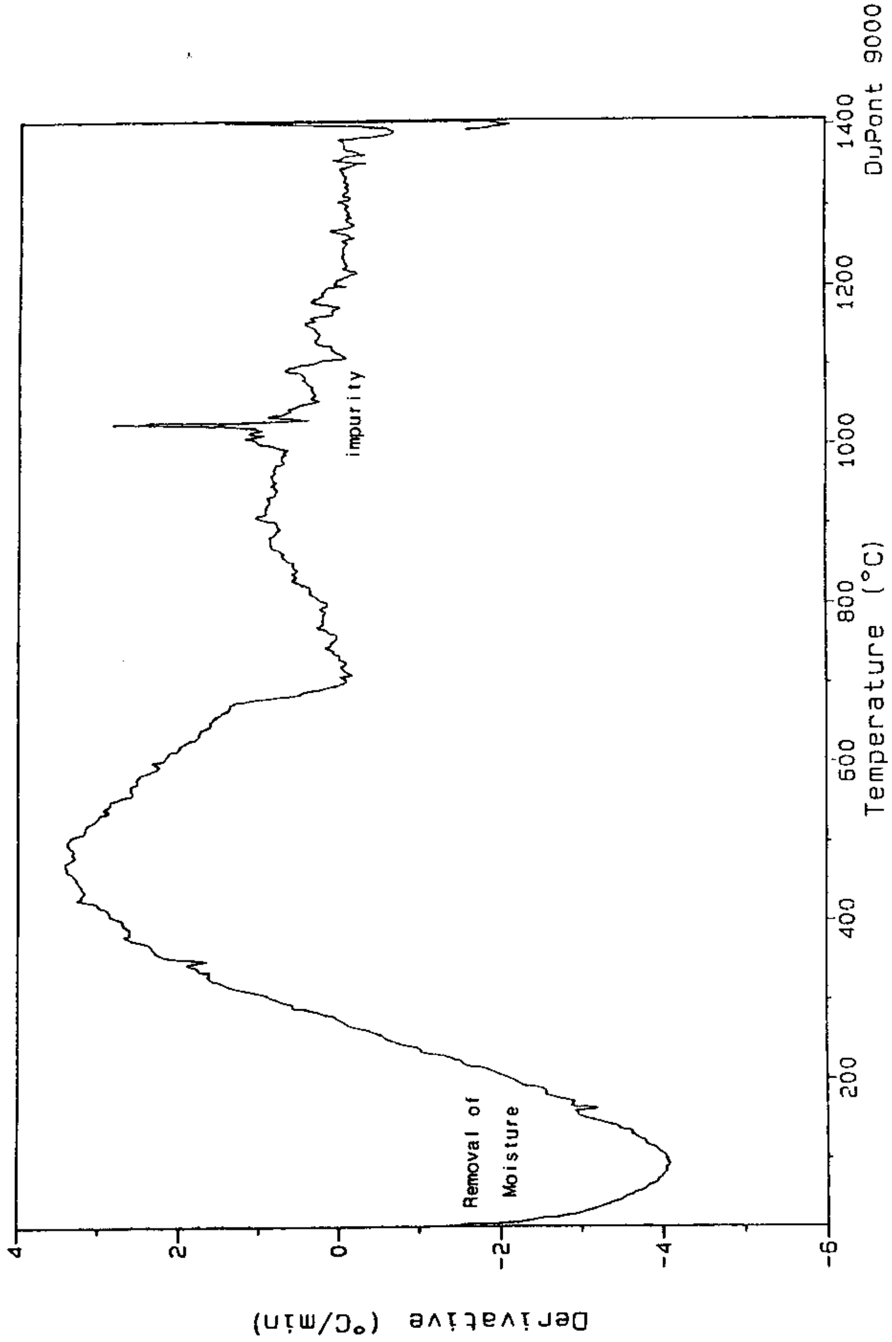

Fig. 6. DTA thermogram of Fe_2O_3 obtained from upgraded iron ore (F_1).

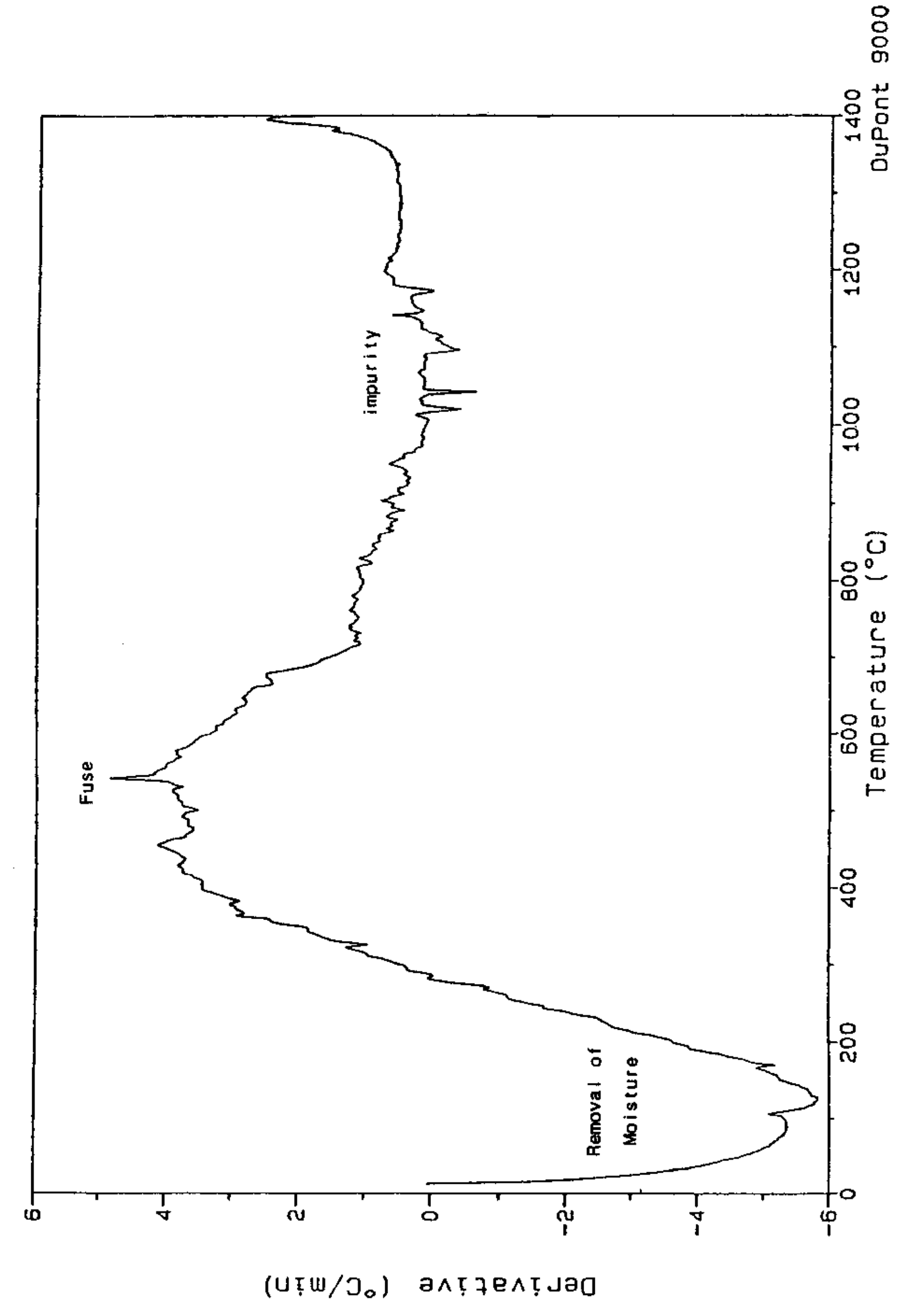

Fig. 7. DTA thermogram of Fe_2O_3 (commercial).

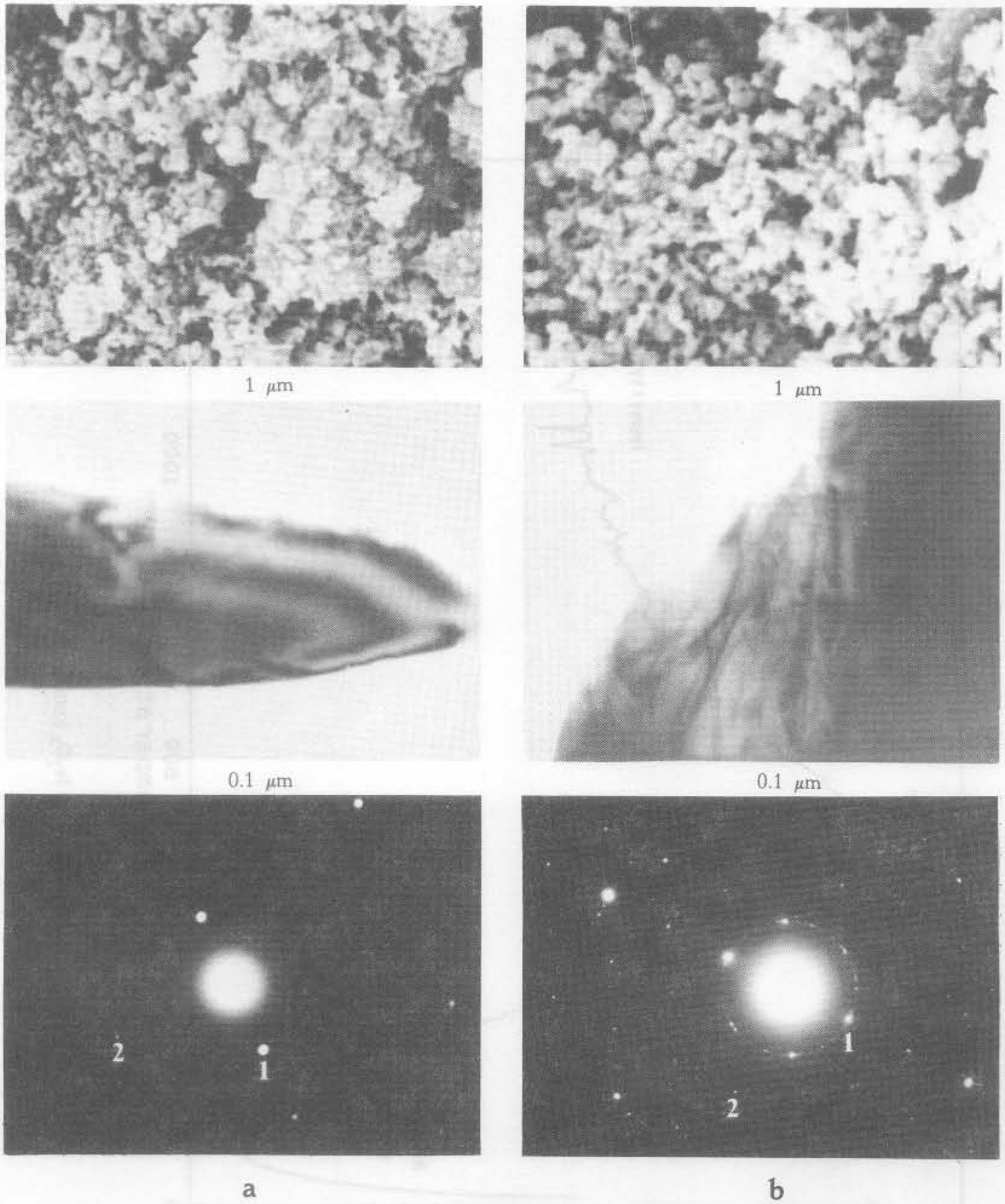

Fig. 8. SEM, TEM and TED pictures of upgraded product (a) and commercial Fe_2O_3 (b) respectively.
1=(010), 2=(210)

Fe-minerals were found to be an intergrowth of haematite and magnetite together with a number of impurities. The starting materials and upgraded Fe_2O_3 were analysed by X-ray fluorescence (XRF), atomic absorption spectrometry (AAS) and X-ray diffractometry (XRD). The impurities were determined and are shown in Tables 2 and 3. Typical XRF peaks are presented in Figs. 3 and 4, X-ray diffractograms of the iron ore and the upgraded product are shown in Fig. 5. Differential Thermal Analysis (DTA) was employed to check the quality of the upgraded products against a commercial one, and the thermograms are shown in Figs. 6 and 7. Scanning electron microscopy (SEM) transmission electron microscopy (TEM) and transmission electron diffraction (TED) were employed to study the particle shapes of Fe_2O_3 as shown in Fig. 8.

Silica and other acid insoluble salts were found to be the main impurities (>50%) by weight of the ore samples, as can be seen in table 1. Small amounts of other impurities were determined as shown in Table 3. A typical X-ray diffractogram of upgraded Fe_2O_3 is compared with commercial Fe_2O_3 in Fig. 5; all peaks belong to Fe_2O_3 according to the Joint Committee on Powder Diffraction Standards number 33-664.[9] There are no significant differences between the upgraded and commercial products, and other compounds were not detected by this method.

By comparing Figs. 6 and 7, the DTA thermogram of upgraded Fe_2O_3 can be compared with that of commercial Fe_2O_3. The results show similarities, i.e. moisture is removed from 0-400°c, and fusing takes place at about 500°c. Slight differences in the thermograms are attributable to unidentified impurities (by this method) present in the samples. The thermogram of upgraded Fe_2O_3 from the second deposit was similar to that shown here.

In Fig. 8 electron micrographs from SEM, TEM and TED of upgraded product are presented. In the SEM micrograph, it is seen that the Fe_2O_3 crystals mostly precipitated into circular shapes. All TED spots in both the upgraded and commercial products are due to Fe_2O_3. Analysis of the TED patterns was carried out according to Andrews *et al.*[10]

Twin spots were found in the TED pattern of upgraded product, while the TED pattern of commercial Fe_2O_3 showed spotty rings, indicating that both Fe_2O_3 are polycrystalline with twin crystals in the upgraded Fe_2O_3.

DISCUSSION AND CONCLUSIONS

From Tables 2, 3, with Figs. 3 and 4, it is clear that the upgrading method can significantly reduce impurities with the exception of antimony. Antimony and gold are not removed from the ore due to the limited extraction capabilities of diethyl ether in 8 Molar solution.[2] However, given the very low initial level of antimony in the ore (and the absence of gold), this should not present any practical problems. An overall purity of 99% was achieved, which is slightly better than the 98% for sample of commercial Fe_2O_3.[11] The commercial products were also investigated using AAS and the results are included in Table 3 Both the upgraded ore and the commercial Fe_2O_3 have the required levels of purity for the production of general-purpose ferrites.[12]

It is likely that for some specialised ferrites, the existence of very small quantities (or traces) of elements will be important. In that case, the data presented here would be useful for determining both the suitability of the ore and of the upgrading process. The data will also show what is required of any alternative upgrading process. If an overall purity of greater than 99% is required, the upgrading process can be repeated (after step b in the upgrading process). On doing so, all the detected impurities will be reduced further (with the exceptions of antimony and gold).

Both the upgraded and commercial products showed good crystallinity and grains which were on average circular with a diameter of less than 500 nm. Analysis of the electron diffraction patterns supported the results of X-ray diffractometry and showed that the upgraded and the commercial Fe_2O_3 powders had some twin spots and spotty rings respectively. The upgraded products were sent to the Materials Science Department, Chulalongkorn University for producing ferrites (antenna rods); and the ferrites yielded satisfactory results.[12]

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REFERENCES

1. Fisher. G., (1984). *Amer. Ceram. Soc. Bull.* 63 [4] P. 569.
2. Morrison, G.H. and Freiser, H., (1957). "Solvent Extraction in Analytical Chemistry". NewYork, John Wiley and Sons, Inc.
3. Tatsuya Sekine and Yuko Hasegawa, (1977). "Solvent Extraction Chemistry" Marcel Dekker, Inc., New York and Basel.
4. Kolthoff. I.M., Sandell, E.B., Meehan, E.J. and Bruckenstein, S., (1969). "Quantitative Chemical Analysis". The Macmillan Company, Collier-Macmillan Limited. London.
5. T. Tunkasari, V. Opasnipat, S. Chantaramee, S. Junhavat, P. Asnachinda and B. Ratanasathien. (1990). The Science and Technology Development Board of Thailand, report on "Ceramic Materials and Products for Electronic Industries" P. 101-109.
6. Tunkasari, T., Opasnipat, V., Chantaramee, S., Ratanasathein, B., Junhavat, S. and Asnachinda, P., on "Characterization and uses of upgraded barytes." Submitted to Journal of Materials Science Letters.
7. Spry, P. G. and Gedlinske, B.L., (1987). "Table for the Determination of Common Opaque Minerals." The Economic Geology Publish, Iowa.
8. Craig, J. R., and Vaughan, D. J., (1981). "Ore Microscopy and Ore Petrography." John Wiley & Sons, N.Y.
9. Joint Committee on Powder Diffraction Standards (JCPDS) No. 33-664.
10. Andrews, K.W., Dyson D.J. and Keown, S.R. (1971). "Interpretation of Electron Diffraction Patterns" Plenum Press, New York.
11. Laboratory grade Ferric oxide purchased from V.O. Chemical Ltd. Chiang Mai, Thailand.
12. Lorprayoon, C., Panyarjun, Uttamasil, L. and Rukhavibul, V. The Science and Technology Development Board seminar on "Ceramic Materials and Products for Electronic Industries" (Development of Ferrite Products for Radio and Television Appliances). Arranged at Chulalongkorn University, 11th, July 1990.

บทคัดย่อ

แร่เหล็ก ที่อยู่ในแหล่งแร่บริเวณตะวันออกเฉียงเหนือ ได้นำมาปรับปรุงโดยกระบวนการสกัดโดยสารละลาย การตรวจหาปริมาณแร่ธาตุและสิ่งเจือปนในแร่ได้กระทำทั้งก่อนและหลังกระบวนการปรับปรุงแร่เหล็กส่วนใหญ่มีธาตุเหล็กประมาณ 40% โดยน้ำหนัก สิ่งเจือปนอื่น ๆ มักเป็นพวกซิลิกาและสารที่ไม่ละลายในกรด หลังกระบวนการปรับปรุงแล้วแร่เหล็กมี Fe_2O_3 บริสุทธิ์ถึง 99% (โดยน้ำหนัก) สิ่งเจือปนอื่น ๆ จะเป็นธาตุอะลูมิเนียม, แบเรียม, สังกะสีและเกลือของทองแดง แต่ละธาตุมีเล็กน้อย น้อยกว่า 0.1% อย่างไรก็ตาม มีร่องรอยของซิลิกอนและพลวงอยู่บ้าง สมบัติกายภาพอื่น ๆ ของ Fe_2O_3 ที่ปรับปรุงแล้ว เช่นความเป็นผลึกที่ดี และความเล็กของอนุภาคก็ได้รับการตรวจสอบด้วย ทั้งคุณสมบัติทางเคมีและฟิสิกส์ของ Fe_2O_3 ที่ปรับปรุงได้ สามารถเปรียบเทียบได้ใกล้เคียงกับ Fe_2O_3 ท้องตลาดที่ใช้ในห้องปฏิบัติการ