Production of M-type strontium hexaferrite magnetic powder with the high-pure magnetite concentrate via the ceramic process

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ABSTRACT
The high-pure magnetite concentrate (HPMC) was studied for a substitution of iron scale to produce the magnetic powder of strontium hexaferrite via the conventional ceramic process in this work. The magnetic powder obtained under the optimum conditions had a magneto plumblite structure, which was confirmed by X-ray diffraction (XRD). Scanning electron microscope (SEM) depicted that ferrite grains were hexagon shaped and evenly distributed with an average particle size of about 1 μm. Furthermore, a comparison of magnetic powders separately produced with HPMC and iron scale was made by detecting the magnetic properties of their sintered magnets using a permanent magnetic measuring system. The results demonstrated that the HPMC magnetic powder had a superiority over iron scale magnetic powder, and it had fully achieved the level of Y30-1 product in China. In the final part, the economic feasibility of using HPMC for magnetic powder production was verified by the cost–benefit analysis.

1. Introduction
The strontium permanent ferrite SrFe$_1$_2O$_9$ (SFO) as a kind of fundamental material is widely applied in automobile and household appliances due to its high curie temperature, large magnetocrystalline anisotropy, cost-effectiveness, and chemical stability [1–3]. The high-performance permanent magnet is made from alloys of rare earth metals, especially neodymium [4,5]. However, due to the increasing scarcity of rare earth metals, their prices have been rising exponentially. The ferrite magnet took the lead over alloy magnets since the 1970s because the former was much cheaper and easier to produce than the latter in industry.

The permanent ferrite or, namely, hard ferrite is generally classified into the bonded magnet and the sintered magnet. The sintered magnet with a high coercivity (Hc) is suitable for certain special applications such as permanent magnet synchronous motor, which requires a good ability to resist demagnetization. In view of the increasing demands globally for motors in electric-powered cars and generators in wind turbines, permanent ferrite will become more attractive. There are various kinds of methods for preparing permanent ferrites: sol-gel [6–10], hydrothermal synthesis [11,12], co-precipitation [13], molten salt [14] and conventional ceramic method [15–17]. Generally, most permanent ferrites are produced by the conventional ceramic process in industry due to its easy operation, low cost, and large production capacity.

The raw iron oxide materials of permanent ferrites mainly include iron oxide red and iron scale. The former is generally applied to mid-grade and high-grade ferrite products, while the latter is used for the low-grade ferrite production due to its detrimental alloying elements such as manganese. The production of iron oxide red is limited now due to the stricter environmental laws, and hence the price of iron oxide red is pretty high due to the short supply [18,19]. Iron scale, a kind of byproduct from steel rolling, could be used as a cooling agent for converter steelmaking or the oxidizing agent for electric furnace steelmaking, and meanwhile the iron element of iron scale is recovered by entering into molten steel. As a result, the supply of iron scale from iron and steel plants has been reducing in recent years because of the internal consumption, especially the high-quality iron scale (Fe >73%) for producing permanent ferrite.

The high-pure magnetite concentrate (HPMC) can be obtained from the magnetite concentrate, a kind of bulk commodity as raw material for ironmaking, by simple magnetic separation having the advantages of no pollution and less energy consumption [20]. Thus, the production of HPMC is cheap and environmentally friendly. Besides, China is rich in high-class magnetite...
resources in Anhui, Sichuan province, etc., and HPMC can be steadily produced in quantity, which is beneficial for its use in permanent ferrite industry.

Conventional raw materials of red iron oxide and iron scale are faced with problems like short supply and high cost, and hence the replacement of these raw materials with HPMC may be a good choice for permanent ferrite production. A minority of researchers have reported that HPMC could be used for low grade permanent ferrite production [21]. However, those works have not been systematically and deeply implemented. In this paper, a systematic work for preparing magnetic powder with HPMC was carried out. The effects of the average particle size of the ground HPMC, the molar ratio of Fe₂O₃/SrO on the composition and the pre-oxidation process on the performance of magnetic powders were studied. The influences of calcination temperature and dwell time on micromorphology and grain size of the magnetic powder were investigated. In addition, the ferrite magnets separately prepared by HPMC and iron scrap were compared in terms of comprehensive magnetic performances. In the final part, a preliminary analysis of the cost and benefit of this preparation process was made. The results of this study are valuable for the substitution of iron scale with HPMC to produce low-grade ferrite magnetic powder, which is widely used among small household applications. The replacement of red iron oxide by HPMC to produce mid-grade or even high-grade ferrite magnetic powders will be introduced in our following study.

2. Experimental

2.1. Materials and reagents

The ash black HPMC powder (Figure 1(a)) used in the study is from Chuanwei Group Mining Co., Ltd in Sichuan province, China. Table 1 illustrates the main chemical compositions of HPMC and its contents of total iron, silicon dioxide, and aluminum sesquioxide are 71.46%, 0.35%, and 0.23%, respectively. The iron content of ideal magnetite is 72.36% according to the chemical formula of Fe₂O₃, and the purity of HPMC in this study is calculated to be 98.8% based on the iron content. The XRD characterizes that the primary mineral in HPMC is magnetite as shown in Figure 1 (b). Reagents like SrCO₃, SiO₂, H₃BO₃, CaCO₃ and Al₂O₃ used here are all analytical grade.

2.2. Experimental setup and procedure

The permanent ferrite in this study was obtained via a conventional ceramic process as shown in Figure 2. In the first stage, HPMC was wet-ground and thoroughly dried at the beginning. The HPMC and strontium carbonate were weighed according to the stoichiometric formula SrO·nFe₂O₃, where n was the molar ratio of Fe₂O₃ to SrO and approximately equal to 6.0. The mixture of starting powder was charged into the planetary grinding mill with an angular velocity of 100 rpm, and the mass ratio of ball to powder to water was 14:1:1.5. The ground mixture was dried in the oven at 110°C for 24 h, and then was shaped into cylindrical briquettes (diameter 8 mm and height 10 mm) under a pressure of 2000 N. The compacted briquettes were pre-oxidated and calcinated in the muffle furnace for a certain time, which was equipped with an air pump to increase oxygen supply, and then were cooled in the furnace under air atmosphere. After crushing, the magnetic powder of strontium hexaferrite was obtained. In the second stage, the magnetic powder was sifted through a 120-mesh screen, and then was wet-milled together with sintering aids, such as CaCO₃, SiO₂, Al₂O₃, H₃BO₃, and so on in the planetary grinding mill with an angular velocity of 300 rpm for 110 min. The mass ratio of ball to powder to water was 14:1:2. The fine-ground slurry with an average particle size of

Figure 1. The appearance and XRD pattern of HPMC.
about 0.8 μm was drained and then pressed into disk-shaped compacts (diameter 30 mm and thickness 15 mm). The compacting was under 100 MPa pressure and 8000Gs induced magnetic field, and the magnetic field direction was parallel to the pressure direction. The green compact was sintered in the muffle furnace and then cooled in furnace under air atmosphere. After polishing and testing, the ferrite magnet was eventually obtained.

### 2.3. Analysis and characterization

The particle size of the sample was detected by Fisher sub-sieve sizer (WLP-216, China). The density of ferrite magnet was tested by an electronic densimeter (DPO-6000, USA). Quantitative chemical assay of the main elements in HPMC was performed by acid digestion followed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PS-6, Baird). Mineralogical composition of the sample was identified by an X-ray diffractometer (XRD, D/Max 2500, Rigaku) with a scanning angle from 5° to 80°. The thermal characteristics of HPMC were obtained from the TG curve using a thermogravimetric analyzer (TGA-5500, British) at a heating increment of 10 K/min in air. Microcosmic morphology of the magnetic powder was observed by scanning electron microscope (SEM, MIA3, TESCAN), following an ImageJ application to analyze and collect grain size of digital photographs. The phase diagram calculations were performed using the software FactSage 7.3 (Thermfact/CRCT, Montreal, Quebec, Canada). The magnetic properties of the magnetic powder were measured at room temperature using a vibrating sample magnetometer (MPMS XL-7, USA) with a maximum field of 20 kOe. The permanent magnetic measuring system (NIM-2000HF, China) was used to test the magnetic properties of sintered ferrite magnet.

### 3. Results and discussion

#### 3.1. Effect of average particle size of HPMC

The average particle size of HPMC has a vital effect both on the mixing effect and thermal reaction rate of solid-state powders [22]. In general, the fine particle size of HPMC is beneficial for solid-state reactions. Therefore, HPMC needs to be finely ground first, whose original average particle size is as coarse as 9.2 μm. HPMC was charged into a planet grinding mill with a ball-material-water mass ratio of 14:1:1.5 and an angular velocity of 150 rpm. The average particle size of HPMC as a function of grinding time is shown in Figure 3.

The average particle size of the ground HPMC sharply decreased as time prolongs within 1 h. After that, the decrease in average particle size became slow. The average particle sizes of HPMC were 1.9 μm and 1.0 μm after milling for 1 h and 4 h, respectively. The fitting curve was nearly horizontal after 4 h, which denoted that HPMC was hard to be levigated when its average particle size approached 1 μm. This was likely because the magnetic agglomeration among particles was intensified when the particle size of HPMC turned too small, causing the decrease in grinding efficiency.

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**Table 1.** Quantitative chemical compositions of HPMC.

| composition | TFe | SiO₂ | Al₂O₃ | CaO | MgO | S   | P   |
|-------------|-----|------|-------|-----|-----|-----|-----|
| content (wt. %) | 71.46 | 0.35 | 0.23  | 0.07 | 0.03 | 0.03 | 0.02 |

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**Figure 2.** The flowchart of preparing ferrite magnet with HPMC by conventional ceramic process.
3.1.1. Phase identification analysis

The magnetic powders were prepared by HPMC with different average particle sizes of 9.2, 1.9, 1.2, and 1.0 μm. The molar ratio n of Fe₂O₃ to SrO for starting materials was 5.9, and slightly excessive strontium carbonate was added to compensate for the burning loss of strontium. Starting powder above was roasted at 800°C for 1 h to eliminate ferrous iron in HPMC, and then calcined at 1300°C for 2 h with a heating rate of 7°C/min in an oxidizing atmosphere.

The XRD patterns of magnetic powders with different average particle sizes of HPMC are presented in Figure 4. The patterns of those magnetic powders were compared with those of standard SrFe₁₂O₁₉ which exhibited hexagonal magneto plumbite crystal structure with space group P63/mmc (JCPDS card, NO. 33–1340). All samples in Figure 4 shows a pure SFO phase and no impurity phase occurred in the magnetic powders. In addition, the positions and intensities of the main peaks of (107) and (114) for these samples were nearly identical, which revealed that the average particle size of HPMC had no evident influence on the crystallinity of SFO in the study range [1].

3.1.2. Magnetic properties

The saturation magnetization (Ms), remanent magnetization (Mr) and intrinsic coercivity (Hcj) of magnetic powder were determined from the obtained hysteresis loops Figure 5(a), and their values are shown in Figure 5(b). The values of Hcj were rapidly increased with the decrease of HPMC particle size before 1.9 μm, while they decreased when the particle size was below 1.9 μm. The values of Ms and Mr slightly increased as the decrease in the average particle size before 1.9 μm, and after that their values fluctuated. The Mr, Hcj and Ms reached their maximum values of 28.38 emu/g, 1162.22 Oe, and 51.78 emu/g at an average particle size of 1.9 μm. The ground HPMC powder inevitably included a part of microparticles (<1 μm), and those microparticles reacted fast during the solid-state reactions causing overgrowth of SFO grains in magnetic powder. The value of Hcj was mainly dependent on the grain size and grain size distribution of magnetic powder [23], and as a result, those coarse grains could be responsible for the decrease of Hcj. While Mr and Ms mainly depended on the intrinsic composition and homogeneousness of materials, and thus the average particle size of HPMC had no evident influence on them. It can be concluded that the optimum average particle size of HPMC for preparing magnetic powder was 1.9 μm.

3.2. Effect of pre-oxidation process

The overall reaction equation for strontium hexaferrite generation is summarized as Eq. (1) [24], and it can be divided into four steps as Eqs. (2–5). The oxidation of Fe₂O₃ starts at around 200°C as shown in Figure 6. The decomposition of SrCO₃ begins at around 840°C. The initial generation of SrFeO₃₋ₓ is generally over 1000°C, and the rapid generation of SrFe₁₂O₁₉ happens over 1200°C [25–28].

Overall reaction:

\[ 4\text{Fe}_2\text{O}_3 + \text{O}_2 + \text{SrCO}_3 \rightarrow \text{SrFe}_12\text{O}_{19} + \text{CO}_2 \]  

Step reactions:

\[ \text{2Fe}_2\text{O}_3 + 1/2\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3 \]  

\[ \text{SrCO}_3 \rightarrow \text{SrO} + \text{CO}_2 \]  

\[ \text{1/2Fe}_2\text{O}_3 + \text{SrO} + 1/2(0.5-x) \text{O}_2 \rightarrow \text{SrFeO}_{3-x} \]  

\[ \text{SrFeO}_{3-x} + 5.5 \text{Fe}_2\text{O}_3 = \text{SrFe}_{12}\text{O}_{19} + 1/2(0.5-x) \text{O}_2 \]
As for the oxidation of HPMC, the thermogravimetry curve (TG) and the derivation curve (DTG) of HPMC ranging from 25°C to 1000°C in air are given in Figure 6. The mass of HPMC increased with increasing temperature in the study range. The first peak of the DTG curve occurred at point I (325°C), which indicated that the surface of the sample was quickly oxidated into ferric oxide. The mass increasing rate decreased after point I probably because the thickened ferric oxide layer impeded oxygen from entering into the inner part of mineral particles causing the decrease in oxidation reaction rate. When the temperature increased to point II (550°C), the mass of the sample increased fast again. High temperature speeded up the heat motion of gas molecules and thus helped oxygen overcome the hindrance of the ferric oxide layer. The DTG curve began to decline after point III (760°C), which implied that the oxidation reaction of the sample was close to the endpoint.

HPMC contains around 30 wt.% ferrous oxides, and ferrous oxide easily reacts with silicon dioxide and produces ferrous silicate, which is a kind of nonmagnetic substance with a relatively low melting point of 1050°C [29]. The binary alloy phase of a FeO-SiO₂ system used to observe the formation of ferrous silicon (Fe₂SiO₄) is given in Figure 7(a). The red curve indicated that the formation temperature of ferrous silicon was above 800°C according to the Y-coordinate intersection. The blue curve implied that the metal iron could be formed if the content of silicon dioxide was over 29 wt.%. The ternary phase diagram of the FeO-SiO₂-SrO system at 1000°C is drawn in Figure 7(b) for the simulation of ferrous silicon occurrence during the early stage of the calcination procedure. It was clear that the ferrous silicate could be generated and stably existed in a wide area when the ferrous iron occurred. The proper amount of ferrous silicate could form a glassy phase between grain boundaries, and thus
the magnetic performance of magnetic powder was improved by impeding the excessive growth of grains. Meanwhile, an overdose of ferrous silicate would decrease magnetic performance as it was a kind of nonmagnetic substance.

The pre-oxidation temperature was set to be 800°C, which was below the temperature of ferrous silicon occurrence. The pre-oxidation time of HPMC here was set from 15 min to 60 min with an increment of 15 min. Hysteresis loops of the magnetic powders with different pre-oxidation time and their magnetic property results are displayed in Figure 8(a). With the increase in pre-oxidation time, the values of Ms and Hcj both increased till 30 min and reached their maximum values of 55.71 emu/g and 1018.39 Oe, respectively, and then their values slightly decreased with time prolonging. The values of Mr basically remained unchanged with pre-oxidation time. The content of ferrous oxide in magnetic powder was reduced rapidly at the early stage, from 0.52% at the pre-oxidation time of 15 min to 0.30% at 30 min in Figure 8(b). The reduction in ferrous oxide improved Ms and Hcj, which contributed to the enhancement of SFO purity and normal grain growth by reducing the production of nonmagnetic substances like Fe$_2$SiO$_4$. The results above indicated that the optimum pre-oxidation time was 30 min, at which the content of ferrous oxide left in magnetic powder was only 0.3%.

3.3. Effect of Fe$_2$O$_3$/SrO molar ratio

Strontium hexaferrite with the stoichiometric formula of SrFe$_{12}$O$_{19}$ or SrO-6Fe$_2$O$_3$ denotes that the theoretical molar ratio of Fe$_2$O$_3$ to SrO is six. Since both partial
burn loss of SrO and inevitable introduction of worn iron during the grinding process increase the molar ratio, a properly excessive amount of SrCO₃ should be added at the beginning. Besides, the deficiency of iron, caused by slightly excessive addition of SrCO₃, produces lattice vacancies, which are favorable for ions immigration [30–33]. As a result, the solid reaction rate is improved. However, overlying addition of SrCO₃ may decrease the magnetic properties of the sample because extra nonmagnetic substances such as strontium silicate (Sr₂SiO₄) are produced, as shown in Figure 7. Therefore, it is of great importance to determine the optimal molar ratio of Fe₂O₃ to SrO, which is implemented under the conditions given as follows: the average particle size of HPMC 1.9 μm, the pre-oxidation temperature 800°C and time 0.5 h, and the calcination temperature 1300°C and time 2 h.

3.3.1. Phase identification analysis

The lattice constants “a” and “c” of magnetic powders are listed in Table 2. Here, “a” and “c” were calculated out from interplanar spacing values d_mkl for the main peaks of (107) and (114) based on equation (6), where h, k and l were the Miller indices [34,35].

\[
d_{mkl} = \left(\frac{4}{3} \frac{h^2 + h k + k^2}{a^2} + \frac{l^2}{c^2}\right)^{-1/2}
\]  

(6)

The X-ray diffraction patterns of magnetic powders with various molar ratios of Fe₂O₃/SrO are depicted in Figure 9. The diffraction peaks of the samples were compared with that of standard SrFe₁₂O₁₉ (JCPDS card NO. 33–1340), which demonstrated that no impurity occurred in all samples. All values of c/a in Table 2 were in the range of 3.91 ~ 3.93. The magneto plumbite structure of the magnetic powder could be verified if the value of c/a < 3.98 [31], and hence the M-type structure of the samples was determined.

3.3.2. Magnetic properties

The hysteresis loops of magnetic powders with various molar ratios are given in Figure 10(a) and the results of magnetic properties are summarized in Figure 10(b). The values of Mr and Ms increased with the increase in molar ratio from 5.7 to 6.0, and reached their maximum values of 29.24 emu/g and 54.07 emu/g at the molar ratio of 6.0. While the values of Hcj kept increasing before the molar ratio of 5.9, and then decreased after that. The maximum value of 1138.6 Oe for Hcj was obtained at a molar ratio of 5.9. The values of Mr, Ms, and Hcj increased significantly from the molar ratio of 5.7 to 5.9 because the practical molar ratio of Fe₂O₃/SrO gradually approached the theoretical value of 6.0, which meant that the proportion of magnetic phase SFO rose in the magnetic powders. When the molar ratio was over 5.9, the values of Mr and Ms increased slowly, while the value of Hcj decreased likely because the generation of α-Fe₂O₃ impurity decreased the material homogeneity, which was not detected by XRD due to its low content [36–39]. The above analyses indicated that the optimum molar ratio of Fe₂O₃/SrO was 5.9 and also confirmed that slightly excessive SrCO₃ addition was necessary.

3.4. Effect of calcination temperature

3.4.1. Phase identification analysis

In this section, the magnetic powder was prepared using HPMC with an average particle size of 1.9 μm under the conditions of molar ratio of Fe₂O₃/SrO 5.9, pre-oxidation temperature 800°C and time 30 min, and calcination time 2 h. The diffraction patterns of samples with different calcination temperatures, as shown in Figure 11, were compared with that of standard SrFe₁₂O₁₉ (JCPDS card, NO. 33–1340). The XRD results of magnetic powders all showed a pure SFO phase. With the increase in the calcination temperature, no impurity phase occurred. In addition, the values of c/a were all <3.98 as indicated in Table 3, and therefore the hexagonal M-type structure of the samples could be identified [31].

3.4.2. Microcosmic morphology study

As shown in Figure 12, the magnetic powder obtained under 1270°C contained a certain number of irregular ferrite grains. When the calcination temperature increased to 1280°C, those grains turned out to be more regular and hexagonal. The micrograph for 1290°C depicted that the hexagonal grains were more evenly aligned. Below the calcination temperature of 1300°C, the mean size of grains increased to be as coarse

Table 2. Crystal parameters of the magnetic powders with various molar ratios.

| Molar ratios | a   | c   | c/a  |
|--------------|-----|-----|------|
| 5.7          | 5.87612013 | 23.04513 | 3.9198 |
| 5.8          | 5.87673237 | 23.04450 | 3.9203 |
| 5.9          | 5.87953237 | 23.03518 | 3.9179 |
| 6.0          | 5.87601237 | 23.05124 | 3.9229 |

Figure 9. The XRD patterns of magnetic powders with various molar ratios.

Figure 10. Hysteresis loops of magnetic powders with various molar ratios.
3.4.3 Magnetic hysteresis

Magnetic phenomena that occur in ferrites include magnetic hysteresis loops and magnetic properties. The magnetic properties were measured using a vibrating sample magnetometer (VSM) at 300 K. Figure 10(a) shows the hysteresis loops of ferrite powders with different molar ratios. The magnetic properties were also calculated using the experimental data. Figure 10(b) shows the magnetic properties of the ferrite powders with various molar ratios. The magnetic properties were calculated using the experimental data. The magnetic properties were nearly independent of the molar ratio, as presented in Figure 13, and thus Mr, Ms, and Hcj all decreased. As a result, the optimum calcination temperature was chosen to be 1290°C.

3.5 Effect of calcination time

3.5.1 Phase identification

The magnetic powder samples in this section were prepared using HPMC with an average particle size of 1.9 μm under the conditions of molar ratio of Fe₂O₃/SrO 5.9, pre-oxidation temperature 800°C and time 30 min, and calcination temperature 1290°C. It was clear that magnetic powder samples with various calcination durations presented a single magneto plumbite structure by comparing their XRD patterns with that of standard hexagonal ferrite (JCPDS card, NO. 33–1340) in Figure 14. With the increase in calcination time, no impurity phase occurred in these samples. In addition, the values of c/a were all <3.98 in Table 4, and hence the M-type structure of the samples could be confirmed [31].

3.5.2 Microcosmic morphology study

As shown in Figure 15, the magnetic powder calcinated for 1.5 h contained quite a few small and irregular ferrite grains (<0.5 μm). The micrograph for 2 h depicted that ferrite grains turned out to be more angular, and that grains were evenly distributed with a mean grain size of 1.03 μm. When the calcination time prolonged to 2.5 h and 3.0 h, grains grew further and some coarse grains (around 3 μm) appeared at 3.0 h due to their overgrowth.

3.5.3 Magnetic properties

The hysteresis loops of magnetic powders with different calcination durations are given in Figure 16(a), and the results of magnetic properties are shown in Figure 16(b). The values of Mr and Ms increased first
and then basically kept unchanged with the calcination time, and separately reached their maximum values of 45.07 emu/g and 73.19 emu·g⁻¹ at 2.0 h. The optimum value of 1331.56 Oe for Hcj was obtained at 2 h, and then it gradually decreased. The ferrite grains become more regular and even in size with the increase in calcination time before 2.0 h, as exhibited in Figure 16, which could be responsible for the

| Time/h | a      | c      | c/a     |
|--------|--------|--------|---------|
| 1.5    | 5.8782 | 23.0453| 3.9205  |
| 2.0    | 5.8782 | 23.0351| 3.9187  |
| 2.5    | 5.8785 | 23.0527| 3.9216  |
| 3.0    | 5.8784 | 23.0427| 3.9199  |

Figure 12. SEM images of the magnetic powders with different calcination temperature.

Figure 13. (a) The hysteresis loops and (b) magnetic properties of magnetic powders with various calcination temperatures.

Figure 14. The XRD patterns of magnetic powders with various calcination times.
improvement of magnetic properties. When the duration was over 2.0 h, the decreased Hcj was possibly due to grain overgrowth. So, the optimal calcination time was 2 h.

3.6. The comparison of HPMC with iron scrap for preparing magnetic powders

It is widely accepted that magnetic properties of magnetic powder are evaluated by testing its sintered ferrite magnet in industry. As depicted in Figure 2, the production of ferrite magnet from magnetic powder includes procedures of grinding, draining, wet-compacting in a magnetic field, sintering, and polishing. The values of remanence (Br), magnetic coercive force (Hcb), Hcj, and the maximum energy product (BHmax) of ferrite magnet were calculated from the demagnetization curves obtained by the permanent magnetic measuring system. To deeply understand the difference between HPMC and iron scrap in producing magnetic powder as iron-containing raw materials, comparative experiments were carried out.

The main chemical compositions of HPMC and iron scale are given in Table 5. The contents of SiO2 and Al2O3 impurities in HPMC were higher than that of iron scrap, while iron scrap contained more manganese oxide, which was detrimental to the magnetic performance of magnetic powder/ferrite magnet [40]. The two kinds of magnetic powders from HPMC and iron scrap were produced under the same experimental conditions.

![Figure 15. SEM images of magnetic powders with calcination durations of 1.5, 2.0, 2.5 and 3.0 h.](image)

![Figure 16. (a) The hysteresis loops and (b) magnetic properties of magnetic powders with different calcination durations.](image)

| Composition (wt. %) | TFe | SiO2 | Al2O3 | CaO | MnO | Particle size |
|--------------------|-----|------|-------|-----|-----|---------------|
| HPMC               | 71.46 | 0.35 | 0.23  | 0.07| <0.001 | 9.2 μm        |
| iron scrap         | 74.31 | 0.12 | <0.01 | 0.03| 0.50  | 2 ~ 5 mm      |

Table 5. Chemical compositions and average particle sizes of HPMC and iron scrap.
conditions of average particle size of HPMC/iron scrap 1.9 μm, molar ratio of Fe₂O₃ to SrO = 5.9, pre-oxidated temperature 800°C and time 0.5 h, calcination temperature 1300°C and time 2 h. Calcium carbonate, aluminum sesquioxide, silicon dioxide and boric acid were added into the obtained magnetic powders before the second grinding, whose mass percentages were 1.0%, 0.3%, 0.2%, and 0.5%, respectively. The sintering was implemented at 1190°C for 2 h with a heating rate of 5°C/min, and the sintered ferrite compacts were cooled in the furnace under an air atmosphere.

The demagnetization curves of sintered ferrite magnets produced by HPMC and iron scrap are shown in Figure 17, and their magnetic properties are displayed in Figure 18. The diameters of these two green magnets were 30 cm, while the diameter of HPMC magnet after sintering was 26.79 cm, which was slightly smaller than that of iron scrap (27.27 cm). The shrinkage of magnet is mainly due to the volatilization of water. Besides, the formation of silicate and aluminate liquid phase densifies the ferrite causing shrinkage. The magnet produced by HPMC shrunk more because there were more SiO₂ and Al₂O₃ in HPMC, which could further transform into a liquid phase during the sintering process. The sintered magnet from HPMC was superior to that from iron scrap in terms of magnetic properties. In particular, the squareness (Hk/Hcj) of the former was as high as 0.98, which indicated that the magnet from HPMC had a remarkable resistance to demagnetization [1]. The data in Figure 18 illustrated that the magnetic properties of ferrite magnet from HPMC had completely reached the level of Y30H-1 product in China (SJ/T 10410–2016).

3.7. Cost-benefit analysis

A preliminary analysis of the cost and benefit of producing per ton HPMC magnetic powder was conducted to evaluate the economic feasibility of the production process. The calculation was based on the experience of related enterprises and the current market quotations. For the total cost, the raw materials, fuel, reagents, electric power, water, workers’ wage, equipment depreciation, etc., were taken into consideration. The expenditures of each project are listed in Table 6. The main costs were raw materials of HPMC and strontium carbonate, which reached 1376 CNY and 2100 CNY for per ton magnetic powder, respectively. The costs of fuel, workers’ wages and electric energy were all over 100 CNY. The investment in equipment was around 10 million CNY for a magnetic powder production line with a production capacity of 10,000 tons per year. Therefore, the equipment depreciation was 100 CNY per ton product assuming that the factory could continually run for 10 years. The total cost of magnetic powder was 4121.66 CNY per ton, and its sale price was 5200 CNY per ton, according to that of the Y30-1 product.
Table 6. Estimated cost and benefit for per ton HPMC magnetic powder.

| Project                     | Price     | Calculation details | Cost/benefit (CNY) |
|-----------------------------|-----------|---------------------|-------------------|
| The raw materials           | HPMC      | 1600 (CNY/ton)      | 1600 × 0.86 a      | 1376              |
|                            | SrCO₃     | 15,000 (CNY/ton)    | 15,000 × 0.14 a    | 2100              |
| fuel                       |           | mixed coal gas from iron and steel plant |               | 270.6             |
| electric energy             |           | 1 (CNY/kw·h⁻¹)      | 5.76               |
| water                       |           | 2.88 (CNY/m³)       | 2.88 × 2           | 140.4             |
| workers’ wage              |           | 200 (CNY/day)       | 200               |
| equipment depreciation      |           | heavy machines like ball mill, rotary kiln, etc. | 100.0           |
| maintenance and others     |           | equipment maintenance |                   | 26.7              |
| total expenditure           |           | summary of the cost involved | 4121.66 |
| revenue                     |           | sale price          | 5200              |
| profit                      |           | sales revenue minus the cost | 1078.34 |
| return on investment        |           | the ratio of profit to investment c | 107.8% |

*The consumption of HPMC was calculated according to the theoretical chemical formula SrO·5.9Fe₂O₄. The dosage of HPMC was 231.4 × 5.9 × 2/(3 × 98.8%) = 921.23 g for per molar ferrite, while SrCO₃ dosage was 147.6/99% = 149.09 g. Here 231.4 and 149.6 were the relative molecular weight of magnetite and strontium carbonate, respectively. 98.8% and 99% were the purity of HPMC and SrCO₃. So, per ton magnetic powder consumed 921.23/(921.23 + 149.09) = 0.86 ton HPMC and 1−0.86 = 0.14 ton SrCO₃.

**The price of magnetic powder was determined according to that of the Y30-1 product.

†The return on investment was 1078.34 × 10,000/10,000,000 = 107.8%. Here 1078.34 CNY was the profit for per ton product, and 10,000 ton and 10 million CNY were the yield and investment of a factory.

Thus, the profit for producing a ton HPMC magnetic powder was 1078.34 CNY. An impressive rate of return on investment 107.8% was obtained without consideration of land cost. The results of cost–benefit analysis indicate that there is a considerable economic benefit for this production process. More importantly, the majority of Y30-1 products are produced with iron scale in China. The price of high-quality iron scale (TFe >73%) for magnetic powder production, around 1800 CNY per ton, is higher than that of HPMC (1600 CNY per ton). Besides, the limited supply of iron scale is hard to satisfy the need for magnetic powder production these days. The magnetic properties of HPMC magnetic powder in this study have fully achieved the level of Y30-1 product, which indicates that the conventional raw material of iron scale can be replaced by HPMC. The cost–benefit analysis illustrates that there is a promising industrial application prospect for this replacement.

4. Conclusion

In this work, HPMC was studied to produce magnetic powder as iron oxide raw material via the conventional ceramic process. The average particle size of HPMC had a vital influence on the magnetic properties of magnetic powder. The pre-oxidation procedure could effectively reduce ferrous oxide content in HPMC, and thus avoided the mass generation of non-magnetic substances like ferrous silicate. The optimum technological conditions of the ceramic process established in this study were as follows: the average particle size of HPMC 1.9 μm, the molar ratio of Fe₂O₃/SrO 5.9; the pre-oxidation temperature 800°C and time 30 min, and the calcination temperature 1290°C and time 2 h. Under the optimum conditions, the magnetic powder with the single magneto plumbite structure was obtained, where ferrite grains were hexagonal shaped and evenly distributed with a mean size of about 1 μm.

The two kinds of magnetic powders, respectively, produced with HPMC and iron scrap were compared by detecting their sintered ferrite magnets. The values of Br, Hcb, Hcj, and BHmax of magnet produced by HPMC were superior to that of iron scrap, and furthermore the former had a better resistance to demagnetization. The HPMC magnetic powder in this study completely achieved the level of Y30-1 product in China. The cost–benefit analysis indicated that there was a promising industrial application prospect for the substitution of HPMC for iron scrap in magnetic powder production.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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References

[1] Pullar RC. Hexagonal ferrites: a review of the synthesis, properties and applications of hexaferrite ceramics. Prog Mater Sci. 2012;57(7):1191–1334.
[2] Luk PKC, Abdulkreem HA, Xia B. Low-cost high-performance ferrite permanent magnet machines in EV applications: a comprehensive review. Etratporation. 2020;6(8):1–13.

[3] Granados-Miralles C, Jenius P. On the potential of hard ferrite ceramics for permanent magnet technology—a review on sintering strategies. J Phys D Appl Phys. 2021;54(30):1–10.

[4] Mounkachi O, Lamour R, Abraime B, et al. Exploring the magnetic and structural properties of Nd-doped cobalt nano-ferrite for permanent magnet applications. Ceram Int. 2017;43(16):14401–14404.

[5] Munir S, Ahmad I, Laref B, et al. Synthesis, structural, dielectric and magnetic properties of hexagonal ferrites. Appl Phys a-Mater. 2020;126(9):1–7.

[6] Liu XS, Zhong W, Gu BX, et al. Exchange-coupling interaction in nanocomposite SrFe12O19/gamma-Fe2O3 permanent ferrites. J Appl Phys. 2002;92(2):1028–1032.

[7] Al-Hwaitat ES, Dmou MK, Bsool I, et al. A comparative study of BaxSr1-xFe12O19 ferrite permanent magnets prepared by ball milling and sol-gel routes. J Phys D Appl Phys. 2020;53(36):1–15.

[8] Manglam MK, Kumari S, Mallick J, et al. Crystal structure and magnetic properties study on barium hexaferrite of different average crystal size. Appl Phys a-Mater. 2021;127(2):1–8.

[9] Trukanov AV, Darwish KA, Salem MM, et al. Impact of the heat treatment conditions on crystal structure, morphology and magnetic properties evolution in BaM nanoferrites. J Alloy Compd. 2021;866:158961–158968.

[10] Chawla S, Kaur P, Mudiajiniyan RK, et al. Effect of fuel on the synthesis, structural, and magnetic properties of M-type hexagonal SrFe12O19 nanoparticles. J Supercond Nov Magn. 2015;28(5):1589–1599.

[11] Liu CC, Liu XS, Feng SJ, et al. Effect of the Fe/Ba ratio and sintering temperature on microstructure and magnetic properties of barium ferrites prepared by hydrothermal method. J Supercond Nov Magn. 2018;31(3):933–937.

[12] Zhang M, Dai JM, Liu QC, et al. Fabrication and magnetic properties of hexagonal BaFe12O19 ferrite obtained by magnetic-field-assisted hydrothermal process. Curr Appl Phys. 2018;18(11):1426–1430.

[13] Wu Z, Zhang RN, Yu ZW, et al. The magnetic properties of permanent ferrite doped with rare-earth material co-precipitation method. Ferroelectrics. 2018;529(1):120–127.

[14] Kim M, Lee K, Bae C, et al. Magnetic and morphological properties of Ca substituted M-type hexaferrite powders synthesized by the molten salt method. Aip Adv. 2021;11(5):1–7.

[15] Sun R, Li X, Xia AL, et al. Hexagonal SrFe12O19 ferrite with high saturation magnetization. Ceram Int. 2018;44(12):13551–13555.

[16] Zhou EM, Zheng H, Zheng L, et al. Synthesis of dense, fine-grained hexagonal barium ferrite ceramics by two-step sintering process. Int J Appl Ceram Tech. 2018;15(4):1023–1029.

[17] Guzmán-Minguez JC, Fuertes V, Granados-Miralles C, et al. Greener processing of SrFe12O19 ceramic permanent magnets by two-step sintering. Ceram Int. 2021;47(22):31765–31771.

[18] Amiri MC. Characterization of iron oxide generated in rusther plant of pickling unit in mobarakeh steel complex. J Mater Sci Technol. 2003;19(6):596–598.

[19] Gao Y, Yue T, Sun W, et al. Acid recovering and iron recycling from pickling waste acid by extraction and spray pyrolysis techniques. J Clean Prod. 2021;312(24):346–358.

[20] Avridson BR. Processing high-grade concentrates from challenging low-grade iron ore deposits. T Indian I Metals. 2013;66(5–6):467–474.

[21] Li JJW, Zhang WH. M-type strontium ferrite prepared from boyan obo super iron concentrate by solid state sintering. Nonferrous metals engineering in China. 2020;10(12):29–37.

[22] Shao LH, Shen SY, Zheng H, et al. Effect of powder grain size on microstructure and magnetic properties of hexagonal barium ferrite ceramic. J Electron Mater. 2018;47(7):4085–4089.

[23] Moon K-S, Kang Y-M. Structural and magnetic properties of Ca-Mn-Zn-substituted M-type Sr-hexaferrites. J Eur Ceram Soc. 2016;36(14):3383–3389.

[24] Li JW. Reaction mechanism of M-type strontium ferrite prepared from boyan obo super iron concentrate by microwave sintering. Baotou: Inner Mongolia University of Science and Technology; 2020. master’s degree.

[25] Yang YJ, Liu XS, Jin DL. Influence of heat treatment temperatures on structural and magnetic properties of Sr0.5Co0.2Zr0.5Fe61.5Co0.25O19 hexagonal ferrites. J Magn Magn Mater. 2014;364:11–17.

[26] Niu XF, Liu XS, Feng SJ, et al. Effects of presintering temperature on structural and magnetic properties of BaMg1.8Cu0.2Fe16O27 hexagonal ferrites. Optik. 2015;126(24):5513–5516.

[27] Chanda S, Bharadwaj S, Srinivas A, et al. Estimation of iron ion distribution at various sites contributing to saturation magnetization in barium hexaferrite at different sintering temperatures. J Phys Chem Solids. 2021;155(34):1–10.

[28] Zhang HB, Fan LN, Cao HC, et al. Microstructure, magnetic, and dielectric properties of Co-Zr co-doped hexagonal barium ferrites based on the sintering temperature and doping concentration. J Mater Sci Mater El. 2021;32(3):2685–2695.

[29] Haberey RLF, Rosenberg M, Sahl K. Preparation and magnetic properties of LPE-grown hexagonal strontium aluminoferrite films. Mater Res Bull. 1980;15(4):8.

[30] Yang YJ, Liu XS, Jin DL. The impact of the iron content on the microstructure and magnetic properties of M-type ferrites Sr0.45Ca0.25La0.3FeCo0.25O19. Mater Sci Eng B-Adv. 2014;186:106–111.

[31] Yang YJ, Liu XS, Jin DL, et al. The effects of the iron content on structural and magnetic properties of Sr0.80La0.20FeZn0.15O19 hexagonal ferrites. J Magn Magn Mater. 2014;355:254–258.

[32] Huang CC, Lin SH, Mo CC, et al. Development of optimum preparation conditions of Fe-Deficient M-type Ca Sr La system hexagonal ferrite magnet. IEEE Trans Magn. 2021;57(2):1–8.

[33] Trukanov AV, Vinnik DA, Trofimov EA, et al. Correlation of the Fe content and entropy state in multiple substituted hexagonal ferrites with magnetoplumponge structure. Ceram Int. 2021;47(12):17684–17692.

[34] Liu XS, Zhong W, Yang S, et al. Influences of La3⁺ substitution on the structure and magnetic properties of M-type strontium ferrites. J Magn Magn Mater. 2002;238(2–3):207–214.
Rehman KMU, Liu XS, Feng SJ, et al. Influence of temperature on Sr0.35La0.40Ca0.25Fe11.6Co0.4O19 hexagonal ferrites against structural, morphological and magnetic properties prepared by conventional ceramic reaction methodology. J Supercond Nov Magn. 2018;31(3):925–932.

Huang TX, Peng L, Li LZ, et al. Low temperature sintering behavior of La-Co substituted M-type strontium hexaferrites for use in microwave LTCC technology. J Rare Earth. 2016;34(2):148–151.

Liu CC, Liu XS, Feng SJ, et al. Microstructure and magnetic properties of M-type strontium hexagonal ferrites with Y-Co substitution. J Magn Magn Mater. 2017;436:126–129.

Chauhan CC, Kagdi AR, Jotania RB, et al. Structural, magnetic and dielectric properties of Co-Zr substituted M-type calcium hexagonal ferrite nanoparticles in the presence of alpha-Fe2O3 phase. Ceram Int. 2018;44(15):17812–17823.

Chen W, Wu WW, Li MY, et al. Al3+ doped M-type hexagonal Ba-Co ferrites synthesized via ball-milling assisted ceramic process: magnetism and its correlation with structural properties. J Mater Sci-Mater El. 2018;29(10):8020–8030.

Ni JL, Feng SJ, Liu XS. Influence of manganese dioxide and Ba2Co2Fe12O22-additives on the magnetic power loss of Ni0.8Zn0.2Fe2O4 ferrites. Materialwiss Werkst. 2018;49(8):986–990.