

PROCESS OF PRODUCING MAGNETIC MATERIAL FROM SLAG

FIELD OF THE INVENTION

The present invention relates to processes of producing magnetic materials, and more particularly to a process of converting slag into magnetic material.

BACKGROUND OF THE INVENTION

Slags are waste products from metal producing and processing processes. Slags may be treated to produce useful materials. For example, slags have been used to produce cement, pozzolan, railway ballast, insulating slag wool, agriculture fertilizer and polishing material.

Slags often contain high contents of iron oxide and silicon oxide. Generally, the majority of iron in slag exists in non-magnetic (paramagnetic, antiferromagnetic and weak-magnetic) forms, such as wustite (FeO), hermatite (Fe_2O_3), iron silicate (Fe_2SiO_4), and ferro-silicate (FeSiO_3). A small portion of iron in slag may be in magnetic forms including metallic iron (Fe), magnetite (Fe_3O_4), and other magnetic ferrites. Magnetic forms of iron are strongly magnetic and are usually ferromagnetic and ferrimagnetic materials.

Heating slags with a reducing agent to elevated temperatures can produce metal iron through a reduction reaction. However, it is typically necessary to heat the reactants to extremely high temperatures, which may be inconvenient, inefficient, difficult or even impractical in certain circumstances or for certain purposes. Further, heat treatment alone may not result in a material with desired properties. The resulting material needs to be further treated. For example, the metal iron produced has to be removed from the rest of the slag.

It is also known that magnetic materials may be extracted from slags after mechanical milling (also known as mechanical alloying). In mechanical milling, the material being treated is ground to fine powders through

mechanical forces. Thus, as the slag is broken up into small particles, where some particles are magnetic and some are not magnetic, the particles can be easily separated by magnetic or other known processes. Although reduction reactions and displacement reactions may occur during mechanical milling, only a small portion of iron is converted from nonmagnetic forms to magnetic forms during known mechanical milling processes. A large portion of the iron content in the treated material is still in nonmagnetic forms. Thus, it is still necessary to separate the magnetic portions of the slag from the rest of the slag in order to obtain a strongly magnetic material. Hence, these known techniques are neither effective nor efficient in converting slag into magnetic materials.

Therefore, there is a need for a process that can efficiently and effectively convert a slag into a magnetic material.

SUMMARY OF THE INVENTION

Disclosed herein is a process for producing magnetic material from a slag including a ferrous component, the process includes, adding an additive induce formation of a ferrite to the slag; and milling the mixture. In a first aspect, there is provided a process for producing magnetic material from a slag comprising a ferrous component, said process comprising: adding an additive to said slag to form a mixture; milling said mixture, causing said additive and said ferrous component to induce a reaction to form a magnetic ferrite having a chemical formula AFe_mO_n , wherein A represents one or more elements, and wherein said ferrite contributes substantially to the magnetic properties of said magnetic material.

The above process may induce a reaction to form a magnetic ferrite having a chemical formula AFe_mO_n that contributes substantially to the magnetic properties of said magnetic material. In the chemical formula AFe_mO_n , A represents one or more elements.

Exemplary additives include barium, cobalt, iron, manganese, nickel, strontium, titanium, and zinc, calcium oxide and silicon oxide. Exemplary formed ferrites include CoFe_2O_4 , NiFe_2O_4 , Ni_2FeO_4 , NiMnFeO_4 , MnFe_2O_4 , Mn_2FeO , ZnFe_2O_4 , $\text{BaFe}_{12}\text{O}_{19}$, $\text{SrFe}_{12}\text{O}_{19}$, $\text{XY}_x\text{Fe}_{12-x}\text{O}_{19}$, where X is barium or strontium, Y is cobalt or titanium, and x is 0 or an integer between 1 and 5; magnetite, barium hexaferrite, strontium hexaferrite, cobalt ferrite, nickel ferrite, manganese ferrite and spinel ferrites having a formula $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ or $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, where $0 < x = 1$.

Disclosed herein is a process for producing a magnetic material from a slag. This

process includes milling a mixture of the slag and at least one additive including a ferrous substance, and heating the mixture to produce a nanocomposite of magnetite and iron.

In a second aspect, there is provided a magnetic material produced in accordance with the process as defined in the first aspect.

In a third aspect, there is provided a process for producing a magnetic material from a slag, comprising milling a mixture of said slag and at least one additive so as to produce a composite of one or more magnetic ferrites and one or more non-magnetic substance.

In a fourth aspect, there is provided a process for producing a magnetic material from a slag, comprising: milling a mixture of said slag and at least one additive including a ferrous substance; and heating said mixture; so as to produce a nanocomposite of magnetite and iron.

In a fifth aspect, there is provided a magnetic material, produced in accordance with the process as defined in the fourth aspect.

Other aspects and features of the present invention will become apparent to those of ordinary skill in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

In the figures illustrating example embodiments of the present invention,

FIG. 1 is a process flow diagram of a process for forming a magnetic material from a slag, exemplary of an embodiment of the present invention; and

FIGS. 2-4 each illustrates two hysteresis curves illustrating changes in magnetic properties of slags treated by a process exemplary of the present invention.

DETAILED DESCRIPTION

FIG. 1 is a process flow diagram, illustrating an exemplary process **10** for forming a magnetic material, exemplary of an embodiment of the present invention. As illustrated, a slag **100** is combined with an additive **102** to form mixture **104** within mill **106**.

Mill **106** used in the exemplary process **10** may be any suitable known type. Generally, mill **106** includes a container for receiving mixture **104**. Mechanical forces are applied to mixture **104** by mill **106** in a manner so as to cause it to repeatedly and continuously come into momentary contact with itself and some other hard objects such as an agitated media, a protruder, or a wall. The impact of contact may cause the material to break up into small

pieces, and eventually, powder-like particles. Fractured particles have fresh and atomically clean surfaces, on which certain chemical reactions may proceed quickly. When two surfaces are in contact for a sustained period of time, such as when welded, inter-diffusion may also occur.

An exemplary suitable mill **106** is a high-energy mechanical ball mill, such as a vibrated ball mill, planetary ball mill, attrition mills (described in, for example U.S. Patent No 2,764,359) and the like, may be used. Typically, the total charge in a ball mill includes a solid material and a number of hard balls. High kinetic energies are applied to the total charge during milling to cause the hard balls and the solid material to repeatedly collide with each other and with the walls of the container. The milling motion causes repeated deformation, fracture and cold welding of powder particles during ball-powder-ball and ball-powder-wall collisions.

Mill **106** produces resultant **108** that may optionally be subjected to heat treatment. Such heat treatment may be effected in any number of know ways. For example resultant **108** may be provided to and heated in heating vessel **110** to produce resultant **112**.

In operation, slag **100** and additive **102** are placed within mill **106** to form mixture **104**, which is the starting material to be treated.

In the example embodiment slag **100** is a by-product of metal refining and other metal processing processes and contains multiple components. One of the components is iron, mostly in the form of iron oxides. Other typical components of slag **100** include silicon oxides as well as impurities such as calcium oxides and aluminum oxides. Slag **100** may be a copper slag or a lead slag, and may contain a significant amount of iron oxides, usually over ten percent by weight (10 wt%). Iron in slag **100** may exist in different forms, such as wustite (FeO), magnetite (Fe_3O_4), and hematite (Fe_2O_3), iron silicate (Fe_2SiO_4), and ferro-silicate (FeSiO_3). Depending on the process that produced the slag, sometimes a small amount of metallic iron or iron alloy may also be present. As is well known, metallic iron, magnetite, as well as magnetic ferrite such as Ni-ferrite (NiFe_2O_4), are strongly magnetic, whereas

hematite, wustite, iron silicate and ferro-silicate are not magnetic or only weakly magnetic. Typically, slag **100** as a whole is not magnetic or only weakly magnetic because the majority of iron in the slag is in nonmagnetic forms, such as hematite, wustite, iron silicate and ferro-silicate.

Additive **102** is chosen so that an iron containing component in slag **100** may chemically react to form magnetic ferrite in resultant **108**. Additive **102** may be a mixture of several chemical components, as detailed below.

Mixture **104** is milled for a time within mill **106**. Typical parameters that can be controlled during milling include collision energy, collision frequency, ball/powder mass ratio, milling time, filling gas composition and pressure in the container, lubricant, and temperature. In the example embodiment, the milling energy is preferably between 0.1 to 1.0 joule and the ball/powder mass ratio between 2:1 to 50:1. The milling time is typically less than forty-eight hours but it may vary depending on the operating parameters of mill **106**, the nature of mixture **104** and any heat treatment performed in vessel **110** after milling. The milling container of mill **106** may be filled with air or inert gas such as argon or nitrogen. Other parameters may vary depending on the particular situation. As can be appreciated, for mill **106** to be effective, at least some of mixture **104** should be in solid phase.

As a result of milling within mill **106**, resultant **108** including a magnetic ferrite is produced. As will be appreciated, a ferrite is a compound with magnetic properties formed from ferric oxide and a basic oxide or from ferric hydroxide and a base. Typically, ferrites have a chemical formula



where **A** may be a suitable element or a combination of elements. For example, **A** may be a metal such as iron, nickel, cobalt, manganese, barium, strontium or the like.

Thus, the magnetic ferrite in resultant **108** may, for example, be one of magnetite, cobalt ferrite, nickel ferrite, manganese ferrite, barium hexaferrite, and strontium hexaferrite. Common magnetic ferrite in resultant **108** may have

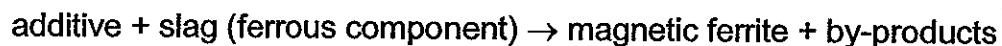
a formula Fe_3O_4 , CoFe_2O_4 , NiFe_2O_4 , MnFe_2O_4 , Ni_2FeO_4 , Mn_2FeO_4 , ZnFe_2O_4 , $\text{BaFe}_{12}\text{O}_{19}$, $\text{SrFe}_{12}\text{O}_{19}$, or $\text{BaM}_x\text{Fe}_{12-x}\text{O}_{19}$ or $\text{SrM}_x\text{Fe}_{12-x}\text{O}_{19}$, (where M may be cobalt or titanium and x is 0 or an integer between 1 and 5).

Similarly, resultant **108** may include spinel ferrites having a chemical formula $\text{A}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, where A is Ni or Mn, and x has a suitable value between 0 and 1, such as .2, .4, .5, .6 and .8.

As is known, mechanical milling can produce both amorphous and crystalline materials. Typically and advantageously, the milled mixture, resultant **108**, consists of small particles, with sizes typically in the range of 0.1 to 10 μm ; different elements or compounds in the mixture are all uniformly dispersed; contact surfaces among different particles are large.

Optionally, mixture **104** or resultant **108** may be subjected to heating, to be heated to high temperatures. In the example embodiment, resultant **108** is provided to heating vessel **110** to form resultant mixture **112**. Optionally, mixture **104** could be subjected to heat treatment within mill **106**. One or more chemical reactions may be induced as a result of heating. These reactions may form the magnetic ferrite or contribute to the formation of the magnetic ferrite in the resultant **108/112**. Advantageously, magnetic ferrite may form at a lower temperature in the resultant **108** than in the mixture **104** that has not been milled.

Generally, the reaction caused by additive **102** and associated milling and optional heating may be expressed as



As should be appreciated, additive **102** and ferrous component of slag **100** need not react with each other directly. Additive **102** may, for example, be a catalyst for a desirable chemical reaction. Additive **102** could similarly participate in an intermediate reaction, or one of a series of such reactions that results in a reactant in the final reaction. For example, additive **102** may be converted into an intermediate as a result of milling; similarly, the slag or its ferrous component may be converted to an intermediate component.

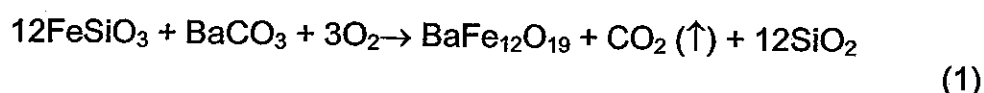
These intermediates may interact with each other; the additive; and/or the slag to create further intermediates or the final magnetic ferrite of interest.

Put another way,

Additive + slag (ferrous component) → intermediates(1) → intermediates(2)
→ ... → intermediates (i) → magnetic ferrite + by-products

Of course, the exact role of the additive **102**; milling and heating will depend on the composition of slag **100**; the specific additive **102**; the length and type of milling; and the length, temperature and properties of heating.

An exemplary additive **102** includes barium carbonate (BaCO_3), which may react with ferro-silicate (FeSiO_3) in slag **100** and produce magnetic barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$) in the ferrite-forming reaction:



Similarly, additive **102** may include nickel monoxide (NiO) that may be added to produce nickel dioxide, which in turn could react with ferro-silicate (FeSiO_3) in slag **100**, in the following reaction,



As is apparent, nickel dioxide could similarly be added directly as an additive. Alternatively, metallic nickel may be added as an additive.

In the above examples, barium carbonate, nickel monoxide, or metallic nickel as additive(s) induce and facilitate a ferrite-forming reaction in which the products include a magnetic ferrite, such as the exemplified barium hexaferrite or nickel ferrite. Other suitable additives include cobalt, manganese, strontium, and their oxides or carbonates, which may respectively induce the formation of Co-ferrite, Mn-ferrite, and Sr-hexaferrite.

Additive **102** may also be added for purposes other than inducing a ferrite forming reaction. For example additive **102** may be added to avoid formation of an undesirable substance or to form a certain desirable

substance. For instance, an additive may be added to inhibit or reduce the formation of nonmagnetic forms of iron during the treatment. Sodium carbonate (Na_2CO_3) may be added for reducing the formation of barium silicates (BaSi_2O_5), which takes away barium available for the desired ferrite forming reaction. Calcium oxide (CaO) or silicon oxide (SiO_2) may be added for forming magnetic cement (based on $\text{SiO}_2\text{-CaO}$).

Additive **102** may include a substance for modifying the magnetic properties of the resultant **108/112**. For example, titanium or cobalt may be added to partially replace the iron in the barium(strontium) hexaferrite.

Additive **102** may also include a component that enriches the iron content in the mixture. For this purpose, additive **102** may include iron. Additive **102** may thus include metallic iron, iron alloy, iron oxides or other ferric or ferrous oxides, iron salts and the like.

The quantity of additive **102** and the concentration of each particular component within additive **102** may vary depending on the purpose and the specific parameters and conditions of the treatment. Additive **102** may be solid, liquid, or gaseous.

Thus, additive **102** and the milling and heating conditions in process **10** may vary so long as they, in combination, induce, facilitate, or promote one or more chemical reactions producing magnetic ferrite in resultant **108/112**.

Resultant **108** (or **112**) of process **10** is a magnetic material including a composite of magnetic ferrite and some other chemical substances. Advantageously, the magnetic ferrite contributes significantly to the magnetic property of resultant **108** (or **112**), as will be demonstrated in the examples described below. The treated mixture can be used as magnetic starting materials without further separation of the magnetic ferrite from the other chemical substances.

As noted, after milling mixture **104**, resultant **108** or a portion of resultant **108** may optionally be subject to heat treatment in heating vessel **110**, which may include annealing or sintering or both. Annealing heats

resultant **108** to a high temperature and then allows it to cool slowly. During milling, internal stress and structural defects may be introduced, which may significantly affect the magnetic properties of the milled material. As is known, annealing may release internal stress and cure internal structural defects in a material, thus causing desirable changes in the material's magnetic properties. Sintering is to coalesce a loose powder into a dense solid by heating. The milled mixture may be heated to any desired and attainable temperature for a particular purpose, which is typically in the range of 200 to 1200°C. Heating to high temperature may facilitate the formation of certain desired substances. For example, hexaferrites typically form at a temperature higher than 600 °C. Sintering may require heating to temperatures up to 1000 °C.

Resultant **108/112** produced by the exemplary process **10** includes a significant amount of magnetic forms of iron, particularly in the form of a magnetic ferrite. The particular forms formed depend on the starting slag **100**, additive **102**, and their treatment. Resultant **108/112** may include composites of magnetic ferrite crystallites in a nonmagnetic matrix. For example, resultant **108/112** resulting from treating a copper slag according to process **10** may include composite of $\text{BaFe}_{12}\text{O}_{19}$ (or $\text{SrFe}_{12}\text{O}_{19}$) in a matrix of non-magnetic oxides such as SiO_2 , CaO , Al_2O_3 , and etc. Resultant **108/112** may be used as starting material for, for example, manufacturing permanent magnets and magnetic recording media.

Resultant **108/112** may also comprise magnetic ferrite particles, such as Ni-ferrite or Co-ferrite, embedded in a calcium silicate matrix, which can be used as magnetic cement. Magnetic cement is potentially of high commercial value as it can be used for microwave absorption, EMC magnetic shielding, non-destructive failure analysis, magnetic concrete structure, and other similar applications. Magnetic cement is at the present not commercially available. In most hydraulic cements produced today, two calcium silicates ($3\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{SiO}$) are the major components. Slag has been widely used as the starting materials for manufacturing cements. However, the cements produced from slag using known technology are not magnetic.

Additive **102** may also contain a ferrous substance. For example, metallic iron may be added as additive **102** to the slag **100** and the resultant **108/112** may comprise nanocomposites of metal iron and magnetite.

While material produced according to embodiments of the present invention is magnetic as a whole, sometimes it is desirable to remove as much as possible the iron content from a slag so the remaining slag can be used as an iron-free starting material. In these cases, the magnetic forms of iron in the resultant **108/112** may be removed by a known magnetic or other process. Advantageously, both the magnetic portion of resultant **108/112** and the nonmagnetic portion (which contains little iron content) are of added commercial value.

As will be appreciated, after treating a sample slag **100** using an exemplary process **10**, the saturation magnetization of the resulting material is substantially higher than that of the original slag. The coercivity of the resulting material may vary in a wide range as it can be adjusted by varying the additives, in addition to heat treatment.

As is well known, the magnetic properties of a material are reflected in its hysteresis curve or loop. A hysteresis curve shows the magnetization of a material as a function of the applied magnetic field. Exemplary hysteresis curves are illustrated in **FIGS. 2 to 4**. On each hysteresis curve there are three significant points, corresponding to three significant characteristics of a magnetic material. The highest point on the curve indicates the maximum magnetization a material can achieve under an external applied magnetic field, which is known as the saturation magnetization. The x-axis intercept of the curve indicates the magnitude of external field needed to bring the magnetization back to zero, which is known as the coercivity. The y-axis intercept gives the magnetization at zero external field, which is known as the remanence. Different materials have different values of saturation magnetization, coercivity, and remanence. Generally, the higher the saturation magnetization value, the stronger the magnetic strength. The desirable range of coercivity and remanence vary depending on the application. Sometimes, hard magnets, which have high coercivities and

remanence, are desirable, and sometimes soft magnets, which have low coercivities and remanence, are desirable.

The above exemplary embodiments of the invention may be better appreciated with reference to specific examples detailed below.

Two types of slags, Slag 1 and Slag 2, were used in the following examples. Their chemical compositions are shown in Table 1.

Table 1. Chemical compositions of sample slags

Constituent	Wt%	
	Slag 1	Slag 2
iron oxide	20	50
Ferro-silicate	38	24
Silicon dioxide	33	21
Aluminum oxide	4.6	2.9
Zinc oxide	1.5	0.94
Calcium oxide	2.1	1.3
Sulfur	0.17	0.11

EXAMPLE 1: Producing NiFe_2O_4 by adding NO

	Material Content	Saturation Magnetization (Am^2/kg)	Coercivity (tesla)
Slag 100	10 g of Slag 1	< 1	-
Additive 102	1 g of NiO	-	-
Resultant 108	Containing NiFe_2O_4	18.5	-

The mixture was mechanically milled for forty hours. A SPEX 8000 vibrated mill was used as mill 106. Several steel balls were loaded with the mixture. The powder/ball mass ratio was 10:1. The resultant is strongly magnetic with a high saturation magnetization value approximately 40% of that of pure Ni-ferrite ($\sim 50 \text{ Am}^2/\text{kg}$).

Experimental results indicate that the milling time materially affect the magnetization of the resultant. For example, another mixture of the same composition was milled for only twenty hours and after the milling the saturation magnetization of the mixture was only 5 Am²/kg, indicating that little Ni-ferrite had been formed. However, subsequent heating of the same mixture to a temperature of 800 °C for 1 hour in air) again resulted in a resultant **112** with a saturation magnetization of 20 Am²/kg. Annealing the same mixture to temperatures of 900 and 1000°C produced no significant increase in saturation magnetization.

Both resultants **108** and **112** described above had very low coercivity values ($< 50 \times 10^{-5}$ tesla) and are suitable for soft magnetic applications.

EXAMPLE 2: Producing NiFe₂O₄, ZnFe₂O₄ or Ni_{0.5}Zn_{0.5}Fe₂O₄ by adding Ni and/or Zn

As is well known, the magnetic properties of a nickel magnetic material can be improved by partial substitution of nickel by zinc (Zn). To demonstrate the possible improvement in magnetic properties, two productions were carried out in this example.

Production 1:

	Material content	Saturation Magnetization (Am ² /kg)	Coercivity (tesla)
Slag 100	20 g of Slag 2	5	-
Additive 102	3.8 g of Ni.	-	-
Resultant 112	Containing NiFe ₂ O ₄	29	$< 50 \times 10^{-5}$

Production 2:

	Material content	Saturation Magnetization (Am ² /kg)	Coercivity (tesla)

Slag 100	20 g of Slag 2	5	-
Additive 102	1.9 g of Ni + 1.9 g of Zn.	-	-
Resultant 112	Containing $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$	43	$<40 \times 10^{-5}$

A Fritsch 5 planetary mill was used as mill 106 for 48 hours with a powder/ball mass ratio of 10:1 for both mixtures and annealed to 900 and 1000 °C for one hour in air atmosphere.

The saturation magnetization of resultant 112 in the two productions were very different. The product of Production 2, which has the additional Zn element, has a much higher saturation magnetization than that of Production 1 and is comparable to that of conventional pure nickel ferrite magnets.

The hysteresis loop of Resultant 112 of Production 2 is shown in FIG. 2 together with the hysteresis loop of samples from untreated Slag 2. As can be seen, Slag 2 is weakly magnetic, probably due to the presence of weakly magnetic material such as hematite and a small amount of magnetic phase, such as metallic iron, magnetite, and ferrite. In contrast, the resultant exhibits good magnetic properties suitable for soft magnetic applications.

EXAMPLE 3: Producing $\text{BaFe}_{12}\text{O}_{19}$ by adding excessive BaCO_3

	Material content	Saturation Magnetization (Am^2/kg)	Coercivity (tesla)
Slag 100	10 g of Slag 1	< 1	-
Additive 102	2 g of BaCO_3	-	-
Resultant 112	Containing $\text{BaFe}_{12}\text{O}_{19}$	13	0.35

The mixture was milled for twenty hours in the same way as described in Example 1. The mixture was then annealed at temperatures ranging between 700 to 900 °C for one hour in air and sintered at 1000 to 1100°C for three hours in air.

The amount of additive 102 added is the minimum amount required to

convert all iron oxides or ferro-silicate in ten grams of Slag 1 into barium hexaferrite ($\text{BaFe}_{12}\text{O}_{19}$). Since there are competing reactions forming compounds such as BaO-SiO_2 , excess BaCO_3 in the mixture is needed to ensure that sufficient barium is available for the formation of $\text{BaFe}_{12}\text{O}_{19}$.

After twenty hours of milling, no significant amount of barium hexaferrite was formed. The resultant **108** had a very low value of saturation magnetization with a small coercivity.

The magnetic property values shown in the above table are measured after annealing. The saturation magnetization of the resulting material is approximately 20% of the saturation magnetization of pure Ba-hexaferrite, suggesting that approximately 20% of the resultant **112** is Ba-hexaferrite. The resultant has a coercivity of 0.35 Tesla, which is nearly twice of the value of conventional Ba-hexaferrite permanent magnets. As may be understood, the high coercivity of the final resultant is likely due to its small particle size, which is close to or below the single domain particle size ($1\text{ }\mu\text{m}$). Small particle size is a convenient benefit of mechanical milling. As can be appreciated, the resultant had good magnetic properties and can be used as permanent magnets or recording media.

After sintering, the powder is nearly fully dense, i.e., its density is close to the theoretical density of the composite. The sintering temperature range is significantly lower than sintering temperature required for conventional Ba-hexaferrite magnets consisting of pure $\text{BaFe}_{12}\text{O}_{19}$ and the reduction of sintering temperature is due to the presence of silicon oxide and other oxides which reduces melting temperature of SiO_2 . The tightly packed dense material is suitable for use as permanent magnets.

In the above example, barium carbonate can be substituted by strontium carbonate (SrCO_3) and a composite of Strontium hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$) may be similarly produced. Either of the composites produced can be used as starting material for, e.g., bonded magnets or magnetic recording media.

EXAMPLE 4: Producing $\text{BaFe}_{12}\text{O}_{19}$ by adding BaCO_3 and NaCO_3

In Example 3, an excessive amount of barium carbonate was added to ensure the formation of $\text{BaFe}_{12}\text{O}_{19}$, which competes with the possible formation of compounds such as BaO-SiO_2 . Alternatively, the formation of BaO-SiO_2 may be avoided by inducing the formation of silicate compounds that are more stable than BaO-SiO_2 , such as $\text{Na}_2\text{O-SiO}_2$, as demonstrated in this example 4.

	Material Content	Saturation Magnetization (Am^2/kg)	Coercivity (tesla)
Slag 100	5 g of Slag 2	5	-
Additive 102	1.2 g of BaCO_3 + 1.76 g of NaCO_3	-	-
Resultant 112	Containing $\text{BaFe}_{12}\text{O}_{19}$	20-25	0.3

The mixture was milled and heated in the same manner as in Example 3.

Ba-hexaferrite was formed after sintering at 900 to 1000°C. The saturation magnetization of the resultant is about 30 to 40% of that of a conventional Ba-hexaferrite magnet.

FIG. 3 illustrates the magnetic hysteresis loop of the resultant 112, in comparison with the hysteresis loop of untreated Slag 2.

EXAMPLE 5 – Producing MnFe_2O_4 by adding Mn

In this example, material including of Mn-ferrite (MnFe_2O_4) have been prepared in a process similar to that of Examples 1 and 2.

	Material content	Saturation Magnetization (Am^2/kg)	Coercivity (tesla)
Slag 100	20 g of Slag 2	5	-
Additive 102	4.7 g of Mn	-	-

Resultant 112	Containing composite of MnFe_2O_4 and silica	30-35	$< 50 \times 10^{-5}$
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The mixture was milled using Fritsch 5 planetary mill for 48 hours. The milled powders were annealed at temperatures in the range of 800 to 1000°C.

The resultant 112's saturation magnetization is about 40% of conventional Mn-ferrite magnets. As in Examples 1 and 2, the resultant is suitable for soft magnetic applications.

EXAMPLE 6: Producing Co-ferrite by adding Co

	Material content	Saturation Magnetization (Am^2/kg)	Coercivity (tesla)
Slag 100	20 g of Slag 2	5	-
Additive 102	3 g of Co	-	-
Resultant 112	Containing CoFe_2O_4	45-50	0.2

The mixture was milled with a Fritsch 5 planetary ball mill for 20 hours with a rotating speed of 250 rpm. The milled mixture was annealed at temperatures between 700 to 1000°C and sintered at 1000°C for three hours in air.

The resultant contained Co-ferrite and had a saturation magnetization about 60% of that of pure Co-ferrite ($80 \text{ Am}^2/\text{kg}$).

After annealing at 900 and 1000°C, the resultant exhibited good magnetic properties, as illustrated in Fig. 4. The coercivity is much higher than that of Co-ferrite produced by conventional methods, which is normally less than 0.1 Tesla. The sintered powders were densely packed.

EXAMPLE 7: Producing CoFe_2O_4 with additional Co and Fe_2O_3

	Material content	Saturation Magnetization (Am ² /kg)	Coercivity (tesla)
Slag	20 g of Slag 2	5	-
Additives	6.1 g of Co + 10 g of Fe ₂ O ₃	-	-
Resultant	Containing CoFe ₂ O ₄	55	0.21

The mixture was milled and subsequently heated in the same way as described in Example 6.

In this example, the saturation magnetization of the resultant has been enhanced by adding extra iron oxide and metallic cobalt to increase the fraction of magnetic ferrite in the final resultant. Compared to the resultant of Example 6, the saturation magnetization was significantly higher whereas the coercivity remained the same.

EXAMPLE 8 – Producing magnetic cement

	Material content	Saturation Magnetization (Am ² /kg)	Coercivity (tesla)
Slag 100	10 g of Slag 2	5	-
Additive 102	20 g of CaO + 1.5 g of Co	-	-
Resultant 112	mainly a mixture of CoFe ₂ O ₄ and CaO-SiO ₂	~30	0.2

The mixture 104 was milled for 24 hours in a Spex mill. The resultant 108 was heated to temperatures from 900 to 1000°C for one hour.

An X-ray diffraction examination of the resultant 112 indicated that the resultant 112 was mainly a mixture of cobalt ferrite and calcium silicates, which is suitable for use as magnetic hydraulic cement. Magnetic hydraulic cement containing other magnetic ferrites such as Ni-ferrite or Mn-ferrite may be produced in a similar process.

EXAMPLE 9 – Producing Fe/Fe₃O₄ nanocomposite by adding metallic

Fe

	Material content	Saturation Magnetization (Am ² /kg)	Coercivity (tesla)
Slag 100	10 g of Slag 1	1	-
Additive 102	2 g of Fe	-	-
Resultant 112	Fe ₃ O ₄ /Fe nanocomposite	~30	

The mixture **104** was milled for 24 hours using a Spex mill with a ball/powder mass ratio of 10:1.

The resultant **108** comprised a nanocrystalline mixture of metal iron and wustite, judging based Mossbauer spectroscopy measurement.

The resultant **108** was heated to temperatures in the range of 200 to 700°C. At these temperatures, wustite decomposed into nanocrystalline Fe and Fe₃O₄. Since metallic Fe and Fe₃O₄ may be oxidized into Fe₂O₃ at temperatures above 700°C, it is preferable in this case that the heat treatment is performed at temperatures below 700°C.

The resultant **112** includes magnetic nanocomposite of Fe and Fe₃O₄ in a matrix of other non-magnetic oxides, which was confirmed by X-ray diffraction, magnetic and Mossbauer measurements.

The magnetic properties of the Fe/Fe₃O₄ nanocomposite can be improved by partially substituting the Fe element in the additives with other ferromagnetic elements such as Co, Ni, Mn, and the like. For example, adding cobalt may result in a product suitable for making permanent magnets and recording media and adding nickel or manganese can resulting in a product suitable for soft magnetic applications.

As can be appreciated, magnetic materials can be extracted from waste slag **100** by applying the exemplary process described herein. The conversion rate of iron from nonmagnetic form to magnetic form is high.

The heating temperature required is not very high and can be lower than what is required in known techniques for producing the same material. The magnetic properties of the resulting materials are good and can be controlled in certain cases. Certain desirable property or structure of the resultant is conveniently obtained without having to subject the resultant to additional processing steps. These properties include, for example, small particle sizes, uniform dispersion of component elements and compounds, formation of composites and nanocomposites, and etc.

The exemplary embodiments of the invention described herein can be modified in any number of ways understood by a person of ordinary skill in the art. For example, while in the exemplary embodiments only slags are used as the starting material, it is possible to use other industrial wastes or other wastes that contain ferrous component. Such other industrial wastes may be wholly or partially solid and may include what are known as sludges. In addition, while mechanical milling is applied in the exemplary embodiments, other mechanical processes and techniques may be used to deform and fracture the slags and to disperse the resulting powders evenly. Further, additives may be mixed with the slag after some milling. Alternatively, additional additives may be added after a step in the process. For instance, certain reactive gases may be introduced during the heating step. Other modifications may include removing or extracting certain materials from the mixture during or after the process.

The invention, rather, is intended to encompass all such modification within its scope, as defined by the claims.

WHAT IS CLAIMED IS:

1. A process for producing magnetic material from a slag comprising a ferrous component, said process comprising:

adding an additive to said slag to form a mixture;

milling said mixture, causing said additive and said ferrous component to induce a reaction to form a magnetic ferrite having a chemical formula AFe_mO_n , wherein A represents one or more elements, and wherein said ferrite contributes substantially to the magnetic properties of said magnetic material.
2. The process of claim 1, wherein said milling comprises high energy mechanical milling.
3. The process of claim 2, wherein said high energy mechanical milling provides a collision energy in the range of 0.1 to 1.0 joule.
4. The process of claim 1, further comprising heating said mixture so as to further induce said reaction.
5. The process of claim 4, wherein said heating comprises at least one of annealing and sintering.
6. The process of claim 5, wherein said mixture is heated to a temperature in the range of 200 to 1200°C.
7. The process of claim 1, wherein said additive acts as a catalyst to form said ferrite.
8. The process of claim 1, wherein said additive impedes a chemical reaction that competes with said reaction to form said ferrite.
9. The process of claim 1, wherein said additive comprises a ferrous substance so as to increase iron content in said mixture.
10. The process of claim 9, wherein said ferrous substance comprises one

or more of iron, iron oxides, and iron salts.

11. The process of claim 1, wherein said additive comprises an element selected from the group of barium, cobalt, iron, manganese, nickel, strontium, titanium, and zinc.
12. The process of claim 1, wherein said magnetic ferrite is one of magnetite, barium hexaferrite, strontium hexaferrite, cobalt ferrite, nickel ferrite, and manganese ferrite.
13. The process of claim 12, wherein said magnetic material comprises a composite of said magnetic ferrite and a nonmagnetic substance.
14. The process of claim 12, wherein said magnetic material comprises a nanocomposite of iron and said magnetic ferrite.
15. The process of claim 12, wherein said magnetic ferrite has a formula selected from the group of NiFe_2O_4 , Ni_2FeO_4 , NiMnFeO_4 , MnFe_2O_4 , and Mn_2FeO_4 .
16. The process of claim 12, wherein said magnetic ferrite has a formula CoFe_2O_4 .
17. The process of claim 12, wherein said magnetic ferrite has a formula $\text{BaFe}_{12}\text{O}_{19}$ or $\text{SrFe}_{12}\text{O}_{19}$.
18. The process of claim 12, wherein said magnetic ferrite has a formula $\text{XY}_x\text{Fe}_{12-x}\text{O}_{19}$, where X is barium or strontium, Y is cobalt or titanium, and x is 0 or an integer between 1 and 5.
19. The process of claim 12, wherein said magnetic ferrite has a formula $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ or $\text{Mn}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$, where $0 < x = 1$.
20. The process of claim 1, wherein said magnetic material is a composite of said magnetic ferrite in a nonmagnetic matrix.
21. The process of claim 1, wherein said magnetic material is a magnetic cement.

22. The process of claim 21, wherein said additive comprises one or both of calcium oxide and silicon oxide so as to form a calcium silicate based magnetic cement.
23. The process of claim 1, wherein said slag comprises more than ten percent of iron oxide by weight.
24. A magnetic material produced in accordance with the process of claim 1.
25. A process for producing a magnetic material from a slag, comprising milling a mixture of said slag and at least one additive so as to produce a composite of one or more magnetic ferrites and one or more non-magnetic substance.
26. A process for producing a magnetic material from a slag, comprising:
 - milling a mixture of said slag and at least one additive including a ferrous substance; and
 - heating said mixture;
 - so as to produce a nanocomposite of magnetite and iron.
27. The process of claim 25 wherein said ferrous substance is selected from the group of iron, iron oxides, and iron salts.
28. A magnetic material, produced in accordance with the process of claim 26.