Magnetic Properties of Ceramic Minerals

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Magnetic minerals and fine iron have plagued ceramic producers since the first glazed pot was produced many thousands of years ago. Early ceramicists adopted elaborate and colorful patterns to cover any imperfections caused by such contamination. Over time, the demand for white or single colored ceramic products increased, making disguising any imperfection increasingly difficult.

Ceramic producers turned to technology, with magnetic separators and screens, to identify and then remove problematic minerals and fine iron. Many ceramic raw material deposits, such as feldspar, silica sand, ball clay and kaolin, have problematic magnetic minerals including micas (muscovite and biotite), hematite, chromite, and iron stained quartz. Additionally, free iron is often introduced into the process from the wear or failure of the process plant (Figure 1). Understanding the minerals' magnetic properties and their reaction within a magnetic field defined the magnetic separator design process.

The behavior that minerals exhibit in a magnetic field is classed under one of five headings:

- Diamagnetic
- Paramagnetic
- Ferromagnetic
- Anti-ferromagnetic
- Ferrimagnetic

These classifications define whether separation is possible with a magnetic separator (Figure 2).

Source of magnetic properties

The magnetic properties of any mineral reside in the electrons of the atoms or ions. In accordance with the principles of wave mechanics, the electron, moving in a closed path about the nucleus, is considered as a current behaving like a wave, and this moving current generates a magnetic field. When a crystal is placed in an external non-uniform magnetic field, there is a force working to align the magnetic fields of the atoms to produce a magnetic moment for the whole crystal. The magnetic susceptibility χ, is the ratio of the resulting magnetic moment, M, to the strength of the external field, H ($\chi = M/H$).

Diamagnetism and paramagnetism

Diamagnetic minerals have a small negative value of χ and are slightly repelled by the magnetic field. In contrast, paramagnetic minerals have a small positive value of χ and are weakly attracted by the field.

Paramagnetism is associated with the spins of the electrons, whereas diamagnetism is related to their distribution in space. Diamagnetism is a property possessed by all atoms. However, when the atom contains an odd number of electrons, or has incomplete electron shells (as in the transition elements) imbalance of the electron spins causes the paramagnetic effect to overshadow the diamagnetic part of the total magnetic susceptibility. Paramagnetism is also found in metals where there is a cloud of free conduction electrons.

This behavior is only applied generally to crystals because the internal crystal field, as a whole, modifies the magnetic effects. The electronic energy levels in a crystal are described as being split and the total magnetic susceptibility depends on the distribution of the electrons in the different levels. Therefore, in complex compounds, it is not possible to predict the magnetic properties.

In minerals, iron-bearing structures are paramagnetic. However, there are paramagnetic minerals without iron. The differences in magnetic susceptibility are sufficient to enable separation using high-intensity magnetic separators.

Bismuth is the sole example of a diamagnetic mineral. Paramagnetic minerals are more widespread and include hematite and biotite mica (Figure 3).

Ferromagnetism

Ferromagnetic minerals possess a magnetic moment even in the absence of an applied magnetic field. They are strongly attracted by even a weak magnetic field and remain permanently magnetized. However, ferromagnetic substances also exist in unmagnetized conditions when, at room temperature, the electronic magnetic moments are permanently in alignment as a result of interaction between neighboring atoms. Iron, cobalt, nickel and pyrrhotite are typical examples of the ferromagnetic species.

Antiferromagnetism and ferrimagnetism

The way in which electrons align in certain crystals produces either an antiferromagnetic or ferrimagnetic effect.

Antiferromagnetism

This occurs when adjacent atoms interact in a manner that aligns the spins in parallel but opposed directions, called antiparallel spins. The two sets of moments cancel one another and there is no permanent magnetic moment. Typical examples include metals such as chromium and oxides such as nickel oxide (NiO).

Ferrimagnetism

Antiparallel alignment, in which the components in opposite directions are not equal, results in a permanent moment which is fer-

Figure 1 Iron speck contamination in fired ceramic tableware (© Paul Fears Photography)

Figure 2 Three fractions after magnetic separation – non-magnetics, middlings and magnetics (© Paul Fears Photography)

rimagnetism. Magnetite is an important example of a ferrimagnetic mineral (Table 1).

Consequence of magnetic particle contamination

The presence of magnetic particles in a ceramic body or glaze, both in mineral form or as free iron, causes a wide range of issues during the firing process. In the past, such flaws were covered by ornate and colorful glazes and decoration. However, modern ceramics producers do not have the luxury of implementing such methods.

Magnetic particles cause both structural and surface defects, as well as color and brightness issues. Lower value, mass-produced ceramics often have very visible black spots and associated glaze deformation. Less visible black or brown particle specking is also common (Figure 1). Such defects occur when magnetic minerals or free iron is present in the glaze during the firing process. The heat is absorbed and retained by the particle, causing a darkening in color and expansion. The particle may also 'pop', causing defects in the surrounding glaze. Another effect is the changing of the final fired glaze color and darkening of the brightness, especially when white or off-white, due to the presence of fine magnetic particles. Defects on ceramic tiles, tableware and sanitaryware, which rely on perfect appearance, result in either partial rework or total rejection and recycling. In plants with insufficient systems to remove the magnetic particles, such rates can be above 10 %. This is costly in both time and materials.

Non-visible magnetic contamination remains problematic. Magnetic particles remaining in the body prior to firing experience the same reaction to heat as those in the glaze. This weakens the surrounding ceramic structure, resulting in fine cracks that develop over time. Failure of a ceramic product due to fracturing is commonly traced back to one or more magnetic particles, which are then visible along the fracture line. A single magnetic particle is

Figure 3 Paramagnetic minerals separated using an electromagnetic filter (© Paul Fears Photography)

Figure 4 Bunting electromagnetic filter in a ceramics plant (© Bunting)

Table 1 Magnetic properties of ceramic related minerals (© Bunting)

Mineral \ Magnetic intensity (Gauss)	Zero magnetic response	1000	2000	3000	4000	5000	6000	7000	8000	9000	10000	11000	12000	13000	14000	15000	16000	17000	18000	19000	20000	21000	22000	23000	24000
Apatite															■	■	■	■	■						
Biotite											■	■	■	■	■	■	■	■	■						
Calcium Carbonate	■																								
Feldspar	■																								
Garnet													■	■	■	■	■	■	■	■					
Goethite																■	■	■	■						
Hematite														■	■	■	■	■	■						
Limonite																	■	■	■	■	■				
Magnetite		■																							
Muscovite																■	■	■	■	■	■	■	■	■	■
Nepheline Syenite	■																								
Olivine (Fayalite)												■	■	■	■										
Quartz	■																								
Quartz (Iron stained)																			■	■	■	■	■	■	■
Talc	■																								

enough to trigger such catastrophic failure.

This poses a risk for many high-performance ceramics, especially as the contamination is not visible from the outset. Failure only occurs over time.

Magnetic separation of minerals

Understanding the magnetic properties of the minerals in a particular ceramic raw material is vital when optimizing magnetic separation. The wide range of magnetic separator designs use different strengths and types of magnetic field to produce a separation. Several designs of magnetic separator may feature in a single mineral processing operation.

The range of high-intensity magnetic separators is divided into dry and wet processing (Table 2). Many ceramic raw materials, such as feldspar, zircon and silica sand are handled and processed in a dry state. Most ceramic mineral processors magnetically treat their own reserves, as higher specification materials generate increased revenue. High-intensity magnetic separators remove magnetic minerals and free iron. Designs include the rare earth roll magnetic separator and rare earth drum magnet, which both utilize permanent magnets, or the electromagnetic induced roll magnetic separator, which is better suited for handling high-temperature materials (for example directly after drying).

Within the manufacturing plant, the spray dry ceramic process commonly introduces free fine iron into the process. Both the

Table 2 High intensity magnetic separators commonly used to process ceramic raw materials, body and glazes (© Bunting)

Magnetic separator	Process	Particle size range	Gauss range
Electromagnetic filter	wet	0-500 µm	0–10,000
Induced roll magnetic separator (IMR)	dry	65–1000 µm	0–22,000
Rare earth roll separator (RE Roll)	dry	65 µm–10 mm	14,000
Wet high intensity magnetic separator (WHIMS)	wet	0–800 µm	0–18,000

rare earth roll magnetic separators and drum magnets are employed to remove such problematic contamination.

Once the ceramic raw materials have been milled and mixed into slips, body and glazes, further magnetic extraction takes place. The milling process often liberates entrapped mineral iron, whilst free iron is reintroduced from the process (for example during screening, pumping, etc).

Electromagnetic filters, producing high magnetic fields, cleanse both the body and the glaze. Larger-sized models, for high capacities, provide the final separation stage for removing very fine and weakly magnetic minerals from the body. Small-sized electromagnetic filters, often mounted on moveable frames, separate fine iron and weak magnetics from the glaze (Figure 4). However, care is needed, as some glaze coloring is magnetic.

As a final check – and to prevent any visible contamination on the glaze – neodymium rare earth tube magnets or magnetic liquid traps with neodymium magnets are positioned as close to or within the glazing station. This captures any magnetic particles introduced to the glaze during transportation to the station.

Future mineral reserves

As traditional ceramic mineral reserves are depleted and more complex deposits are mined, understanding the mineralogy in terms of magnetic susceptibility is vitally important. Magnetic separator suppliers work closely with mineral processors and plant designers, often at the project feasibility stage, providing advice on the optimum design of magnetic separator and stage within the process. This often involves extensive test work in magnetic separation laboratories and at site. The ongoing demand for white and pattern-free ceramics means that there is no rest for ceramic producers and raw material suppliers in the battle to eradicate magnetic minerals and free iron.

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