

Mine Water Treatment Using Iron Ferrites and Magnetite

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Abstract

Iron ferrites and magnetite are effective for the removal of heavy metals from liquid effluents. The mineral magnetite, or synthetically prepared iron ferrite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$), is typically used. Iron ferrite can be utilized in a batch mode by adding preformed ferrite to the liquid or by preparing the ferrite in situ, thus using the existing iron in the effluent. Natural magnetite can also be used in a batch mode or in a column mode. This paper will review previous work on the use of iron oxides for wastewater treatment and discuss the potential of the process for mine water treatment and remediation.

Introduction

Iron oxides are widely used for the treatment of liquid wastes containing radioactive and hazardous metals. These processes include adsorption, precipitation, and other chemical and physical techniques (King and Navratil 1986, Driscoll 1986, Freeman 1988, Macasek and Navratil 1992). For example, a radioactive wastewater precipitation process utilizes ferric hydroxide to remove radioactive contaminants, such as americium, plutonium, and uranium (Boyd et al. 1983). Some adsorption processes for wastewater treatment have utilized ferrites and a variety of iron-containing minerals, such as akaganeite, ferroxhyte, ferrihydrite, goethite, hematite, lepidocrocite, maghemite, and magnetite (Schwertmann and Cornell 1991). Ferrite is a generic term for a class of magnetic iron oxide compounds (Reynolds 1980). Ferrites possess the property of spontaneous magnetization and are crystalline materials soluble only in strong acid. Iron atoms in iron ferrite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) can be replaced by many other metal ions without seriously altering its spinel structure (Boyd et al. 1986).

Various ferrites and natural magnetite were used in batch modes for actinide and heavy metal removal from wastewater (Boyd et al. 1986, Kochen and Navratil 1987, Navratil 1989, Navratil 1990, Navratil 1988). Supported magnetite was also used in a column mode, and in the presence of an external magnetic field, enhanced capacity was found for removal of plutonium and americium from wastewater (Kochen and Navratil 1997, Navratil et al. 1995, Ebner et al. 1999). These observations were explained by a nanolevel high gradient magnetic separation (HGMS) effect, as americium, plutonium, and other hydrolytic metals are known to form colloidal particles at elevated pH levels (Ebner 1999). Recent modeling work supports this assumption and shows that the smaller the magnetite particle, the larger the induced magnetic field around the particle from the external field (Ebner et al. 1997). Other recent studies have demonstrated the magnetic enhanced removal of arsenic, chromium, cobalt, iron, and uranium from simulated groundwater and wastewater (Cotten et al. 1999a, Cotten et al. 1999b, Navratil 2008).

The magnetic field-enhanced filtration/sorption process differs significantly from magnetic separation processes used in the processing of minerals and, more recently, for water treatment and environmental applications. Conventional processes use, for example, a fine stainless steel wool to form a magnetic matrix within a flow field of a solution containing mineral particles to be separated. For this reason, in order for such processes to remove metal ions and nanoparticles from solution, precipitating or flocculating agents must first be added to effect formation of large particles. In contrast, the magnetic filtration/sorption process is unique because a highly porous adsorbent material not only acts as a magnetic matrix, it also contributes an adsorptive component to the system. This adsorptive component allows for the removal of complex metal species and ions from solution, while the relatively low field magnetic matrix allows for the removal of nanoparticles through a HGMS effect.

This paper reviews previous work on the use of iron oxides for wastewater treatment and work leading to the development of the magnetic filtration/sorption process. The potential of magnetite and iron ferrites for simple and inexpensive mine water treatment will also be discussed.

Ferrite Wastewater Treatment

Metals are removed in most conventional wastewater treatment processes in the form of metal hydroxides because they have low solubilities. As noted above, ferric hydroxide is often added to scavenge a wide variety of heavy metal contaminants (Dzombak 1990). However, the metal hydroxide solids can form gelatinous precipitates, which are difficult to filter. Consequently, filter aids must sometimes be added to facilitate the filtration process.

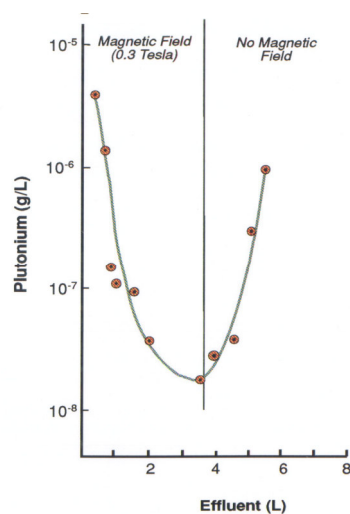
The use of iron ferrite and magnetite in wastewater treatment has a number of advantages over conventional flocculent precipitation techniques for metal ion removal (Boyd et al. 1986). Ferrite solids are crystalline materials, unlike hydroscopic metal hydroxide sludges, and can be more readily filtered; their ferromagnetic character permits use of magnetic separation of the solids from solution. A wide variety of metal ion impurities can be effectively removed in one treatment step, and their removal is not seriously affected by high salt concentrations (Boyd et al. 1986, Navratil 1988). The ferrite method does not require expensive chemicals, and because iron is usually a constituent of waste solutions, its oxidation states can be adjusted by chemical or electrolytic means to form ferrite. In situ and preformed ferrite methods have been used in wastewater treatment applications (Boyd et al. 1986). Most commonly with the in situ method, ferrous ions are added to the waste solution (usually heated to 60–90°C) followed by the addition of base and subsequent oxidation (usually by aeration). Ferrite is formed within the waste solution itself. In this technique, metal ions undergo ferrite formation and can be incorporated into the lattice of ferrite crystals. In the preformed case, ferrite is prepared separately using the in situ procedures described and added in solid or slurry form to the waste solution. Magnetite, a naturally occurring ore prevalent in most parts of the world, can also be used in place of preformed ferrite. However, natural magnetite needs activation to have the same capacity as preformed ferrite (Kochen and Navratil 1997).

The ferrite functions as an adsorption medium to remove contaminating species from solution. In addition to its chemical incorporation capabilities, in situ ferrite can also function in this manner. The adsorption mechanism of ferrite occurs through metal hydroxide species. In alkaline solution, most metal ions form insoluble species, which may be complexed with additional hydroxide ions, depending the chemistry of the metal and the pH of the solution. Hydroxide ions are strongly adsorbed onto the surface of ferrite particles so that metal ions can bond to the ferrite surface through the hydroxide ions to which they are bound. Alkali, alkaline, and other metals, which do not form insoluble hydroxides, and metals that form soluble hydroxide complexes at high pH, such as aluminum and zinc, are not removed by ferrite (see Table 1)

Table 1 Trace Metal Ions Removable from Solution using Iron Ferrites (Boyd et al. 1986)

Aluminum*	Erbium	Nickel
Americium	Gallium*	Plutonium
Antimony*	Germanium*	Rhodium*
Arsenic	Indium*	Silver
Beryllium	Iron	Tin
Bismuth	Lead*	Titanium
Cadmium	Lithium*	Tungsten*
Calcium*	Magnesium*	Uranium
Chromium	Manganese	Vanadium*
Cobalt	Mercury	Zinc*
Copper	Molybdenum*	Zirconium

Figure 1 Plutonium Removal using Epichlorohydrin Resin Coated with Magnetite (Ebner et al. 1997)



Supported Magnetite Process

Magnetite from natural and waste sources is usually only available as a fine powder. To achieve low backpressure and good water flow in a column of magnetite, it must be supported with another material. The first tests of supported magnetite involved using a column containing a nonporous polyamine-epichlorohydrin resin bead coated with activated magnetite surrounded by an electromagnet of 0.3 tesla (Kochen and Navratil 1997). In this work, the capacity of the magnetite-coated resin for both plutonium and americium removal from water increased by a factor of five compared with using unsupported magnetite particles in the absence of a magnetic field (see Figure 1). The above observations were explained by a nanolevel HGMS effect, as americium, plutonium, and other hydrolytic metals are known to form colloidal particles under alkaline conditions (Ebner et al. 1999). The pores of the magnetite-coated resin are large enough to permit the free displacement of the colloidal particles. When the field of the electromagnet is turned on, the magnetite particles are magnetically induced, creating a field that contributes to the net field sensed by the colloidal particles. When the magnetic force is sufficiently greater than the force associated with Brownian (thermal) motion, the magnetic force created by the field can be attractive and sufficiently large to allow the magnetite to sorb the colloidal particles, provided they have sufficient magnetic susceptibility. Recent modeling work has shown that the smaller the magnetite particle, the larger the induced magnetic field around the particle from the external field (Ebner et al. 1997). When the electromagnet is turned off, the nanoparticles are released and dispersed in solution by thermal motion (metal hydroxide complexes would still be adsorbed, however, and would need to be removed by an eluent solution). Recent studies have demonstrated the magnetic-enhanced removal of arsenic, chromium, cobalt, iron, and uranium from simulated groundwater and wastewater using the experimental setup shown in Figure 2 (Cotten et al. 1999a, Cotten et al. 1999b, Navratil 2008). These results (selected results shown in Figure 3) also indicate that natural components of groundwater, such as calcium and magnesium, do not interfere and are not removed with the process. Several suitable support media, including glass beads, were tested for mixing with natural magnetite and achieving satisfactory flow characteristics while retaining the magnetic field-enhanced sorption properties of magnetite (Cotten et al. 1999b).

Figure 2 Experimental Column Apparatus Cotten et al. 1999b)

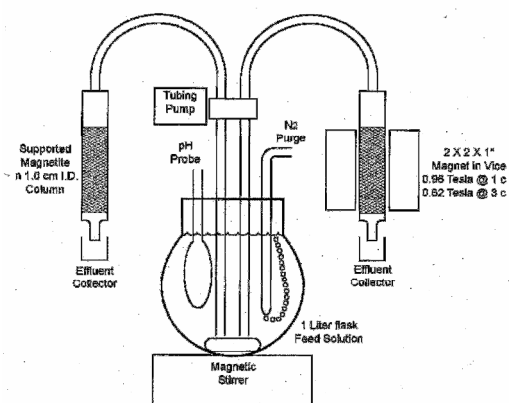
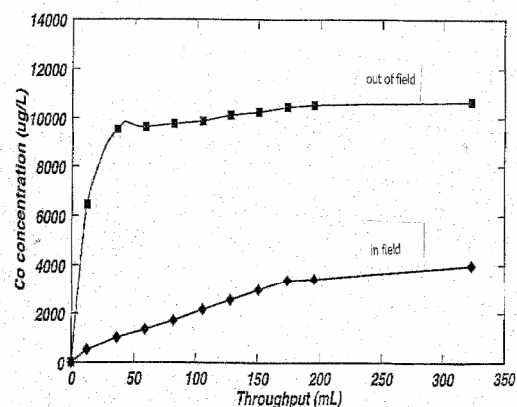


Figure 3 Effect of Magnetic Field with Cobalt Loading on Glass Wool/Magnetite Column (Cotten et al. 1999b)



Operation of the Magnetic Process

One inexpensive device for containing supported magnetite is simply some type of static-bed column with screens at the entrance and exit for holding the support in place while permitting the flow of the smaller magnetite particles in and out of the column. The first step in operating the column would be to pass a slurry of activated magnetite down the column containing a support material such as glass beads (Cotten et al. 1999b). After the column is loaded with magnetite, the magnets (either electro or rare earth) would be placed around it to hold the magnetite in place. The water to be treated would be passed upflow through the column until contaminant breakthrough is reached. The magnetic field

would then be removed and an additional amount of fresh magnetite slurry added to the top of the column to displace a portion of loaded magnetite and the captured contaminant particles. The magnets would be replaced around the column, and more water would be passed in an upflow direction. The spent magnetite could be regenerated or discarded depending on the contaminants and operational situation. Discarding the material would be useful for contaminants that sorb strongly onto the adsorbent material (thus perhaps serving as a favorable waste form for final disposal).

Besides ferrite treatment, wastewater could also be pretreated with standard flocculation, precipitation, and filtration steps to remove gross amounts of metal ions from solution. The magnetic filtration/sorption device would then be used as a polishing step for the water to remove colloids, small particles, and complex ions not removed in the precipitation and filtration steps.

Conclusions

Iron oxides in various forms have been used in water and wastewater treatment technology. The use of ferrites and magnetite has some advantages for batch treatment of a broad range of aqueous wastes, including mine water treatment. Activated magnetite, supported and used in a column mode in the presence of an external magnetic field, shows enhanced capacity in removal of a wide variety of contaminants from wastewaters. The magnetic field-enhanced filtration/sorption process is ideal for use as an improved, simple, and inexpensive method for mine water treatment and remediation.

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