

TRACE METAL RECOVERY AND CONCENTRATION USING FERRITES

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Ferrites have been used to separate a wide range of substances such as dissolved metal species, particulate matter, and organic and biological materials; they have been used almost exclusively for metal waste treatment applications. However, ferrites can be used to remove and concentrate selected trace metals in a wide variety of feed solutions requiring analysis. A brief overview of ferrite properties and recent applications for trace metal recovery and concentration will be presented.

Ferrites are a class of mixed valence iron oxide compounds having the crystal structure of spinel, MgAl_2O_4 . Iron atoms in iron ferrite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$), or magnetite, can be replaced by many other metal ions without seriously altering the spinel structure. They are ferromagnetic crystalline materials which are soluble only in strong acid.

Ferrites have been used for a wide variety of waste treatment techniques for separating not only metals from aqueous waste but also biological matter, organic materials, particulate matter and suspended solids.¹ Furthermore, ferrites and activated magnetite² have the potential to remove impurities from metal feed solutions to effect purification of metal ions, such as alkali and alkaline earth metals.³ Thus ferrites make excellent magnetic adsorbents for pre-analysis separation and concentration of trace elements.

Experimental

Preparation methods: The in situ ferrite preparation method has been used extensively in waste treatment applications.⁴ Most commonly, ferrous ion is added to the waste solution (usually heated to between 60 and 90 °C) followed by the addition of base and subsequent oxidation, usually by aeration, and ferrite is formed within the waste solution itself. In this technique, metal ions undergo ferrite formation and are incorporated into the lattice of ferrite crystals. The resulting mixture of ferrites forms a solid which is not susceptible to leaching by alkaline, neutral, or even weakly acidic aqueous solutions.

Ferrous ions are usually added in the form of ferrous sulfate. Alternatively, metallic iron can be dissolved in acidic waste media to produce ferrous ions. A third method of

introducing ferrous ions are by electrolytic means. Ferrite can be produced directly from ferrous and ferric ions present in the waste solution. Addition of ferrous chloride and ferric chloride in a molar ratio 1 : 1 to 1 : 2.5 to a waste solution, followed by addition of base, produces ferrite.

The second general method of application is referred to as the preformed ferrite technique. In this case, ferrite is prepared separately and subsequently added in solid or slurry form to the waste solution. The ferrite functions as an adsorption medium to remove contaminating species from solution. In situ ferrite can also function in this manner in addition to its chemical incorporation capabilities. Preformed ferrite is prepared separately using the in situ procedures described above and is subsequently placed in contact with a waste solution. Contaminants are adsorbed onto the ferrite surface and are not generally susceptible to leaching by water from natural sources.

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 upon 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. This mechanism is consistent with the observation that adsorbed species can be removed with acid, since acid would react with hydroxide and thereby destroy the link between the ferrite surface and the metal. It is also consistent with the fact that alkali, alkaline earth and other metals, which do not form insoluble hydroxides, are not removed from solution by ferrites. Metals which form soluble hydroxide complexes at high pH, such as aluminum and zinc, also are not affected by ferrite. Preformed ferrite can be applied to pre-analysis separation in various physical forms. For example, barium ferrite ($\text{BaO} \cdot \text{Fe}_2\text{O}_3$) has been used successfully as granules, powder, or pellets. Iron ferrite, or magnetite can also be used in much the same manner. In the latter case, adsorbed species can be removed by washing with acid solution and the ferrite reused.

Magnetite is a naturally occurring ore and very prevalent in Australia. However, natural magnetite needs activation to have the same capacity as preformed ferrite.² We have found that the magnetite can be effectively activated by treatment with certain alkali and alkaline earth hydroxides, water, steam and other treatments to increase the surface area and absorptive characteristics of the material. Recently a synergistic effect has been discovered in using supported magnetite in a column mode with an external magnetic field for concentration of plutonium and americium from waste water.⁵ Thus the material achieves and can even surpasses the metal removal capacity of ferrite.

Separation and concentration of trace metals with ferrites: Some conventional precipitation processes operate where metal ions are removed in the form of metal hydroxides. While most metal hydroxides have low solubilities, optimum precipitation conditions for different metals are not the case of aluminum and zinc, for instance, metal

hydroxide can form a soluble complex if the hydroxide concentration is high enough. Other species, such as chromate and permanganate, require reduction prior to hydroxide precipitation. As a result, multiple treatment steps are often required to effectively remove and concentrate various dissolved metal ions. The metal hydroxide solids can form gelatinous precipitates which are difficult to filter. Consequently, flocculating agents, diatomaceous earth, coagulating agents, or other filter aids must be added to facilitate the filtration process.

Compared to conventional flocculant precipitation techniques for trace metal ion removal and concentration, ferrite treatment has a number of advantages:

(1) Unlike hygroscopic metal hydroxide sludges, ferrite solids are crystalline materials. As a result, they can be more readily filtered, and their ferromagnetic character allows for their separation from solution by magnetic means as well.

(2) Most trace metal ions can be effectively removed in one step. Furthermore, such species as chromate and permanganate can be removed directly by the ferrite method without a prior reduction step. Nor is the ferrite method affected by high salt concentrations.

(3) Ferrites are very insoluble in aqueous media, and the trace metals adsorbed by ferrite or captured within the ferrite crystal structure are not readily redissolved by water from natural sources.

(4) The ferrite method does not require expensive chemicals. A convenient source of ferrous ions used to form ferrite is readily available as an industrial by-product in the form of ferrous sulfate. Also iron is usually a constituent of waste and feed solutions and the ferrous-to-ferric ratio can be adjusted by chemical or electrolytic means.

Table 1
Trace metal ions that can be removed from concentrated
solution using ferrites, taken from References 1 and 2

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

*May not be removed by activated magnetite/preformed ferrite and pH control. Thus, these metals could remain in solution and be effectively purified by ferrite treatment.

Use of ferrite to remove a wide variety of soluble metal species from many different types of solutions has been reported. These metals are listed in Table 1. The removal of titanium and silicon as their dioxides has also been reported. There is also a patent which describes the use of barium ferrite and magnetite for the removal of "radioactive material" from solution, but no specific elements or compounds are mentioned.⁶

Magnetic polymer resins capable of efficient removal of actinides and heavy metals from contaminated water has been disclosed together with methods for making, using and regenerating them.⁵ The resins comprise polyamine-epichlorohydrin resin beads with ferrites attached to the surfaces of the beads. Markedly improved water decontamination is demonstrated using these magnetic polymer resins in the presence of a magnetic field, as compared with water decontamination methods employing ordinary ion exchange resins or ferrites taken separately.

Conclusions

Magnetic ferrites can be used to separate and concentrate a wide range of trace metals from solutions containing various cations and anions. The ferrites can be prepared in situ in the solution or added as preformed ferrite or activated magnetite. However, a column of supported ferrite operated in the presence of an external magnetic field could be one of the most efficient methods for pre-analysis concentration of trace elements from environmental samples as well as for large scale separations.

References

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