Chapter

Magnetic Separation of Impurities from Hydrometallurgy Solutions and Waste Water Using Magnetic Iron Ore Seeding

Haisheng Han, Wenjuan Sun, Wei Sun and Yuehua Hu

Abstract

The removal of iron ion from leaching solution is critical for the recovery of value metals, with the method of choice commonly being crystallization (precipitation). This paper summarized the new improvements in iron removal by precipitation methods in recent years and proposed a novel process, magnetic seeding and separation. The new process can promote iron precipitate aggregation and growth on the surface of the magnetic iron ore seeds. A core-shell structure was formed of iron precipitate and magnetic iron ore seeds, which can be magnetized and coalesced in magnetic field, accelerating the solid-liquid separation. The efficient magnetic floculation and separation offset the poor settleability and filterability of the residues, contributing to the development of the hydrometallurgy process. Moreover, magnetic seeding and separation was also used for the removal of organic and inorganic contaminants from wastewater, significantly improving the purification efficiency. Therefore, iron ore not only played an important role in mining and steel manufacture, but also can be used to solve some problems in crossing fields.

Keywords: leaching solution, goethite process, iron removal, magnetic seed

1. Introduction

Iron is one of the most abundant elements in the earth’s crust. It always coexists with metals in the ore, mainly exists in the form of hematite, magnetite and muscovite on the surface of particles or in the inclusions inside crystals [1]. In hydrometallurgy, iron, although is converted into insoluble precipitates and removed in advance by sulfation roasting, soda roasting, acid leaching, etc. during ore pretreatment, still inevitably goes to the aqueous solution with the dissolution of the target metal during the leaching process [2–4]. The classical methods for removing iron in the leaching solution are precipitation, extraction, ion exchange, displacement, and electrowinning [4]. The commonly used method is the precipitation method, which separates iron ions by converting to iron precipitation compounds. According to the different iron precipitation compounds, it can be divided into jarosite [5–6], hematite [7], iron(III) oxide-hydroxide [8] and goethite [9–10] method, etc. The jarosite method produces a large amount of low-grade iron-bearing slag in the application, which is difficult to handle, consumes a large amount of sulfate, and
causes certain environmental problems [5–6]; the hematite method needs to be carried out under high temperature and pressure, which consumes large energy and high CAPEX (capital expenditure) [7]. The filtration efficiency of Fe(OH)_3 colloid precipitation method is low, and it is easy to adsorb a large amount of other valuable metals, causing large metal loss [8].

The goethite method is widely used in hydrometallurgical plants for zinc, copper and nickel as the main process for removing iron because of its low CAPEX and environmentally friendly products [9–10]. In order to ensure the effect and efficiency of iron removal, the goethite process must strictly control the concentration of Fe^{3+} below 1 g/L, and thus developed the two commonly used processes – VM method and EZ method [8–9, 11]. The former firstly reduces all the iron ions to Fe^{2+}, and then slowly oxidizes the Fe^{2+} to Fe^{3+} under hydrolysis conditions to control the content of Fe^{3+} [9], and the latter slowly adds the concentrated pressure leachate containing Fe^{3+} in the precipitation vessel with addition rate of less than the Fe^{3+} hydrolysis rate, thereby forming goethite precipitation [11]. The pH in goethite process is common lower than 4.0, and calcium hydroxide or calcium carbonate is usually used as neutralizer, which will result in a large amount of calcium sulfate mixed with the goethite residue [12]. These mixed residues reduce the filtration efficiency and cause the loss of valuable metals such as Zn and Ni [5, 13–14]. In addition, the residue mixture accumulated in the tailings pond contains heavy metals such as Pb, As, and Cr, which causes pollution of local water and soil. Therefore, improving filtration performance and reducing the loss of valuable metals are two problems that need to be solved urgently in the traditional goethite precipitation method.

This article summarizes the new improvements in iron removal by precipitation methods in recent years, and on this basis, proposes a novel iron removal process - magnetic seeding and separation. A core-shell structure is formed by precipitating and growing iron on the magnetic seeds surface, and achieves high-efficiency solid-liquid separation by magnetic separation. The new process remarkably reduces the loss of valuable metals in iron removal. Magnetic seeding and separation processes have not only been successfully used in the removal of iron from hydrometallurgical leachate, but also shown good application prospects in wastewater and soil pollution treatment.

2. Iron removal in nickel and zinc leaching solution

2.1 Magnetite precipitate process

Magnetic flocculation and separation based on the magnetic difference of materials can easily separate magnetic solids from mixtures. It shows higher selectivity and efficiency than centrifugation and filtration, and has been widely used in water treatment, biotechnology and minerals separation [15–18]. As is shown in Figure 1, Han et al. [3] studied the feasibility of magnetite precipitation in the hydrometallurgical nickel leaching solution. Under lower oxidation potential, at pH 2.0–2.2 and 90–100°C, the iron ions in the leachate may slowly oxidize and partially precipitate in the form of magnetite. Magnetic flocculation and separation can effectively separate the precipitate from the solution. Unfortunately, the iron precipitation from solution is still dominated by goethite, the magnetite composition is relatively small, and it is difficult to truly achieve effective magnetic separation in industrial applications. But this research of magnetite process of iron removal provides other new ideas of magnetic separation.
2.2 Induced crystallization goethite process

The goethite process can be divided into four stages: (a) hydrolysis to monomers and dimers; (b) the reversible stage involving rapid growth to small polymers; (c) formation of slowly reacting large polymers; and (d) precipitation of a solid phase [19–20]. The goethite precipitation system is a complex system, and the presence and content of different components and iron phases have a greater impact on the precipitation and filtration performance of goethite. As shown in Figure 2, the pH and temperature conditions of the sulfate-containing solution determine the existence and content of different iron phases such as hematite, goethite, iron hydroxide and hydroxyl salt [21]. The goethite residues that cause

![Figure 1.](image1)

*Potential/pH diagram for Fe-H$_2$O system at 100°C.*

![Figure 2.](image2)

*Temperature and pH conditions for the precipitation of hematite, goethite, ferric hydroxide, and hydroxy salts (including jarosites) from 0.5 M ferric sulfate solution [21, 23].*
filtration difficulties and metal loss are composed of amorphous iron phase, six-line ferrihydrite, poor crystalline goethite, solid solution jarosite phase and silica [2, 22]. Therefore, the crystallinity, size and content of the goethite particles can be controlled by adjusting the pH, thereby improving the separation performance and the loss of valuable metals.

Yue and Han [23] study that as the pH value decreases from 5.0 to 2.0, as shown in Figure 3, the crystallinity of goethite decreases, the goethite particles tend to agglomerate, the particle size increases significantly, and the filterability of the precipitate improves. Nickel is lost in the iron precipitate by being incorporated into the crystal lattice and adsorbed on the surface of the goethite particles, and the nickel adsorption loss are related to the specific surface area of the goethite particles. When goethite is in an intermediate transition state at low pH (2.5–3.3), which is between the crystalline state and the colloidal state, the loss of nickel is the least. However, the improvement by only adjusting the pH of the goethite precipitation process is minimal. Chang et al. [24] carefully reduced the pH from 4.0 to 2.5, and the loss of nickel is only reduced by about 10% in the iron precipitation. Moreover, it is not realistic to achieve such detailed condition control in actual industrial applications.

Figure 3.
(a) SEM images of the goethite precipitate at different pHs and (b) pH effect for the nickel loss, the crystallinity, and the specific surface area of the precipitate [23, 25].

![Figure 3](image)

Figure 4.
The specific surface area and the nickel grade of iron precipitates with limonite seeds in different size ranges (2 g/L limonite seeds, pH 2.1–2.5, 85°C) [30].

![Figure 4](image)
The traditional goethite precipitation method needs to overcome high barriers to the formation of crystals, and often requires a few days of reaction time. The amorphous iron phase appears at this stage, making precipitation separation difficult. Seed induced crystallization can make crystals precipitate and crystallize from the solution at lower solution saturation, pH value and temperature, and has been widely used in the preparation and production of drugs and nanomaterials [26–29]. Han [30] choose natural limonite as the seed crystal of goethite and induce crystallization to improve the problem of poor filterability at the low pH goethite precipitate. As is shown in Figure 4, by adding limonite seeds, the particle size of the goethite precipitate is significantly increased. The goethite particles in the particle size range of 37–74 μm have the largest yield and the smallest specific surface area, which can result iron precipitates with a nickel grade of <1%. However, the reduction of metal loss and improvement of filterability are difficult to achieve at the same time by pH control and induced crystallization, one of them must be sacrificed. The intermediate transition state goethite with good filtration performance and minimum metal loss is difficult to accurately induce formation in the actual field industry. It is a need to find other ideas to achieve qualitative progress.

3. Magnetic iron seeding and separation

Han et al. [25, 31–32] combined seed induced crystallization and magnetic separation, and proposed a novel magnetic seeding and separation process, as shown in Figure 5. Before the iron is precipitated as goethite, fine-grained maghemite or magnetite particles are added to the leaching solution to make the goethite precipitate and grow on the surface of the magnetic particles, thereby avoiding mixing with the calcium sulfate precipitation in the solution. The iron precipitates on the surface of the goethite to form large magnetic particles with a core-shell structure, and the precipitates are efficiently settled and separated by magnetic separation. The results show that the iron content in the dry iron residue is more than 52% and the Ni content is less than 0.6%, which can be used in industrial applications to deal with a large amount of iron precipitation. After the calcium sulfate precipitation is roasted, 99% of S and As can be removed, and the roasting residue can be respectively used as raw materials for ironmaking and building materials.

![Image](image-url)

**Figure 5.** The process of iron precipitation on the magnetic seeds and the magnetic flocculation in magnetic field [3, 25].
Yue et al. [31] applied magnetic iron seeding and separation to separate goethite from calcium sulfate in zinc leaching with maghemite fine particles as carrier. As is shown in Figure 6, the magnetic goethite-maghemite aggregates were separated effectively from calcium sulfate precipitates by magnetic drum separator, and 90% of Fe and Ca is respectively recovered in two corresponding products. Roasting goethite precipitate with coal powder under the optimum conditions removed 99% of S and As. Goethite products can be directly used in the ironmaking industry, and calcium sulfate precipitation can also be used to produce cement and building materials.

Yue et al. [32] establish the surface complex and precipitation model of goethite on magnetite and maghemite magnetic nanoparticles, as shown in Figure 7. The formation of Fe (III) surface complexes are directly related to the nucleation and
precipitation of goethite on the solid surfaces of the two magnetic nanoparticles. The more polynuclear surface complexes produced on the particle surface, the more precipitation of heterogeneous forms. Fundamentally, it is possible to screen out the best material as the crystal nucleus to separate goethite from calcium sulfate or other heterogeneous precipitation.

4. Application and prospect

4.1 Recycling Fe and Cr in Cr-bearing electroplating sludge

The Cr-bearing electroplating sludge is produced from the treatment of Cr wastewater and metallurgical processes [33–36]. It contains excessive amounts of heavy metals, such as Cr, Fe, Ni, Cu, Pb and Zn, or potential dioxin pollutants [37–38], therefore must be treated before stacking. Many methods have been applied to recover Cr from the acid leaching solution of electroplating sludge, such as electrochemical precipitation (ECP) [39], selective extraction [35, 40], adsorption or biosorption [41–44] and Cr-Fe coprecipitation [45–48]. Compared with other methods, recovering Cr by Cr-Fe coprecipitation is simple, economical and practical for industrial applications. In addition, the advance coprecipitation of Fe and Cr can avoid their interference on the recovery of Ni, Cu and Zn.

Yue et al. [49] use the novel magnetic seeding and separation process to recover Cr(III) and Fe(II) synchronously by forming the Cr(III)-Fe(III) coprecipitates on the surface of maghemite (γ-Fe₂O₃) fine particles. The active hydroxide radicals on the surface of magnetic seeds induce the nucleation and growth of goethite, which results in enhanced Cr(III)-Fe(III) coprecipitation. As shown in Figure 8, the maghemite particles, served as the crystal nuclei, could induce the formation of the core-shell structured Cr(III)-Fe(III) coprecipitates on its surface and accelerate the sedimentation of the coprecipitates in the magnetic field. The results of the two-stage coprecipitation showed that the total recoveries of Cr and Fe were 96.17 and 99.39%, respectively, and the grades of Ni, Cu, and Zn in the precipitates were 0.41, 0.38, and 0.22%, respectively. The obtained coprecipitates can be recycled as the feed material of chromium smelting after heat treatment. This method is simple and efficient for high-concentration Cr³⁺ solution treatment, which is beneficial for the sustainable development of resources and environment.

Figure 8. SEM images of the Cr(III)-Fe(III) coprecipitates without maghemite fine particles (a) and with maghemite fine particles (b), respectively; scheme (c) of the formation of γ-Fe₂O₃/CrₓFe₁₋ₓOOH with core-shell structure [49].
4.2 Removal of As in arsenic alkali residue

Arsenic (As) is contained in most metal deposits, and therefore a large amount of arsenic-containing wastewater, flue gas and residues will be produced in mineral processing and smelting, posing a huge threat to the environment [50–52]. Commonly used methods for removing arsenic from solution include precipitation, electrocoagulation, ion exchange, membrane technology and adsorption [53–56]. In order to remove arsenic and recover valuable metals at the same time, these methods all require acid leaching of the waste, which will produce highly toxic and deadly arsine gas [54, 57]. As is shown in Figure 9(a), Yue [58] developed a safer alkaline leaching method - oxidation alkali leaching of the wastes to transform arsenic compounds into arsenate (\( \text{AsO}_4^{3-} \)) and subsequently recycling the alkali solution after arsenate removal, to treat the arsenic bearing wastes at a lower risk level.

There are a large number of reports that iron oxides have excellent adsorption and precipitation effects on heavy metal ions impurities in aqueous solutions, such as Cr, U and As. García-Sánchez et al. [59–60] found that goethite has a special adsorption effect and capacity for As ions. Wei Jiang [61] considers that arsenic (\( \text{AsO}_4^{3-} \)) absorbs on the surface of goethite by forming a bidentate-binuclear complex, and that pH and other metal ions in the solution will affect the distance and coordination number of As/Fe. His et al. [62] found that Uanyl can be adsorbed on goethite, amorphous ferric oxyhydroxide, and hematite sols at 25°C, and the adsorption effect on amorphous iron oxide is the strongest. Yue et al. [58] synthesized a series of high-concentrated ferric oxyhydroxide gels (HFGs) at different supersaturation to adsorb arsenate at high alkalinity, achieving zero-consume of the alkali resources. As is shown in Figure 9(b), using HFG (I) that synthesized under the lowest super-saturation condition as the sorbent to treat the oxidation alkali leaching solution of the copper slag from real industry, the residual concentration of arsenic (As (V)) could decrease from 2084 to 71.8 mg/L, which fully meet the requirements for high-concentrated arsenic stabilization at high alkalinity and alkali resource recycling. To further improve the efficiency of filtration and separation, magnetic seed sowing and separation technology can also be introduced to make this process more complete. Related research is underway.

4.3 Removal of phosphate and starch in wastewater

Phosphorus and starch reportedly are the main wastewater contaminants that are difficult to remove efficiently [63–64]. When the phosphorus concentration in water exceeds 0.02 mg/L, phosphorus becomes a polluting element and causes eutrophication of water bodies [65–67]. Starch is a commonly used and cheap material, widely used in many chemical and material industries, but it produces high concentration of organic wastewater, which will affect the environment [68–70]. Therefore, phosphate and starch removal from wastewater has become the focus of many studies. The main phosphate and starch removal methods are similar, such as chemical precipitation [71–74], biological methods [75–79] and adsorption techniques [80–83]. Among them, Chemical precipitation and adsorption technology is commonly used in wastewater treatment due to the simple operation with low cost and large processing capacity compared to other methods [84–86]. However, chemical precipitation inevitably produces a large amount of fine precipitation and suspended solids, which seriously affect the sedimentation and filtration efficiency [84, 87]. And the adsorbents currently used in adsorption technology, such as activated carbon [70, 88], silica gel [89–90], membranes [91–93], etc., have
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High production costs and poor adsorption performance, which greatly limits the adsorption effect and industrial applications.

Magnetic flocculation is an effective way to remove ultrafine suspended solids in water treatment [94–95]. It adds magnetic seeds to the aqueous solution to form magnetic flocs with the ultrafine suspended solids in the wastewater, and then passes through a magnetic separator to achieve rapid precipitation and separation [3, 95–96]. The combination of magnetic flocculation and chemical precipitation can make up for the shortcomings of ultrafine suspended solids and low separation efficiency of chemical precipitation. Magnetic flocculation has been widely used to treat wastewater with high pollution concentration [71], high turbidity [96] and high chemical oxygen demand (COD) [97]. It is worth noting that in many studies, iron-bearing minerals have shown the characteristics of removing phosphorus from aqueous solutions [98–99]. The iron-bearing minerals can be coordinated with phosphate and therefore have the potential to be used as adsorption materials for phosphorus and starch in wastewater [100–101].

Figure 9.
(a) Flow diagram of the comprehensive treatment of the arsenic alkali residue and (b) arsenic removal from arsenic alkali solution with different HFG samples synthesized at pH 3(I), 7(II), and 11(III) [58].

Figure 10.
The chemical precipitation and magnetic flocculation of removed hydroxyapatite contaminants [103].
Du et al. [102–103] combined the magnetic flocculation technology with iron-containing materials to prepare porous magnetic seeds with core-shell structure, which achieved simultaneous removal of starch and phosphate in wastewater. As shown in Figure 10, the core-shell magnetic seeds prepared by sulfation roasting of fine magnetite particles have a porous $\alpha$-Fe$_2$O$_3$ structure on the surface, and the specific surface area is three times larger [103–106]. As shown in Figure 10, the phosphate and starch in the wastewater can be adsorbed on magnetic seeds surface, and then separated from the wastewater by magnetic separation. The phosphorus and starch content in the wastewater are reduced to 1.51 and 9.51 mg/L, respectively, and the removal rate reaches more than 75% [102].

5. Conclusion

The iron removal method of the hydrometallurgical leachate is still dominated by the goethite process. The goethite process faces the disadvantages of high loss rate of valuable metals and difficulty in separation and filtration, which must be solved to get qualitative improvement. Careful adjustment of the pH value can help reduce metal loss, and inducing crystallization can increase the crystallinity of goethite and improve the separation and filtration efficiency. However, both methods can only focus on solving one of the problems and cannot reduce loss and promote filtration at the same time. The magnetite produced during the precipitation (crystallization) process opened a new path for magnetic separation, while the magnetite method is currently limited to laboratory research. In the present paper, the authors combined the goethite precipitation (crystallization) method with magnetic seed separation technology and developed a novel route. Goethite precipitates on the surface of the external magnetic seeds to form core-shell structured particles, which are efficiently separated by magnetic separation, and at the same time solve the two major problems of the traditional goethite process. This new method also shows advantages in the fields of arsenic and chromium removal from the leachate, phosphorus, and starch removal from wastewater and other fields. Goethite is the most common and stable crystalline iron oxide in soil and sediment. We expect that the goethite method combined with magnetic seed separation technology will show better results in the removal of organic dyeing, heavy metal ions, anions in wastewater and soil, and the adsorption and passivation of chemicals, nutrients, and harmful compounds in environments.

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