Proceeding Paper

Reduction of Ferric Iron in Hydrometallurgical Solutions Using Zero-Valent Iron †

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Abstract: Most hydrometallurgical solutions usually contain high levels of ferric iron, which is often regarded as a major and problematic impurity. Precipitation of Fe(III) by raising the solution pH results in a voluminous amorphous residue that is particularly difficult to handle. Prior complete or partial reduction of Fe(III) to the divalent state facilitates the precipitation of crystalline iron oxides such as magnetite or goethite. The aim of this research was to investigate the effectiveness of zero-valent iron (ZVI) for the reduction of Fe(III) to Fe(II), which is a crucial pretreatment step for the efficient removal of iron. The effects of pH, reaction time and type of coexisting anions, i.e., sulphates or chlorides, were evaluated by conducting batch tests in an agitated reactor. It was found that using ZVI, Fe(III) is rapidly reduced to Fe(II), with higher reduction kinetics achieved in sulphate solutions at acidic pHs of 0.5–1.

Keywords: zero-valent iron; ferric iron reduction; reduction kinetics; iron separation; ZVI oxidation

1. Introduction

Hydrometallurgical treatment of ores and concentrates to dissolve the valuable metals is commonly carried out using sulphuric or hydrochloric acid solutions. However, this treatment results in the co-dissolution of iron minerals and the generation of high Fe(III) levels in the pregnant leaching solution (PLS) [1–3]. Iron is commonly removed from leaching liquors by adding a base (NaOH, CaCO₃), which increases the solution pH and causes the precipitation of iron in the form of amorphous hydroxides. This process generates a large quantity of a gelatinous solid which is difficult and costly to manage, and it usually also adsorbs the valuable metals coexisting in the PLS [4].

The reduction of Fe(III) to the divalent form can facilitate the precipitation of iron in the form of low-volume crystalline oxides, which can be easily separated from the aqueous phase and recovered in the form of potentially marketable products. This is the principle of the goethite process, which involves the reduction of iron to the ferrous state followed by an oxidation step under controlled conditions for the final precipitation of Fe in the form crystalline goethite [4,5]. Ferrous iron solutions can be also used as precursors for the precipitation of nano-magnetite, a high-added-value material with a wide variety of biomedical and technological applications [6].

The aim of this research was to investigate the effectiveness of zero-valent iron for the reduction of Fe(III) to the divalent state. Microscale zero-valent iron (ZVI) is an inexpensive, non-toxic and moderate reducing reagent which has been successfully used to remediate groundwater due to its negative reduction potential. ZVI donates electrons and is then oxidized in the presence of species with more positive reduction potentials. ZVI has mostly been applied for the treatment of polluted waters via the construction of a permeable reactive barrier (PRB) [7,8]. ZVI has been efficiently used for the removal of various pollutants such as Cr(VI) and Se(VI), through reductive and adsorptive processes [7–9].

In this study, ZVI was selected as a reducing agent for the reduction of ferric to ferrous iron, since it does not affect the solution chemistry or pH and therefore eliminates the need for the external addition of chemical reagents for pH control or solution purification. To the best of our knowledge, there has been no attempt until now to use granular elemental iron for ferric iron reduction. A few previous studies dealing with the reduction of ferric iron have used hydrogen [10], ascorbic acid [11] and sulphites [12]. The effects of pH and the type of iron source for ferric reduction using ZVI were evaluated by conducting batch tests.

2. Materials and Methods

Microscale elemental iron (H$_2$Omet 86) was supplied by Rio Tinto Metal Powders Ltd. H$_2$Omet 86 is a high-density fine granular zero-valent iron (ZVI), >99% Fe, with a bulk density equal to 3.28 g/cm^3 and a particle size of less than 250 μm. H$_2$Omet 86 was mainly designed for injection in field-scale remediation applications and as a filler for permeable reactive barriers.

The salts iron(III) sulphate hydrate (>97% Merck, Darmstadt, Germany) and ferric chloride hexahydrate of analytical grade (>99.0%, Merck, Germany) were used as sources of ferric iron solutions. The iron solutions were prepared by dissolving Fe$_2$(SO$_4$)$_3$·xH$_2$O and FeCl$_3$·6H$_2$O in deionized water (DW) to yield a 0.22 M concentration of Fe(III). The deionized water was previously boiled in order to remove the dissolved oxygen. In each experiment, 0.5 L of ferric iron solution with an initial concentration of 0.22 M was prepared, and the pH was adjusted to the desired value using either hydrochloric or sulphuric acid. Elemental iron was then added to the solution in an amount equivalent to 0.18 moles/L. Taking into consideration the stoichiometry of reduction (reaction 1), the added amount of ZVI corresponds to an excess of 64%.

The experiments were carried out in a glass reactor (1 L) which was purged with nitrogen gas during the reaction, and the suspension was stirred by a mixer at a speed of 500 rpm. The temperature of the reactor was kept constant at 25 °C. Aliquots of samples (5 mL) were withdrawn at various reaction times (t = 2, 5, 10, 20, 40 and 60 min) and analysed for Fe(II). Ferrous iron concentration was determined by redox titration using potassium permanganate. The Fe(III) concentration was calculated based on the stoichiometry of reaction (1).

$$2\,\text{Fe(III)} + \text{Fe(0)} \rightarrow 3\text{Fe(II)} \qquad (1)$$

3. Results and Discussion

The effects of pH and of the coexisting anions on the kinetics of ferric ion reduction by ZVI are shown in Figure 1. It can be seen that Fe(III) reduction is more rapid at lower pHs and in the presence of sulphate anions. At pH 0.5, 100% reduction of Fe(III) was achieved within 40 min in the presence of SO$_4$, whereas it reached 96% after 60 min in the presence of chlorides. At pH 1.0, the reduction of Fe(III) was equal to 99% and 92% after 60 min of reaction in the sulphate and chloride media, respectively. At pH 1.5, the corresponding reduction percentages were 84% and 73%.
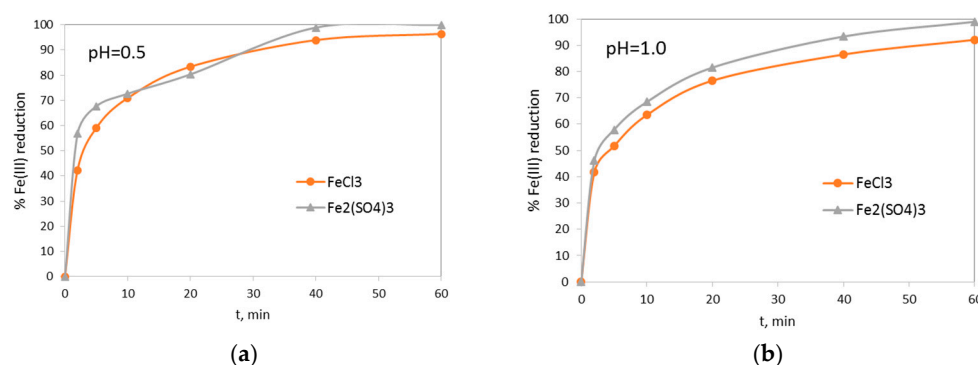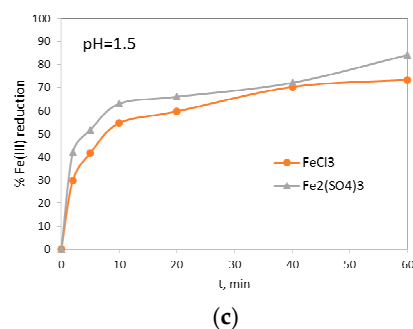

(a)

(b)

Figure 1. *Cont.*

(**c**)

Figure 1. Evolution of Fe(III) reduction with ZVI at (**a**) pH 0.5, (**b**) pH 1.0 and (**c**) pH 1.5 (initial concentrations: Fe(III) 0.22 M; ZVI 0.18 M).

During the reduction of Fe(III), the elemental iron is oxidized in the divalent state, as shown in reaction (1). The aqueous solution is thus enriched in ferrous iron at values exceeding the initial concentration of Fe(III). The evolution of the Fe(II) concentration in comparison with the initial Fe(III) content and the corresponding depletion of Fe(0) is shown in Figure 2 for the experiments carried out at pH 0.5.
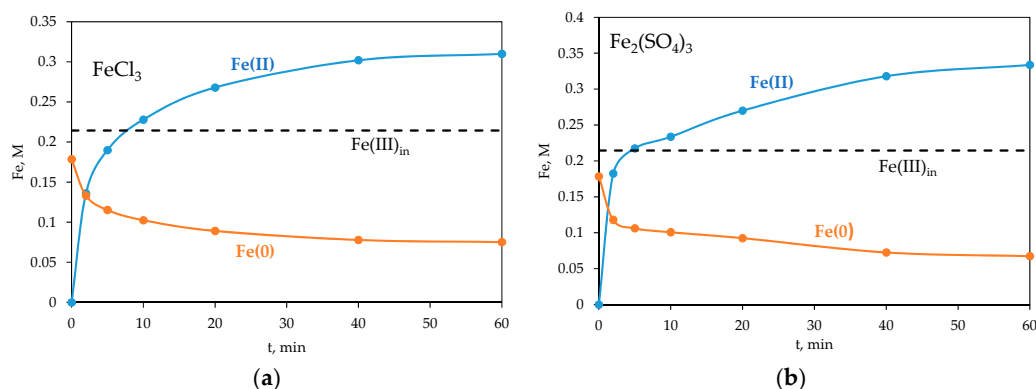
Figure 2. Evolution of Fe(II) concentration and depletion of Fe(0) in the experiments carried out at pH 0.5 for (**a**) $FeCl_3$ and (**b**) $Fe_2(SO_4)_3$ solutions.

4. Conclusions

Microscale zero-valent iron can be efficiently used as reducing agent for the rapid reduction of ferric to ferrous iron at acidic pHs, in order to proceed to the following precipitation steps for the final recovery of iron in the form of low-volume crystalline oxides with a possible market potential. The sulphate anions were found to favour the reduction kinetics in comparison with the chloride medium. Reduction was also found to be faster in the lower range of tested pHs.

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