



Chemical stability and extent of isomorphous substitution in ferrites precipitated under ambient temperatures

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ABSTRACT

The ferrite process is an established method for treating wastewaters containing dissolved toxic metals, using precipitation at temperatures above 65 °C. Various ambient-temperature operation methodologies have also been proposed, but the effects of temperature reduction on product stability, and on the extent of isomorphous substitution (in terms of x in $\text{Me}_x\text{Fe}_{3-x}\text{O}_4$, Me representing a non-iron metal), have not been adequately quantified. At ambient temperature precipitation, maximal x of Zn^{2+} , Co^{2+} , Ni^{2+} and Cd^{2+} was found in the current study to be approximately 0.73, 0.67, 0.39 and 0.17, respectively. These values are 73% to 50% of the corresponding values attained by precipitation at 90 °C. The chemical stability of the ferrites produced under ambient temperatures was found to deteriorate upon high Me^{2+} incorporation levels, in stark contrast with the trend observed in ferrites precipitated at 90 °C. Both observations were ascribed to the increased importance of Fe^{2+} – Fe^{3+} interaction under ambient conditions in driving spinel ordering. In the presence of high Me to Fe ratio in the initial solution, this interaction is weaker, resulting in impeded dehydration.

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1. Introduction

Ferrites ($\text{Me}_x\text{Fe}_{3-x}\text{O}_4$, Me represents a non-iron metal), also termed substituted or doped magnetites (magnetite = Fe_3O_4), are ceramic materials with a spinel structure. Because they are chemically stable under environmental conditions and easily precipitated from aqueous solutions at temperatures >65 °C, these materials have been frequently proposed to serve as a terminal sink for several toxic metal ions found in laboratory, industrial and mining wastewater streams [1–4]. This approach, commonly referred to as “the ferrite process” (FP), is advantageous over the metal hydroxide precipitation treatment as the product may be either safely discarded or even reused in a variety of applications [5]. Energy considerations have driven modification of the ferrite process to ambient temperature operation, under which, normally, amorphous phases predominate, probably because of much slower hydrolysis and dehydration rates of the precursor [6]. In order to minimize the formation of such phases in this so-called “ambient temperature ferrite process” (ATFP), seed addition [7–10], slow $\text{Fe}(\text{II})$ oxidation rates [11], prolonged aging times [6] and elevated pH levels [6] have been suggested. Nevertheless, high non-iron

metal to total iron concentration ratio (Me/Fe_T) in the inlet solution has been reported to promote non-spinel phases [9,10] and reduce Me incorporation efficiency [12], for reasons not fully understood. Furthermore, the incorporation capacity of most non-iron metal ions into the ferrite structure under these conditions, has not, to date, been adequately quantified. This property is imperative for assessing the external iron and base chemical demands. The effect of Me-for-Fe substitution on the chemical stability of the product seems also to be missing, although this property reflects the immobilization degree of the toxic metal, and may also shed light on the formation mechanism.

The present work proposes the incorporation limits of four divalent non-iron metal ions into the structure of ferrites precipitated at ambient temperature. The effect of metal incorporation on the relative chemical stability of these ferrites was deduced from their complete dissolution rates. The results are compared to corresponding characteristics of ferrites produced under 90 °C in order to assess the effect of temperature on the reaction. Mechanistic aspects and implications to process design are discussed.

2. Experimental

2.1. Procedures

2.1.1. Preparation of ferrites at 90 °C

In order to prepare high quality ferrites, the procedure used by Sidhu et al. [13] and Regazzoni et al. [14] was followed. 655 mL of

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deionized water (DW) were heated to $90 \pm 5^\circ\text{C}$ and simultaneously deoxygenated using N_2 gas. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and Me salt (metal sulfate salts, >98% purity) were added in amounts designated to attain x (as in $\text{Me}_x\text{Fe}_{3-x}\text{O}_4$) values between 0.0 and 1.0, and 196 mmol of total metals. A basic oxidizing solution (prepared by dissolving 52 g KOH, 7.65 g KNO_3 and 21 mg hydrazine sulfate in 281 mL DW) was added drop-wise for a period of 20 min. The solution was then aged for 1 h under the same conditions (or several hours if black precipitates had not been obtained after 1 h). The precipitates were washed twice after settling for 1 h using 5 L DW. A third wash with DW at pH 2.0 (“pH 2 solution”, adjusted with 98% H_2SO_4) was employed in order to remove any adsorbed or hydroxide metal species (approximately 97% removal, assuming the volume of precipitates was less than 0.3 L out of the 5 L pH 2 solution). The rinsing pH was selected based on preliminary experiments with cobalt and on reported adsorption behavior of some Me on various iron oxides [15–18]. A final volume of 1000 mL was established using DW, and pH was adjusted to 8.0–9.0 using 5 M NaOH solution. This final solution is referred to hereafter as the “ferrite sample”, and its solid phase “the particles” or “the product”.

2.1.2. Preparation of ferrites at ambient temperature – batch experiments

In order to precipitate ferrites at ambient temperatures under the most favorable known conditions, two seed-promoted methods were employed following Refs. [8] and [12]. These methods were termed in this paper StFP (stoichiometric ferrite process) and OxFP (oxidation ferrite process).

2.1.2.1. Laboratory setting. Ferrite synthesis by Fe(II) oxidation (OxFP) and from stoichiometric Fe(II)–Fe(III) solutions (StFP) were conducted in a batch manner in identical 2.5 L vessels with an open top. Except for Co–ferrites produced at an initial Me/Fe_T ratio of 0.2, both StFP and OxFP vessels were placed in the same water bath and stirred by one jar-test machine to attain equal temperature and mixing (~100 rpm) conditions. A 5 M NaOH solution was used for pH adjustment using a dosing pump (ProMinent, Gamma/4) and a pH controller (EUTECH pH 200 series).

2.1.2.2. Operational conditions. Influent solutions were prepared by the addition of metal sulfate salts (>97% purity) at required molar ratios. The initial magnetite seed was produced by the ambient temperature procedure [7], and the ferrite seed concentration was maintained during all experiments at approximately $20 \pm 2 \text{ g L}^{-1}$ as Fe. The mixed solution volume was 2 L. pH was maintained at 10.5 ± 0.1 , unless otherwise stated. The reactor solution was initially purged with N_2 to remove any dissolved oxygen. More than 40 cycles were employed in each batch experiment to ensure that the system reached steady state conditions (i.e., when practically all of the original ferrite particles had been replaced by new ones). Subsequently, samples were prepared for analyses according to the procedure described in the previous section

2.1.2.3. OxFP procedure. A mixed 2 mL sample was taken daily from the reaction vessel in order to establish the concentration of ferrous intermediate species (FI). This was done by immersing the sample in 100 mL acidified distilled water (pH 2.0) for 15 min, after which the Fe(II) concentration was determined. In each synthesis cycle, 400 mL divalent metal solution was then added to the vessel over a ~1 min period during which pH was manually corrected (5 N NaOH), in order to establish FI concentration of ca. $3000 \text{ mg Fe}^{2+} \text{ L}^{-1}$. Subsequently, $\text{N}_{2(\text{g})}$ purging was replaced by air, adjusted at an appropriate flow rate in order to reduce FI to ca. $1500 \text{ mg Fe}^{2+} \text{ L}^{-1}$ over a 2.5 h reaction period [10]. At the end of the reaction, an appropriate amount of mixed solution was removed to maintain the seed concentration constant. Subsequently, mixing

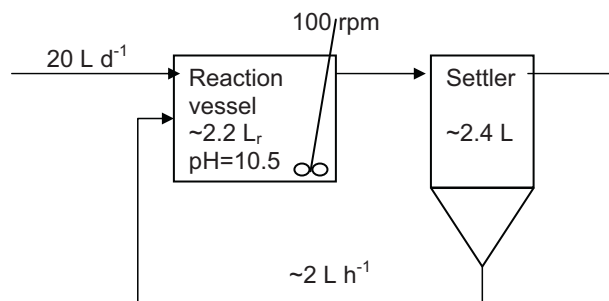


Fig. 1. Schematic diagram of a continuous system.

was stopped and the precipitates were left to age overnight. Before the next-cycle, an appropriate volume of supernatant (resembling the process effluents) was removed to allow for the addition of a new reagent solution

2.1.2.4. StFP procedure. 400 mL metal solutions were prepared using 40% FeCl_3 (around 200 g Fe L^{-1}) solution and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The ratio between the trivalent to (total) divalent metals concentration in the inlet solution in the Co–ferrite experiments was usually 1.7. However, this ratio was reduced when the precipitates started losing their visible ferrite characteristics (charcoal black color, settling and magnetic properties). For example, in the experiment with an initial Fe/Co of 3 this ratio was lowered to 1.5 by adding more Fe(II) and less Fe(III). In the Ni–ferrite experiments, the initial trivalent to divalent metals ratio was reduced to 1.25, corresponding to a Fe(III)/Fe(II) ratio of 2.0, and to ~1.125 (Fe(III)/Fe(II) = 1.74) during 20°C experiments, in order to establish only black precipitates. The required Fe(II) excess could not be explained by dissolution of atmospheric O_2 . Metal solutions were added over 2.5 h period using a dosing pump (ProMinent, Gamma/4) in order to maintain the lowest possible concentration of Fe(III) species in the system, while keeping the same reaction time that was applied in the OxFP. All other steps were as described for the OxFP procedure

2.1.3. Preparation of ferrites at ambient temperature – continuous experiments

Because of the large amount of operation cycles required in this work, a continuous system was built and operated in order to reduce the time required to attain steady state conditions. The continuous system set-up is depicted in Fig. 1. Operational parameters were similar to those applied in the StFP batch experiments. A relatively high recycle flow-rate was employed in order to prevent line clogging. This led to a very short retention time of the ferrite solids in the settler (only gravitational separation was employed). Excess solids were drawn out once a day from the settler. Before solids removal, the recycle flow rate was increased significantly for ~1 min, followed by 0.5 h settling period, in which the recycling pump was turned off. The removal of approximately 1 L of sludge from the settler following this procedure was usually sufficient to maintain a constant seed concentration in the reactor on day to day basis. The total metal ion concentration in the inflow was maintained at 24 mM. The resulting total metal flux (per reactor volume L_r) was thus $7\text{--}9 \text{ mg } L_r^{-1} \text{ min}^{-1}$, i.e. in the same range of that employed in the batch experiments. No major differences were observed regarding the quality of the product attained using the different operation modes.

2.2. Analyses

The chemical composition of the washed particles was determined by dissolving 4 mL of filtered ($0.7 \mu\text{m}$ fiberglass filter) rinsed ferrite sample in 10 mL 32% HCl solution. Metal concentrations

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