



# 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  $Me_xFe_{3-x}O_4$ , 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 ( $Me_xFe_{3-x}O_4$ , 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  $Fe(II)$  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  $\text{N}_2$  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  $\text{KNO}_3$  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%  $\text{H}_2\text{SO}_4$ ) 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<sub>T</sub> 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  $10.5 \pm 0.1$ , unless otherwise stated. The reactor solution was initially purged with  $\text{N}_2$  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

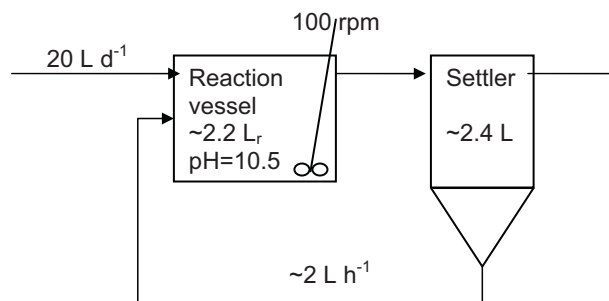


Fig. 1. Schematic diagram of a continuous system.

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%  $\text{FeCl}_3$  (around  $200 \text{ g Fe L}^{-1}$ ) 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  $20^\circ\text{C}$  experiments, in order to establish only black precipitates. The required Fe(II) excess could not be explained by dissolution of atmospheric  $\text{O}_2$ . 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

**Table 1**  
Maximal incorporation of four divalent metal ions into ferrites produced under ambient and elevated temperatures.

Metal	Max. $x^a$	Max. Me/Fe <sub>T</sub> <sup>b</sup>	Initial Me/Fe <sub>T</sub>	Process	React. T (°C)	React. pH	Max. x at elevated T [21]
Zn <sup>2+</sup>	0.73	0.32	0.33	StFP	30	10.5	1.0
Co <sup>2+</sup>	0.67	0.29	0.33	StFP	30	10.5	1.0
	0.66	0.28	0.33	OxFP	30	10.5	
Ni <sup>2+</sup>	0.39	0.15	0.2	StFP	30	10.5	0.78
	0.39	0.15	0.2	StFP	20	10.5	
Cd <sup>2+</sup>	0.17	0.06	0.07	StFP <sup>c</sup>	30	9.0	0.35

<sup>a</sup>  $x$  in Me<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub>.

<sup>b</sup> Me/Fe<sub>T</sub> ratio in the product, Fe<sub>T</sub> = total iron.

<sup>c</sup> Continuous system.

were determined by ICP (Optima 3000 DV, Perkin Elmer) and were used to calculate the value of  $x$  in the formula Me<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub>, under the assumption that the oxygen atoms are present according to this formula. Fe(II) was determined by the phenanthroline method, modified for possible ferric iron interference [19] using UV–vis spectroscopy at 510 nm (Milton Roy Spectronic 601, Ivyland). Fe(III) was measured using the sulphosalicylic acid method [20]. Ferrite samples were dried at 40 °C before analysis by X-ray diffraction (XRD, Siemens D500), using Cu K $\alpha$  radiation at 30 mA and 40 kV with step-scanning in the range of 10–70° 2 $\theta$  at a rate of 1° 2 $\theta$ /min (step width 0.05° 2 $\theta$  for 3 s). Exact peak positions were taken at half height after position correction using lead nitrate as internal standard. XRD spectra were established and evaluated using the Bruker EVA software. Dissolution tests were performed by adding 2 mL of ferrite sample to a 1 L of 12.8% HCl solution, stirred continuously at room temperature. 5 mL samples for dissolved metal analysis were extracted at different time intervals and filtered immediately by 0.22  $\mu$ m pore size filter. The iron release rate was determined in the initial linear stage of the dissolution process. Specific dissolution rates were obtained by further division by the solids concentration and by the specific surface area. Effective surface area of the particles was estimated by N<sub>2</sub> adsorption at 77 K after conditioning for 2 h at 150 °C (Flowsorb II 2300, Micromeritics). Solid concentration was determined from the weight of a filtered ferrite sample (with a predetermined volume), after 1 h of drying at 100 °C. Thermo-gravimetric analysis (TGA) tests were carried out with a TA Instruments module SDT 2960. TGA runs were recorded at a scan rate of 10 °C/min up to 500 °C. The sample compartment was flushed with dried, UHP argon.

### 3. Results and discussion

From an operational standpoint, seed-aided ferrite precipitation at room temperature was found in this work to be an efficient process, under both routes (i.e., OxFP and StFP), as long as the Me/Fe<sub>T</sub> ratio was not excessively high. The concentration of metal ions in the effluents was normally below 0.02 mg L<sup>-1</sup>, and in many cases below detection limits. Settling properties were excellent, with sludge volume index (SVI) values ranging from 4 to 8 mL g<sup>-1</sup> (typically around 4.0). Effective surface area of the particles was normally 8–45 m<sup>2</sup> g<sup>-1</sup>. The precipitates were characterized by charcoal black color and reacted strongly to a magnetic field.

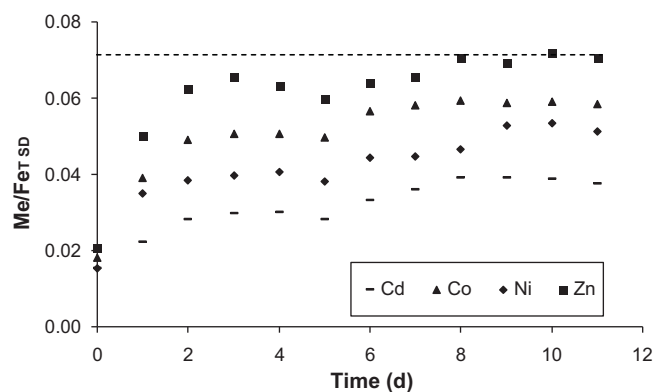
#### 3.1. The effect of reaction temperature on the incorporation extent of non-iron metals

In order to estimate the maximal incorporation level of four Me<sup>2+</sup> into the ferrite lattice under ambient temperature precipitation, an extensive set of experiments was performed using seed-aided precipitation by either the StFP or OxFP techniques, under both batch and continuous conditions. The highest incorporation values obtained in these experiments are presented in Table 1, which also includes, for comparison purposes, the

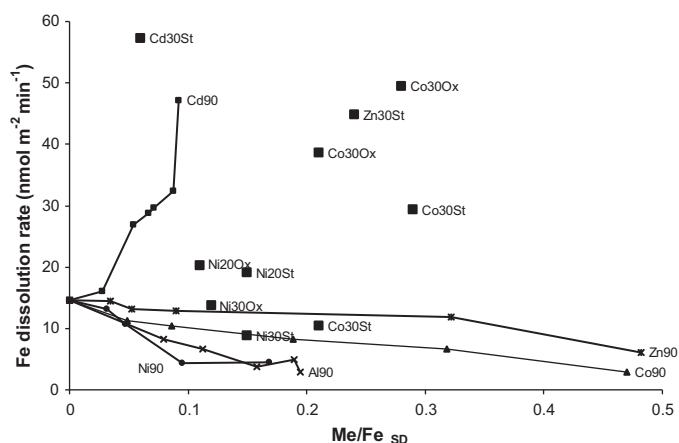
corresponding values obtained by oxidation-induced precipitation under elevated temperatures (80–100 °C) [21]. Because the XRD spectra of all the ferrites precipitated under ambient temperatures corresponded to a spinel structure only, and because each of the non-iron metals and Fe dissolved congruently in all of these samples, it was concluded that the products did not contain significant amounts of either crystalline or amorphous non-ferrite phases [21]. It should be noted that when magnetic, settling and/or color properties started to deteriorate or when the Me/Fe<sub>T</sub> ratio in the product (Me/Fe<sub>T,SD</sub>) was much lower compared to the Me/Fe<sub>T</sub> ratio in the inlet solution, attempts to attain higher incorporation levels were discontinued. Therefore, the maximal incorporation levels presented in Table 1 may reflect a certain (small) underestimation.

Table 1 shows that the maximal incorporation levels attained by applying the ambient temperature precipitation methods were between 50% and 73% of the respective values attained in the elevated temperature synthesis methods. The results presented in Table 1 refer to experiments in which each toxic metal was incorporated alone (i.e., in the presence of iron ions only). To assess these results, an experiment was carried out in the presence of all four metal ions at equal initial concentrations. The ratio between each of the metal ions to the total iron concentration in the inlet solution was 0.071. The resulting Me/Fe<sub>T</sub> ratios in the solid ferrite product (Me/Fe<sub>T,SD</sub>) are presented in Fig. 2, as a function of time. Note that the initial ferrite seed in this particular experiment was formed from an initial solution, which contained equal but lower concentrations of the same four metal ions.

Fig. 2 shows that the ease-of-incorporation order of the metal ions conformed to the order obtained in the single metal ion experiments (Table 1), i.e. the incorporation ease followed the order Zn > Co > Ni > Cd. This order also agrees with the sequence reported for ferrites precipitated under elevated temperature [21]. The latter observation suggests that the fundamental processes responsible for metal ions incorporation under both elevated and ambient



**Fig. 2.** Me/Fe<sub>T,SD</sub> ratios in ferrite crystals produced at 30 °C from a solution containing Cd<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup> at equal concentrations using the StFP in a continuous fashion. The dashed line indicates the theoretical maximal ratio between each Me and total iron in the solids (i.e., the ratio in the inlet solution).



**Fig. 3.** Iron dissolution rates (at 12.8% HCl,  $23 \pm 2^\circ\text{C}$ ) of ferrites produced by different methods as a function of the metal content in the solid product. The number following each metal refers to synthesis temperature. St and Ox stand for StFP and OxFP, respectively. Only data points related to ferrites produced at  $90^\circ\text{C}$  are connected by a solid line.

temperature ferrite syntheses are at least related and even more probably, analogous.

### 3.2. The effect of reaction temperature and metal substitution on the chemical stability of the ferrites

The chemical stability of the final ferrite product reflects the immobilization degree of the toxic metals and may have major implications on the ultimate application of the product. The chemical stability is also interesting from a mechanistic standpoint, as this parameter can be affected by Me-for-Fe substitution and by insufficient dehydration. Because of the relatively high stability of the ferrite structure (compared to metal (oxy)-hydroxides), standard leaching procedures such as the “toxicity characteristic leaching test” (TCLP), are not suitable as they can only provide indication to the stability of the ferrite’s surface [10]. Instead, the chemical stability of the ferrites was ascribed in the current work to the inverse of the iron release rate from the product during its complete dissolution (12.8% HCl stirred solution at room temperature). It is noted that although this method provides indication to the relative stability of the different ferrites, it is not intended to replace a more fine-tuned analysis, which nature depends on the environment in which the product is ultimately placed.

Specific iron dissolution rates (normalized for the specific surface area and solid concentration) of various ferrites precipitated under  $90^\circ\text{C}$  and ambient temperatures ( $20$  or  $30^\circ\text{C}$ ) are depicted in Fig. 3. It is noted that fewer ferrite samples were produced under ambient temperature, because of the much longer time (on the order of months) required in these procedures for attaining steady state with respect to the solid product. Fig. 3 shows that except for Cd-ferrites, the dissolution rate of ferrites produced at  $90^\circ\text{C}$  was reduced with increased Me-for-Fe substitution ratios. It can thus be concluded that the incorporation of Co, Ni, Zn, and Al acted to stabilize the ferrite structure formed in the  $90^\circ\text{C}$  procedure, while incorporation of Cd into the ferrite lattice had the opposite effect. The observed effect of these different metals on the dissolution rate is in good agreement with similar experiments conducted with Zn, Cu, Co and Ni substituted magnetites prepared by calcination or sintering processes at  $1200$ – $1300^\circ\text{C}$  [22,23].

The effect of the metal type on the dissolution rate was suggested to be a function of either the Me–O bond strength [16], free energy of formation [23], or the rate of  $\text{H}_2\text{O}$  loss from the inner hydration sphere of the cation ( $k_{-w}$ ) [23,24]. According to Fig. 3, and considering the fact that all cations dissolved congruently with iron,

it may be concluded that Al and Ni have the largest stabilization effect on the ferrite structure, followed by Co and Zn. This behavior is in agreement with the  $k_{-w}$  trend of these metals ( $7 \times 10^7$ ,  $2 \times 10^6$ ,  $3 \times 10^4$  and  $1 \text{ s}^{-1}$  for  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Al}^{3+}$ , respectively [21]), suggesting this parameter is indeed related to stabilization. The effect of corresponding lattice energies, calculated according to established procedures [25] cannot however be ruled out. The adverse effect of Cd on the ferrite’s stability observed in the current work can be logically ascribed to its relatively large ionic radius relative to that of iron, which may promote structural strain [21].

Fig. 3 also reveals that the dissolution rates of ferrites produced under ambient temperatures are of the same order of magnitude as those obtained for ferrites precipitated under  $90^\circ\text{C}$ . However, while the dissolution rates of the latter decrease with increased Me content, the opposite trend seems to characterize the ferrites which were produced under ambient temperatures.

The reduced stability observed in ferrites produced under ambient temperatures upon increased Me content cannot be associated with Me incorporation (with the exception of Cd), because of the opposite trend observed in the ferrites produced at  $90^\circ\text{C}$ .

Because dehydration is known to be a crucial step in ferrite formation and its rate to depend reversibly on the precipitation temperature [6], it was hypothesized that the reduced stability in some of the ambient-temperature-produced ferrites resulted from retention of  $\text{H}_2\text{O}$  molecules in their structure. This postulation was strongly corroborated by a thermo-gravimetric analysis of ferrite samples (containing similar and high amounts of cobalt), produced under different temperatures and via different analysis methods. The results, illustrated in Fig. 4, show a very small weight loss upon heating a ferrite sample produced at  $90^\circ\text{C}$  from room temperature to  $\sim 200^\circ\text{C}$ , with no further weight loss upon additional heating. This weight loss can be ascribed mostly to evaporation of sorbed water. However, a much larger and lingering weight loss was observed in ferrite samples produced at  $30^\circ\text{C}$  upon heating to  $400^\circ\text{C}$  and higher temperatures. This weight loss has to be associated with the evaporation of water trapped in the crystalline structure. The higher water content observed in the StFP sample as compared to the OxFP sample probably stems from a non-optimized Fe(II)/Fe(III) ratio in the inlet solution (Section 2.1.2). The fact that the specific iron dissolution rate of the StFP sample was actually lower compared to the corresponding OxFP sample (“Co30St” and “Co30Ox” in Fig. 3) was ascribed to the higher specific surface area of the former ( $79$  vs.  $45 \text{ m}^2 \text{ g}^{-1}$  in the StFP and OxFP samples, respectively). When correction for specific surface area was omitted, the iron dissolution rate of that StFP sample was in fact slightly higher than that of the OxFP sample.

The results presented in Figs. 3 and 4 imply that the combined effects of a high initial Me/Fe<sub>T</sub> ratio and low precipitation temperature leads to high water retention within the solid structure, which apparently reduces the chemical stability of the formed ferrite.

### 3.3. Interpretation of the results

A probable explanation to all of the observations discussed above is as follows: It is generally accepted that ferrites precipitate under elevated temperatures ( $80$ – $100^\circ\text{C}$ ) mainly through a dissolution and recrystallization mechanism [21,26,27]. However, according to Jolivet et al. [28,29], magnetite nano-particles produced by addition of ferrous/ferric mixtures into solution maintained at a basic pH and  $25^\circ\text{C}$ , are formed by transformation of an unstable  $\text{Fe}^{2+}$ -ferrihydrite precursor ( $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$ ) in two competing pathways: (i) solid state reactions followed by dehydration and spinel ordering, and (ii) dissolution of  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  from the surface, followed by spinel crystallization. These authors suggested that the high electron mobility between  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in the precursor drives local spinel ordering in the fine particle

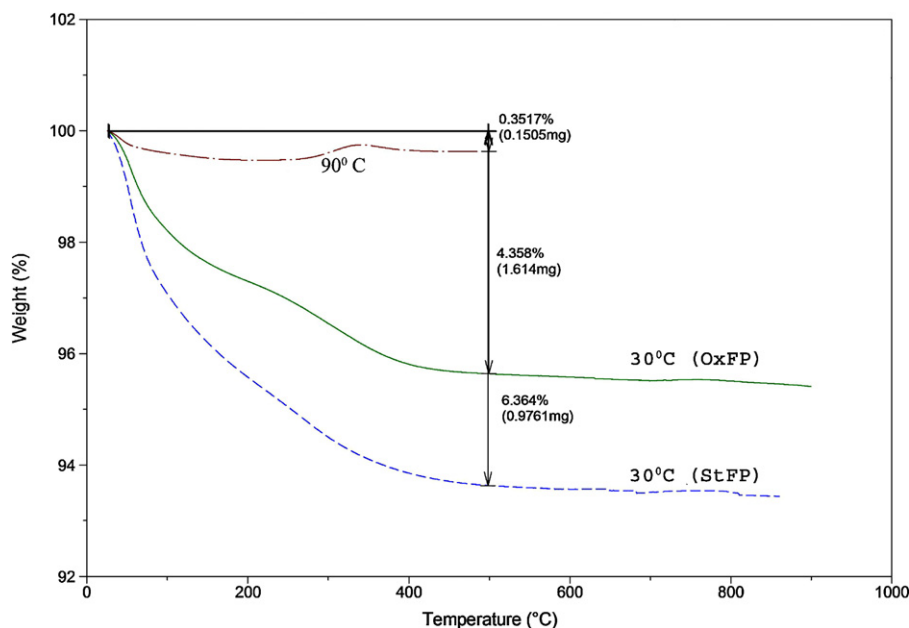


Fig. 4. TGA of Co-ferrites produced under 90 °C ( $x=0.74$ ), and 30 °C ( $x=0.67$ ).

in process (i) which extends to the growing particle by process (ii). Thus, it seems that lowering the precipitation temperature, increases the importance of process (i). Because electron mobility between  $\text{Me}^{2+}$  and  $\text{Fe}^{3+}$  is considered negligible [28], under ambient temperatures and high  $\text{Me}^{2+}$  content in the initial solution (i.e., a high  $\text{Me}/\text{Fe}_T$ ), electron mobility in the precursor is reduced, impeding spinel ordering by process (i), which results in an interference with the overall ferrite crystallization process. This sequence could lead to a dehydration difficulty, as occurs normally when magnetite precipitation temperature is decreased [6], circumventing the special conditions employed in the AFTP. This hypothesis explains well the observed retention of water molecules in the crystalline structure, which was associated in this study with the reduced chemical stability with respect to ferrites obtained at 90 °C. It also explains the promotion of amorphous phases under ambient temperature precipitation reported elsewhere (Section 1). Additionally, according to the proposed hypothesis, under high initial  $\text{Me}^{2+}/\text{Fe}_T$  ratio and low temperature, a certain Fe(II) excess (and Fe(III) shortage) in the initial solution should improve ferrite crystallization to some extent, as observed experimentally in the current study. However, as the  $\text{Fe}^{2+}-\text{Fe}^{3+}$  interaction (process (i)) becomes limiting, it is also expected that iron incorporation will be preferred, leading to an overall reduced  $\text{Me}^{2+}$  incorporation level, compared to levels attained under elevated temperature precipitation techniques (Section 3.1). It is noted, that because the dissolution-recrystallization process under ambient temperature synthesis (i.e., process (ii)) is not impeded by an increase in the initial  $\text{Me}^{2+}/\text{Fe}_T$ , higher incorporation levels than those reported in the current work are possible, though a much higher amount of non-spinel phases are expected.

#### 4. Conclusions

The results of the current work reveal that seed-aided ferrite precipitation performed under ambient temperature is a promising method for treating wastewaters containing toxic metals. However, the process is hindered at high  $\text{Me}/\text{Fe}$  ratios because of a reduced dehydration rate. Counter-intuitively, it was evident that increasing the Fe(II)/Fe(III) ratio in the initial solution improved ferrite precipitation to a certain degree. Nonetheless, a significant

incentive to employ the FP at elevated temperatures exists, as both the Me-for-Fe substitution degree and the chemical stability of the product can be significantly higher than those obtained under ambient temperature precipitation, irrespective of the synthesis process applied (i.e., StFP or OxFP). The cost of energy for heating should thus be weighed against the costs of additional iron and base required in the ambient temperature process. Alternatively, heating costs may be significantly reduced by employing an ambient temperature contact-reactor stage, as suggested by Morgan et al. [9] in order to concentrate the dissolved metals into a small water volume, which can then be more economically heated.

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#### References

- [1] J. Yang, J. Peng, K.C. Liu, R. Guo, D.L. Xu, J.P. Jia, Synthesis of ferrites obtained from heavy metal solutions using wet method, *J. Hazard. Mater.* 143 (2007) 379–385.
- [2] Y. Tamaura, T. Katsura, S. Rojarayanont, T. Yoshida, H. Abe, Ferrite process – heavy-metal ions treatment system, *Water Sci. Technol.* 23 (1991) 1893–1900.
- [3] M. Erdem, F. Tumen, Chromium removal from aqueous solution by ferrite process, *J. Hazard. Mater.* 109 (2004) 71–77.
- [4] E. Barrado, F. Prieto, J. Medina, F.A. Lopez, Characterisation of solid residues obtained on removal of Cr from waste water, *J. Alloys Compd.* 335 (2002) 203–209.
- [5] K. Yang, M. Misra, R.K. Mehta, in: G. Warren (Ed.), Ambient temperature treatment of Noranda tailing and Berkeley pit acid mine water by modified ferrite coprecipitation and magnetic separation, EPD Congress, San Francisco, CA, TMS, Warrendale, PA, 1994, pp. 363–373.
- [6] J. Wang, T. Deng, Y.J. Dai, Study on the processes and mechanism of the formation of  $\text{Fe}_3\text{O}_4$  at low temperature, *J. Alloys Compd.* 390 (2005) 127–132.
- [7] O. Lahav, B.E. Morgan, G. Hearne, R.E. Loewenthal, One-step ambient temperature ferrite process for treatment of acid mine drainage waters, *J. Environ. Eng. – ASCE* 129 (2003) 155–161.
- [8] B.E. Morgan, O. Lahav, G.R. Hearne, R.E. Loewenthal, A seeded ambient temperature ferrite process for treatment of AMD waters: Magnetite formation in the presence and absence of calcium ions under steady state operation, *Water SA* 29 (2003) 117–124.
- [9] B.E. Morgan, O. Lahav, R.E. Loewenthal, Advances in seeded ambient temperature ferrite formation for treatment of acid mine drainage, *Environ. Sci. Technol.* 39 (2005) 7678–7683.

- [10] L. Petrick, Y. Dubowski, S. Klas, O. Lahav, Stable incorporation of  $\text{Co}^{2+}$  into ferrite structure at ambient temperature: effect of operational parameters, *Water Air Soil Pollut.* 190 (2008) 245–257.
- [11] O.P. Perez, Y. Umetsu, H. Sasaki, Precipitation and densification of magnetic iron compounds from aqueous solutions at room temperature, *Hydrometallurgy* 50 (1998) 223–242.
- [12] W. McKinnon, J.W. Choung, Z. Xu, J.A. Finch, Magnetic seed in ambient temperature ferrite process applied to acid mine drainage treatment, *Environ. Sci. Technol.* 34 (2000) 2576–2581.
- [13] P.S. Sidhu, R.J. Gilkes, A.M. Posner, Synthesis, Some properties of Co, Ni, Zn, Cu, Mn and Cd substituted magnetites, *J. Inorg. Nucl. Chem.* 40 (1978) 429–435.
- [14] A.E. Regazzoni, G.A. Urrutia, M.A. Blesa, A.J.G. Maroto, Some observations on the composition and morphology of synthetic magnetites obtained by different routes, *J. Inorg. Nucl. Chem.* 43 (1981) 1489–1493.
- [15] K. Ito, Y. Tamaura, T. Katsura, Cadmium(II)-bearing, magnesium(II)-bearing and zinc(II)-bearing ferrites formed from Gamma-FeOOH at various reaction pHs, *Bull. Chem. Soc. Jpn.* 57 (1984) 2820–2823.
- [16] R.M. Cornell, U. Schwertmann, *The Iron Oxides* 2nd, completely rev. and extended Ed., Wiley-VCH, Weinheim, 2003.
- [17] S. Music, M. Ristic, Adsorption of trace-elements or radionuclides on hydrous iron-oxides, *J. Radioanal. Nucl. Chem.* 120 (1988) 289–304.
- [18] H. Katsumata, S. Kaneko, K. Inomata, K. Itoh, K. Funasaka, K. Masuyama, T. Suzuki, K. Ohta, Removal of heavy metals in rinsing wastewater from plating factory by adsorption with economical viable materials, *J. Environ. Manage.* 69 (2003) 187–191.
- [19] L. Herrera, P. Ruiz, J.C. Aguillon, A. Fehrmann, A new spectrophotometric method for the determination of ferrous iron in the presence of ferric iron, *J. Chem. Technol. Biotechnol.* 44 (1989) 171–181.
- [20] Y.A. Zoltov, *Fundamentals of Analytical Chemistry. Practical Guide*, Visshaya Shkola, Moscow, 2001, p. 461.
- [21] S. Klas, Y. Dubowski, G. Pritosiwi, J. Gerth, W. Calmano, O. Lahav, Extent and mechanism of metal ion incorporation into precipitated ferrites, *J. Colloid Interface Sci.* 358 (2011) 129–135.
- [22] Z.Y. Lu, D.M. Muir, Dissolution of metal ferrites and iron-oxides by HCl under oxidizing and reducing conditions, *Hydrometallurgy* 21 (1988) 9–21.
- [23] T. Kishi, T. Miki, T. Nagai, Anodic behavior of cobalt ferrous ferrites in acid-solutions, *Surf. Technol.* 20 (1983) 279–286.
- [24] T. Kishi, T. Nagai, Cathodic dissolution of nickel ferrous ferrites in acid-solutions, *Surf. Technol.* 19 (1983) 9–15.
- [25] G. Ottonello, Energetics of multiple oxides with spinel structure, *Phys. Chem. Min.* 13 (1986) 79–90.
- [26] R.M. Cornell, R. Giovanoli, Effect of cobalt on the formation of crystalline iron-oxides from ferrihydrite in alkaline media, *Clays Clay Miner.* 37 (1989) 65–70.
- [27] R. Giovanoli, R.M. Cornell, Crystallization of metal substituted ferrihydrites, *J. Plant Nutr. Soil Sci.* 155 (1992) 455–460.
- [28] J.P. Jolivet, E. Tronc, C. Chaneac, Synthesis of iron oxide-based magnetic nanomaterials and composites, *C. R. Chim* 5 (2002) 659–664.
- [29] J.P. Jolivet, E. Tronc, C. Chaneac, Iron oxides: from molecular clusters to solid. A nice example of chemical versatility, *C. R. Geosci.* 338 (2006) 488–497.