

Precipitation of Heavy-Metal Ions from Aqueous Solutions as Spines-Type Compounds(Ferrites) at Ambient Temperature(**重金属イオンのスピネル型化合物(フェライト)としての常温における水溶液からの析出**)

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論 文 内 容 要 旨

Chapter 1. Introduction.

In the aqueous processing field the generation of a precipitate involves different critical factors. This figure includes a high efficiency of ions removal, a quick solid-liquid separation and a suitable stability of generated sludges to be disposed without any damage to influenced ecosystems. Under these premises, this work was undertaken with the aim of the precipitation of heavy metal ions as magnetic and stable spinel-type compounds at ambient temperature.

Ordinarily, to produce a metal-bearing ferrite from aqueous solutions it is necessary the heating-up of the hydroxides suspension at temperatures above 90 °C. Evidently, those high temperatures will limit the applicability of this alternative to treat large volumes of polluted industrial effluents. In this regard, the main feature of our proposal is the generation of those magnetic oxides but at a temperature as low as 25 °C and even without further heating. What makes it possible is the partial aerial oxidation of ferrous iron under well controlled oxidizing conditions and a simultaneous control of the pH. In turn, the attractiveness of our proposal is increased by the potential utilization of those magnetic-quality materials.

Chapter 2. The feasibility to produce the iron ferrite in an open-to atmosphere operation at room temperature.

As a first step, the feasibility to generate magnetite by neutralization and controlled aerial oxidation of ferrous solutions at room temperature was investigated. The standard precipitation and oxidation procedure consisted in the simultaneous neutralization and aeration of the solutions under a constant mechanical stirring. Air was injected into the reaction vessel during the adjustment of pH up to the set value ("conditioning stage") as well as during the subsequent "contacting stage" at constant pH. Our results suggest a close relation between precipitation pH and the kinetic of conversion of

intermediate green rust-II into γ -FeOOH and/or Fe_3O_4 . A precipitation pH among 10 and 11 and a moderate aeration of solutions promoted the stability of magnetite rapidly generated at ambient temperature.

Chapter 3. The magnetite forming-reaction at low temperatures.

This chapter includes the study of the stability conditions for the generation of magnetite by aerial oxidation of ferrous sulfate solutions. The progress of the magnetite-forming reaction was followed by monitoring the oxidation-reduction potential (ORP) at constant pH and the rate of proton releasing associated with the oxidation of ferrous entities. The concentration of ferrous iron in starting solutions was 0.012 M for all tests including the subsequent Fe-M (M= Zn, Cd, Cu) systems.

Under our experimental conditions only a moderate oxidation rate of ferrous entities, represented by a rate of proton releasing of 0.08 mmoles/min and an ORP of -120 mV established at pH 11.0, was favorable for the conversion of intermediate green rust-II into magnetite at 25 °C. Fast oxidation, promoted by extremely high air flow-rates and vigorous stirring deteriorated or even destroyed incipient ferrite frameworks.

When the formation of magnetite was still incipient, the aging of the sludges in contact with their mother liquor (24 hours at 25 °C, without stirring) would promote the further oxidation of Fe(II) entities in the intermediate and its final conversion (de-hydration), into crystalline magnetite. Furthermore, the promoting effects of stirring on oxidation rates and the associated Activation Energy of 4.9 Kcal/mol (in the temperature range between 10 and 40 °C) suggested that a mass-transfer step, attributed to the oxygen transference into aqueous phase, controlled the oxidation of ferrous entities at low temperatures.

Chapter 4. The Zn-bearing ferrite forming-reaction at 25 °C.

The generation of a Zn-bearing ferrite from aqueous solutions was investigated. It was found that well controlled oxidizing conditions permitted the generation of this ferrite at pH 11.0 and 25 °C, even without aging. Moreover, Fe and Zn ions contained in starting solutions were completely precipitated.

As seen in Figure 1, the ORP value established during the contacting stage was found to be dependent on the Fe/Zn mole ratio, "r". When "r" was 5, 7 or 10, a common ORP value of -150 mV was established. Under those conditions only black and magnetic sludges of a Zn-bearing ferrite, evidenced by the XRD patterns of Figure 2, were produced. Moreover, the higher the Zn/Fe mole ratio, the stronger the magnetic response of the precipitates. This trend was attributed to the further oxidation of ferrous entities and the progress of the de-hydration reaction in the intermediate compound.

The beginning of the liberation of protons associated with the progress of the oxidation reaction was retarded when higher proportions of Zn, i.e., lower Fe/Zn mole ratios, were contained in the intermediate compounds.

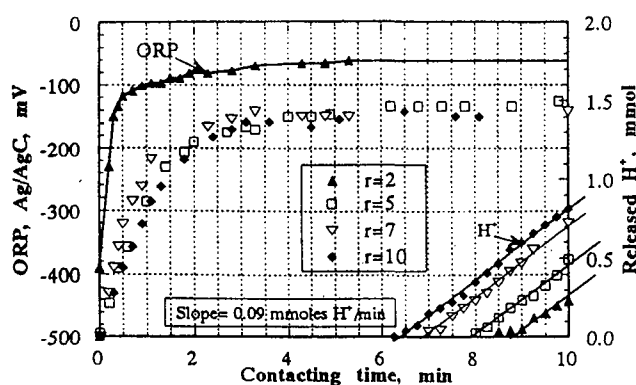


Fig. 1 Variation in ORP and amount of released protons with contacting time for different Fe/Zn mole ratios, "r". Air flow-rate 0.1 l/min; 500 rpm; pH 11.0; 25 °C.

Thus, it seems that Zn ions may inhibit the oxidation of ferrous entities during the contacting stage. However, the rate of protons releasing (0.09 mmol/min) was constant, irrespective of the selected Fe/Zn mole ratio. Based on the EPMA analysis, the more compact appearance and stronger magnetic response of the precipitates obtained at $r=10$ would be attributed to the satisfactory elimination of sulfur, as H_2SO_4 , from the precipitates and the inherent de-hydration of the intermediate. On the other hand, an excessively long contacting period promoted the increase in ORP and the overoxidation of ferrous entities. Poorly crystalline, voluminous and weakly magnetic precipitates were generated under that condition.

The degree of crystallinity of the Zn-bearing ferrites was enhanced by aging of the sludges in contact with their mother liquors at 25 °C.

Chapter 5. The Cd-bearing ferrite forming-reaction at 25 °C.

The effect of the Fe/Cd mole ratio on the feasibility to produce a magnetic Cd-bearing precipitate was investigated. The results could be grouped according to the ORP established in the contacting stage and the magnetic nature of the precipitates. The first group, that includes tests at molar ratios 2, 5 and 10 was characterized by a common ORP value of -40 mV and the precipitation of non-magnetic poorly crystalline solids. In turn, an ORP of -110 mV was established when magnetic precipitates were generated at molar ratios between 20 and 40. The enhancement in the rate of protons releasing observed at higher Cd proportions, i.e., lower Fe/Cd mole ratios, may be caused by some structural distortion in the framework of the host iron precipitates because of the incorporation of Cd ions. This structural effect would also explain the requirements of high Fe/Cd mole ratios (above 10) to generate the corresponding ferrites at 25 °C. The formation of the magnetic Cd-bearing ferrites took place with the elimination of Fe and Cd ions (terminal concentrations < 0.001 mg/l).

The levels of sulfur, as sulfate ions, in the intermediates could be decreased by prolonging the contacting stage or by aging of the sludges. In both cases, the suitable oxidation of ferrous entities and the progress of the de-hydration reactions would have been promoted. Furthermore, the degree of crystallinity of the Cd-bearing ferrite was also enhanced by aging.

Chapter 6. The Cu-bearing ferrite forming-reaction at 25 °C.

The generation of a Cu-bearing ferrite resulted a viable process at 25 °C. An intermediate precipitate consisting of Cu(I) and Fe(III) entities, formed by the partial oxidation of Fe(II) by Cu(II) ions preceded the formation of the Cu-bearing ferrite.

Under our experimental conditions, an air flow-rate of 0.10 l/min permitted a moderate oxidation rate and the establishment of an ORP value of -140 mV at pH 11.0. Those parameters favored the suitable oxidation of ferrous entities and the de-hydration conducive to the Cu-ferrite structures. The formation of the ferrite-type compounds also permitted the complete removal of Fe

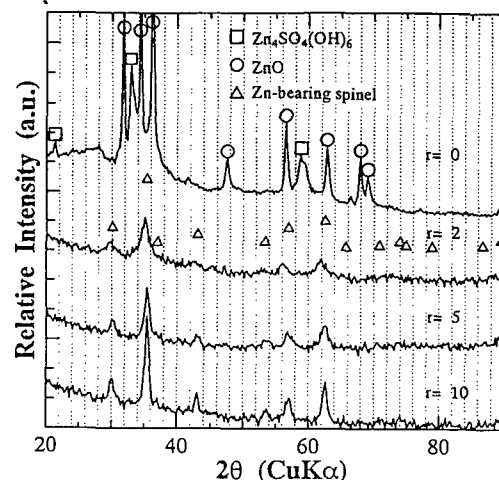


Fig. 2 X-ray diffraction patterns of non-aged Zn-bearing iron precipitates produced at different Fe/Zn mole ratios, "r". Ferrous ions were not contained in the starting solution of the test at $r=0$.

and Cu ions from starting solutions. The levels of sulfate ions incorporated in the Cu-bearing intermediates can be controlled by a suitable duration of the contacting period or by aging of the sludges at 25 °C. In all cases, sulfate ions would be released as H₂SO₄. Moreover, the degree of crystallinity of the sludges was enhanced by decreasing the sulfate contents in the precipitates.

A larger proportion of Cu(II) ions in starting solutions or an excessive aeration of the intermediates will destroy the spinel-type frameworks because of the overoxidation of ferrous iron. Poorly crystalline and voluminous sludges were produced under those extreme conditions.

Chapter 7. Characterization of metal-bearing ferrite powders produced at 25 °C.

The magnetic quality of the ferrite powders, the nature of the water and sulfate contents and the structural arrangement of Zn atoms in the ferrite structure were investigated.

It was found that the larger the Fe/M mole ratios, the higher the saturation magnetization, *M_s*, of the precipitates. A similar trend in *M_s* was obtained by prolonging the contacting stage; however, extremely long contacting times were deleterious for the magnetic quality of the solids. Furthermore, the magnetic quality of the solids was also promoted by aging. The growth of incipient ferrite particles and the progress of the oxidation and de-hydration reactions during aging were related to the enhancement in the saturation magnetization values. The ferrite powders produced at 25 °C exhibited *M_s* values as high as 83 emu/g.

The infrared (IR) analysis demonstrated the incorporation of molecular water and sulfate ions in the Zn-bearing iron precipitates. The IR spectra, complemented by the thermogravimetric analysis (TG) of the ferrite powders indicated that the de-hydration of the solids can be promoted by: (i) increasing the Fe/Zn mole ratios; (ii) a suitable duration of the contacting stage or (iii) by aging. These conditions also favored the diminution of the sulfate contents in the produced solids.

The incorporation of Zn ions into the structure of the magnetic precipitates has been demonstrated by EXAFS. The analysis of the local structural arrangement indicated that Zn ions were fully incorporated into a ferrite structure and occupied its most stable position (A-site).

Chapter 8. General Conclusions.

The formation of magnetite and other metal-bearing ferrites resulted in a viable process at a temperature as low as 25 °C. At pH 11.0, an air flow-rate of 0.10 l/min and a constant mechanical stirring at 500 rpm permitted a moderate oxidation rate and a mildly oxidizing environment represented by ORP values among -110 and -150 mV. These conditions favored the conversion of the metal-bearing intermediates into the corresponding ferrites. The formation of the ferrites took place simultaneously with the elimination of the heavy-metal ions from starting solutions.

Higher Fe/M mole ratios in the precipitates or a suitable length of the contacting stage permitted higher saturation magnetization values, *M_s* (>60 emu/g). The magnetic quality of the ferrites was also enhanced by aging. According to the FT-IR analyses of the ferrite powders, the loss of molecular water and the decrease in the SO₄²⁻ contents of the precipitates (related to the de-hydration and ferrous iron oxidation in the precipitates, respectively) would be promoted by increasing the Fe/Zn mole ratio, a suitable duration of the contacting stage or by aging of the sludges at 25 °C. The analysis of the local structure by EXAFS suggested Zn atoms were fully incorporated in the ferrite lattice occupying their most stable position, i.e., the A-sites.

The mentioned features enable this "Low-Temperature Ferrite Process" to be considered a promising alternative not only for the treatment of large volumes of polluted effluents but also as a potential route to produce re-usable magnetic-type materials.

審査結果の要旨

重金属イオンを低濃度で含む排水の高度な浄化技術の開発は、環境汚染防止の緊急課題の一つである。廃水処理における現行のフェライトプロセスは通常60℃以上の温度で操業されている。本研究では、常温で硫酸第1鉄および亜鉛、カドミウム、銅などの重金属イオンを含む水溶液のpH調整と空気吹き込みを同時に行うことによって、重金属を含むスピネル型化合物（フェライト）粒子を作製する方法を提案したうえ、その生成過程、固相の特性等を明らかにした。本論文は、この研究成果についてまとめたもので、全編8章からなる。

第1章は緒言であり、本研究の背景、研究の目的を述べている。

第2章では、硫酸第1鉄溶液について、pH調整および適度な速さの空気酸化を行わせ、25℃においてもマグネタイトが生成することを示した。これは、極めて重要な知見である。

第3章では、0.01mol/L程度の硫酸第1鉄溶液について、溶液中の残留鉄イオン濃度、酸化還元電位および水素イオン生成量の変化の測定結果と沈殿のX線回折の結果を総合して沈殿生成・酸化過程で起こる反応について考察した。また、25℃、24時間の熟成がフェライトの結晶化を著しく進めることを見出した。これは実用化を考える上で非常に有用である。

第4章、第5章および第6章では、それぞれ、亜鉛、カドミウムおよび銅イオンを共存させた溶液で同様な操作により、pH11.0、25℃において各金属イオンを取り込んだフェライトが生成することを示した。いずれも、ORP値に基づいた空気供給量の制御により残留金属イオンの濃度も十分に低下し、沈降性が優れたフェライト粒子を得た。

第7章では、生成した沈殿について赤外線吸収スペクトルや磁化曲線の測定、EXAFSによる解析を行い、それぞれの金属を取り込んだスピネル型化合物が生成していることを示し、水溶液から生成したフェライトは高温焼成したフェライトと同様な原子配列をとり、同じ水準の飽和磁化を有するという興味深い結果を得た。

第8章は結論である。

以上要するに本論文は、酸化反応を適度な速さで進めることにより25℃において水溶液から重金属イオンを取り込んだスピネル型化合物を析出させるプロセスの基礎的知見を明らかにしたものであり、地球工学とくに汚染防御工学および素材合成工学の分野で発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。