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A study on antimony-bearing ferrite

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Abstract

Ferrite containing heavy metals is precipitated by the wet method of the ferrite process when heavy metal ions come to coexistence. Based on this process, this paper investigated the treatable limit, existing shape after treatment, and properties of sludge formed on antimony compounds that have been restricted by Basel convention as a hazardous heavy metal. We determined that the ferrite process can be applied in initial concentrations up to 75 ppm in Sb^{3+} and Sb^{5+} solutions. For the initial concentrations of antimony exceeding 75 ppm, formation of α-FeOOH (Goethite) appeared gradually and showed difficulties of treatment by the ferrite process. Applicable limits of Sb^{3+} and Sb^{5+} from the results of this study were expected to be around 75 ppm and 100 ppm. Ferrite precipitate formed was a spherical particle cohering strongly at an approximate size of 0.1 μm. © 1998 Elsevier Science B.V.

Keywords: Ferrite; Waste-water treatment; Magnetite; Spinel structure; Saturation magnetization; Mössbauer spectra; Antimony

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1. Introduction

The global community has been facing serious social problems brought about by heavy metals in environmental pollution. Of the many methods used to treat waste-water containing heavy metals, the ferrite process, the precipitate aggregation method, the electrolytic floating method, and the resin adsorption method are the most common [1]. Of these methods, the ferrite process has merit because the formed ferrite compounds

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can be easily separated into liquids and solids using magnets. This is due to the property of ferromagnetism and its insolubility in water owing to its spinel structure. The chemical formula of ferrite is generally expressed as $MO \cdot Fe_2O_3$ (where M can be Fe, Zn, Mn, Co, Ni, Cd, Cu, etc.) if M is Fe, it will become Fe_3O_4, a well known magnetite. A magnetite is chemically stable material with the property of magnet [2]. The particularity of universities' and institutes' laboratory waste-water, containing various mixed compounds, differs from factories [3] but the ferrite treatment process is especially suitable for this type of waste-water. For this reason, the ferrite process is the most popular at Japan's universities and institutes [4]. Recently, much has been reported on the removal of heavy metals from waste-water by the ferrite process. Temperature, reaction time, pH levels, quantity and types of metal ions have been reported to have effects on this process [5–11]. Although many studies on the ferrite process have been reported, sufficient information about the ferrite process application for antimony compounds has yet to be gathered. Antimony compounds have been frequently used as material for plating, fireworks, alloy and semiconductors. These compounds have been restricted by the Basel convention which restricts the transport and disposal of hazardous wastes outside the national boundary. Until now, the treatable limit by the ferrite process has not been satisfactorily reported with regard to the existing shape of antimony compounds when these go beyond an applicable limit.

Therefore, Sb^{3+} and Sb^{5+} compounds treated by the ferrite process were investigated on the treatable limit and the properties of sludge recovered in this study.

2. Method of experiment

2.1. Reagent

All reagents used in this study were of an extra grade and obtained from WAKO Chemical. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) was used to form ferrite and antimony compounds having different valency ($SbCl_3$ and $SbCl_5$) were used as heavy metal ion substances. Bearing-antimony solutions containing known initial concentrations of 0, 5, 10, 25, 50, 75, 100, 150 ppm [Sb/Fe(total) = 0 ~ 0.00821 mol ratio] were used. Also, sodium hydroxide (5 N) was used to control pH levels.

2.2. Experiment

A total of 200 ml of standard solution of inorganic antimony compounds (Sb^{3+} and Sb^{5+}) was added to 300 ml beaker. Next, ferrous sulfate 8.34 g, (0.15 mol/l concentration as a Fe^{2+} ion) was added and then the solution was dissolved slowly with an agitator. After this solution was controlled to pH 9.5 ~ 10.5 by adding sodium hydroxide (5 N), it was oxidized by air through the G1 glass filter (flow rate 500 ml/min; surface area of air bubbles was 14 m^2/min) at 65 ~ 70°C. As the pH level of the solution decreased, due to alkali consumption with progressing reaction of ferrite process, sodium hydroxide (5 N) was added in order to maintain pH 9.5 ~ 10.5 at the same temperature. Reaction termination was confirmed by an Oxidation Reduction

Potential (ORP) meter when the value was increased abruptly from about −800 to 120 mv. After reaction, the solution was left to stand, then cooled to room temperature and filtrated to liquid and solid using cellulose nitrate filter paper of 1.0 μm pore. The precipitate was washed five times by distilled water and then dried in a desiccator. In case of leaching test, after sufficiently drying in a desiccator, the precipitates underwent and distilled water (pH 5.8 ~ 6.3) was added to the precipitates at a 10% ratio of weight cubic volume, and precipitates were shaken continuously for 6 h at room temperature. After settling, the suspension was filtered using 5C filter paper.

2.3. Sample analysis

The ferrite compound formed was identified by X-ray Diffraction (Rigaku Electric, Geigerfle 2013 model, target Fe, filter Mn) and the shape of the powder was observed using a Transmission Electron Micrograph (Hitachi HU-11Ds, accelerating voltage 100 KV). Saturation magnetization of the ferrite compound formed was measured by a DC hysteresis loop tracer (Toei, Vibrating Sample Magnetometer-5S model, maximum magnetic field 10 KOe). After the reaction, concentrations of untreated antimony ions in the filtrate and concentrations of leaching test on the precipitates were analyzed by Inductively Coupled Plasma-1000IV (Shimadzu, wave length 206.838 nm) with Hydride Vapor Generator-1 based on Japanese Industrial Standard (JIS) method and official announcement No. 13 of the Ministry of Environment in Japan. In order to evaluate the strength of magnetism and stability of ferrite, Mössbauer spectra method was carried out side-by-side using the Mössbauer Spectra Scope (Seiko EG, EG&G ORTEC 5500, velocity ± 12 mm/s 6 Hz).

3. Results and discussion

3.1. Formation of ferrite and waste-water treatment

Treatment of heavy metal ions by the ferrite process causes a reaction making Fe_3O_4 with air oxidation from green rust or $Fe(OH)_2$ formed by adding sodium hydroxide to ferrous sulfate solution. The mechanism of ferrite formation can be expressed as follows. When an amount of equivalent alkali is added to a solution of bivalent metal ions with ferrous ion, mixed hydroxide or its compound is formed from the basic reaction of the ferrite formation.

$$\begin{aligned} xM^{2+} + (3-x)Fe^{2+} + 6OH^- \rightarrow \quad & MxFe_{3-x}(OH)_6 \\ & \text{or } xM(OH)_2 + (3-x)Fe(OH)_2. \end{aligned}$$

When this suspended hydroxide solution is heated to 60 ~ 70°C and oxidized by air, the ferrite process takes place as follows:

$$MxFe_{3-x}(OH)_6 + 1/2\,O_2 \rightarrow MxFe_{3-x}O_4 + 3H_2O.$$

Though the reaction mechanism is not yet accurately confirmed, according to Kiyama, oxidation reactions (after pH control) of ferrite formation take place not on particle surface of $Fe(OH)_2$ but on oxidation of $(FeOH)^+$ dissolved into liquid phase from one of $Fe(OH)_2$ As for the oxidation rate, the dissolution rate of oxygen to liquid phase in air and of $(FeOH)^+$ is proven to be the rate-determining step [12]. Misawa et al. reported that in pH 9 ~ 11, the growth of the Fe_3O_4 particle with repetition of adsorption and oxidation on particle surface of Fe_3O_4 occurs during reaction because Fe^{2+} is adsorbed easily on the surface of iron oxide mixtures and oxidation of Fe^{2+} ion by oxygen is more easily adsorbed on surfaces than in solution [13]. If the above mentioned mechanism is correct, the growth of ferrite particles of spinel type can be expected by adsorption of metal ion (M^{2+}) and Fe^{2+} ion. However, adsorption reactions of metal ion (M^{2+}) to the surface of iron oxide mixtures are studied in detail by Davis and Leckie and other researchers [14]. These facts lend support to the above claim that the growth of crystals of ferrite happens by repeating adsorption and oxidation of Fe^{2+} and M^{2+} ions. Once the spinel structure is formed, metal ions will be situated in a lattice with strong bonds.

3.2. X-ray diffraction

In the treatment of the antimony-bearing ferrite process, we wanted to discover the existing shape of antimony when the formation and applicable limits of ferrite were surpassed. The X-ray diffraction results of precipitates obtained by ferrite processing of the solution at various concentrations of antimony are shown in Fig. 1. The vertical and the horizontal axes indicate the intensity and the angle of diffraction (2θ). Continuous variance of the lattice constant shows that the formed ferrite was decreased with increasing concentrations of antimony. This occurs because of the destruction of the lattice faces by the formation of by-products such as iron oxides and oxyhydroxide compounds. The precipitates obtained from Sb^{3+} and Sb^{5+} solutions of less than 75 ppm of initial concentration have the magnetite peaks due to the spinel type compound and are shown to be complete crystal ferrites of spinel type. Testing of the solution of 100 ppm showed the precipitate from Sb^{5+} had the most ferrite peaks and the precipitate from Sb^{3+} lost some ferrite peaks around 74 and 81 in 2θ and showed peaks around 42 and 53 in 2θ. This means that Sb^{5+} solution forms ferrite with less impurities than the Sb^{3+} solution at the concentration of 100 ppm. When the concentration of antimony ions is higher, α-FeOOH (Goethite), β-FeOOH (Akaganeite), γ-FeOOH (Lepidocrocite), and δ-FeOOH (Feroxyhite) formation are expected [15], but in fact, α, β, δ-FeOOH peaks were observed and their intensity ratios were $\alpha > \delta > \beta$. If the green rust formed by oxidization of ferrous hydroxide is oxidized rapidly by air, formation of γ-FeOOH can be expected but, in this study, their peaks were not observed and thought to be generated in the transition to α-FeOOH from γ-FeOOH as advocated by Misawa et al. [16]. The reason why γ-FeOOH, which is generally expected by the rapid oxidation of ferrous hydroxide products (green rust), was not observed in this experiment might be the transformation from γ-FeOOH to α-FeOOH as studied by Misawa et al. The transition to α-FeOOH consisting of oxygen in only one kind of bonding state seems to be more stable in configuration due to an increase in entropy than γ-FeOOH, having a regular array of two kinds of oxygen, formed in ferrous sulfate solution. These variations in chemical state can be due to γ-FeOOH dissolution, and

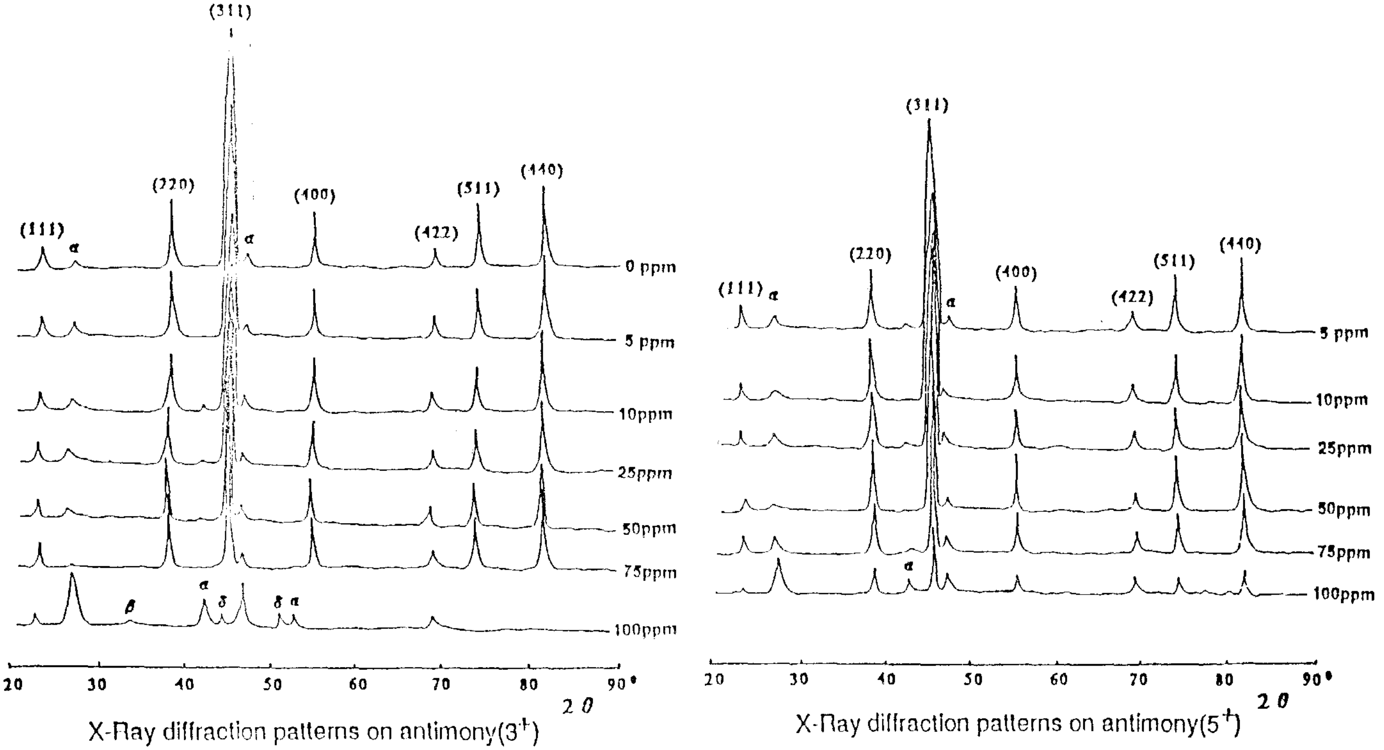

Fig. 1. X-ray powder diffraction patterns of ferrites obtained from the solutions containing various concentrations of antimony (the numbers in parenthesis are points corresponding to lattice faces of crystal using Fe target and Mn filter).

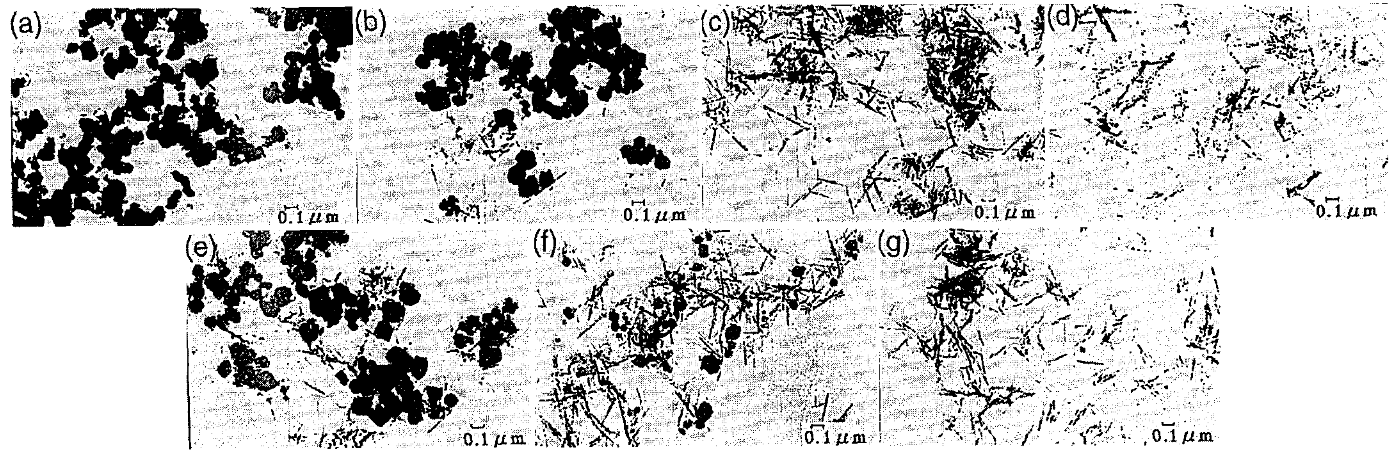

Fig. 2. Transmission electron micrographs of ferrites obtained from the solutions containing antimony of: (a) 0 ppm, (b) 50 ppm (3^+), (c) 100 ppm (3^+), (d) 150 ppm (3^+), (e) 50 ppm (5^+), (f) 100 ppm (5^+) and, (g) 150 ppm (5^+).

β-FeOOH compound is said to be formed easily when chloride and fluoride ions were existing. In the ferrite process treatment Sb^{3+} and Sb^{5+}, α-FeOOH formation was also confirmed as a major by-product.

3.3. Transmission Electron Micrograph (TEM)

After the ferrite process reaction, particle sizes of formed compounds in the precipitates, obtained from the solution of Sb^{3+} and Sb^{5+} having initial concentrations of 0, 50, 100, 150 ppm, were observed by TEM (paste method, 28200 times) and shown in Fig. 2. In the case of no antimony, only ferrite crystals (spherical–cubic shape) were observed, but needle shape crystals appeared and increased gradually with increasing concentration of antimony. Magnetite particles were observed in precipitates from the solution of Sb^{3+} and Sb^{5+} having an initial concentration of 50 ppm due to the spinel type compound and showed to be complete crystal ferrite of spinel type. A light yellow solid, which was identified as a needle shape crystal of α-FeOOH by X-ray diffraction and Mössbauer spectra, was observed in the precipitate from Sb^{3+} 150 ppm solution but not in one from Sb^{5+} 150 ppm solution. In the case of 100 ppm of Sb^{3+} and Sb^{5+}, a small amount of ferrite crystals (spherical–cubic shape) was observed. Ferrite of Sb^{5+} was formed better than ferrite of Sb^{3+} due to the above mentioned reason. On the whole, formed particles of ferrite cohered strongly with a fine grain of about 0.1 μm. When antimony did not exist, particle sizes of ferrite increased to about 0.15 ~ 0.2 μm and were identified with magnetite by X-ray diffraction and Mössbauer spectra.

3.4. Magnetization measurement

Ferrite formed can be easily isolated to liquid and solid by a magnet because of its ferromagnetism. This process has been used as one of the important processes in waste-water treatment system. To evaluate the magnetic properties of ferrite sludge (obtained from the ferrite process reaction of about six times at each antimony concentration) saturation magnetizations of each precipitate were measured and the mean values were shown in Fig. 3 at maximum magnetic field (10 KOe). A typical hysteresis loop of ferromagnetism was observed and more than 60 emu/g of saturation

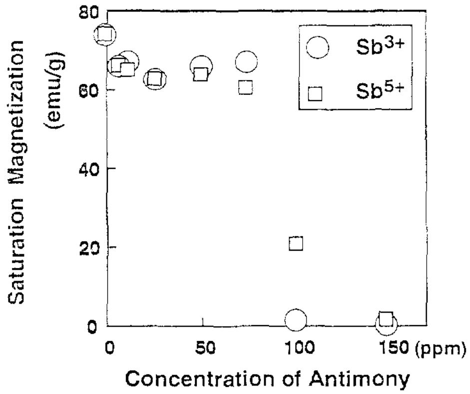

Fig. 3. Relationship between saturation magnetization and concentration of antimony.

magnetization was indicated for the precipitates from up to 75 ppm of initial concentration of Sb^{3+} and Sb^{5+} solution. The figure of 60 emu/g is known to be a sufficient value for separation by a magnet. These ferrites, which also showed high magnetic permeability (μ) with about 100 Oe of coercive force (Hc) and about 10 emu/g remanence magnetization (Mr), can be said to be ferromagnetic spinel crystals. The value of the saturation magnetization of the brown precipitate at 100 ppm of the Sb^{3+} solution decreased abruptly, while that of the black precipitate at 100 ppm of Sb^{5+} solution decreased slightly and was 18 emu/g (a reported limit value for magnetic separation) [17]. The precipitates from 150 ppm of Sb^{3+} and Sb^{5+} solutions had values of saturation magnetization of almost zero, in both cases, which indicated no ferrite formation and no possibility of separation by a magnet. Heavy metal ions in waste-water might be removed by incorporation into the spinel structure of ferrite from oxidation of ferrous ion. Heavy metal ions might also be removed by physical–chemical adsorption due to the character of ferrite particles.

3.5. Residual antimony concentration after the ferrite process

The results of mean concentration of residual antimony after the ferrite process are shown in Fig. 4. In the past, antimony compounds in the ferrite process were reported to disturb its reaction [18], but a possibility of removing antimony by using the ferrite process was shown in this study. Fig. 4 shows that the residual concentration of antimony from the Sb^{3+} solution was higher than that from the Sb^{5+} solution at the same initial concentration of antimony, in a range of 0 ~ 150 ppm. The removal ratios of Sb^{3+} and Sb^{5+} were 99.08 ~ 99.66% and 99.4 ~ 99.9%. There was a linear relationship between the initial concentration and the residual concentration of antimony. The residual concentration linearly increased with increasing initial concentration of antimony. The removal ratio for the Sb^{5+} solution of 150 ppm was calculated to be 99.8% from the molar ratio of Sb/Fe_{total} (0.00821) and the residual concentration of antimony (223 ppb), and for Sb^{3+} solution of the same initial concentration was

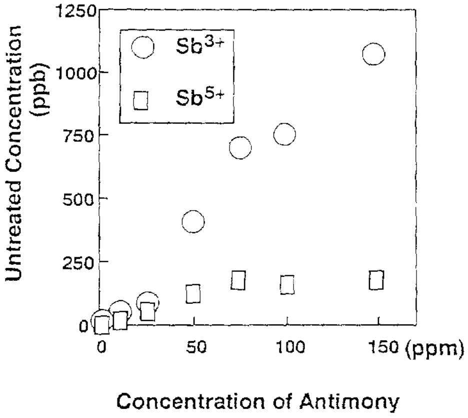

Fig. 4. Relationship between untreated concentration and concentration of antimony.

calculated to be 99.3%. From these results, applicable limits for Sb^{3+} and Sb^{5+} were expected around 75 ppm ($0.075/121.75 = 0.000616$ mol/l as Sb^{3+}/Fe ratio was 0.0041) and around 100 ppm ($0.1/121.75 = 0.000823$ mol/l as Sb^{5+}/Fe ratio was 0.0055). If these values are to quantities of iron, the spinel structures of Sb^{3+} and Sb^{5+} could be estimated by recalculation and expressed as follows:
Sb^{3+}: $Fe^{2+} \cdot Fe^{3+}_{1.988}Sb^{3+}_{0.012}O_4$; Sb^{5+}: $Fe^{2+} \cdot Fe^{3+}_{1.984}Sb^{5+}_{0.016}O_4$.

Since the half diameter of an Sb^{3+} ion (0.76 Å) is bigger than that of an Sb^{5+} ion (0.61 Å), incorporation of Sb^{3+} into spinel structures might be more difficult than that of Sb^{5+}. This might explain the different removal ratio of Sb^{3+} and Sb^{5+}. However, it is said that the effect of the ferrite process applied to the solution containing heavy metal was explained not only by the theory of lattice point exchange, but also by the complex physical–chemical adsorptions such as coprecipitations with iron oxide mixtures. The different adsorption properties of Sb^{3+} and Sb^{5+} might be another reason for the discrepancy. Regardless of the different removal ratio of Sb^{3+} and Sb^{5+}, it has been proven that it is sufficiently safe to treat up to 100 ppm of initial concentration of both Sb^{3+} and Sb^{5+}, when the target concentration is 1 ppm after treatment.

3.6. *Mössbauer spectra*

To investigate the distribution of cations incorporated into the spinel structure in detail, Mössbauer spectra were measured for the precipitates and the results are shown in Fig. 5. The Mössbauer spectrum of perfect ferrite, such as $NiFe_2O_4$ at room temperature, should show a spectra of absorption with double of 6 peaks [19]. Spinel structure is incorporated with heavy metal ions in oxygen of cubic closed packed structure enclosed by 4 oxygens, tetrahedral site (A site), and by 6 oxygens, octahedral site (B site). Six strong peaks of typical Zeeman splitting were shown, and Fe^{2+} was identified with inverse spinel ferrite incorporated into B site in Fig. 5. In general, the internal magnetic field is decreased with increasing concentration of heavy metals. The spinel lattice was shown to increase gradually stoichiometrically with an incorporation of heavy metal ions into the spinel structure [20]. Values of isomer shift, quadruple splitting, and magnetic splitting of the precipitates from up to 75 ppm of initial concentration of Sb^{3+} and Sb^{5+} solution almost never changed and a magnetite structure was indicated. Internal magnetic fields of A and B sites up to 75 ppm of initial concentration of Sb^{3+} and Sb^{5+} solution were $49.067 \sim 49.246$ and $45.83 \sim 45.866$ T (Tesla). Evaluation of the formation state of ferrite can be traced stoichiometrically by Mössbauer spectra, but an internal magnetic field of 33 ± 3 T at 150 ppm of Sb^{3+} was observed and recognized as an α-FeOOH (Goethite) which was not fitted to the ferrite pattern. Almost all of the results agreed with the X-ray diffraction.

3.7. *Leaching test*

When precipitate containing heavy metals formed by waste-water treatment is buried in the ground, heavy metal ions will be dissolved, and pollution will take place. Leaching tests to evaluate the safety and stability of precipitates were conducted based

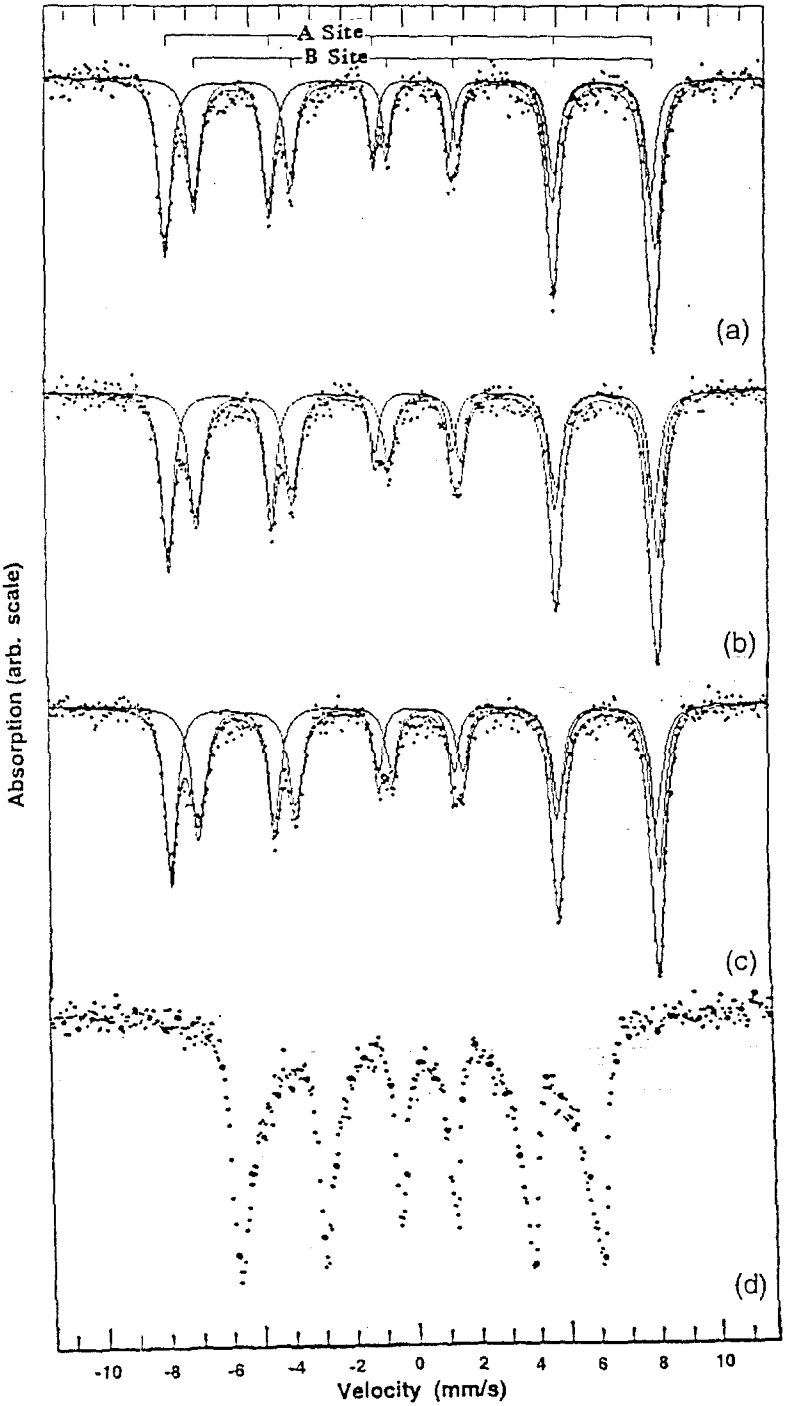

Fig. 5. Mössbauer spectra at room temperature of the precipitates obtained after ferrite process reaction at antimony of: (a) 0 ppm, (b) 50 ppm (5^+), (c) 75 ppm (3^+) and, (d) 150 ppm (3^+): A and B sites are indicated.

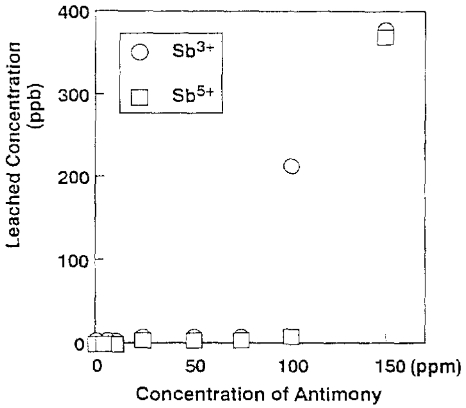

Fig. 6. Relationship between leached concentration and concentration of antimony.

on official announcement No. 13 of the Ministry of Environment in Japan. The results of its mean concentration of leaching test are shown in Fig. 6. Leaching concentrations of filtrates up to 75 ppm of initial concentration of Sb^{3+} and Sb^{5+} were very low, under 10 ppb. Most of the antimony ions were thought to be incorporated into spinel lattice of ferrite. While leaching concentrations of filtrates came from 100 ppm of initial concentration of Sb^{3+} and Sb^{5+} solution were 212 and 8.5 ppb. We believe that the Sb^{5+} ion was incorporated more strongly into the spinel lattice as its composition element than the Sb^{3+} ion. This result matched with X-ray diffraction and Mössbauer spectra. Antimony is limited to a guide value of 2 ppb as an item of caution in Japan. In general, if some compounds not designated in environmental standard are discharged to a river or a drainage, they will be regulated at 10 times the amount of the environmental standard, and the discharging value for criterion of antimony based on this will be 20 ppb. If the final treatment of industrial waste precipitates is to bury them in the ground, leaching tests must be performed in advance. Generally, if the antimony criterion for leaching test is regulated to 3 times the discharging value to a river or a drainage, it will be 60 ppb. Therefore, for up to 100 and 75 ppm of initial concentration of Sb^{5+} and Sb^{3+}, as shown in Fig. 6, leaching concentration of antimony from precipitates was low and can be treated by burying as industrial waste.

4. Conclusion

The ferrite process of single-stage simultaneous removal is applicable to mixed waste-water containing many kinds of heavy metal ions, discharged from institutes and universities. Compounds of heavy metal ion treated by the ferrite process have more stable structures than hydroxide and sulfide compounds that are dissolved, and continuous separation to liquid and solid can be easily accomplished by use of magnets. Ferrite compounds formed by treatment are worthy of recycling for use in creating computer materials, antenna rods and magnetic amplifiers. These compounds have been used in radio-wave absorbers, metal scavengers, reduction of NO_x and oxidation of CO as catalysts. Ferrous sulfate as a raw material can be recycled because it is discharged from industrial waste. In this study, solutions containing antimony ions, which were reported to have no capability of forming ferrite, were examined in the ferrite process. It has been proven that the solutions containing up to 75 ppm of initial concentration of Sb^{3+} and Sb^{5+} can be treated by the ferrite process to produce a fairly stable precipitate which releases less than 10 ppb of antimony in the leaching test. The existence of the ferrite in the precipitate is also proven by obtaining ferrite peaks in the X-ray diffraction, ferrite crystals (spherical–cubic shape) in the TEM observation, typical hysteresis loop of ferromagnetism in the magnetization measurement, and six strong peaks of typical Zeeman splitting in the Mössbauer spectra analysis. As for solutions which contain more than 75 ppm of initial concentration of Sb^{3+} and Sb^{5+}, the gradual formation of α-FeOOH (Goethite) is also demonstrated by those analyses. From these results, we have determined that the applicable limits of Sb^{3+} and Sb^{5+} are around 75 ppm and 100 ppm, and their spinel structures are thought to form $Fe^{2+} \cdot Fe^{3+}_{1.988}Sb^{3+}_{0.012}O_4$ and $Fe^{2+} \cdot Fe^{3+}_{1.984}Sb^{5+}_{0.016}O_4$. We conclude that treatment of Sb^{5+} is better than treatment of Sb^{3+} because of the difference of half distance of ions.

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