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Treatment of tellurium containing stream using ferrite process and its characterization

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ABSTRACT

Ferrite containing heavy metals is precipitated when heavy metal ions come into coexistence in the wet method of the ferrite process. Based on this theory, this paper examines the treatable limitation, actual shape beyond that limitation, and the property of the sludge formed on tellurium compound restricted by the Basel Convention as a hazardous heavy metal. We have discovered that the ferrite process treatment could be applied in tellurium solution with the initial concentration up to 25 ppm. Furthermore, we are able to confirm that when the initial concentration exceeds 25 ppm, tellurium ion tends no longer to be incorporated into the spinel structure of ferrite with causing difficulties in the ferrite process. The applicable limitation from the experiment results of this study on tellurium treatment by ferrite process appears to be around 25 ppm for both Te^{4+} and Te^{6+}. In both cases, needle shaped crystal of α-FeOOH (Goethite), which is a by-product of ferrous hydroxide, can no longer be observed in accordance with hindrance to the growth of ferrite crystal particles in the ferrite sludge obtained at 500 ppm. Sizes of ferrite particles become smaller, that is to say, approximate 0.01~0.02 μm and the growth of crystals shows no progress.

Keywords: Ferrite; Tellurium; Magnetite; Spinel structure; Saturation magnetization

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1. Introduction

Various kinds of environmental pollution and ecological destruction, resulting from economic growth and development, must be dealt with by the world community as a whole and not by a single State. Environmental issues arising from toxicity of heavy metals have a long history and are still being raised on a broad scale. The main methods to treat wastewater containing heavy metals are the ferrite process, the precipitate aggregation, the electrolytic floating, the resin adsorption, etc [1,2]. Since the formed ferrite compounds are strong magnetism, they allow to separate easily the wastewater into liquid and solid by a magnet in the ferrite process. Therefore, attention is given to the ferrite process because recycling technology makes efficient use of the sludge formed as a magnetic substance. The chemical formula of ferrite is generally expressed as MO Fe_2O_3 (whereas M is divalent metal ions). The ferrite has been commonly used in communication equipment as a magnetic substance for a long time and it has wide practical usage. Therefore, active researchers have developed techniques to produce useable ferrite and the ferrite process by the wet method is discovered in the early 80's. The M in the case of many metals stands not only for divalent metal ions, but also for mono to six valent ion. M is incorporated into the spinel structured ferrite because iron ions in the

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ferrite lattice may be replaced with other metal ions [3]. Currently, treatment system using this method are being operated in numerous facilities like universities, institutes, waste processes, refuse disposal sites, and factories [4]. The ferrite process method incorporates heavy metal ions into crystal lattice points of ferrite produced by the air oxidation of the ferrous ion in wastewater. Several merits may be also attached thereto: it is possible to treat various metal ions at the same condition and time. The magnetic separation method due to ferrite being a strong magnetic substance may be used and danger of leaching heavy metal is unlikely in regards to the sludge produced, and it can be used again [5]. Tellurium compound is frequently used in coloring agents for plating, electro-alloy, semiconductor, catalyst, and thermocouples. Tellurium does not constitute an environmental standard item in Japan, but it is restricted by the Basel Convention as a harmful heavy metal substance. It is an established rule that harmful waste should be disposed in the state of origin. However, there have been insufficient studies on treatment methods for tellurium. Therefore, this study investigates the applicable limitation, actual shape beyond the limitation, and the properties of leaching from the sludge recovered by the ferrite process method on tellurium (Te^{4+} and Te^{6+}) compounds.

2. Method of experiment

2.1. Reagent

All reagents used in this study were of an extra grade and supplied from Wako Pure Chemical Industries. Ferrite was formed by using ferrous sulfate ($FeSO_4$ $7H_2O$). Telluriums used as a heavy metal ion substance were sodium tellurate ($Na_2H_4TeO_6$) and sodium tellurite (Na_2TeO_3). Initial concentrations for tellurium-bearing solutions were 0, 5, 10, 25, 50, 75, 100, 250 and 500 ppm. The ranges of their $Te/Fe_{(total)}$ mol ratios were 0≈0.026 and they were used as standard solutions. Furthermore, sodium hydroxide (5N) was used to control pH levels.

2.2. Experiment

A 200 ml of tellurium standard solution was added to a 300 ml tall beaker. Ferrous sulfate in amount of 8.34 g (0.15 mol/l concentration as a Fe^{2+} ion) was added to the solution and dissolved slowly with an agitator. After the solution was controlled to pH 9.5≈10.5 by adding sodium hydroxide (5N), heat was added to keep the temperature at 65≈70 × °C. The solution was oxidized by air through the G1 glass filter, where the flow rate was 500 ml/min and the surface area of air bubbles was 14 m^2/min. As the pH level decreased of the solution due to alkali consumption with the progressing reaction of ferrite process, sodium hydroxide (5N) was added in order to maintain at pH 9.5≈10.5. Reaction termination was confirmed by an oxidation reduction potential (ORP) meter when the value was increased abruptly from approximate –800 to 120 mV. After reaction, the solution was cooled to room temperature and filtrated using cellulose nitrate filter paper of 1.0 μm pore. The precipitate was washed 8× with distilled water to remove sodium sulfate (Na_2SO_4) and then naturally dried for more than 3 wk in room temperature.

2.3. Sample analysis

The ferrite compound formed was identified by X-Ray Diffraction (Rigaku Electric Co., RINT 2200 model, target Fe) 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 Corporation, Vibrating Sample Magnetometer-5S model, maximum magnetic field 10 KOe). After the reaction, the concentration of untreated residual tellurium ions in the filtrate was measured based on (JIS) Japanese industrial standard) method and a leaching test based on official announcement No. 13 of the Environment Agency in Japan was conducted on the ferrite compounds [6]. The untreated residual and leached concentrations were measured with Inductively Coupled Plasma-1000IV (Shimadzu, wave length 214.275 nm) with Hydride Vapor Generator-1 to increase the sensitivity.

3. Results and discussion

3.1. Formation of ferrite and removal of heavy metal ion

Treatment of heavy metal ions by the ferrite process involves a reaction producing Fe_3O_4 through 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.

$$\begin{aligned} &XM^{2+} + (3-x)Fe^{2+} + 6\,OH^- \rightarrow M_xFe_{3-X}(OH)_6 \\ &\quad \text{or}\quad xM(OH)_2 + (3-x)Fe(OH)_2 \end{aligned} \tag{1}$$

When this suspended hydroxide solution is heated to 60≈70 °C and oxidized by air, ferrite process takes place under the following reaction:

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

where, metal ions are incorporated into ferrite crystals of spinel (or reverse spinel) structure. Through relevant choice of x in Eq. (1) and conditions of reaction in Eq. (2) such as temperature, pH, oxidization rate, etc., size of the particle over the control of ferrite formation is possible to enable the crystal of ferrous-excessive MO Fe_2O_3-Fe_3O_4 compound to be created [7,8].

3.2. Residual concentration in the treated solutions

The results of mean residual concentration in the treated solutions after the ferrite process reaction are shown in Fig. 1. In the past, it has been said that the tellurium ion from a simple beaker test cannot be removed by ferrite process when it comes into co-existence [9]. However, a possibility of tellurium removal using the ferrite process is shown in this study. Fig. 1 shows the residual tellurium concentration in the filtrate at initial concentration ranging from 0≈500 ppm. Untreated residual concentration of Te^{6+} in the filtrate was slightly higher than that of the Te^{4+} at the same initial concentration of tellurium. The removal ratios for the Te^{4+} and Te^{6+} at the initial concentration up to 25 ppm were 99.0≈99.04% and 98.18≈98.61%, and residual concentrations of tellurium ions in the filtrate were 0.038≈0.25 ppm and 0.091≈0.347 ppm. This seems to be due to the fact that the tellurium ions in the solution were sufficiently incorporated or adsorbed into spinel structure of ferrite. As for the relationship between the initial and the residual concentration after the ferrite process reaction, the residual concentration linearly increased with increasing initial concentration of tellurium ions beyond 25 ppm level with Te^{6+} slightly higher values. Furthermore, as the initial concentration of tellurium exceeded 25 ppm, the treatment ratios for the Te^{4+} and Te^{6+} declined to 41.6% and 36.2% at 500 ppm, respectively. The molar ratio of Te/Fe_{total} at initial concentration of 25 ppm for Te^{4+} and Te^{6+} was 0.0013 and their residual concentrations were 250 ppb and 347 ppb, respectively. Applicable limitations from these results for Te^{4+} and Te^{6+} were expected around 25 ppm (0.025/127.6 = 0.000196 mol/l as $Te^{4+,6+}/Fe$ ratio was 0.0013); if these values convert into quantities of used iron, the spinel structures of Te^{4+} and Te^{6+} could be estimated by recalculation as follows: Fe^{3+} at A site; $0.996Fe^{3+}$, $0.004Te^{4+,6+}$, $1.0Fe^{2+}$ at B site; i.e. $Fe^{2+}\ Fe^{3+}_{1.996}Te^{4+,6+}_{0.004}O_4$ of spinel has been formed. Both Te^{4+} and Te^{6+} have the same applicable limitations. However, since the radius of the Te^{6+} ion (0.56 Å) is slightly greater than that of the Te^{4+} (0.52 Å), the former seems to have more difficulty being incorporated into spinel structure. Also, the effect of the ferrite process on heavy metal ions is explained as a complex action of physical-chemical adsorption caused by co-precipitation with an iron oxide substance not only by the theory of lattice point exchange. As for Te^{6+}, Fe^{2+} reduces Te^{6+} to Te^{4+} as follows:

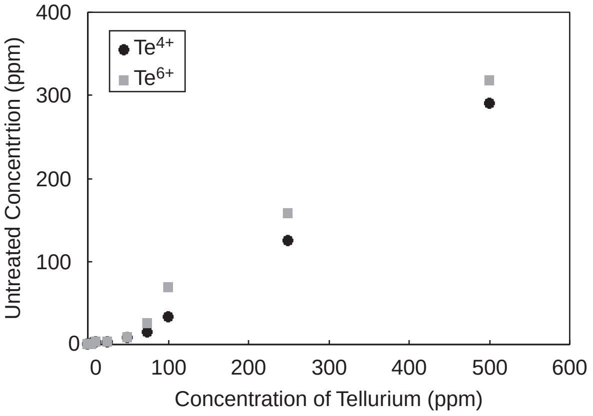

Fig. 1. Relationship between untreated concentration and concentration of tellurium.

$$2Fe^{2+} + Te^{6+} = 2Fe^{3+} + Te^{4+}$$

If $FeTe_2O_4$ and Fe_3O_4 are considered to be formed, the ratio of $FeTe_2O_4/Fe_3O_4$ would be 1/2. If this solution is to be alkalified, it will be possible immediately to form the ferrite precipitate of the spinel type even in a nitrogen because the oxidization of the Fe^{2+} does not require an air [10]. Since Te^{6+} is more or less reduced to Te^{4+} at first and then incorporated into spinel structure, it is possible that Te^{6+} could be more difficult than Te^{4+} to enter into it. In either case, if the target concentration of effluent is 1 ppm, it will be shown that the initial concentration up to 25 ppm for both Te^{4+} and Te^{6+} is sufficiently safe to treat.

3.3. X-Ray diffraction

The evaluation on the treatment of tellurium ion by ferrite process requires knowledge of the existing shape of tellurium compound when the ferrite formation occurs and its applicable limitations surpass. The X-ray diffraction results of precipitates obtained by ferrite process from the solution at various concentrations of Te^{4+} and Te^{6+} are shown in Figs. 2 and 3. The vertical and the horizontal axes indicate the intensity and the angle of diffraction (2θ), respectively. In general, continuous variance of the lattice constant shows that lattice faces of formed ferrite will decrease with increasing tellurium concentration. This is due to the destruction of lattice faces as a result of the formation of by-products such as iron oxides and oxyhydroxide compounds. However, the by-product peaks like α-FeOOH in this study were not observed at initial concentration up to 500 ppm of Te^{4+} and Te^{6+}. This indicates that a complete crystal

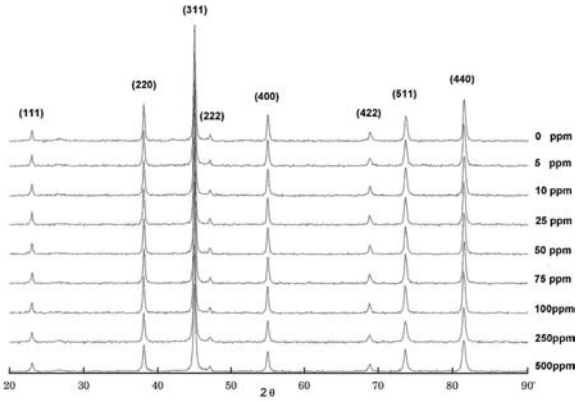

Fig. 2. X-Ray powder diffraction patterns of ferrites obtained from the solutions containing various concentrations of Te^{4+} (The numbers in parenthesis are points corresponding to the lattice faces of crystal using Fe).

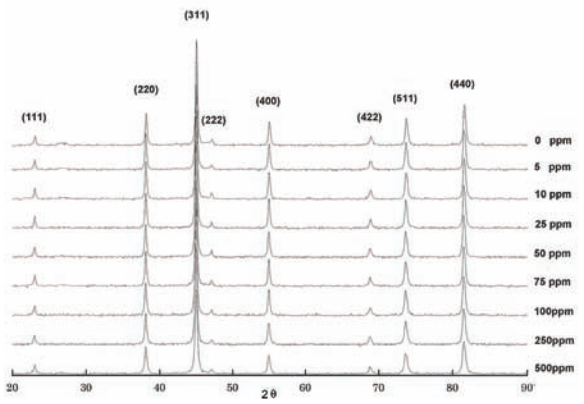

Fig. 3. X-Ray powder diffraction patterns of ferrites obtained from the solutions containing various concentrations of Te^{6+} (The numbers in parenthesis are points corresponding to the lattice faces of crystal using Fe).

ferrite of the spinel type was formed. As for the peak intensity, some variance is given due to the density of measuring sample. Therefore, the intensity is compared at approximate 45 (311) degrees in 2θ, which is the highest among ferrite peaks. It was decreased slightly when initial concentration of Te^{4+} and Te^{6+} exceeded 100 ppm and 75 ppm, respectively. In cases where concentration of heavy metal is high or reaction conditions are bad, formation of α, β, γ, δ-FeOOH formed by rapid oxidization of ferrous hydroxide or green rust could not be observed at all. In general, value of half width of peak tends to become wider in accordance with initial heavy metal concentration since heavy metal ions are coercively incorporated into spinel lattice of ferrite. Therefore, values of half width were measured for lattice at 81.4 (440) degrees in 2θ in order to examine this change. However, almost no change was observed for both Te^{4+} and Te^{6+} ranging from 0.33 (100%) ≈ 0.37 (112%) during initial concentrations between 0 ppm and 500 ppm. Therefore, it is perceived that crystal ferrite of spinel type was formed at initial concentration up to 500 ppm for both Te^{4+} and Te^{6+}.

3.4. Transmission electron micrograph (TEM)

After the ferrite process reaction, particle sizes of ferrite compound obtained from the tellurium-bearing solution at initial concentration of 0, 50, 100, 500 ppm were observed by TEM (paste method, 28,200×) and shown in Fig. 4. In the case of no heavy metal, only ferrite crystals (spherical-cubic shape), being simply intensively magnetite, were observed and size of the particles was relatively evenly distributed in approximate 0.1 μm in diameter. Some needle shaped crystals can be seen for Te^{4+} and Te^{6+} solutions at initial concentration up to 100 ppm and 50 ppm. However, magnetite particles, indicating attributable ferrite to relatively even compound of

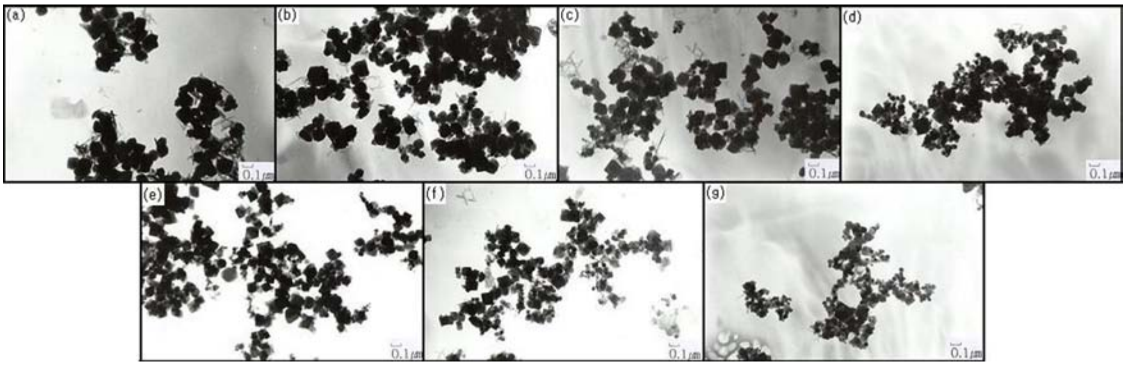

Fig. 4. Transmission electron micrographs of ferrites obtained from the solutions containing tellurium of: (a) 0 ppm; (b) 50 ppm (4+); (c) 100 ppm (4+); (d) 500 ppm (4+); (e) 50 ppm (6+); (f) 100 ppm (6+); and (g) 500 ppm (6+).

spinel type, are observed and hence formation of complete crystal ferrite of spinel type can be perceived. In this case, ferrite particles are crystal (spherical-cubic shape) of about 0.07≈0.1 μm on average in size when concentration was increased up to 500ppm for both Te^{4+} and Te^{6+} coinciding the results from X-ray diffraction. Needle shape crystals of α-FeOOH (Goethite) can also no longer be observed with the growth of ferrite crystal particles and their sizes become about 0.01≈0.02 μm with no more growth of the crystal. It was further observed that growth of ferrite particles in regards to the influence of tellurium concentration greatly deteriorated when the initial concentration was increased up to 100 ppm for both Te^{4+} and Te^{6+}, in spite of optimal reaction condition formed only spherical-cubic shaped ferrite. The growth of needle shaped crystal of α-FeOOH (Goethite) was not progressed.

3.5. Magnetization measurement

The formed ferrite sludge is primarily a ferromagnetic compound that plays an important role in the treatment of heavy metal wastewater by ferrite process through magnetic separation and connection. For the wastewater treatment system, it is important not only to transform the heavy metal ions into ferrite sludge, but also to isolate the sludge from the treated suspension using high gradient magnetic separation (HGMS) equipment in wastewater. Lately, much of the load can be treated in a short time by HGMS method and researches for its application such as the treatment of iron mine wastewater and river sludge, magnetic dressing of ores, extraction of resources, etc., have been carried out in the field. To evaluate the magnetic properties of ferrite sludge, saturation magnetization of each precipitate obtained from the ferrite process reaction was measured for each concentration level. The measured values are shown in Fig. 5 at maximum magnetic field of 10 KOe. A typical hysteresis loop of ferromagnetism was observed even at initial concentration up to 500 ppm for Te^{4+} and Te^{6+}, and saturation magnetization values of about 72≈80 emu/g were indicated, so that solid and liquid separation would be feasible. These ferrites, which also show high magnetic permeability (μ) with coercive force (Hc) of about 70≈100 Oe and remanence magnetization (Mr) of about 15 emu/g, can be said to be ferromagnetic spinel crystals. In general, many heavy metal ions act as an obstacle to the formation of ferrite and a low value of saturation magnetization is found when the concentration of heavy metal is high. Saturation magnetization tends to increase when zinc ferrite contains Mn, Co, or Ni. This similar tendency seems to be shown slightly in case of tellurium. For both Te^{4+} and Te^{6+} at initial concentration up to 500 ppm, color of precipitates was black and satisfactory ferrite compounds were formed relatively.

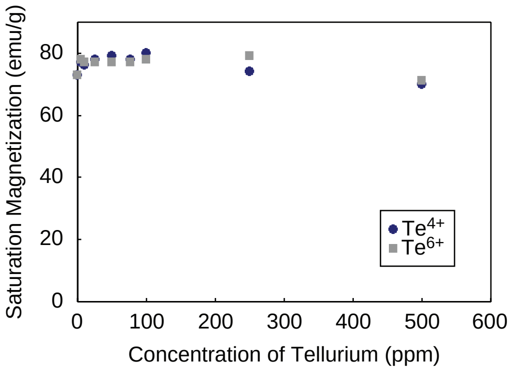

Fig. 5. Relationship between saturation magnetization and concentration of tellurium.

3.6. Leaching test

Among the methods for the treatment of heavy metals, the precipitate aggregation method is the most commonly one used when only a few kinds of heavy metals are involved. Solutions containing heavy metal ions are neutralized and induced to be precipitated as hydroxide substances after their solubility have been lowered. However, the most suited pH for each metal differs from one another. Reclamation in the acidified ground would allow these harmful heavy metals to leach with causing possible secondary pollution. Therefore, a leaching test was conducted to evaluate the safety and stability on tellurium-bearing ferrite. The test was also conducted based on official announcement No. 13 of the Environment Agency in Japan. After sufficient natural drying, the precipitates underwent a leaching test. Distilled water (pH 5.8≈6.3) was added to the precipitates at a 10% ratio of weight cubic content and the precipitates were shaken continuously for 6 h at room temperature. After setting, the suspension was filtered using cellulose nitrate filter paper with 1.0 μm pore size. The mean concentration levels of tellurium after leaching test are shown in Fig. 6. The concentration of tellurium leached at the initial concentration up to 500 ppm for both Te^{4+} and Te^{6+} was extremely low, below 12≈16 ppb. This result showed that most of the tellurium ions were incorporated into ferrite precipitate. One conceivable reason for this condition is that the tellurium ion is incorporated as a constituent element of strong spinel structure in both cases of Te^{4+} and Te^{6+}. However, the treatment limitation from the analysis results of residual concentration of tellurium in the filtrate became troublesome at the initial concentration over 25 ppm for Te^{4+} and Te^{6+}. As a result, the tellurium ion not incorporated into the spinel structure remained unchangeably in the solution and did not pose an obstacle to formation of ferrite like other

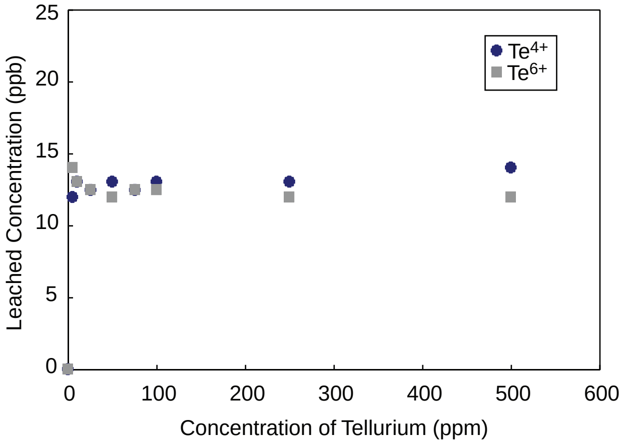

Fig. 6. Relationship between leached concentration and concentration of tellurium.

metals. Tellurium is not designated as a cautionary item in Japan. In general, if some compounds not designated in environmental standard are discharged to a river or a drain, they will be regulated to 10× of the amount of the environmental standard. If the precipitate as industrial wastes for the final treatment is to reclaim in the ground, the leaching test must be performed in advance. Generally, the criterion for leaching test is regulated to 3× of the discharging value to a river or a drain. Based on reverse calculation, leached tellurium concentration from the formed ferrite is low at the initial concentration up to 500 ppm for both Te^{4+} and Te^{6+} even though a guidance value of 0.6 ppb will be designated as an item requiring caution in Japan. This is able to reclaim as an industrial waste with the sufficiently feasible treatment in the ground.

4. Conclusion

In this study, solutions containing tellurium ions (Te^{4+} and Te^{6+}) were examined by using the ferrite process. According to the results of X-ray diffraction, TEM, saturation magnetization, leaching test, and residual concentration of tellurium ions for produced ferrite, ferrite process treatment is feasible for both Te^{4+} and Te^{6+} up to 25 ppm initial concentration. This suggests that incorporated tellurium ion exists in the center enclosed by oxygen atoms constituting ferrite, so that the once spinel structured ferrite compound is stable due to strong adsorption of ferrite in regards to leaching. Tellurium is conceivably incorporated into the spinel structure of the ferrite lattice to a certain level for the lower concentrations. It also has to be pointed out that the tellurium ion could strongly reflect the physical-chemical adsorption function through co-precipitation with iron oxide compound when compared with lattice exchange. This coincides with results from X-ray diffraction, saturation magnetization, and TEM. It has been confirmed that the ferrite process for both Te^{4+} and Te^{6+} gradually becomes difficult when initial concentrations surpass 25 ppm. Furthermore, if the target residual concentration for tellurium ion at some country is 1 ppm, initial concentration up to 25 ppm for both Te^{4+} and Te^{6+} will sufficiently feasible to treat. From these results of experiments, applicable limitation for Te^{4+} and Te^{6+} is measured at approximate 25 ppm and formed spinel of $Fe^{2+}Fe^{3+}{}_{1.996}Te^{4+,6+}{}_{0.004}O_4$ with incorporation into ferrite lattice. The reason for the treatment ability of Te^{4+} being better than that of Te^{6+} seems to rest with the difference in the radius of ion and reduction.

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