

Removal of Arsenic(?) in Aqueous Solutions by Controlling Oxidation Potetial (酸化ポテンシャルの制御による水溶液中のAs(?)の除去)

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論文内容要旨

1. Introduction

Recently more stringent regulations against arsenic have been established because of its toxic nature. Arsenic is one of the common impurities in most of the concentrates of non-ferrous minerals. The treatments of such feeds necessarily lead to build-up of arsenic in metallurgical processes and generation of arsenic-bearing intermediates, by-products, effluents and waste waters. These arsenic-bearing materials and process wastes have to be treated in an environmentally acceptable manner. In industrial processes to separate and remove arsenic from aqueous solutions, various types of operation were developed and came into practice with varying success. These processes, however, in most cases result in the generation of a big mass of sludges contaminated by arsenic. Furthermore, the reactions actually occurring in these processes were not fully understood. The development of technology to separate and remove arsenic from aqueous solutions effectively requires well-refined understanding of the reactions taking place under various conditions.

The present work was undertaken with the aim of fundamental data for (1) separation of arsenic from process solutions as insoluble phase of high arsenic content and (2) removal of arsenic from effluents to meet the environment protection regulation of 0.1 mg/L for waste water. One of the most important points to realize such arsenic removal process may be almost complete oxidation of trivalent arsenic, As(III), to pentavalent arsenic, As(V), and production of insoluble arsenate with ferric species, Fe(III). Then, the oxidation of As(III)

species and oxidative precipitation of As(III) at different oxidation potentials, in other words, with different oxidizing reagents, have been systematically investigated. The oxidizing reagents considered here are hydrogen peroxide, potassium permanganate and oxygen. The oxidation and oxidative precipitation reactions were analyzed under various conditions for the determination of factors governing the removal of arsenic from solutions of two different levels of arsenic concentrations: the high concentration solution of 0.1 mol/L and the dilute solution of 0.0005 mol/L (38 mg As/L) in As. The progress of the reactions and the delicate changes in the principal reactions were clearly determined by continuous monitoring of oxidation reduction potential (ORP), amount of hydrogen ion generated or consumed in the course of the oxidation and precipitation reactions, in term of NaOH or H₂SO₄ consumption for keeping pH constant, and chemical analysis for As, Fe, Mn and S species.

2. Oxidative Precipitation of Arsenic(III) in the Presence of Iron(II,III) with Hydrogen Peroxide

Firstly, it is clearly demonstrated that As(V) is more amenable to the precipitation method using Fe(III) than As(III). When As(III) in arsenic-bearing solutions is oxidized to As(V), it is possible to effectively separate arsenic in the solution of high concentration as ferric arsenate at fairly low pH where the hydrolysis of Fe(III) does not take place, and also to remove arsenic in the extremely dilute solution to a sufficiently low level less than that of the arsenic regulation (0.1 mg/L) for waste water, at Fe(III)/As mole ratio as small as 5 in a wide pH region from low pH of 3.5. Secondly, the oxidation of As(III) with hydrogen peroxide proceeds readily in the alkaline solution, but slowly in the acidic solution. The oxidation of As(III) in the acidic solution is promoted to some extent by a rise in temperature and an increase in the concentration of H₂O₂, but is not sensitive to the concentration of As(V). In the presence of Fe(II,III) ions, H₂O₂ in the acidic solution can act as a more powerful oxidizing agent to As(III) even at ambient temperature due to the catalysis of Fe(II, III) ions through the reactions with H₂O₂. It is interesting that the dissolved oxygen can positively contribute to the oxidation of As(III) in the coexistence of H₂O₂ and Fe(II). The possible reaction path for the oxidation of As(III) in the system is discussed. By use of H₂O₂ in the presence of Fe(II) or Fe(III), As(III) in the acidic solution of high concentration is oxidized to As(V) and precipitated as ferric arsenate over a fairly low pH region where hydrolysis of ferric ion is not yet detected. As(III) in its dilute solution can be removed to a sufficiently low concentration below 0.1 mg As/L by the oxidative precipitation with H₂O₂ at Fe/As mole ratio of 5. The favorable pH range is between 3.5 and 5.0 for Fe(II)-added solution and between 2.5 to 3.0 when Fe(III) is added. Hydrogen peroxide coupled with Fe(II) or with aid of Fe(III) staying in the solution provides adequate oxidizing power to eliminate arsenic from the aqueous solutions without hydrolysis of the coexisting metal ions.

3. Oxidative Precipitation of Manganese(II), Iron(II) and Arsenic(III) with Potassium Permanganate

The oxidation and oxidative precipitation reactions in the solutions of (1) Mn(II), (2) Mn(II)-As(V), (3) Mn(II)-As(V)-Fe(III) and (4) Mn(II)-As(III)-Fe(II) by use of KMnO₄ as an oxidizing agent are described. In the solution of MnSO₄, KMnO₄ oxidizes Mn(II) to form MnO₂ nearly stoichiometrically even at low pH. In the

oxidation of Mn(II) in the presence of As(V), $\text{MnAsO}_4 \cdot n\text{H}_2\text{O}$ is precipitated preferentially over MnO_2 , especially in the fairly acidic solution. By the oxidative precipitation method using the Mn(II)- KMnO_4 couple, As(V) can be precipitated out in the fairly acidic solution where formation of $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ does not take place. Furthermore, the coexistence of Fe(III) gives rise to the incorporation of both Fe and Mn in the precipitate to form $(\text{Fe},\text{Mn})\text{AsO}_4 \cdot n\text{H}_2\text{O}$, which reduces the concentration of remaining As(V) to a considerably low value in a low pH range. In the oxidative precipitation of Mn(II), As(III) and Fe(II) with KMnO_4 in a low pH range, oxidation of Fe(II) is observed first and then As(III) is oxidized prior to the start of oxidation of Mn(II). The iron(III)-manganese arsenate is preferentially precipitated similarly to that in the solution of Mn(II), As(V) and Fe(III). This indicates that the use of KMnO_4 brings As with Mn(II) and Fe to the oxidative precipitation of arsenic-bearing precipitate containing both Mn and Fe, independently of the oxidation states of As and Fe in the starting solution. In this series of experiment, KMnO_4 not only acts as an oxidizing reagent for Fe(II), As(III) and Mn(II), but also provides a precipitate-forming species Mn(III). Thus, the concentrations of As and Mn remaining in the solution after the oxidative precipitation are significantly reduced at ambient temperature. Based on these observations, it is concluded that the oxidative precipitation method based on Mn(II)- KMnO_4 couple is effective in the separation and removal of arsenic from aqueous solutions at fairly lower pH than by formation of ferric arsenate and that the incorporation of both Fe and Mn in the precipitate brings the concentration of remaining arsenic to less than those with individual simple arsenates of iron and manganese.

4. Oxidation of Arsenic(III) and Sulfur(IV) with Oxygen

While As(III) is hardly oxidized to As(V) with oxygen alone under moderate conditions, it is observed that the coexistence of S(IV) favors the oxidation. In the solution containing S(IV) with As(III), the oxidation of As(III) is detected at pH above 5.0 and remarkably enhanced by a rise in pH. At pH of 9.0 a maximum oxidation rate is reached but a further rise in pH significantly lowers the oxidation reaction rate. A rise in temperature and an increase in the initial concentration of S(IV) lead to a significant acceleration of the oxidation. The addition of As(V) brings about a slightly promoted oxidation of As(III). The oxidation of S(IV) and As(III) takes place simultaneously in a complicated manner and is very sensitive to pH of solution. It is noted that As(III) can be oxidized by oxygen under the conditions where oxidation of S(IV) is favored, in other word, the oxidation of As(III) is induced by the oxidation of S(IV) and the progress of the two oxidation reactions is affected by each other. Under appropriate conditions, for instance, at pH 9, 50°C and the initial S(IV)/As(III) mole ratio of 10, the oxidation of As(III) with oxygen proceeds at a considerable rate to completion. It is clear that O_2 coupled with S(IV) can be used for the effective oxidation of As(III) in a higher pH range.

5. Oxidative Precipitation of Arsenic(III) in the Presence of Iron(II,III) and Sulfur(IV) with Oxygen

As noted previously, As(III) is hardly oxidized with oxygen coupled with S(IV), sulfite or dissolved SO_2 , in the acidic solution. However, it is found that the coexistence of S(IV) and Fe(II,III) significantly enhances the

oxidation of As(III) with oxygen at low pH. In this system, S(IV) is oxidized to S(VI) with oxygen favorably in the presence of Fe(II) or Fe(III) species, and Fe(III) is considered to play an important role as a promoter of the oxidation reaction. In the Fe(II)-added solution, the oxidation reactions of S(IV) to S(VI), Fe(II) to Fe(III) and As(III) to As(V) occur in parallel in the acidic solution. The first reaction is promoted remarkably by the second redox system in direction to oxidation and these two reactions induce the oxidation of As(III) to As(V). The oxidative precipitation of As(III) with the SO₂-O₂ gas mixture in the presence of Fe(II,III) is carried out under various conditions. Here, SO₂ is a source of S(IV) and is mixed up to 30 mL/min with O₂ stream of 500 mL/min. It is observed that SO₂ is absorbed into the solution and oxidized rapidly by oxygen, and As(III) is simultaneously oxidized at considerable rate. The resulting As(V) comes into precipitation with Fe(III) species at lower pH, and the concentration approaches the terminal values observed for the Fe(III)-As(V) solution after pH adjustment. A rise in temperature and an increase in the feed rate of SO₂ in the oxygen stream can accelerate the oxidative precipitation of As(III) with Fe(III). By using this method, arsenic in the acidic solution of high As(III) concentration can be effectively separated as amorphous scorodite FeAsO₄·2H₂O from the solution in a fairly low pH range where excess ferric ion stays in the solution. The oxidative precipitation method with O₂ also proves to be effective for the removal of arsenic in the solution of low As(III) concentration. Both sulfite salt (Na₂SO₃) and SO₂ gas can be used as the source of S(IV). Based on the present observation, some processes are proposed for the separation of arsenic in acidic leach solutions of high arsenic(III) concentration and for the removal of arsenic from effluents and waste waters of low arsenic(III) concentration.

6. Conclusions

The above-described results indicate that hydrogen peroxide coupled with Fe(II,III) species, potassium permanganate and oxygen coupled with S(IV) and Fe(III) oxidize As(III) at low pH both in the solution of high As concentration and in its dilute solution. The redox systems considered in the present work make it possible to effectively separate arsenic from the solution separately from the hydrolyzed ferric hydroxide precipitate and remove arsenic to less than the level of the arsenic regulation of 0.1 mg/L through the oxidative precipitation of As(III). By putting the redox systems, S(IV)/S(VI) and Fe(II)/Fe(III) together, the oxidation of As(III) with oxygen is significantly induced at lower pH. In view of the availability, cost, oxidation effectiveness and least possible adverse effect on the environment, the use of oxygen coupled with S(IV) is a promising method for the oxidation of As(III) and for the oxidative precipitation of As(III) in the presence of Fe(II,III).

審査結果の要旨

製錬、素材製造、使用済み材料の再生等において排水中のヒ素の処理が大きな課題とされているが、現在広く行われている水酸化鉄による共沈法では、大量のスラッジが生じ、ヒ素の挙動のコントロールも困難である。本研究は、酸性溶液中でヒ素を酸化・析出させる新プロセスの開発を目的として、 H_2O_2 、 KMnO_4 、 SO_2-O_2 混合ガスなどの各種酸化剤を用いた場合の水溶液中の3価ヒ素イオンの酸化反応とヒ素塩の析出反応を検討したもので、全編6章からなる。

第1章は序論であり、水溶液中のヒ素の化学的性質と従来の酸化、分離法について概括し、研究の背景と研究目的を述べている。

第2章では、 H_2O_2 によるAs(III)の酸化の進行について検討し、単味溶液中のAs(III)の酸化がpH、As(III)濃度および温度の上昇によって著しく加速されること、Fe(III)が共存すると酸性溶液中のAs(III)の酸化が著しく加速して、 FeAsO_4 の析出が低pHで進むことなどを明らかにしている。これは重要な知見である。

第3章では、As(III)とMn(II)が共存する溶液における KMnO_4 による酸化・析出反応について検討し、 FeAsO_4 の析出よりも低いpHにおいて MnAsO_4 の形でヒ素を除去できること、Fe(II)が共存すると(Mn, Fe)AsO₄の析出により、残留ヒ素濃度がさらに低下することなどを明らかにしている。これは実用上重要な成果である。

第4章では、 SO_3^{2-} (S(IV))と共存するAs(III)の酸素による酸化について検討し、As(III)の酸化が5よりも高いpHで進みS(IV)の酸化が進行する環境下で促進されることを示している。これは新しい知見である。

第5章では、As(III)、Fe(II, III)とS(IV)が共存する溶液中での酸素による酸化・析出反応について検討し、Fe(II)–Fe(III)系の酸化の進行とともにS(IV)の酸化が促進されること、これにより低pHでAs(III)の酸化が誘引されて、 FeAsO_4 が生成することを示している。すなわち、複数の酸化還元系を共存させることによって単一系では起こりにくい酸化反応を進めることができ、共存金属イオンが加水分解しない低いpHにおいて酸素によってヒ素を難溶性塩として除去することが可能であることを明らかにしている。

第6章は結論であり、本研究を総括している。

以上要するに本論文は、種々の条件の下でのAs(III)の酸化・析出反応の進行を明らかにし、共沈法に代わる水溶液からのヒ素の除去プロセスを検討したもので、金属工学の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。