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A study on hydrothermal disposal of sodium arsenate waste from Ga-As processing

N. YAMASAKI, F. ZHANG*
Research Laboratory of Hydrothermal Chemistry, Faculty of Science, Kochi University, 2-5-1 Akebono, Kochi 780, Japan
E-mail: Zhang@sniri.go.jp

Hydrothermal disposal of sodium arsenate waste was investigated with the aim of removing As from solution, and its precipitation as crystalline iron arsenate. The precipitate was characterized by XRD and SEM, and leach tests were conducted to examine the precipitates solubility. The optimum formation condition for crystalline iron arsenate was pH 0.3–1.7, temperature 150–200 °C, Fe/As 1.0 and time 10–40 min. Over 98% arsenic in the waste can be precipitated. The solid product is mainly iron arsenate which has a solubility below 5 mg/l. The preliminary work showed that hydrothermal disposal is a feasible option for treatment of sodium arsenate waste. © *1999 Kluwer Academic Publishers*

1. Introduction

Sodium arsenate waste is produced during Ga-As processing. Because of its high solubility and toxicity, the waste must be suitably treated without any adverse environmental impacts. Various methods have been suggested for the disposal of arsenic [1–8]. A typical treatment method for a solution containing arsenic is to make arsenic coprecipitate with iron, where lime is used as the neutralizing agent, producing bearing arsenic ferrihydrite [1, 7, 9, 10]. However, there still exists some controversy about the constitution [11, 12] and stability [13–18] of the precipitate. Consideration thermodynamic data suggests that arsenic-bearing ferrihydrite, which is a voluminous, high surface area material, immobilizes arsenic mainly by adsorption and is unstable because of its possible conversion to crystalline iron oxide phases (such as goethite). These crystalline materials have a lower specific area than that of the ferrihydrite phase, which would result in arsenic being released into solution during the transformation process [15].

Crystalline iron arsenate (scorodite) currently is considered to be an acceptable approach for final disposal of arsenic based on studies of solubility and natural arsenate minerals [13, 14]. Much work about the hydrothermal treatment of arsenical wastes has been undertaken at Imperial College, London [19]. The crystalline iron arsenate (up to 10 μm in size) has relatively low surface area which would give rise to a slow reaction rate when contacted with water. Scorodite is unlikely to undergo any significant physical or chemical changes, is the most abundant arsenate mineral in nature, and can be found in a wide range of climatic and pH regimes, which suggest that it is a suitable compound for final disposal of waste containing arsenic.

Hydrothermal process which could produce crystalline iron arsenate compounds (principally scorodite) at elevated temperature have shown potential for final disposal of arsenic [20, 21]. Baghurst *et al.* [22] have studied the hydrothermal microwave synthesis of scorodite and suggested that optimal condition is pH 1.1, temperature 130 °C, and time 20 min. Swash *et al.* [19] reported that crystalline product can be formed at temperatures higher than 175 °C, time 30 min in a solution with Fe/As 1, and considered that hydrothermal treatment can be adapted to treat a volume of arsenic-bearing solutions and solids such as flue dusts and sludge.

This paper is a study on the conditions of formation of crystalline iron arsenate and the feasibility of disposal of sodium arsenate waste by hydrothermal processing. The optimum conditions for hydrothermal treatment should be that arsenic in the waste is not only precipitated as a crystalline iron arsenate, but also that the percentage precipitated is high.

2. Experimental

The waste containing arsenic used in this experiment is sodium arsenate waste derived from the treatment of Ga-As waste. The chemical composition of the sodium arsenate waste is As 17.5%, Na 16.1%, Ga 0.2%, H_2O 50.1% and arsenic solubility 45 g/l. The autoclave used in this experiment has a liner of Hastelloy-C (volume 35 cm^{-3}), as described elsewhere (e.g. [23]).

In order to avoid the rapid formation of ferrihydrite, ferrous sulfate was used as an additive of iron. Firstly, the sodium arsenate waste, ferrous sulfate and water were stirred and mixed by magnetic agitator, to achieve a Fe : As mole ratio of 1. The initial arsenic concentrations in the slurry was in the range from 25 to 30 g/l. Hydrogen peroxide, two times the theoretical amount required for oxidation of Fe^{2+} to Fe^{3+}, was added into

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* Present address: Shikoku National Industrial Research Institute, 2217-14 Hayashi, Takamatsu, Kagawa 761-0395, Japan.

the autoclave. Sulfuric acid and sodium hydroxide were used for adjusting solution pH in this experiment. The reactants in the autoclave were heated (50 °C/min) to designed temperatures with stirring.

After treatment the samples were taken out and cooled to room temperature, and the slurry filtered. The solid products were washed in de-ionized water, and dried in an oven at 120 °C for 12 h. The phase of arsenic existed in solid product is analyzed by X-ray diffraction (XRD) and the shape and size of solid products were observed on a Scanning Electron Microscope (SEM). The content of arsenic and iron in the solutions were analyzed by ICP. Percentage of arsenic precipitated was calculated by mass balance calculations.

Leach test for the precipitate was carried out using the following procedure: 1.6 g precipitate was dispersed in 100 ml distilled water, solution pH of was adjusted with 0.5 M H_2SO_4 or 1 M NaOH solution and was checked every 12 h intervals; the solutions were analyzed by ICP.

3. Results and discussion

3.1. Influence of pH

The effect of solution pH (final solution pH after reaction) on the percentage of arsenic precipitated is showed in Fig. 1, where the other factors are constant (Fe/As 1.0, temperature 200 °C, time 60 min). No precipitate was produced at a pH lower than 0.2, but arsenic was obviously precipitated when solution pH increased to 0.3. Maximum percentage of arsenic precipitated is reached at pH 1.3, then the percentage of arsenic precipitated becomes progressively less as the pH is increased.

H_3AsO_4 is easily dissociated at higher pH, which is favorable to the precipitation of arsenic. But when pH continues to rise, especially above 2, arsenic is coprecipitated with ferrihydrite following hydrolysis. Since there is not enough surface of ferrihydrite (Fe/As only 1.0) for adsorption of arsenic, the arsenic is not adequately adsorbed and will remain in solution. The formation of ferrihydrite as a result of increasing pH results in a fall in removal rate of arsenic.

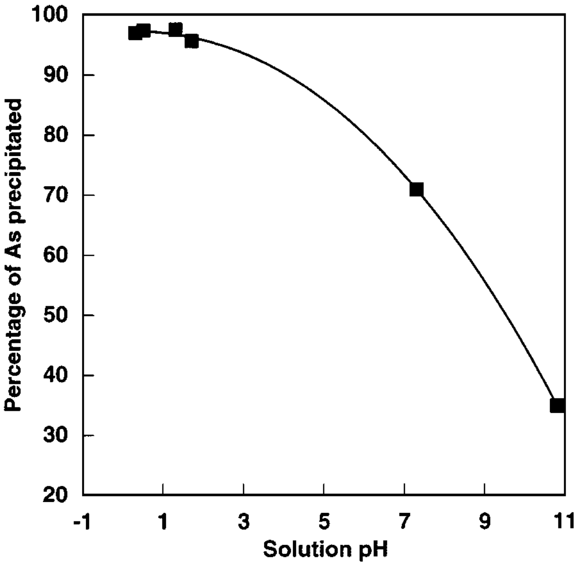

Figure 1 Percentage of arsenic precipitated as a function of solution pH. Reaction temperature 200 °C, Fe/As 1.0 and time 60 min.

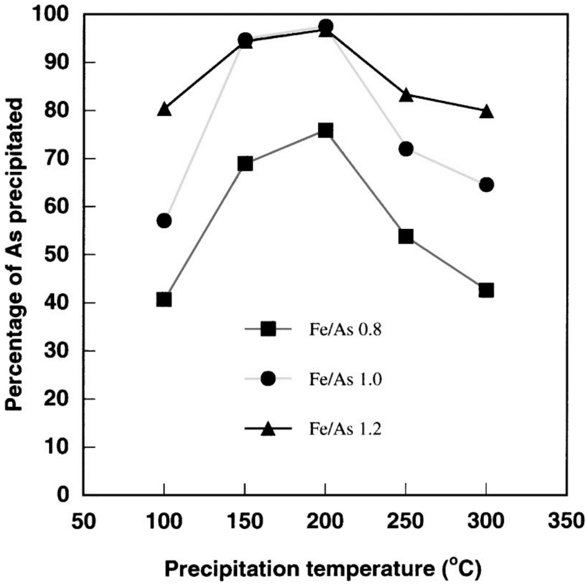

Figure 2 Effect of precipitation temperature on percentage of arsenic precipitated at different Fe/As (0.8, 1.0, 1.2). Solution pH 0.9, time 60 min.

3.2. Influence of temperature

Fig. 2 depicts the effect of precipitation temperature on percentage of arsenic precipitated at different Fe/As proportion, where the solution pH is 0.9 and the precipitation time is 60 min. It is found that temperature lower than 100 °C or higher temperature 250 °C is disadvantageous to precipitation of arsenic. Appropriate temperature for precipitation of arsenic is in the range from 150 to 200 °C. The effect of Fe/As relies on precipitation temperature. The removal rate of arsenic increases as Fe/As increases at temperature lower than 150 °C or higher than 200 °C; but when temperature is between 150 and 200 °C, solution with Fe/As 1 demonstrates the best removal effect for arsenic. Lower precipitation rate at Fe/As 0.8 is obviously due to the insufficient amount of iron; but high Fe/As (1.2) also does not result in a high precipitation ratio, this is possibly the result of chemical interference during the nucleation and growth of the scorodite crystallites, in a solutions containing relatively high concentrations of Fe^{3+}, there may exist co-precipitation of amorphous iron compounds with iron arsenate compounds at $pH > 2$ [19].

3.3. Influence of time

The relationship between precipitation time and removal rate of arsenic at temperatures 150, 200 and 250 °C is illustrated in Fig. 3, where the solution pH is fixed at 0.9 and Fe/As 1. Appropriate precipitation time relies on precipitation temperature. The arsenic can be removed more perfectly from solution at a temperature higher than 200 °C than that at a temperature lower than 150 °C. However there is an adverse tendency at 250 °C; the longer the reaction time, the lower the percentage of arsenic removed is achieved.

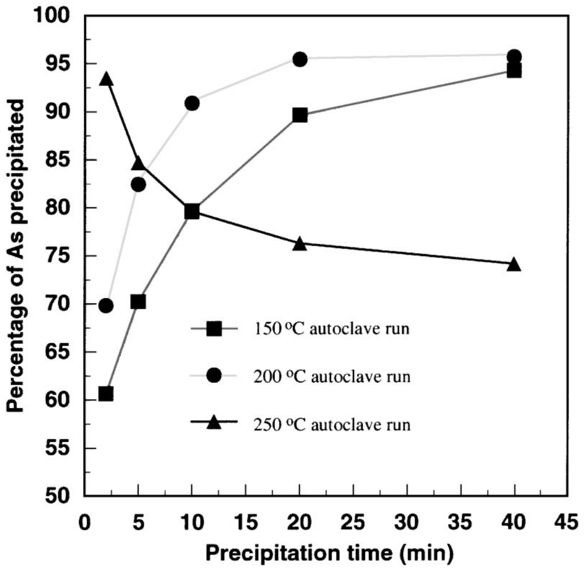

Figure 3 Relationship between reaction time and percentage of arsenic precipitated at different temperatures (150, 200, 250 °C). Solution pH 0.9, Fe/As 1.0.

3.4. Characterizations of solids

Fig. 4 displays the XRD patterns of the hydrothermal precipitate synthesized in different pH solution. The precipitates formed at pH 0.5 and 1.7 crystallized a compound comparable to the mineral scorodite ($FeAsO_4 \cdot 2H_2O$). Although there exists small amount of iron arsenate in the precipitate at pH 7.3, the main crystalline products are $Fe(OH)SO_4$ and FeOOH. As pH rises to 10.8, the main crystalline product in the precipitate is Fe_2O_3.

It is found that crystalline iron arsenate can not be formed when temperature is lower than 100 °C, Higher temperature (200 °C) could improve the crystallinity of iron arsenate. But, a new compound is formed at 250 °C, which is different from that formed at 150 and 200 °C (Fig. 5). This is the Type-2 compound $[Fe_3(AsO_4)_2(OH)_x(SO_4)_y$, where $x + 2y = 3]$ as reported by Swash and Monhemius [19]. Precipitate formed at 250 °C has a composition of Fe/As between 1.4 to 1.6 according to material balance. It is deduced that crystalline scorodite will be decomposed to another structure at temperatures between 200 and 250 °C.

The SEM micrographs indicate that the precipitate formed at low temperature (100 °C) is aggregates of colloid particles. The precipitate occurs as disperse fine particles when precipitation temperature is higher than 150 °C. The disperse particles get coarser at 200 °C. But the particles adversely become finer and are near spherical at 250 °C (Fig. 6).

XRD patterns reveal that temperatures higher than 100 °C are necessary for the formation of crystalline iron arsenate. When temperature is lower than 100 °C, arsenic is precipitated mainly adsorbed on ferrihydrite as described in reaction (1).

$$mFe^{3+} + nOH^- + xAsO_4^{3-} \longrightarrow Fe_m(OH)_n \cdot xAsO_4^{3-} \downarrow \qquad (1)$$

In order to provide sufficient surface of ferrihydrite for adsorption of arsenic, the molar Fe/As ratio must be above 3 [9].

As temperature rises to 150 °C, arsenic precipitates as crystalline iron arsenate (principally $FeAsO_4 \cdot 2H_2O$) as described in reaction (2). The higher the temperature, the more rapidly the gelation precursor of iron arsenate is formed, which may be the cause of the percentage of arsenic removed increases as temperature increases from 100 to 200 °C.

$$2AsO_4^{3-} + 2Fe^{2+} + H_2O_2 + 2H_2^+ \longrightarrow 2FeAsO_4 \cdot 2H_2O \downarrow \qquad (2)$$

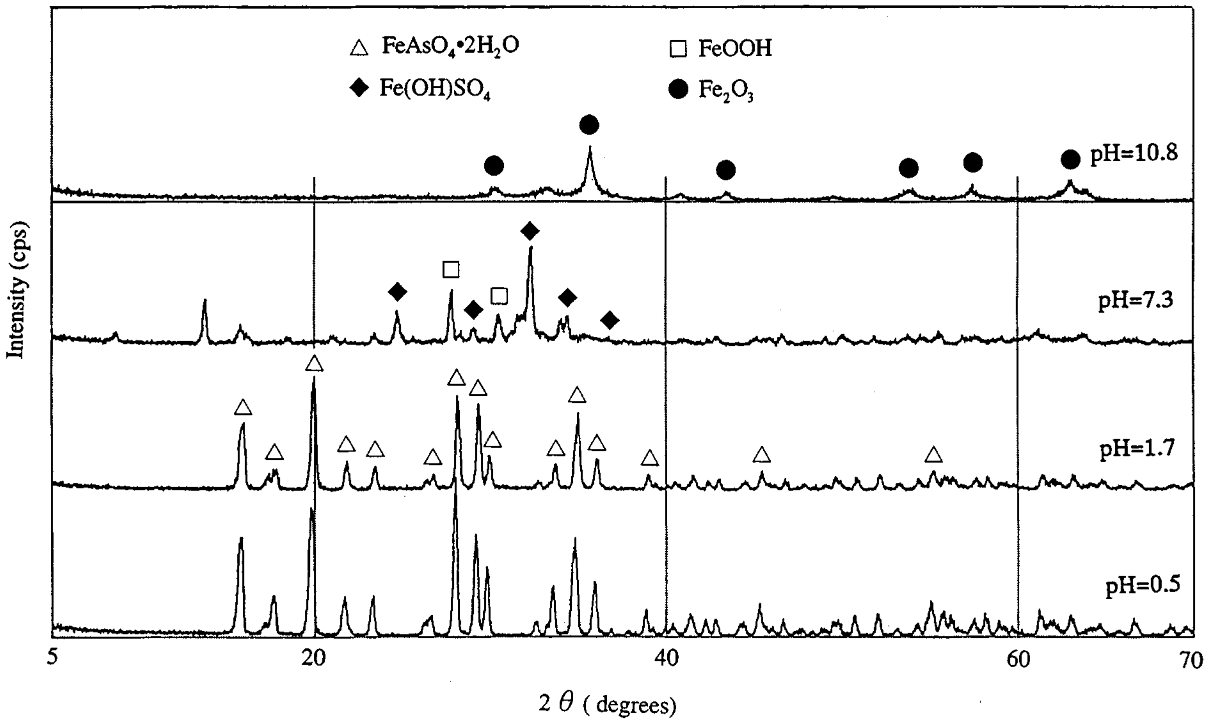

Figure 4 X-ray diffraction patterns of precipitates produced at different solution pHs. Reaction temperature 200 °C, Fe/As 1.0, and time 60 min.

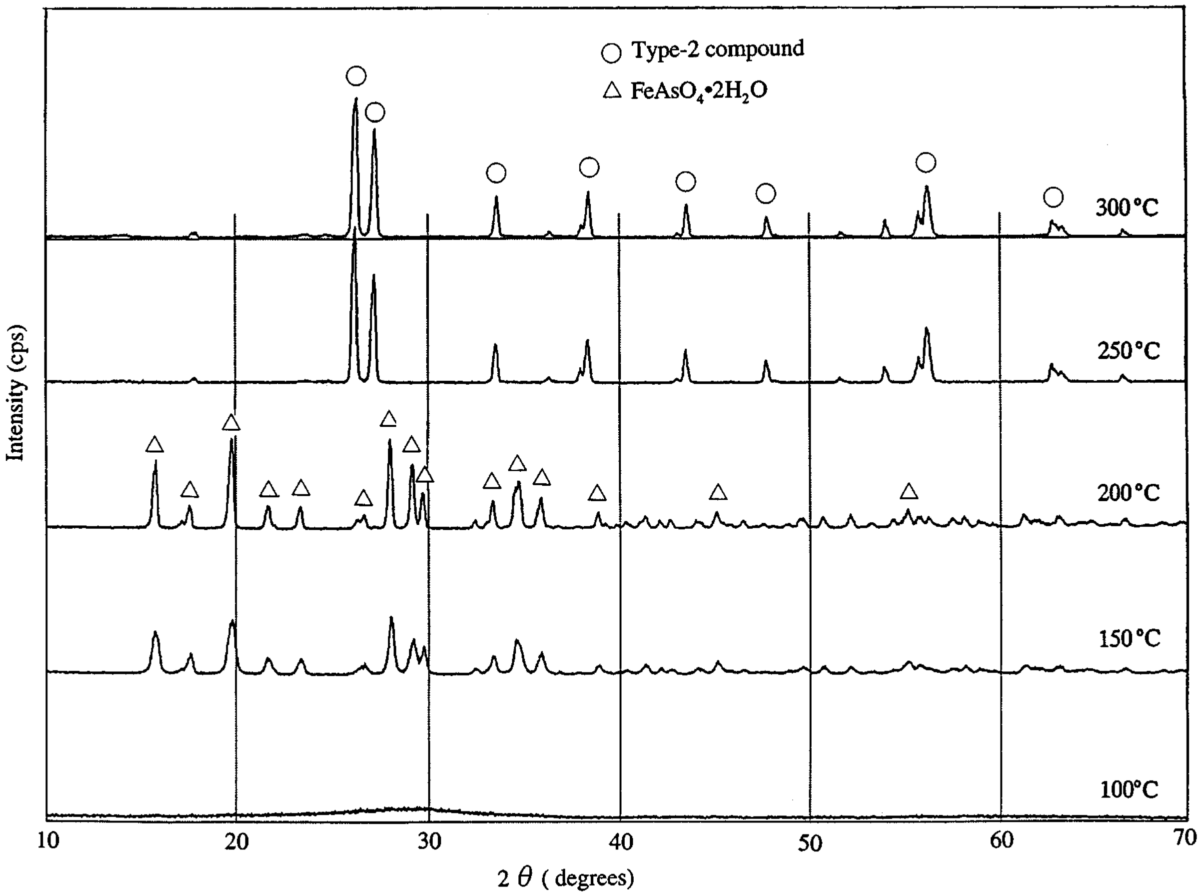

Figure 5 X-ray diffraction patterns of precipitates produced at different temperatures. Reaction time 60 min, Fe/As 1.0 and solution pH 0.9.

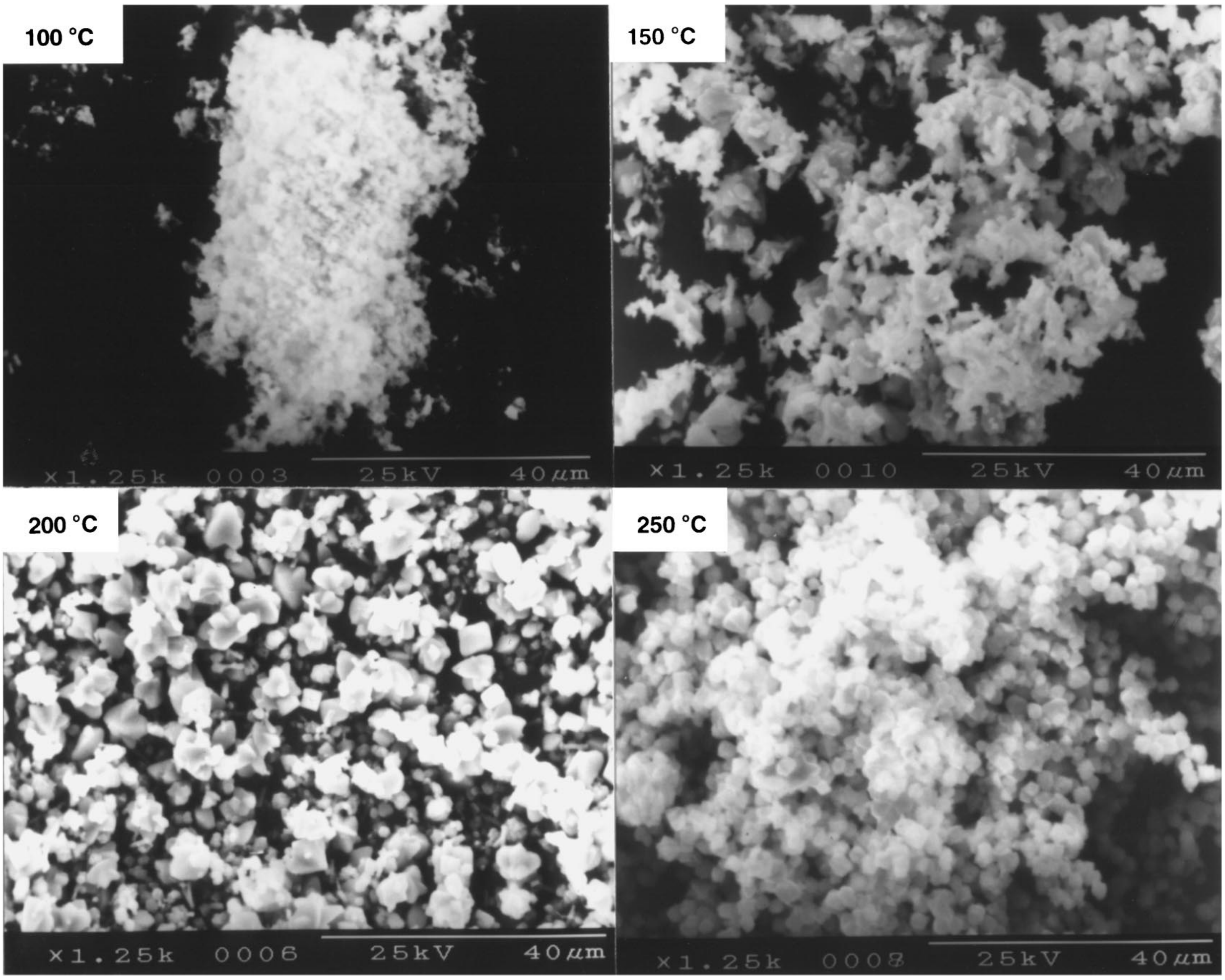

Figure 6 SEM microphotographs of precipitates produced at different temperatures. Reaction time 60 min, Fe/As 1.0 and solution pH 1.3.

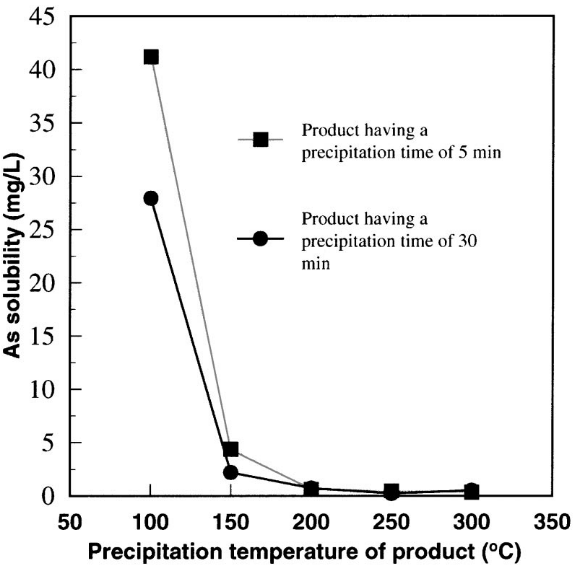

Figure 7 Effect of precipitation temperature on solubility of precipitate. pH 1.3, Fe/As 1.0.

There is possibly a transformation of scorodite to Type-2 compound when temperature is between 200 and 250 °C, as shown in Fig. 5, which would result in releasing of arsenic into solution again (reaction (3)).

$$3FeAsO_4 \cdot 2H_2O + ySO_4^{2-} + xOH^- \longrightarrow Fe_3(AsO_4)_2(OH)_x(SO_4)_y \downarrow + AsO_4^{3-} + 6H_2O \quad (3)$$

Reaction (3) is consistently supported by experiment results, where the percentage of arsenic removed is lower at temperature 250 °C than that at temperature 200 °C (Fig. 2), percentage of arsenic removed at temperature 250 °C decreases as increasement of reaction time (Fig. 3).

Whether the arsenic precipitates as crystalline iron arsenate or not also depends on solution pH. Crystalline iron arsenate can be formed only in the acid solution. As pH increases, the crystalline products are mainly iron compounds which is $Fe(OH)SO_4$ and FeOOH (pH 7.3), and Fe_2O_3 (pH 10.8); arsenic is removal in the form of amorphous absorption on the surface of iron compounds (Fig. 4).

3.5. Optimum processing conditions

Based on the above results, optimum hydrothermal condition for treatment of sodium arsenate waste can be obtained, which is a solution pH 1.3, Fe/As 1.0, temperature 150–200 °C and time 10–40 min. Table I summarizes the disposal result of sodium arsenate waste under the condition. After hydrothermal reaction, over 98% of arsenic in the waste can be removed, the concentration of arsenic remaining in solution is lower than 0.5 g/l. A secondary ambient neutralization precipitation may be required to treat the arsenic remaining in solution, but the sludge from ambient precipitation can be return back to hydrothermal process, whole arsenic in sodium arsenate waste can be disposed and discharged as stable crystalline iron arsenate. Ongoingly, future investigation will focus on the industrial application of combining hydrothermal and ambient neutralization precipitation.

TABLE I Hydrothermal precipitation conditions and results of the treatment of sodium arsenate waste

Temperature (°C)	200	180
Time (min)	10	20
Percentage of As precipitated (%)	98.6	98.9
Concentration of As remaining in solution (g/l)	0.42	0.31

Note: pH 1.3, Fe/As 1.0, starting As concentration 30 g/l.

TABLE II Arsenic solubility for precipitated product at different pHs

Solution pH	1	2	3	4	5	6	7	7.5	8	9
As solubility (mg/l)	3.2	2.2	1.4	1.2	2.1	2.7	4.2	4.8	17	83

3.6. Solubility of arsenic in precipitate

Leach test concerning the effect of precipitation temperature on the solubility of precipitation product was conducted in a solution with pH 2.5 for 96 h. The precipitates are produced at a hydrothermal condition: pH 1.3, Fe/As 1.0, time 30 min. Fig. 5 demonstrates that precipitation temperature can improve the stability of the precipitates. The solubility decreases sharply when precipitation temperature rises from 100 to 150 °C. The precipitate produced at above 150 °C has a low solubility of arsenic which does not exceed 5 mg/l.

Solubility results at different pH for 120 h are presented in Table II. The precipitate tested is the hydrothermal product at temperature 200 °C, pH 1.3, Fe/As 1.0, time 30 min. The stable pH region (As $<$ 5 mg/l) is extended to more acid condition (pH 1–7.5), comparing to that (pH 3–8) of residue from ambient temperature precipitation [9]. The product has a higher solubility ($>$5 mg/l) in alkaline solution (pH $\geq$ 8), this is consistent with the solubility tendency of precipitate obtained at ambient temperature, which also has high solubility in alkaline solution.

4. Conclusions

Crystalline iron arsenate can be formed by hydrothermal treatment of slurries with pH 0.3–1.7 and Fe/As lower than 1 at 150–200 °C for 10–40 min, the arsenical precipitate has low solubility and is therefore inferred to be relatively stable under environmental conditions (pH 4–7). Hydrothermal treatment of sodium arsenate waste does appear to be a feasible option with the formation of a crystalline iron arsenate.

References

1. R. G. ROBIN, J. Y. HUANG, T. NISHIMURA and G. H. KHOE, in "Arsenic Metallurgy Fundamentals and Applications," edited by R. G. Reddy, J. L. Hendrix and P. B. Queneau (TMS publication, Phoenix, 1988) p. 99.
2. T. M. DOUGLAS, *Environmental Progress* **2** (1987) 82.
3. R. J. BOWELL, *Applied Geochemistry*, **9** (1994) 279.
4. C. P. HUNG and P. L. K. FU, *J. Water Pollution Control Fed.* **56** (1984) 233.

5. D. EVAN, I. SOCRATES and P. GEORGE, *Water Resources* **12** (1993) 1773.
6. A. I. ZOUBOULIS, K. A. KYDROS and K. A. MATIS, *Separation Science and Technology* **15/16** (1993) 2449.
7. M. M. GLOSH and J. R. YUAN, *Environmental Progress* **8** (1987) 150.
8. M. CHANDA, K. F. ODRISCOLL and G. L. REMPEL, *Reactive Polymers*, **7** (1988) 251.
9. N. PAPASSIOPI, E. VIRCIKOVA, V. NENOV, A. KONTOPOULOS and L. MOLNAR, *Hydrometallurgy* **41** (1996) 243.
10. V. NENOV, A. I. ZOUBOULIS, N. DIMITROVA and I. DOBREVSKY, *Environ. Pollution* **83** (1994) 283.
11. J. BARRETT, M. N. HUGHES, A. N. ISLAM and C. SIMONS, "Randol Gold Forum" (Cairns, Australia, 1991) p. 179.
12. S. THERDKIATTIKUL and D. A. DAHLSTROM, "Randol Gold Forum" (Beaver, Creek, Colorado, 1993) p. 373.
13. E. VIRCIKOVA, L. MOLNAR and P. LECH, *Hydrometallurgy* **38** (1993) 111.
14. N. PAPASSIOPI, M. STEFANAKIS and A. KONTOPOULOS, EMC'94, 1994, p. 203.
15. R. G. ROBINS, *Metall. Trans.* **12B** (1981) 103.
16. T. NISHIMURA, C. T. ITO and K. TOZAWA, in "Arsenic Metallurgy Fundamentals and Applications," edited by R. G. Reddy, J. L. Hendrix and P. B. Queneau, (TMS publication, Phoenix, 1988) p. 321.
17. G. B. HARRIS and S. MONETTE, in "Arsenic Metallurgy Fundamentals and Applications," edited by R. G. Reddy, J. L. Hendrix and P. B. Queneau, (TMS publication, Phoenix, 1988) p. 469.
18. M. T. EMETT and G. H. KHOE, in EPD Congress 1994, edited by G. Warren, (TMS Publication, 1994) p. 153.
19. P. M. SWASH and A. J. MONHEMIUS, Hydrometallurgy '94, 1994.
20. N. YAMASAKI and FARAO ZHANG, in Proceedings of the Second International Conference on Solvothermal Reactions, Organizing Committee Ed., Takamatsu, Japan, 1996, p. 122.
21. R. S. KUNTER and W. E. BEDAL, *J. Mineral and Metal Society* **44** (1992) 35.
22. D. V. BAGHURST, J. BARRETT and D. M. P. MINGOS, *J. Chem. Soc., Chem. Commun.* **3** (1995) 323.
23. N. YAMASAKI, in "Hydrothermal Science Handbook," 1st ed. (Editing committee of Hydrothermal Science Handbook, Ed., Tokyo, 1997) p. 227.

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