Completely treating heavy metal laboratory waste liquid by an improved ferrite process

Jie-Chung Lou *, Chien-Kuei Chang

Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, Len-Hai Road No. 70, Kaohsiung 80424, Taiwan

Abstract

This work proposes a scheme for completely treating heavy metal laboratory waste liquid. Ten common heavy metals and various anions were adopted to synthesize the simulated laboratory waste liquid. Experimental results demonstrated that although conventional ferrite process (FP) could not be used to treat the simulated waste liquid completely, the enhanced FP, i.e., the extended reaction ferrite process (ERFP), could be used to satisfy regulatory limits. FeSO₄ can be added in the extended stage of ERFP intermittently rather than continuously. Elutriation was conducted to reduce the cost of ERFP and ensure that the sludge met toxicity characteristic leaching procedure (TCLP) standards. The pH of the elutriation liquid should be greater than 2.88. This work also establishes that FP or ERFP can be applied directly to treat dichromate and permanganate without a prior reduction step.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Laboratory waste liquid; Improved ferrite process; Elutriation; Heavy metal

1. Introduction

Laboratory waste liquid (LWL) refers to liquid waste generated in experiments performed for educational purposes, research and examinations. The amount of LWL is minute, explaining why it must be either collected over extended periods or derived from various sources to obtain an appropriately operational amount. Therefore, LWL is highly complex and varied. Treating LWL is more difficult than treating either industrial waste liquid or wastewater owing to the inability to identify its constituents.

Classified collection is critical to reducing the complexity of LWL. “Heavy metal laboratory waste liquid (HMLWL)” is classified as such because it contains hazardous metals. These cannot be eliminated by either physical or chemical means; at best, they can merely be stabilized. According to the environmental laws of Taiwan, the effluent may be discharged into a public water body only when it fulfills effluent standards, and sludge can be discharged into a landfill when it fulfills toxicity characteristic leaching procedure (TCLP) standards. A treatment procedure must satisfy these two conditions before it can be deemed to be “complete”.

Conventional technologies for treating heavy metals in solution are based on chemical precipitation. Hydroxide, carbonate and sulfide precipitations are the most common methods. The sludge generated by chemical precipitation has a loose structure, precipitates slowly, difficult to be filtered, and dissolves easily in acid. Hence, it must be further solidified before it can be deposited in a landfill. However, solidification increases the volume of a landfill by a large factor. It is particularly wasteful in areas where landfills are scarce.

The ferrite process (FP), which is employed currently in Japan, is another effective technique [1–4]. FP has many advantages over chemical precipitation methods. It can be applied directly to treat anions that contain heavy metals, such as Cr₂O₇²⁻, CrO₄²⁻, MnO₄⁻ and others. It can simultaneously remove various heavy metals, and the remaining concentration is extremely low. The sludge produced from this process is compact and easy to be separated and it also fulfills TCLP standards without further solidification.

FP was originally developed to produce magnetite (Fe₃O₄) by wet-synthesis. The reaction equation is as follows:

\[
3\text{Fe}^{2+} + 6\text{OH}^- + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{O} \quad \text{(1)}
\]
The reaction equation becomes Eq. (2) when the solution contains other metal ions (for example with divalent cations):

\[ xM^{2+} + (3 - x)Fe^{2+} + 6OH^- + \frac{1}{2}O_2 \to M_xFe_{3-x}O_4 + 3H_2O \]

(2)

Treating heavy metal wastewater by FP involves the reaction of Eq. (2) by inserting heavy metal ions into the spinel structure formed from iron and oxygen.

Various studies indicated that three important factors determine the performance of FP [5–7]. First, the range of commonly used pH is 9–11 because FP must be conducted under basic conditions. Second, the reaction temperature must exceed 70 °C to ensure that the spinel crystal of ferrite is large and includes no other mixed crystal phase. Third, the dosage of Fe^{2+} is typically 5–10 times the total metal content to ensure the quality of ferrite. Aeration was used to provide oxygen for chemical oxidation. It has ascertained that the air supply rate of 1 L/min is enough to support the reaction by previous research [8].

As well as offering the advantages elucidated above, the FP-treated sludge is stable and exhibits soft magnetism; it can be recycled as a magnetic material, such as used in blind guide bricks, magnetic symbols and electric wave absorbents. Also, it can be resourced as catalyst to treat isopropyl alcohol and carbon monoxide in waste gas [9]. Accordingly, this approach has great potential. FP will interfere with chelating agent. This problem has been solved by Fenton method [10].

This work develops a procedure for completely treating HMLWL that improves upon the FP. Although various past studies have claimed that FP can be adopted to treat heavy metal-containing wastewater, all treatment targets have simple compositions and low concentration, and exist only in the liquid phase [11–15]. HMLWL is obviously more complex than such wastewater. Its composition is difficult to anticipate, and heavy metal precipitates or complex compounds may be present. Although Tamura [1] reported the treatment of HMLWL by FP, they considered only the effluent. Therefore, whether FP can be adopted to treat completely HMLWL must be verified. Besides, to establish an assistant procedure to improve treatment efficiency of FP is worthy.

2. Materials and methods

2.1. Preparing simulated laboratory waste liquid

This study attempts to develop a procedure for effectively treating almost all HMLWL, hence an extremely difficult treating target-simulated waste liquid was designed. The total concentration of heavy metals of the simulated waste liquid is 0.02 M. It contains 10 heavy metals—Cd, Pb, Cu, Cr, Zn, Ag, Hg, Ni, Sn and Mn, each at a concentration of 0.002 M. Various anions are adopted to elucidate their interactions (precipitation, complexation, redox and others). Table 1 presents the chemicals that were used. The 0.1 M solution of each heavy metal reagent was prepared in advance; 20 mL was mixed with each of the other solutions. Then, the mixture was diluted to 1 L by adding deionized water. K₂Cr₂O₇ and KMnO₄, which are highly toxic and often used in laboratories, were adopted as sources of Cr and Mn. These two compounds must be reduced before the heavy metals can be placed into the spinel structure of ferrite. Therefore, they can be used to test the reductive power of FP.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chemical</th>
<th>Metal</th>
<th>Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>Cd(NO₃)₂·4H₂O</td>
<td>Ag</td>
<td>AgNO₃</td>
</tr>
<tr>
<td>Cu</td>
<td>CuSO₄·5H₂O</td>
<td>Hg</td>
<td>Hg(NO₃)₂</td>
</tr>
<tr>
<td>Pb</td>
<td>Pb(NO₃)₂</td>
<td>Ni</td>
<td>NiSO₄·6H₂O</td>
</tr>
<tr>
<td>Cr</td>
<td>K₂Cr₂O₇</td>
<td>Sn</td>
<td>SnCl₂·2H₂O</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn(NO₃)₂·6H₂O</td>
<td>Mn</td>
<td>KMnO₄</td>
</tr>
</tbody>
</table>

2.2. Analytical methods and instruments

Heavy metal concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (ELAN5000, Perkin-Elmer, Germany). Although the TCLP test corresponded to the regulations on methods allowed the Environmental Protection Administration of the Republic of China (NIEA R201.13C), the volume of the sludge was modified. The extraction agent was prepared by adding 5.7 mL of glacial acetic acid and 64.3 mL of 1 M NaOH to a 1 L volumetric flask that contained 500 mL deionized water; then, the solution was diluted to 1 L by adding deionized water. The pH of the extraction agent was 4.93 ± 0.05 and it should be checked before testing. About 4 g of dry sludge was placed in a 100 mL extraction bottle, and 80 g of extraction agent was added. The extraction bottle was placed on the rotator and the bottle rotated at a frequency of 30 ± 2 rpm for 18 ± 2 h. Following this procedure, the concentration of the heavy metals in the extraction liquid was measured.

2.3. Reaction equipment

The FP reactor is a 2 L stainless steel tank. The temperature of the system is automatically controlled and a pH monitor is used. An agitator is used to mix the solution thoroughly. An air supply tube provides oxygen to the reaction from the bottom of the reactor. The maximum air supply rate is 4 L/min. The pH value is maintained in the range ±0.2 by adding NaOH or HNO₃.

2.4. Treating HMLWL by conventional FP

About 1 L of the simulated waste liquid was poured into the reactor. FeSO₄ was added, the solution was agitated and it was mixed uniformly. The pH of the solution was adjusted in advance by adding NaOH or HNO₃; then, heat the solution to the preset reaction temperature. Next, air was supplied and the reaction was timed. Reaction times of 20, 40, 60, 80 and 120 min were used separately. The solution was filtered after it was cooled. The sludge was dried in an oven at 105 °C. The concentration of each heavy metal in the filtered liquid was analyzed and, finally, TCLP was applied to the sludge.
A full-factorial experiment is performed to determine the efficiency of conventional FP. Twenty-seven reaction conditions with the following levels of factors are used: pH 9, 10, 11; temperature 70, 80, 90°C; dosage of FeSO₄ 0.1, 0.14, 0.2 mol; air supply rate 3 L/min.

2.5. Treating HMLWL by ERFP

The extended reaction ferrite process (ERFP) comprises two stages. The initial stage is similar to a conventional FP, but it is followed by an extended stage. In this work, the conditions of the initial stage are: dosage of FeSO₄ 0.2 mol, pH 9, temperature 90°C, air supply rate 3 L/min and reaction time 40 min. Apart from the manner in which FeSO₄ is added, the conditions of the extended stage are the same as those of the initial stage. In the extended stage, a 1 M solution of FeSO₄ is added to the reaction system. The adding of FeSO₄ is separated into two ways—continuous dosing and intermittent dosing. In continuous dosing, the FeSO₄ solution was delivered using a peristaltic pump at fixed rates of 2, 5 and 10 mL/min. In intermittent dosing, a pipette was used to add instantly the FeSO₄ solution at a fixed frequency, as follows: (1) 2 mL FeSO₄ solution was added at 1 min intervals, (2) 10 mL FeSO₄ solution was added at 5 min intervals, (3) 20 mL FeSO₄ solution was added at 5 min intervals. Following the extended stage, the temperature was maintained and the air supplied for 40 min to ensure that the ferrite was mature enough. Every experiment was repeated three times.

2.6. Treating sludge by elutriation

The 5.7 mL glacial acetic acid was placed into a 1 L volumetric flask; adding 1 L of deionized water, and the pH was adjusted by adding HNO₃ or NaOH yielded the elutriation liquid at pH 2, 2.88, 4 and 4.93. Some of the sludge that had already been generated in conventional FP was mixed thoroughly before further use. The 10 g of mixed sludge was placed in a 500 mL bottle, to which 400 mL of the elutriation liquid was added. Five bottles were prepared for each pH, and then put the bottles in a shaker. Following 0.5, 1, 2, 6 and 18 h of shaking, samples were obtained; the concentration of each heavy metal in the elutriation liquid was analyzed, and the sludge underwent TCLP. Every experiment was repeated three times.

3. Results and discussions

3.1. Treating HMLWL by conventional FP

This work examined 27 reaction conditions for conventional FP, covering reasonable operating ranges. In none of the 27 sets was the simulated waste liquid treated completely. Tables 2 and 3 summarize representative data obtained from these experiments. Most samples of the filtered liquid are qualified. A few filtered liquid is unsatisfactory because the concentration of Cd or Hg slightly exceeds the effluent standards. Any qualified reaction condition set can be adopted or this problem can be solved by adding an ion exchange unit. The difficulty concerns the sludge.

2.5. Treating HMLWL by ERFP

The extended reaction ferrite process (ERFP) comprises two stages. The initial stage is similar to a conventional FP, but it is followed by an extended stage. In this work, the conditions of the initial stage are: dosage of FeSO₄ 0.2 mol, pH 9, temperature 90°C, air supply rate 3 L/min and reaction time 40 min. Apart from the manner in which FeSO₄ is added, the conditions of the extended stage are the same as those of the initial stage. In the extended stage, a 1 M solution of FeSO₄ is added to the reaction system. The adding of FeSO₄ is separated into two ways—continuous dosing and intermittent dosing. In continuous dosing, the FeSO₄ solution was delivered using a peristaltic pump at fixed rates of 2, 5 and 10 mL/min. In intermittent dosing, a pipette was used to add instantly the FeSO₄ solution at a fixed frequency, as follows: (1) 2 mL FeSO₄ solution was added at 1 min intervals, (2) 10 mL FeSO₄ solution was added at 5 min intervals, (3) 20 mL FeSO₄ solution was added at 5 min intervals. Following the extended stage, the temperature was maintained and the air supplied for 40 min to ensure that the ferrite was mature enough. Every experiment was repeated three times.

3. Results and discussions

3.1. Treating HMLWL by conventional FP

This work examined 27 reaction conditions for conventional FP, covering reasonable operating ranges. In none of the 27 sets was the simulated waste liquid treated completely. Tables 2 and 3 summarize representative data obtained from these experiments. Most samples of the filtered liquid are qualified. A few filtered liquid is unsatisfactory because the concentration of Cd or Hg slightly exceeds the effluent standards. Any qualified reaction condition set can be adopted or this problem can be solved by adding an ion exchange unit. The difficulty concerns the sludge.
All samples of the TCLP are unqualified because of Cd, Pb and Cu. Their extracted concentrations significantly exceed the allowed values, but those of the other heavy metals do not. Therefore, the claim of Tamaura [1] that the FP can be utilized to treat all heavy metals simultaneously does not hold in the light of current Taiwanese environmental laws, because the claim neglects the quality of the sludge. The main benefit of FP is that the quality of the sludge it produces satisfies legal environmental standards, reducing the costs of solidification and landfill treatment. In Taiwan, unless FP can be improved to increase the quality of the sludge, it will no longer be applied because it is more expensive than the precipitation procedure.

Further analyzing the TCLP data of the sludge formed over various reaction periods reveals that the quality of the sludge does not alter after 40 min. Using Cd, Pb and Cu as examples, Fig. 1 reveals that increasing the reaction time does not improve the quality of the sludge.

Kiyama [5] indicated that the first step in forming the heavy metal into the spinel structure of ferrite is to form M(OH)+ (with a divalent metal, for example). FP must be conducted under basic conditions, under which the most of precipitates are metal hydroxide, which must be dissociated before it can be treated. FP can extract heavy metals from the liquid phase to yield the solid of ferrite and to reduce the concentration of M(OH)+ in the liquid phase. Chemical balance causes the dissociation of metal hydroxide precipitate. Based on a similar principle, FP also causes the dissolution of non-metal hydroxide precipitates. Accordingly, FP can also treat them effectively.

Conventional FP adds all FeSO4 immediately before reaction. Thus, the concentration of Fe2+ falls rapidly with time. The mechanism that promotes heavy metal precipitate dissociation then terminates. Therefore, increasing the reaction time is ineffective.

3.2. Treating HMLWL by ERFP

ERFP is based on adding Fe2+ as necessary to sustain a continuous reaction. The result of so doing shows that the sludge following a suitable ERFP comprehensively satisfies the relevant standards.

Fig. 2 compares the effects of continuous dosing ERFP at various rates of addition of Fe2+. Experimental results reveal that addition rates of 5 and 10 mL/min can effectively improve the quality of sludge. The rate of addition of 2 mL/min was found to yield the lowest efficiency. The amount of Fe2+ added at a rate of 2 mL/min for a reaction time of 300 min is the same as that added at 5 mL/min for a reaction time of 120 min, but the effects differ considerably. This finding demonstrates that, in this reaction system, FP offers better treatment efficiency as the concentration of Fe2+ is increased. Only a high concentration of Fe2+ can reduce the concentration of M(OH)+ in the liquid phase sufficiently to make the precipitates dissolve quickly. Fig. 3 shows the comparison of treatment efficiency of four different dosing modes. Intermittent dosing is more effective than continuous dosing. Continuous dosing can be regarded as intermittent dosing with an infinitesimal interval. Fig. 3 shows that continuous dosing offers the worst performance. The treatment efficiency of intermittent dosing with mode (3) (10 mL FeSO4 solution once every 5 min) exceeds that of mode (2) (2 mL FeSO4 solution once every minute). Accordingly, the extended stage yields better-quality sludge when the dose of Fe2+ is larger and the interval is longer for a particular total amount of Fe2+. This finding establishes again that if the transient concentration of Fe2+ is high enough, then the treatment efficiency of extended stage will be high. By comparing the results of modes (3) and (4) of Fig. 3, it reveals that increas-
Fig. 3. Treatment efficiency of (a) Cd, (b) Pb, and (c) Cu by four FeSO₄ adding modes: (1) continuous dosing, 2 mL/min; (2) intermittent dosing, 2 mL FeSO₄ solution once at 1-min interval; (3) intermittent dosing, 10 mL FeSO₄ solution once at 5-min interval; (4) intermittent dosing, 20 mL FeSO₄ solution once at 5-min interval.

The dosage in mode (4) is double that in mode (3), but the effectiveness of the treatment is only slightly stronger. The cost of FeSO₄ represents most of the expense of ERFP. The performance of unit FeSO₄ is maximized by the intermittent dosing—by adding 10 mL FeSO₄ solution at 5 min intervals, throughout the 80 min of the reaction.

The FP is capable of reducing hexavalent chromium and permanganate because there is no unqualified record of Cr or Mn in all experiments of this work. This function represents an advantage of FP because chemical precipitation cannot be applied to treat these metals directly.

3.3. Treating unqualified sludge by elutriation

Although the results herein showed that extending FP without limit would enable all heavy metals to be completely treated, the economic benefit of ERFP would be lost. Moreover, LWL is very complex and variable, so a fixed process cannot be guaranteed to treat all HMLWL completely, and unqualified sludge will probably be present. A further strategy must be studied to treat the general unqualified sludge.

Some of the sludge that had been generated in earlier conventional FP experiments was mixed thoroughly to simulate unqualified sludge. This work uses elutriation to wash out the easily dissolved components of the sediment, ensuring that the sludge satisfies TCLP standards. Four pH values (2, 2.88, 4 and 4.93) of the elutriation liquid were used. The experimental results show that the elutriation liquid at any of these four pH values can dissolve the rest of the heavy metals, enabling the sludge to meet TCLP standards. Less time is required as the pH of the elutriation liquid decreases. Heavy metal precipitates have various physical or chemical characteristics, and so exhibit various behaviors during elutriation. For example, the very small dissociation constant of Cd causes it to exist in the form of Cd(OH)₂ [11]. Fig. 4(a) shows that the Cd that is not captured in the ferrite will almost completely be dissolved after 0.5 h of elutriation. Fig. 4(b) indicates that the Pb requires more time for elutriation. A part of Pb should exist in non-hydroxide form in the sediment. The most likely form is PbSO₄ because high concentration of SO₄²⁻ ion is present in the reaction solution of FP. Fig. 4(c) shows that the Cu exhibits in a similar characteristic to that of Pb. Some studies have demonstrated that CuO and Cu₂O are the main forms of non-ferrite Cu in the sediments [15,16].

Fig. 4. Sludge’s TCLP extracted concentration vs. elutriation time: (a) Cd, (b) Pb, and (c) Cu.
charged to ensure that it is harmless. Fig. 6 presents a suggested FP should be treated using an ion exchange unit before it is dis- be more discreet attitude toward environment. The effluent from liquid of FP or ERFP can meet the effluent standards, we should contains concentrated heavy metals. It should be returned to FP and an elutriation time of 6 h. We therefore recommend an operating pH from 2.88 to 4 acid is used without a buffer and the sludge formed by FP makes the solution alkaline, an elutriation liquid pH of 4.93 is not fea-
ible. When strong acid is used without a buffer and the sludge formed by FP makes the solution alkaline, an elutriation liquid pH of 4.93 is not feasible. We therefore recommend an operating pH from 2.88 to 4 and an elutriation time of 6 h.

The waste elutriation liquid cannot be discharged because it contains concentrated heavy metals. It should be returned to FP to be treated. Though experiment result shows that the filtrated liquid of FP or ERFP can meet the effluent standards, we should be more discreet attitude toward environment. The effluent from FP should be treated using an ion exchange unit before it is discharged to ensure that it is harmless. Fig. 6 presents a suggested flowchart for the treatment of HMLWL.

4. Conclusions
ERFP effectively improves the efficiency of conventional FP. ERFP is required to treat large amounts of Cd, Pb or Cu to form ferrite. If the amounts of Cd, Pb and Cu are small, then the LWL can be treated with just a short extended stage, or even conventional FP only. This work verified that $\text{Cr}_2\text{O}_7^{2-}$, $\text{CrO}_4^{2-}$ and $\text{MnO}_4^{-}$ can be directly treated and need not be reduced beforehand. Elutriation is an effective approach for ensuring the quality of the sludge at reasonable cost. Based on the find- ings herein, a procedure was proposed for treating completely HMLWL. For the simulated waste liquid of this work, the optimum operating parameters in the initial stage are pH 9, $\text{FeSO}_4$ dosage 0.2 mol/L, temperature 90 °C, air supply rate 3 L/min and reaction time 40 min; in the extended stage, they are intermittent dosing, adding 10 mL 1 M $\text{FeSO}_4$ solution every 5 min, pH 9, temperature 90 °C, air supply rate 3 L/min and reaction time 80 min; in elutriation, the pH of the elutriation liquid should be 2.88, and the elutriation time 6 h.

Acknowledgement

The authors would like to thank the National Science Council of the Republic of China, Taiwan for financially supporting this research under contract number NSC 90-MOE-S-110-002-X.

References