Mn2+ oxidation, playing counteractive role in electro-oxidation of ammonia, hinders the generation of free chlorine

Xiaoxia Ma, Jinning Tang, Yunan Yuan, Zuohua Liu, Changyuan Tao

Abstract:
Ammonia in electrolytic manganese residue (EMR) constitutes potentially severe environmental risks. As an efficient, environment-friendly technology, electro-oxidation of ammonia in EMR was investigated in the present work. The influence of different metal ions coexisting with ammonia in EMR on the electro-oxidation of ammonia was evaluated and the relevant mechanism was deduced through phase transformation analysis. Results showed that (1) Mn2+, Ca2+, Mg2+, Na+, and K+ coexist with ammonia in the water-leach liquor of EMR, (2) Mn2+ inhibits the reaction whereas Ca2+ and Mg2+ demonstrate no distinct influence on the electro-oxidation of ammonia, and (3) Mn2+ and Cl− react emulsiously on the anode. MnO2 can generate free chlorine; thus, the presence of Mn2+ exerts a crucial impact on ammonia removal. So, it can be considered that further utilization of EMR can be realized by recycling Mn2+ first and then removing effectively ammonia through electro-oxidation method.

Introduction
With the rapid development of electrolytic metal manganese (EMM) industries in China, the country is facing enormous resource and environmental pressure, especially in terms of developing harmless methods to treat electrolytic manganese residue (EMR). The EMM industry would discharge 12 metric tons of EMR per ton manganese product at present. There are about 10 million tons of EMR discharged each year, and the accumulated amount during the past many years is about 50 million tons. EMR, the by-product of the electrolytic manganese metal process with soluble manganese and ammonia, is produced by the acid leaching, neutralization, and pressure filtration treatment of manganese carbonate powder. Currently, EMR is primarily dumped into the environment without pretreatment in China. The EMR piled up in the open field releases excess manganese and ammonia, which flow into nearby rivers via rainwater flushing and poses serious threats to both the economy and the health of people. These threats mainly include lake eutrophication and carcinogenicity.

Studies have reported about the disposal and utilization of the EMR. Liu et al. used EMR as supplementary cementitious materials. Li et al. used fly ash and burned EMR as complex additives for cement. Applications of EMR as soil amendment and roadbed backfill were also investigated. In addition, some scholars have reported that alkaline ions in the electrolyte can affect the electrochemical reaction. Nobumitsu Hirai et al. showed a specific anodic oxidation peak while discussing the effect of various alkaline metal ions on the electrochemical behavior of lead.
The main chemical composition of EMR was analyzed via X-ray fluorescence (XRF; LAB CENTER XRF-1800, Shimadzu, Japan), and its mineralogical composition was identified via X-ray diffraction (XRD; XRD-6000, Shimadzu, Japan; scan rate: 2°/min, 5–90 °C) and field emission scanning electron microscopy (JSM-7800F, Japan). Precipitations from the anode plate and reaction vessel were collected via vacuum suction filtration, dried in a vacuum oven at 80 °C, and then ground into powder. The chemical composition of these precipitates was characterized by XRD.

Leaching experiment of EMR

The leaching experiment was performed according to the Chinese solid waste-extraction procedure for determining leaching toxicity via the horizontal vibration method (HJ 557-2009). Add the water slurry in which the ratio of EMR to deionized water was kept 1:10 to the leaching experimental setup, stir for 8 h at room temperature, statically place for 16 h to ensure a steady concentration of NH₃ was obtained.

The contents of leached metals were measured by flame atomic absorption spectrometry (FAAS; Hitachi z-2000).

Electrochemical measurements

A total of 300 ml of EMR leach liquor was measured after tenfold dilution for the electrochemical experiments. Many scholars had mentioned that the treatment of ammonia wastewater by chloride ion had good effect and our previous repeated research also demonstrated the optimal electro-oxidation conditions as follows: current density of 80 mA/cm², chloride ion concentration of 300 mg/L, and pH=7 where the ammonia removal rate reached the highest. During the experiment, a syringe connected to a 0.45 µm membrane was used to draw 2 ml of the reaction liquid. Another 2 ml of distilled water was added to the liquor to maintain a constant concentration in the liquid. The reaction was stopped when the ammonia absorbance (Abs) became constant. The concentration of ammonia was determined by Water quality–Determination of ammonia nitrogen–Nessler’s reagent spectrophotometry (HJ 535-2009). Nitrate was measured by UV-Vis spectrophotometer (HJ/T 34–2007). To minimize interference from chloride ions, the UV spectra of the electrolyte solutions were used as the background for nitrate analyses. The concentration of nitrite nitrogen was determined by Water quality-Determination of nitrogen(nitrite)-Spectrophotometric method (GB 7493-87). NOx in the evaluated gases was analyzed by using a NOx detector tube (Gastec Co., 11HA). In experiments, The contents of total nitrogen was calculated as

\[ TN = (C_1 + C_2 + C_3) \quad , \]

Where TN is the contents of total nitrogen (mg/L), C₁ is the contents of ammonia (mg/L), C₂ is the contents of nitrate nitrogen (mg/L), and C₃ is the contents of nitrite nitrogen (mg/L).

The ammonia removal rate (%) was calculated as

Removal rate (%) = \( \frac{(C_0 - C_e)}{C_0} \times 100\% \),

where \( C_0 \) (mg/L) and Ce (mg/L) are the initial and equilibrium ammonia concentrations in the solution, respectively.
Analyzing the chemical composition of EMR and water-leach liquor of EMR

XRF analysis was performed as a complementary technique to examine the chemical composition of EMR. The EMR leach liquor was subjected to FAAS, and the results are listed in Tables 1 and 2. Fig. 1 illustrates the XRD patterns of EMR before and after leaching; the inset in the figure describes the appearance and scanning electron micrograph of the residue. As shown in Table 1, the EMR contains high silicon contents, as well as some metals, such as high contents of Ca, Al, Fe, Mn, and Mg; low contents of Na, P, Ti, and Zn. Table 2 reveals that the leach liquor contains high contents of Mn$^{2+}$ and NH$_4^+$-N (1552 and 553.6 mg/L, respectively). The contents of Ca$^{2+}$, Mg$^{2+}$, Na$^+$, and K$^+$ in the liquor are 386.2, 105, 91.32, and 65.02 mg/L, respectively; comparatively, the contents of other metal ions in the liquor, such as Zn$^{2+}$ and Cu$^{2+}$, are much lower.

The XRD pattern of EMR in Fig. 1 shows the presence of ammonia in the forms of (NH$_4$)$_2$SO$_4$ and (NH$_4$)$_2$Mn$_2$(SO$_4$)$_2$·6H$_2$O. Comparison of the XRD patterns of EMR before and after leaching shows apparent phase shifts. After processing by water, the characteristic peaks of solubilized ammonium sulfate crystals also partially disappear. These results indicate that these salts dissolved in water and leached out in the form of ions. Parts of the characteristic peaks of CaSO$_4$·0.62H$_2$O also disappeared or weakened, thus suggesting the dissolution of some calcium salts. In addition, it can be observed that the characteristic peaks of the SiO$_2$, Fe$_2$O$_3$, CaSO$_4$·0.5H$_2$O, CaSO$_4$·2H$_2$O, CaSO$_4$, and (NH$_4$)$_2$SO$_4$ have been existed before and after leaching. The inset of Fig. 1 suggests that the EMR particles are irregular in shape, distributed unevenly, and overlap with each other randomly and loosely.

Results thus far demonstrate that the concentrations of manganese and ammonia nitrogen far exceed Chinese Standards (GB8978-1996). And ammonia leaches easily in EMR and that Mn$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, and K$^+$ are the main metal ions coexisting with ammonia.

**Ammonia removal from EMR by electro-oxidation**

The results of electrolysis of the EMR leach liquor and (NH$_4$)$_2$SO$_4$ solution are shown in Fig. 2. The ammonia removal rate of the EMR leach liquor is only 10% when electrolysis is performed for 2 h; thereafter, a steady ammonia concentration is obtained. Obviously, the removal effect in this system is not ideal. By contrast, the ammonia content is close to or zero after electrolysis for 1.5 h in the solution of 48 mg/L (NH$_4$)$_2$SO$_4$. The results of the (NH$_4$)$_2$SO$_4$ solution show that electro-oxidation is feasible for ammonia removal, consistent with Li’s study, which showed nearly 100% oxidation efficiency in a reaction system containing chloride ions.

By comparing the two experiments above, it can be found that different experimental phenomena. Dark brown-black precipitates can be observed in the reaction vessel and anode plate of the EMR water-leach liquor but not in (NH$_4$)$_2$SO$_4$ solution. Table 2 and Fig. 2 show the metal ions coexisting with ammonia may affect the treatment of ammonia from EMR.

### Table 1 Composition of EMR (wt%)

<table>
<thead>
<tr>
<th>Name</th>
<th>O</th>
<th>Si</th>
<th>S</th>
<th>Ca</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>P</th>
<th>Ti</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content wt%</td>
<td>46.78</td>
<td>15.32</td>
<td>13.05</td>
<td>9.26</td>
<td>4.14</td>
<td>3.89</td>
<td>2.35</td>
<td>2.07</td>
<td>1.83</td>
<td>0.61</td>
<td>0.28</td>
<td>0.34</td>
<td>0.013</td>
</tr>
</tbody>
</table>

### Table 2 Composition of the leach liquor of EMR (mg/L)

<table>
<thead>
<tr>
<th>Name</th>
<th>Mn$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Zn$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>NH$_4^+$-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration mg/L</td>
<td>1552</td>
<td>386.2</td>
<td>105.5</td>
<td>91.32</td>
<td>65.02</td>
<td>0.8842</td>
<td>0.2251</td>
<td>553.6</td>
</tr>
</tbody>
</table>

Simulation experiments and determination of free chlorine

Simulation experiments of the water-leach liquor of EMR were performed according to Table 2. In this experiment, the contents of Mn$^{2+}$, Ca$^{2+}$, and Mg$^{2+}$ which were respectively added into (NH$_4$)$_2$SO$_4$ solution ([NH$_4^+$]=48 mg/L) with 300 mg/L Cl$^-$ were maintained at [Mn$^{2+}$]=155.2 mg/L, [Ca$^{2+}$]=38.62 mg/L, and [Mg$^{2+}$]=10.55 mg/L; these concentrations are about one-tenth of those shown in Table 2. Each of the mixtures was stirred vigorously, and then electrolysis was initiated. Determination of free chlorine was also performed according to Chinese Water Quality guidelines [Determination of free chlorine and total chlorine—Spectrophotometric method using N,N-diethyl-1,4-phenylenediamine (DPD) (HJ/586-2010)] in this reaction system. The solution containing Mn$^{2+}$ was numbered 1, the solution containing Ca$^{2+}$ was numbered 2, the solution containing Mg$^{2+}$ was numbered 3, and the solution with no metal ions was numbered 4. The free chlorine in these solutions was then measured 1 h after reaction.

Results and discussion

Analyzing the chemical composition of EMR and water-leach liquor of EMR

Figure 2 shows the metal ions coexisting with ammonia may affect the treatment of ammonia from EMR.

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Influence of coexisting metal ions on the electro-oxidation of ammonia from EMR

To evaluate the influence of coexisting metal ions on ammonia removal from EMR leachates, simulation experiments were performed. On the basis of analyzing the chemical composition of EMR and EMR’s water-leach liquor, it can be seen that Mn$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, K$^+$, and Na$^+$ with higher concentration might lead to different phenomena in the electrolysis of the EMR leach liquor and (NH$_4$)$_2$SO$_4$ solution. According to Li et al.,$^{28}$ K$^+$ cannot generate precipitates and only migrates to the cathode; this activity does not affect the efficiency of anode reaction. Thus, further exploring the influence of K$^+$ or Na$^+$ is unnecessary in this work (the chemical properties of Na are similar to those of K). From this point onward, only the impacts of Mn$^{2+}$, Ca$^{2+}$, and Mg$^{2+}$ on ammonia removal are investigated. Fig. 3 shows that the ammonia contents of solutions containing Ca$^{2+}$ or Mg$^{2+}$ tend to be zero after electrolysis for 1.5 h, similar to the curve of the (NH$_4$)$_2$SO$_4$ solution without metal ions added to it from the Fig. 2. Therefore, addition of Ca$^{2+}$ and Mg$^{2+}$ does not affect the treatment of ammonia. By contrast, the removal rate of ammonia significantly decreased to only at 15.8% in solutions containing Mn$^{2+}$. In other words, Mn$^{2+}$ affects the ammonia removal rate. The dark brown-black precipitates in solution containing Mn$^{2+}$ also obtained from the anode plate and reaction vessel.

Analyzing the results of the above reveals that depositions containing Mn$^{2+}$ on the anode plate prevent oxidation of ammonia, which seriously affects its removal. Thus, Mn$^{2+}$ should be removed from the EMR water-leach liquor before electrolysis. A solution of 0.2 mol/L NaOH was added to the EMR water-leach liquor until precipitation no longer formed in the supernatant. The Abs of Mn$^{2+}$ in the EMR leach liquor was measured as 0.007 by the spectrophotometric method. This result suggests that nearly all of the Mn$^{2+}$ in the solution had been removed. After sediment filtration, electrolysis was conducted on the liquor. Fig. 4 reveals that when the reaction is conducted after 1.5 h, the concentration of ammonia tends to be stable. Moreover, the removal rate of ammonia reached 93.57%. Thus, Mn$^{2+}$ exists the inhibiting effect during electro-ammonia, whereas Ca$^{2+}$ and Mg$^{2+}$ exert no distinct influence on the reaction. So, it can be considered firstly recycling Mn$^{2+}$, and then removing effectively ammonia by electro-oxidation method can realize the reuse of EMR.

Mechanism of the influence of coexisting metal ions on electro-oxidation of ammonia from EMR

In order to further evaluate the effect of electro-oxidation of ammonia, the results of concentration change of ammonia, total nitrogen, and oxidation products -nitrate nitrogen, nitrite nitrogen at pH=7, 28 are shown in Fig. 5. The concentration of nitrite nitrogen is too small to show because the amount was only 0.078 mg/L which is equal to 0.159% of the initial total nitrogen. The concentration of nitrate nitrogen, by comparison, shows a higher proportion. The reason is that the more ammonia is oxidized indirectly, the more by product: nitrate nitrogen is generated according to the reaction (12)$^{30}$. It is worth noting that, in this column, the height difference of ammonia and total nitrogen is equal to the column height of nitrate nitrogen. Besides, gas ammonia was not detected. NOx gas detected in the anodic and cathodic chambers was negligible at less than 1 ppm. This means that the ammonia was mainly converted into nitrogen and nitrate nitrogen. Additionally, Kwang-Wook Kim et al.$^{30}$ showed that a chlorination current of the adsorbed chloride ion generates before the oxidation of the adsorbed ammonia to nitrogen at the anode. Nigel J. And Bunce et al.$^{30}$ proposed that ammonia is oxidized by electro-generated positive chlorine, therefore, after the anode reaction (4), the reaction of the production of active chlorine and the oxidation of ammonia nitrogen occurred in the reactor, as shown in Eqs. (8)- (12). Meanwhile, a part of hypochlorite produced at the cathode could produce the side reaction (7)$^{30}$. 
Influence of coexisting Mn\(^{2+}\), Ca\(^{2+}\), and Mg\(^{2+}\) on the electro-oxidation of 48 mg/L ammonia. (a) Solution of 152.2 mg/L Mn\(^{2+}\), (b) solution of 38.62 mg/L Ca\(^{2+}\), and (c) solution of 10.55 mg/L Mg\(^{2+}\).

Removal of ammonia from EMR water-leach liquor without Mn\(^{2+}\).

Precipitates from the anode plate and reaction vessel, were analyzed by XRD, and the relevant results are shown in Fig. 6. Fig 6(a) shows characteristic diffraction peaks representing CaSO\(_4\)-H\(_2\)O, CaCl\(_2\)-Ca(H\(_2\)O\(_4\)\(_2\))\(_2\), (NH\(_4\))\(_2\)Mn(SO\(_4\))\(_2\)(H\(_2\)O)\(_6\), and (NH\(_4\))\(_2\)Mg(SO\(_4\))\(_2\)6H\(_2\)O. This result implies that the depositions in the reaction vessel are formed by Mn\(^{2+}\), Mg\(^{2+}\), and Ca\(^{2+}\) from the EMR leach liquor, and the reaction equation can be expressed as (13)-(16). Fig. 6(b) also shows sharp, clear peaks, which indicate the presence of MnO\(_2\). In other words, the oxide layer formed on the anode was MnO\(_2\), as the equation (5). In addition, we all know that the standard electrode potentials of Mn\(^{2+}\) and Cl\(^-\) are 1.228 and 1.35827 v, respectively, as shown in Eqs. (1) and (2). The presence of Mn\(^{2+}\) in the reaction system affects ammonia removal because this ion has competitive effect in consuming electrons and hinders the generation of free chlorine on the anode when it is oxidized to MnO\(_2\). Although Ca\(^{2+}\) and Mg\(^{2+}\) can generate a small amount of precipitation (Fig. 6), they cannot be easily oxidized at the anode plate. Experiments demonstrating the colorimetric determination of free chlorine are shown in Fig. 7. The solution containing Mn\(^{2+}\) presents no colour, whereas the solutions containing Mn\(^{2+}\), Mg\(^{2+}\), and no ions exhibit similar pink colours. Such coloration indicates the reaction of free chlorine with DPD. These different experimental phenomena can explain the observed variations in ammonia removal yields with coexisting metal ions in Fig. 3.

\[
\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4\text{H}^+ + 2e^- (\phi^o = 1.228v) \\
(1)
\]

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 (g) + 2e^- (\phi^o = 1.35827v) . \\
(2)
\]

Based on the XRD patterns and experimental results obtained, a simple mechanistic model of the main processes occurring during electro-oxidation of ammonia in EMR water-leach liquor is shown in Fig. 8. The reactions involved in this process are as follows:

On the anode:

(1) Ammonia accompanying its adsorption on the anode can directly be oxidized into nitrogen by hydroxyl radicals electro-generated from water at the electrode surface. The electrochemical reaction of ammonia to nitrogen is generally considered to be a three-electron exchange reaction, as shown below:\(^{30}\).

\[
\text{NH}_3 \rightarrow \frac{1}{2}\text{N}_2 + 3\text{H}^+ + 3e^- , \\
(3)
\]

(2) Cl\(^-\) is oxidized into free chlorine on the anode, as shown below.

\[
2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- , \\
(4)
\]

(3) Mn\(^{2+}\) diffusing to the surface of the anode is oxidized, and a layer of manganese oxide can be formed on the anode.
$\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 \downarrow + 2\text{e}^- + 4\text{H}^+$,  

(5)

$2\text{NH}_4^+ + 3\text{HClO} \rightarrow \text{N}_2 \uparrow + 3\text{HCl} + 3\text{H}_2\text{O}$,  

(10)

On the cathode:

Water molecules induce hydrogen evolution on the cathode.

$4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{H}_2 \uparrow + 4\text{OH}^-$,  

(6)

$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Cl}^- + 2\text{OH}^-$.  

(7)

In the reactor:

(1) Free chlorine is formed in the aqueous solution and reacts with ammonia as a strong oxidizer to produce nitrogen, as shown below.

$\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{HClO} + \text{Cl}^- + \text{H}^+$.  

(8)

$\text{HClO} \rightarrow \text{ClO}^- + \text{H}^+$.  

(9)

(2) $\text{Mn}^{2+}$, $\text{Mg}^{2+}$, and $\text{Ca}^{2+}$ produce a large amount of precipitation that eventually spreads to the entire reactor via diffusion and advection.

$\text{Ca}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  

(13)

$2\text{Ca}^{2+} + 2\text{OH}^- + 2\text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{CaCl}_2 \cdot \text{Ca(OH)}_2 \cdot \text{H}_2\text{O}$  

(14)

$2\text{NH}_4^+ + \text{Mg}^{2+} + 2\text{SO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{Mg(SO}_4)_2 \cdot 6\text{H}_2\text{O}$  

(15)

$2\text{NH}_4^+ + \text{Mn}^{2+} + 2\text{SO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{Mn} \left( \text{SO}_4\right) _2 \cdot 6\text{H}_2\text{O}$  

(16)

According to the reaction mechanism described above, removing the $\text{Mn}^{2+}$ can substantially prevent reaction (5). In this
way, reaction (4) occurs smoothly without precipitation of manganese dioxide at the anode plate. The continuous generation of free chlorine rapidly prompts indirect reactions (10) and (11) and, thus, contributes to ammonia removal.

Conclusions

(1) The EMR leach liquor presents a diverse composition, mainly including NH₄⁺, Mn²⁺, Ca²⁺, Mg²⁺, Na⁺, and K⁺.

(2) The removal rate of ammonia reached 93.57% in the system with Mn²⁺ removal; this rate is 83.57% higher than that obtained under the same conditions but without Mn²⁺ removal.

(3) Electrochemical oxidation of the ammonia leached from EMR is very inefficient because the Mn²⁺ in the leachate competed for oxidation and also fouled the anode by producing MnO₂ which hinders the generation of free chlorine. By contrast, Ca²⁺ and Mg²⁺ exert no distinct influence on the reaction.

(4) A new train of thought and method which can be considered firstly recycling Mn²⁺, and then removing effectively ammonia by electro-oxidation was provided for the further utilization of EMR.

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Notes and references

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Mn$^{2+}$ oxidation, playing counteractive role in electro-oxidation of ammonia, hinders the generation of free chlorine.

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Ammonia, which is one of the hazardous materials from EMR, was studied by a safe and clean electro-oxidation technology. The cause of influencing the ammonia removal was explored in the current work by studying the effect of coexisting metal ions and the concentration changes of intermediate products in the process of electro-oxidation. And the removal rate of ammonia reached 93.57% by removing Mn$^{2+}$ which seriously affected ammonia removal. This method provided a new idea to develop harmless methods to treat EMR.