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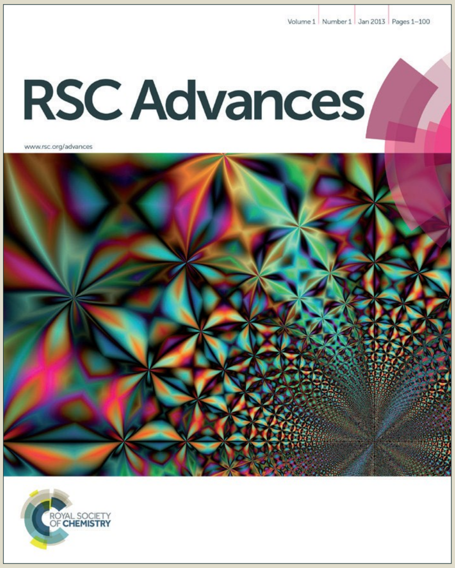

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ARTICLE

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

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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 by phase transformation analysis through X-ray diffraction, X-ray fluorescence, scanning electron microscopy, flame atomic absorption spectrometry, and spectrophotometry. Results showed that (1) Mn^{2+}, Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} coexist with ammonia in the water-leach liquor of EMR, (2) Mn^{2+} inhibits the reaction whereas Ca^{2+} and Mg^{2+} demonstrate no distinct influence on the electro-oxidation of ammonia, and(3) Mn^{2+} and Cl^{-} react emulously on the anode. MnO_2 hinders the generation of free chlorine; thus, the presence of Mn^{2+} exerts a crucial impact on ammonia removal. So, it can be considered that further utilization of EMR can be realized by recycling Mn^{2+} 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)[1-3]. The EMM industry would discharge 12 metric tons of EMR per ton manganese product at present[4]. 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[5]. 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[6, 7].

Studies have reported about the disposal and utilization of the EMR. Liu et al.[8] used EMR as supplementary cementitious materials. Li et al.[9] used fly ash and burned EMR as complex additives for cement. Applications of EMR as soil amendment and roadbed backfill were also investigated[10-11]. Although there are many prospects to build materials, these applications could not be generalized in practice due to the low quantity of added EMR and the leaching of ammonia. Duan et al.[12] pointed out that about 36.5 Kg NH_3 was lost to the EMR per ton of EMM product while the addition amount of NH_3 was 82.78 Kg. Currently, measures to control ammonia pollution are an urgent necessity.

In recent years, a variety of technologies for processing ammonia in EMR, such as replacing ammonia during production[13-14] and ammonia recycling/removing[5,15-16], have been explored. However, these methods present several shortcomings; for example, no appropriate alternative materials to ammonia are available, washing of slag easily damages the water balance system and causes secondary pollution, and stabilizing EMR cannot effectively utilize the ammonia it contains. Over the last several years, electrochemical treatment of ammonia has attracted considerable attention in various fields, such as landfill leachate[17], wastewaters containing synthetic organic dyes[18], tannery wastewater[19], and textile wastewater[20-21]. Electrochemical treatment presents a number of advantages, including minimal generation of secondary waste, remote control, and easy operation[22-24]. In addition, some scholars have reported that alkaline ions in the electrolyte can affect the electrochemical reaction. Nobumitsu Hirai et al.[25] showed a specific anodic oxidation peak while discussing the effect of various alkaline metal ions on the electrochemical behavior of lead

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electrode in sulfuric acid. A review by Zhang et al.[26] mentioned that oxidative precipitation of MnO_2 has been applied to the removal of manganese impurities from Zn, Co, and Ni processing circuits. Above all, in the current work, electro-oxidation was applied to remove ammonia in EMR for the first time and the effect of coexisting metal ions on the oxidation reaction was also comprehensively investigated. In order to effectively remove the ammonia in the EMR by this method and provide a new train of thought and method for the further utilization of EMR. The reaction mechanism was further discussed by analyzing factors associated with the experimental phenomena.

Experimental

Materials

The EMR was sampled according to Technical Specifications on Sampling and Sample Preparation from Industry Solid Waste guidelines (HJ/T20-1998) from a manganese industry factory in Chongqing, China. This EMR sample had been deposited in an open field for approximately 5 years. The physicochemical properties of EMR are summarized in Table 1. The chemical components of EMR are complex. The sample was dried in a vacuum drying oven at 105 °C to a constant weight, ground by an XQM-2L frequency conversion planetary ball mill, and then screened by dry-sieving to obtain particles with diameters of 80 mesh.

All aqueous solutions were prepared using distilled water supplied by a Human Power II type water purifying apparatus (South Korea).

Apparatus

The leaching experiments were conducted in a 500 ml beaker connected to a mechanical agitator. A vacuum suction filter was used to separate the residue and leach liquor.

The electrolysis experiment was performed in a rectangular plexiglass reactor (15 cm × 9 cm × 9 cm). A Ti/RuO_2-IrO_2-SnO_2 anode (5 cm × 10 cm, Long Sheng Co., China) and a stainless steel plate cathode (5 cm × 10 cm) were fixed to the reactor with an electrode gap of 2.5 cm. A DC power supply (WYJ-10A30V, Hangzhou Ping Guo Co., China) was applied to generate a stable and continuous electric field.

Characterization of material structure

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 drying 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 NH_3 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/cm^2, 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)-Spectrophotmtrlc 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

$$TN = （C_1+C_2+C_3）,$$

Where TN is the contents of total nitrogen (mg/L), C_1 is the contents of ammonia (mg/L), C_2 is the contents of nitrate nitrogen (mg/L) ,C_3 is the contents of nitrite nitrogen (mg/L).

The ammonia removal rate (%) was calculated as

$$\text{Removal rate (\%)} = [(C_0 - Ce)/C_0] \times 100\%,$$

where C_0 (mg/L) and Ce (mg/L) are the initial and equilibrium ammonia concentrations in the solution, respectively.

Table 1 Composition of EMR (wt%)

Name		O	Si	S	Ca	Al	Fe	Mn	K	Mg	Na	P	Ti	Zn
Content wt%	EMR	46.78	15.32	13.05	9.26	4.14	3.89	2.35	2.07	1.83	0.61	0.28	0.34	0.013

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

Name	Mn^{2+}	Ca^{2+}	Mg^{2+}	Na^+	K^+	Zn^{2+}	Cu^{2+}	NH_4^+-N
Concentration mg/L	1552	386.2	105.5	91.32	65.02	0.8842	0.2251	553.6

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 $(NH_4)_2SO_4$ solution ($[NH_4^+\text{-N}]$=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

XRF analysis was performed as a complementary technique to examine the chemical composition of EMR. The EMR leach liquor was subjects 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 metal elements， such as high contents of Ca, Al, Fe, Mn, K, 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 $(NH_4)_2SO_4$ and $(NH_4)_2Mn_2(SO_4)_2{\cdot}6H_2O$. Comparison of the XRD patterns of EMR before and after leaching shows apparent phase shifts. After processing by water, the characteristic peaks of salts such as $(NH_4)_2Mn_2(SO_4)_2{\cdot}6H_2O$, $MnSO_4{\cdot}4H_2O$, and $MgSO_4$ disappear completely. The characteristic peak of soluble 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 $CaSO_4{\cdot}0.62H_2O$ 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, FeS_2, $CaSO_4{\cdot}0.5H_2O$, $CaSO_4{\cdot}2H_2O$, $CaSO_4$ and $(NH_4)_2SO_4$ 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 $(NH_4)_2SO_4$ 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 $(NH_4)_2SO_4$. The results of the $(NH_4)_2SO_4$ solution show that electro-oxidation is feasible for ammonia removal, consistent with Li's[27] study, which showed nearly 100% oxidation efficiency in a reaction system containing chloride ions.

By comparing the two experiments above, it can been found other 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 $(NH_4)_2SO_4$ solution. Table 2 and Fig. 2 show the metal ions coexisting with ammonia may affect the treatment of ammonia from EMR.

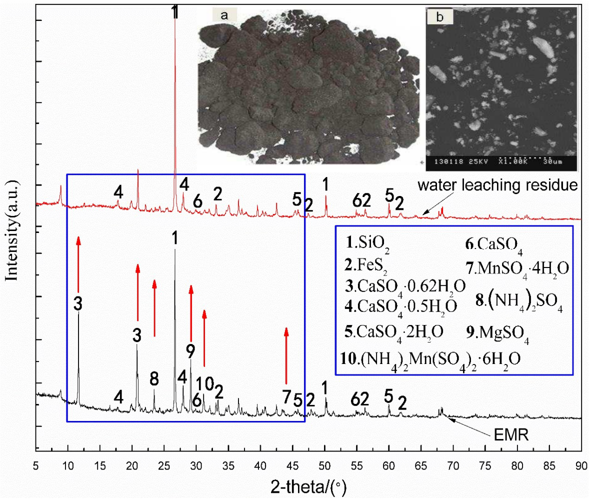

Fig. 1 XRD patterns of EMR before and after leaching. Inset: (a) Appearance and (b) scanning electron micrograph of EMR.

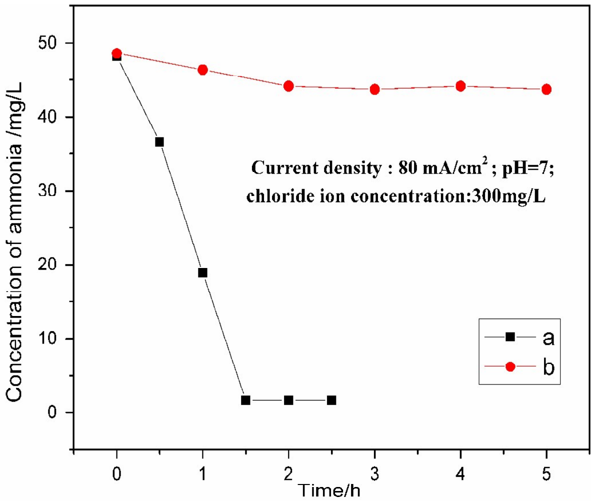

Fig. 2 Ammonia removal from (a) a solution of 48 mg/L $(NH_4)_2SO_4$ and (b) the EMR water-leach liquor

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 $(NH_4)_2SO_4$ 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 $(NH_4)_2SO_4$ 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 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)[22]. 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.[29] 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].

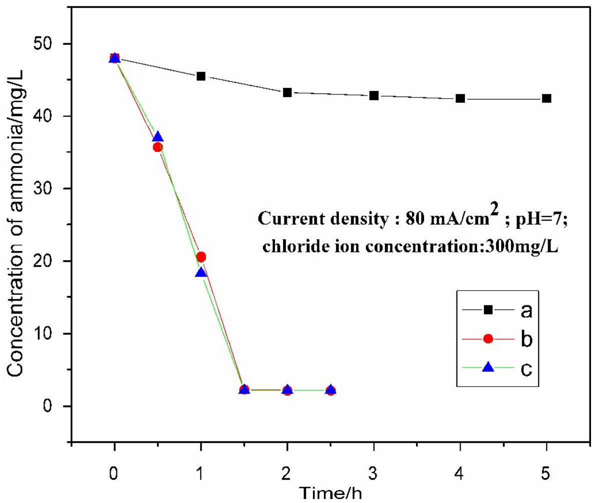

Fig. 3 Influence of coexisting Mn^{2+}, Ca^{2+}, and Mg^{2+} on the electro-oxidation of 48 mg/L ammonia. (a) Solution of 152.2 mg/L Mn^{2+}, (b) solution of 38.62 mg/L Ca^{2+}, and (c) solution of 10.55 mg/L Mg^{2+}

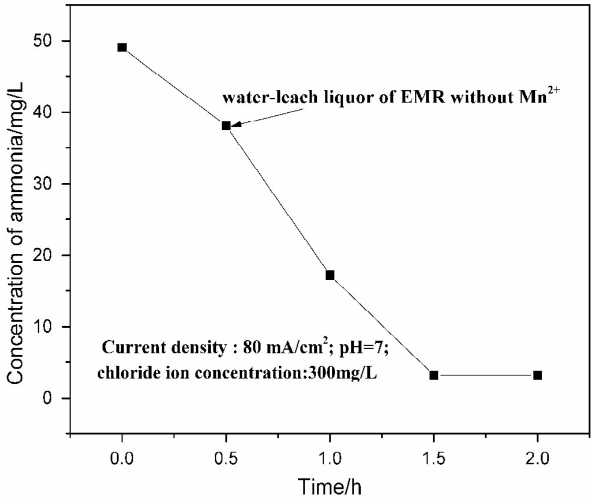

Fig. 4 Removal of ammonia from EMR water-leach liquor without Mn^{2+}.

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 $CaSO_4 \cdot H_2O$, $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$, $(NH_4)_2Mn(SO_4)_2(H_2O)_4$, and $(NH_4)_2Mg(SO_4)_2 6H_2O$. 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 electronics 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.

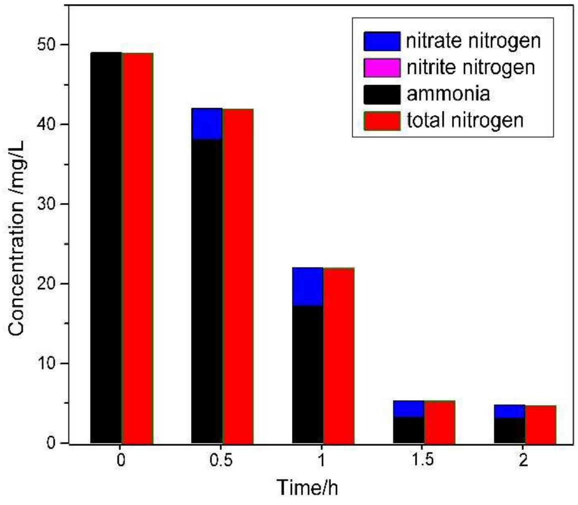

Fig. 5 Concentration change of ammonia, total nitrogen, nitrate nitrogen , nitrite nitrogen at pH=7

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 \downarrow + 2e^- + 4H^+ (\varphi^0 = 1.228v)$$

(1)

$$2Cl^- \rightarrow Cl_2(g) + 2e^- (\varphi^0 = 1.35827v) . \quad (2)$$

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].

$$NH_3 \rightarrow \frac{1}{2} N_2 \uparrow + 3H^+ + 3e^- , \quad (3)$$

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

$$2Cl^- \rightarrow Cl_2 \uparrow + 2e^- , \quad (4)$$

(3) Mn^{2+} diffusing to the surface of the anode is oxidized, and a layer of manganese oxide can be formed on the anode.

$$Mn^{2+} + 2H_2O \rightarrow MnO_2\downarrow + 2e^- + 4H^+ , \quad (5)$$

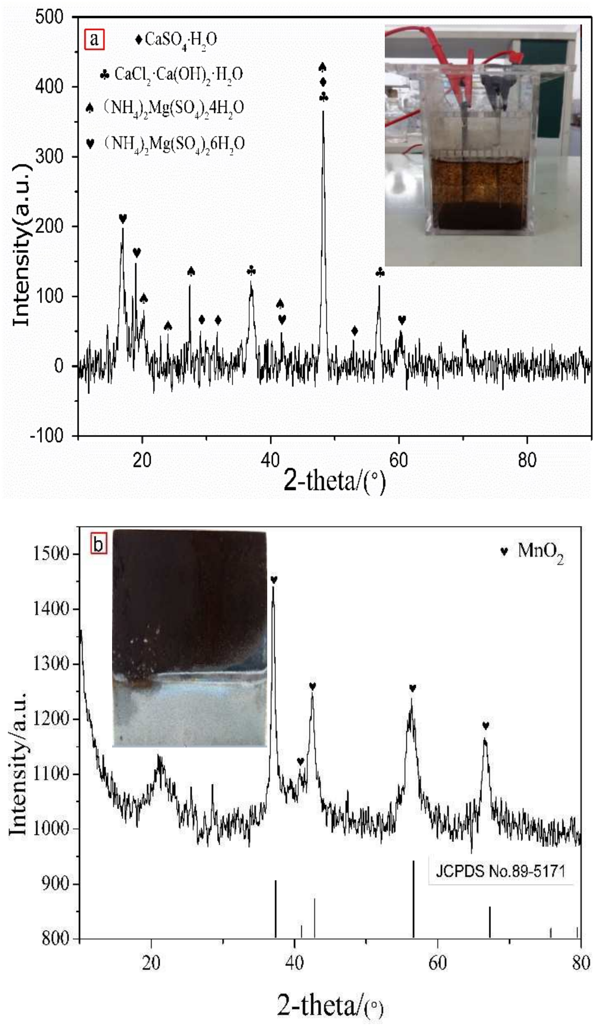

Fig. 6 XRD patterns of the precipitates obtained from (a) the reaction vessel(b) the anode plate.

On the cathode:

Water molecules induce hydrogen evolution on the cathode.

$$4H_2O + 4e^- \rightarrow 2H_2\uparrow + 4OH^- , \quad (6)$$

$$ClO^- + H_2O + 2e \rightarrow Cl^- + 2OH^- . \quad (7)$$

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.

$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ , \quad (8)$$

$$HClO \rightarrow ClO^- + H^+ , \quad (9)$$

$$2NH_3 + 3HClO \rightarrow N_2\uparrow + 3HCl + 3H_2O , \quad (10)$$

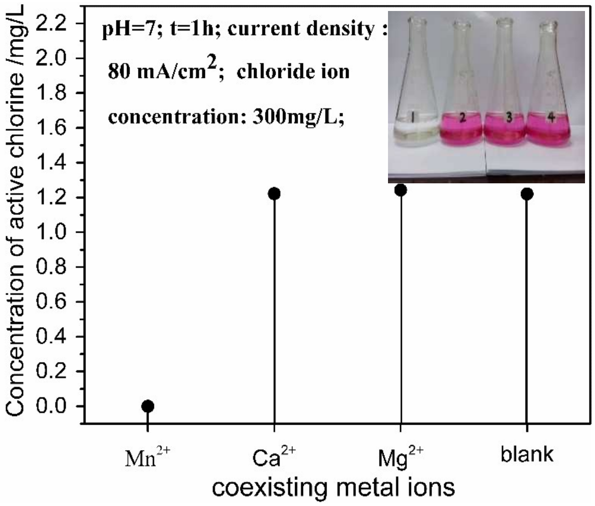

Fig. 7 Influence of coexisting metal ions on the production of free chlorine; insets 1, 2, 3, and 4 illustrate the colorimetric detection of free chlorine in solutions containing Mn^{2+}, Ca^{2+}, Mg^{2+}, and no metal ions, respectively

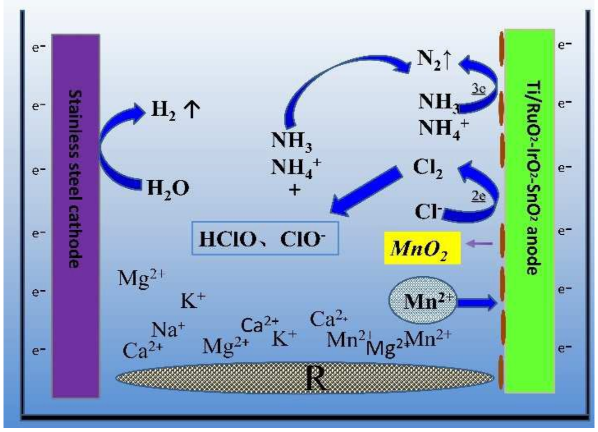

Fig. 8 Mechanism of the electro-oxidation ammonia-nitrogen (R represents precipitation of reaction vessel)

$$2NH_3 + 2ClO^- \rightarrow N_2\uparrow + 2HCl + 2H_2O . \quad (11)$$

$$HOCl + (1/4)NH_4^+ \rightarrow (1/4)NO_3^- + (1/4)H_2O + (3/2)H^+ + Cl^- \quad (12)$$

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

$$Ca^{2+} + SO_4^{2-} + H_2O \rightarrow CaSO_4H_2O\downarrow \quad (13)$$

$$2Ca^{2+} + 2OH^- + 2Cl^- + H_2O \rightarrow CaCl_2Ca(OH)_2H_2O \quad (14)$$

$$2NH_4^+ + Mg^{2+} + SO_4^{2-} + 6H_2O \rightarrow (NH_4)_2Mg(SO_4)_2 6H_2O\downarrow \quad (15)$$

$$2NH_4^+ + Mn^{2+} + SO_4^{2-} + 4H_2O \rightarrow (NH_4)_2Mn(SO_4)_2(H_2O)_4\downarrow , \quad (16)$$

According to the reaction mechanism described above, removing the 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 NH_4^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Na^+, and K^+.

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

(3) Electrochemical oxidation of the ammonia leached from EMR is very inefficient because the Mn^{2+} in the leachate competed for oxidation and also fouled the anode by producing MnO_2 which hinders the generation of free chlorine. By contrast, Ca^{2+} and Mg^{2+} exert no distinct influence on the reaction.

(4) A new train of thought and method which can be considered firstly recycling Mn^{2+}, 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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Table of Content

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

Xiaoxia Ma, Jinjing Tang, Yunan Yuan, Zuohua Liu and Changyuan Tao

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.