Treating electrolytic manganese residue with alkaline additives for stabilizing manganese and removing ammonia

Changbo Zhou*,†, Jiwei Wang*, and Nanfang Wang**,†

**Chinese Research Academy of Environmental Sciences, 8 Dayangfang, Beiyuan Road, Beijing 100012, China
**School of Chemistry and Chemical Engineering, Hunan Institute of Engineering,
88 Fuxing East Road, Xiangtan 411104, China*
(*Received 25 June 2013 • accepted 20 August 2013*)

Abstract−Electrolytic manganese residue (EMR) from the electrolytic manganese industry is a solid waste containing mainly calcium sulfate dihydrate and quartzite. It is impossible to directly use the EMR as a building material due to some contaminants such as soluble manganese, ammonia nitrogen and other toxic substances. To immobilize the contaminants and reduce their release into the environment, treating EMR using alkaline additives for stabilizing manganese and removing ammonia was investigated. The physical and chemical characteristics of the original EMR were characterized by XRFS, XRD, and SEM. Leaching test of the original EMR shows that the risks to the environment are the high content of soluble manganese and ammonia nitrogen. The influence of various alkaline additives, solidifying reaction time, and other solidifying reaction conditions such as outdoor ventilation and sunlight, and rain flow on the efficiencies of Mn^{2+} solidification and ammonia nitrogen removal was investigated. The results show that with mass ratio of CaO to residue 1 : 8, when the solidifying reaction was carried out indoors for 4 h with no rain flow, the highest efficiencies of Mn^{2+} solidification and ammonia nitrogen removal (99.98% and 99.21%) are obtained. Leaching test shows that the concentration and emission of manganese and ammonia nitrogen of the treated EMR meets the requirements of the Chinese government legislation (GB8978-1996).

Key words: Electrolysis Manganese Residue, Harmless Disposal, Solidification of Manganese, Removal of Ammonia Nitrogen

INTRODUCTION

The electrolytic metal manganese (EMM) industry is known as high consume, high pollution, high danger, and low output (three high and one low) [1]. With the demand of manganese metal increasing in the global market, the development of EMM industry has been promoted recently, which generates some environmental problems, especially electrolytic manganese residue (EMR) [2]. EMR is a solid waste in which manganese ore is leached in sulfuric acid to obtain a solution containing Mn^{2+} and a great amount of impurities in the ore turned into EMR containing mainly soluble manganese, ammonia and other toxic substances [3]. It is reported that, with the grade of manganese ore decreased, the EMM industry discharges 10-12 metric tons of EMR per ton manganese product. About 10 million tons of EMR are discharged each year, and there are about 50 million tons to be disposed over the years [1,2,4]. Furthermore, it is very difficult to dispose of the EMR due to its diversity of pollutants and its humidity, fineness and viscosity. Currently, almost all EMRs are dumped in the open field. Thus, pollutants can seep into the natural environment, migrate and transfer continuously, and seriously pollute the surface and ground water [3]. Such a large mount of EMRs without pretreatment poses a serious threat to the environment, as well as the health of the people and the economy. The development of the EMR disposal technologies is urgent.

Although there are some researches about EMR disposal and its utilization, they can not solve the essential problems. Feng et al. [5] used manganese slag as the cement setting retarder. Li et al. [6] used the burned EMR and fly ash as a complex additive for the cement. But the amounts of the added Mn-slag were too low (<15%), which was not applied in a large scale. Usage of EMR for crops [7-9] and application of Mn-slag to roadbed backfill [10] was investigated, but these applications could not be generalized in practice due to the low efficiency and immaturity of the technology.

Due to high efficiency, low cost, and simple procedure, stabilization/solidification technology is extensively applied to harmlessly dispose of the pollutant [11-16]. As for EMR, it can stabilize or demobilize contaminants in solid waste materials, and impart some strength to EMR, which is favorable to its utilizations such as landfills, building materials, roadbeds. Currently, as for evaluation of harmless disposal of solid wastes, leaching toxicity method is commonly adopted to determine the potential environmental risk of the disposed products. Palfy, et al. [17] found original arsenic solubility of 6430 mg/L from untreated waste to 0.823 mg/L from final solidified product with leaching tests. Roussel et al. [18] performed a mineralogical and chemical investigation on the site of the Cheni mine (France) and found that oxidation fixation decreased the soluble arsenic concentration. Wang et al. [19] used the arsenical sludge and clay mixed with a defined for the brick and found that solidification for As, Zn, Pb, and Cd was very good and the leaching toxicity of arsenical sludge bricks was lower than that of the national standard.

In this paper, solidification/stabilization technology was applied for EMR for the first time. On the basis of analysis data of the original EMR, the alkaline additives, such as quicklime (CaO), sodium hy-

Table 1. Chemical composition of the original EMR

Component	SiO₂	SO₃	CaO	Al₂O₃	Fe₂O₃	MnO	MgO	K₂O	P₂O₅	Ignition loss
wt%	17.17	19.89	8.85	5.03	3.89	3.05	1.14	1.36	0.631	38.17

Original EMR characterization

Moisture (%)	24.98	Average particle size (μm)	17.37			
Real density (g/cm³)	2.64	Loose density (g/cm³)	0.64	Tap density (g/cm³)	1.02	

droxide (NaOH), potassium hydroxide (KOH) and so on, could be used as solidifying agents. Due to the higher price of KOH, CaO and NaOH were chosen as the alkaline additives in this work. The effect of various solidifying agents (CaO and NaOH), solidifying reaction time, and other solidifying reaction conditions such as outdoor ventilation and sunlight, and rain flow on the leaching toxicity of the solidified EMR was mainly investigated.

EXPERIMENTAL

1. Materials

The EMR sample used in the present study was collected from a manganese industry factory in Chongqin, China. The sample was taken at random from the stockyard and stored in an airtight container until used. The quicklime (CaO) and sodium hydroxide (NaOH) were commercially available.

2. Procedure of Solidification

Prior to solidification, the EMR sample was dried at 105 °C to remove the moisture, then demolded and ground to pass through a 9.5 mm sieve, kept in dry oven before use. In a typical procedure of solidification, we weighed the solidifying agent (CaO or NaOH) and 100 g dry EMR sample was mixed fully in a 100 mL beaker. Then 50 mL deionized water was poured and quickly stirred to a homogeneous paste. The paste was placed in a ventilated cabin to react for 2 h, and then dried at 40 °C for testing. The testing results were given as the arithmetic means of three replicated experiment samples, unless otherwise stated.

3. Characterization

Moisture of samples was determined according to the procedure in the section 4.1.2 of GB/T 5086.2-1997: test method for leaching toxicity of solid wastes - horizontal vibration extraction procedure. Average particle size of the residue samples was determined on a Micro-Plus particle size analyzer (Malvern, Britain). Real density was determined on a Quantachrome Ultrapycnometer 1000 (Quantachrome, USA). Loose density was measured on a TBX-25 loose density tester (Xiamen, China). Tap density was measured on an F2S4-4 tap density tester (Nibong, China). The chemical composition of the EMR (in oxide form) was determined by X-ray fluorescence spectrometry (XRFS) (ARL ADVANT XP⁺, thermo electro corporation, USA) under measurement conditions of an Rh anode in the X-ray tube, 50 kV and 50 mV for generator voltage and current, the working condition temperature and relative humidity (R.H.) at 22 °C and 40%, respectively. XRD was conducted by an MXPAHF X-ray diffractometer from 5° to 70° with a Cu Kα of 1.54056 Å. SEM was observed by a JSM-6360LV scanning electron microscope. Before XRFS, XRD and SEM testing, the EMR sample was dried at 105 °C, demolded and ground to pass through a 100 mesh sieve.

4. Leaching Test

Leaching test was performed according to the procedure in HJ 557-2009 (Solid waste-extraction procedure for leaching toxicity - Horizontal vibration method). 10 g of solidified sample was weighed and placed into a 300 mL borosilicate glass flask. About 100 mL deionized water was added to maintain a solid to liquid ratio 1 : 10. The sample solution was agitated at 110±10/min on a bath reciprocal shaker at room temperature for 8 h, and then statically placed for 16 h. The upper clear liquid of the sample solution was filtered to remove the solid particles. The concentration of Mn²⁺ and ammonia nitrogen in leaching solution was determined according to ref. [20] respectively: manganese was determined using the potassium periodate spectrophotometric method, a wavelength of 525 nm, and ammonia was determined spectrophotometrically with Nessler's Reagent at a wavelength of 420 nm on a UV-vis spectrometer (UV-3802). The pH of leaching solutions was measured using an FE20 pH meter with an LE438 combined plastic electrode (Mettler Toledo, Shanghai, China).

RESULTS AND DISCUSSION

1. Characterization of EMR Sample

The chemical analyses (Table 1) by XRFS showed the original EMR mainly contains SO₃, SiO₂, CaO, Al₂O₃, Fe₂O₃, and MnO, which is similar to the common metasilicate materials. This was also verified by XRD pattern of EMR. Fig. 1 shows that there are mainly four crystalline phases in the XRD pattern, which are corresponding to Gypsum (CaSO₄·2H₂O), Quartz (SiO₂), Albite (KAl₂Si₃AlO₁₀(OH)₂), and Muscovite ((Na,Ca)Al(Si,Al)₃O₈), respectively. Due to the acid oxidates higher than the alkali oxidates, it makes the original EMR present acidity. It is generally considered that the main composition of original EMR is similar to clay minerals, but the content of the silicon aluminum components is too low to use as the building materials. Table 1 shows that the ignition loss of the EMR is highly
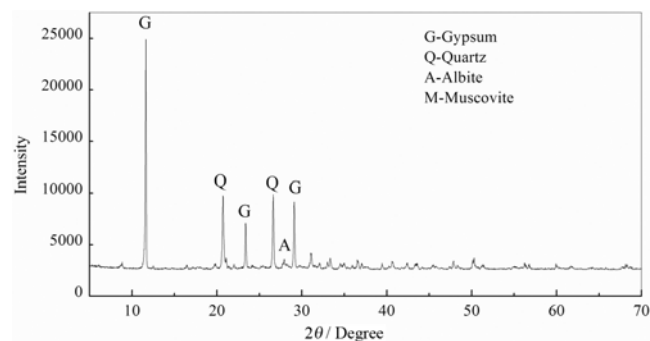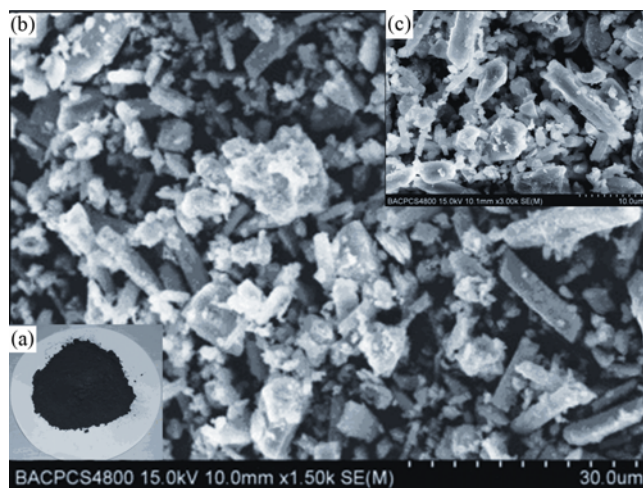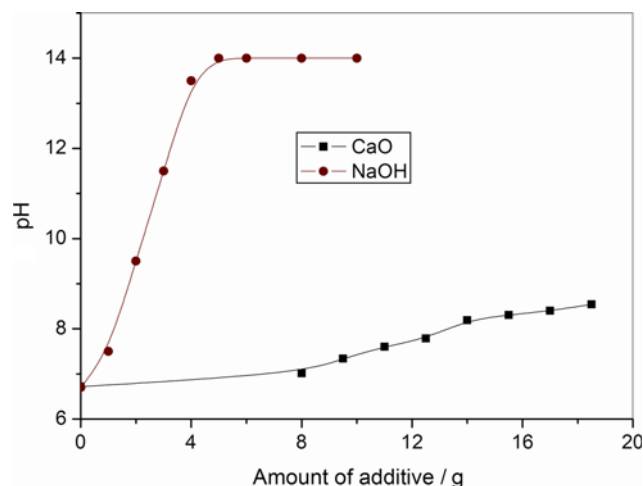

Fig. 1. XRD pattern of the original EMR.

Table 2. Leaching test result of the original EMR

Pollutants	Pollutant concentration/mg/L	Integrated wastewater discharge standard (GB8978-1996)/mg/L
Mn^{2+}	2270	5.0
NH_3-N	678.12	25
Hg^{2+}	NF	0.05
Pb^{2+}	0.567	1.0
Cd^{2+}	0.060	0.1
Cr^{3+}	0.802	1.5
Cr^{6+}	0.0065	0.5
Cu^{2+}	0.047	2.0
Zn^{2+}	1.72	5.0
Be^{2+}	NF	0.00
Ba^{2+}	0.055	-
Ni^{2+}	0.44	1.0
Ag^+	0.268	0.5
As^{3+}	0.0114	0.5
Se ions	0.019	0.5
Fluoride	0.789	20
Cyanide	NF	1.0

attributed to the high level content (678.12 mg/L NH_3-N in Table 2) of $(NH_4)_2SO_4$, which can be decomposed at 100 °C to release NH_3 gas. If these ammonia nitrogen chemicals are released into the natural environment, they could lead to eutrophication in water bodies [2]. Moreover, the original EMR contains a great quantity of $CaSO_4 \cdot 2H_2O$ which can release the crystal water and partly decompose itself at 950-1,000 °C, contributing to the ignition loss. The high moisture of the original EMR results in caking when drying. The real and tap density is more than water density, leading to depositing in the water. Table 2 presents toxic substances content of the original EMR by means of leaching test and the integrated waste-water discharge standard (GB8978-1996). It is obvious that the concentrations of Mn^{2+} and NH_3-N are much higher than the limits of the discharge standard (454 and 27 times, respectively). So the origi-
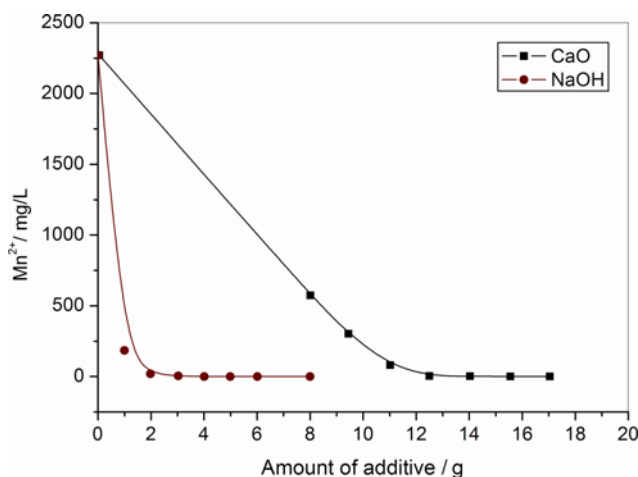
nal EMR poses a significant threat to the environment once the pollutants are released into water. In our research, Mn^{2+} and NH_3-N concentrations are used as characterization and evaluation of the effect and feasibility of the solidification with the solidifying additives.

Fig. 2 displays SEM of the original EMR. Fig. 2(a) shows its visual image is a black powder. In general, EMR is a non-magnetic and insoluble fine powder which likes sludge paste when absorbing moisture and changes into a hard block when deposited. The color of the residue power changes with the raw material and process of EMM industry. Fig. 2(b) and Fig. 1(c) show there mainly are regularly cylindrical particles and irregularly shaped particles which overlap each other randomly and loosely. In the spaces formed by them, there is a small amount of irregular floccule residues. The sizes of particles are not uniform, varying from several microns to hundreds of microns. There are no obvious bonds among the particles.

2. Various Solidifying Agents

Fig. 3 shows the relationship between pH of leaching solution from EMR treated by various additives and the dosage. With the dosage of CaO and NaOH increasing, the tendency in increase of leaching solution pH of EMR treated by NaOH is sharper than that

Fig. 3. pH of leaching solution with various additives.

Fig. 2. The SEM of the original EMR ((a) visual image, (b) ×1500, (c) ×3000).

Fig. 4. Mn^{2+} concentration of leaching solution with various additives.
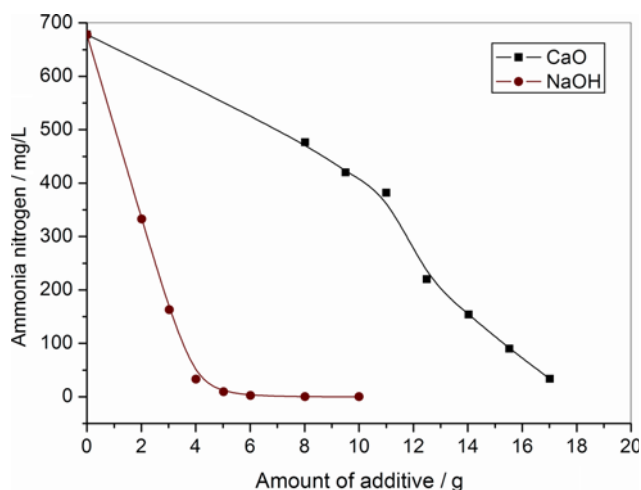
Fig. 5. Ammonia nitrogen concentration of leaching solution with various additives.

by CaO, due to the higher alkalinity and solubility of NaOH. Additionally, when the dosage of NaOH exceeds 5 g, the pH remains at 14 due to the high alkalinity beyond the measuring range of pH meter, which cannot represent the constant alkalinity.

It is seen from Fig. 4 and Fig. 5 that with the additive CaO and NaOH increasing, the Mn^{2+} concentration and ammonia nitrogen concentration of leaching solutions for the treated EMRs are significantly decreased at first and then remain nearly unchanged. The decrease of the Mn^{2+} concentration concentration from EMR treated with the additive CaO and NaOH is attributed to the fact that the soluble Mn^{2+} and OH^- introduced by the additive CaO and NaOH can transfer into $Mn(OH)_2$. $Mn(OH)_2$ can be oxidized by oxygen in air into the insoluble MnO_2 to solidify the soluble Mn^{2+} in the EMR and eliminate the hazard from Mn^{2+}. The total reaction from Mn^{2+} to MnO_2 is depicted as the following equation [21].

$$2Mn^{2+}(aq)+O_2(g)+2H_2O(l)\rightarrow 2MnO_2(s)+4H^+(aq) \qquad (1)$$
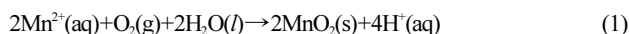
In Eq. (1), it is obvious the reaction can produce H^+, which decreases the pH of the solution. If the alkalinity of the system is not high enough, it will lower the efficiency of this reaction into MnO_2. Accordingly, with the additive CaO and NaOH increasing, the concentration of OH^- increases so as to increase the velocity and efficiency of the reaction. Owing to the higher alkalinity, less input amount of NaOH can obtain the same Mn^{2+} and ammonia nitrogen concentration compared to CaO.

In terms of the decrease of ammonia nitrogen concentration, the ammonia nitrogen in EMR exists in the form of free NH_3 molecular and NH_4^+ ion between which there is an equation reaction as follows.

$$NH_4^+ + OH^- \text{€} NH_3 + H_2O \qquad (2)$$

In Eq. (2), when the alkalinity of the EMR increases, NH_4^+ ion can be transformed into NH_3 gas released into the air to remove ammonia nitrogen in the residue.

In Fig. 4, when the amount of additive for CaO and NaOH is 12.5 g and 2.5 g, respectively, the inflection point values of the Mn^{2+} curve are obtained (4.5 and 4.6 mg/L respectively lower than the limit of the integrated wastewater discharge standard in Table 2), where solid-

ification efficiency for Mn^{2+} is above 99%. In Fig. 5, when CaO and NaOH are set at 12.5 g and 2.5 g, the ammonia nitrogen concentration reaches 200.92 and 210.37 mg/L, respectively, where gasification efficiency for ammonia nitrogen is above 70%. The ammonia nitrogen concentration of the treated EMR is much higher than the limit (25 mg/L) of the discharge standard in Table 2 because the transformation from NH_4^+ to NH_3 is slow. If stripping for a certain time is introduced to solidification procedure, the ammonia nitrogen concentration will be controlled in the limit of the discharge standard. In doing so, the treated EMR does not pose great risk to the environment any more.

From the point of the efficiencies of the Mn^{2+} solidification and ammonia removal in EMR, when the mass ratio of additive CaO to EMR is 1 : 8 and the ratio of NaOH to EMR is 1 : 40, respectively; the treated EMR is basically harmless and meets the standard of landfill or utilization. Therefore, to attain the same the treatment result, the consumption of CaO is five times of NaOH. But the present price per ton of CaO is one-fifth of NaOH so that the discrepancy in the use cost for both additives is little. In the use manner, owing to low solubility, CaO requires molding into fine powder to facilitate a homogeneous mixture with EMR. Adversely, there is not the above problem on the NaOH additive, which is favorable to the process design. However, the treatment with CaO has its special advantages. The one is that compared to NaOH, CaO with lower alkalinity and milder reactivity is less harmful to humans and cannot form secondary pollution with better safety. The other is that NaOH with higher alkalinity and stronger corrosion can severely do harm to the equipment. Additionally, in terms of the solidifying mechanics, the mixing of contaminated soils with quicklime promotes a number of reactions in the soil/porewater including flocculation, ion exchange, lime carbonation, dissolution of clay minerals and pozzolanic reactions, which may result in formation of macroaggregates [22]. Considering the advantages, CaO is chosen as the solidifying additive and the optimal mass ratio of additive CaO to EMR is 1 : 8 for the further investigation.

3. Solidifying Process

3-1. Time

Fig. 6 shows the effect of the solidifying time on the concentrations of Mn^{2+} and ammonia nitrogen in the leaching solution from
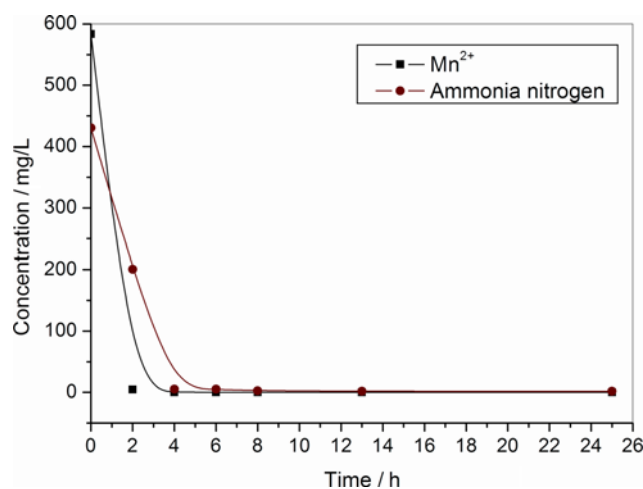

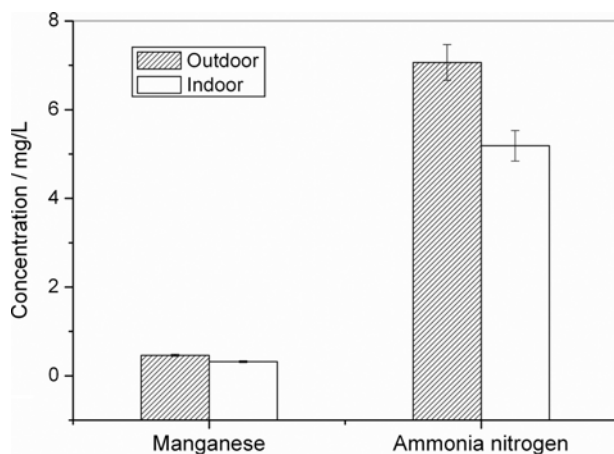**Fig. 6. Mn^{2+} and ammonia nitrogen concentration vs. time.**

Fig. 7. Mn²⁺ and ammonia nitrogen concentration vs. outdoor and indoor (error bars present standard deviations).
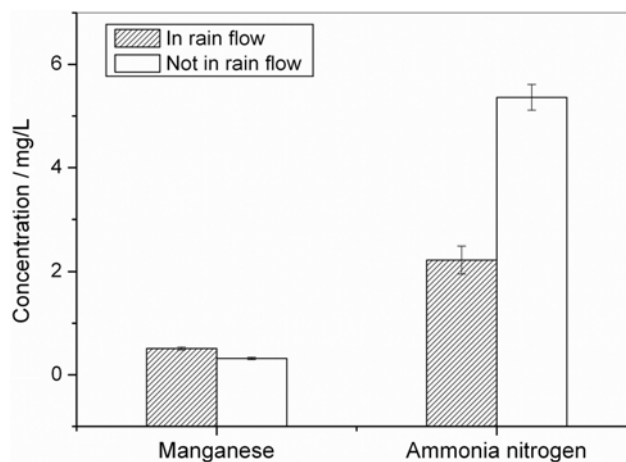

Fig. 8. Mn²⁺ and ammonia nitrogen concentration vs. rain flow (error bars present standard deviations).

the EMR treated by CaO. It is clear from the two curves for Mn^{2+} and ammonia nitrogen that the concentrations are sharply decreased at the beginning of 0-2 h and remain unchanged (0.32 and 5.35 mg/L, respectively) with time increase from 4 to 25 h, indicating that the reaction of the Mn^{2+} solidification and the ammonia nitrogen removal with CaO has been completed within 4 h. So the technology of Mn^{2+} solidification and ammonia nitrogen removal with CaO for EMR has a good stability and high practical value.

3-2. Ventilation and Sunlight

The EMR mixed with CaO is generally laid outdoors, in which ventilation and sunlight are important factors. It is required to consider the effect of ventilation and sunlight on the efficiency of solidification. In the experiment, temperature, relative humidity and air speed of the outdoor and indoor were recorded as follows: 28-30 °C, 36-40%, 0.2-0.3 m/s and 24-26 °C, 40-60%, 0 m/s, respectively. Fig. 7 displays the Mn^{2+} and ammonia nitrogen concentration under the different storage conditions (outdoor and indoor) for 4 h, respectively. The Mn^{2+} and ammonia nitrogen concentrations from the sample placed in the outdoor condition are both higher than that in the indoor condition, indicating that solidification in the indoor condition is optimal. The reason for this result is that the hydration reaction of CaO is highly exothmic and generates significant amounts of heat energy, which results in evaporation of porewater and drying of soil [22]. Therefore, evaporation of water or moisture in the EMR mixed with CaO in the outdoor condition is faster than that in the indoor condition, and meantime the CaO powder cannot be fully dissolved, so that the system pH decreases quickly, resulting in the lower efficiency of solidification compared to that in the indoor condition.

3-3. Rain Drops

Rain drops are also an important factor of the storage condition. To simulate the condition of rain drops, a water spray apparatus was employed. In this study, 5-6 mL water was sprayed on each sample with the interval of 1-1.5 h when the sample surface appears dry and hard. Fig. 8 displays the Mn^{2+} and ammonia nitrogen concentration with rain flow and without. As for Mn^{2+}, the concentration of rain flow sample is much higher than that of non rain flow sample, indicating lower efficiency of solidification in rain flow. In rain flow, the pH of the residue with the additive CaO is decreased

quickly, which hinders the proceeding of the solidification reaction, resulting in lower efficiency of solidification for Mn^{2+}. As for ammonia nitrogen, removal of ammonia nitrogen is mainly dependent on pH and temperature according to Eq. (2). In rain flow, the pH and temperature of the residue tend to decrease, which is not favorable for removing the ammonia nitrogen. However, the tested concentration of ammonia nitrogen of the rain flow sample is surprisingly lower than that of the non-rain flow sample. The reason for this is that a great mount of NH_4^+ leaks out of the residue with the rain flow rather than releases out as NH_3 gas produced by the solidifying reaction.

CONCLUSION

To eliminate its hazards and improve resource utilizations of EMR, a harmless disposal of EMR using additives was adopted to stabilize manganese and remove ammonia in the EMR. The chemical and physical characterization of the original EMR shows that the risks to the environment are the high concentration of soluble manganese and ammonia nitrogen. Comparing the effect of various additives on the efficiencies of Mn^{2+} solidification and ammonia nitrogen removal reveals that two additives (CaO and NaOH) both can effectively solidify Mn^{2+} and remove ammonia nitrogen, but CaO has better safety and ease of operation than NaOH. Influence of solidifying time and other solidifying reaction conditions such as outdoor ventilation and sunlight and rain flow on the efficiencies of Mn^{2+} solidification and ammonia nitrogen removal was investigated. With mass ratio of CaO to residue 1 : 8, when the solidifying reaction was carried out in the indoor for 4 h with no rain flow, the highest efficiencies of Mn^{2+} solidification and ammonia nitrogen removal (99.98% and 99.21%) were obtained, and that the Mn^{2+} and ammonia nitrogen concentrations from leaching solution of the treated EMR are lower than the limit of the integrated wastewater discharge standard (GB8978-1996).

ACKNOWLEDGEMENTS

REFERENCES

1. N. Duan, Z. Dan, F. Wang, C. Pan, C. Zhou and L. Jiang, *J. Clean. Prod.*, **19**, 2082 (2011).
2. N. Duan, F. Wang, C. Zhou, C. Zhu and H. Yu, *Res. Conserv. Rec.*, **54**, 506 (2010).
3. J. Qian, P. Hou, Z. Wang and Y. Qu, *J. Wuhan Univ. Technol.*, **27**, 45 (2012).
4. B. Xin, B. Chen, N. Duan and C. Zhou, *Bioresour. Technol.*, **102**, 1683 (2011).
5. Y. Feng, F. Liu and X. Bao, *Cement*, 22 (2006).
6. T. Li, H. Xie, X. He and X. Zhou, *Bull. Chin. Ceram. Soc.*, 567 (2007).
7. J. Lan, *China's Manganese Ind.*, 27 (2005).
8. J. Lan, *China's Manganese Ind.*, 43 (2006).
9. J. Lan and K. Wang, *China's Manganese Ind.*, 23 (2006).
10. F. Xu, *China's Manganese Ind.*, 5 (2001).
11. V. Bednarik, M. Vondruska and M. Koutny, *J. Hazard. Mater.*, **122**, 139 (2005).
12. J. R. Conner, Ed., *Chemical fixation and solidification of hazardous wastes*, Van Nostrand Reinhold, New York (1993).
13. R. Malviya and R. Chaudhary, *J. Hazard. Mater.*, **137**, 267 (2006).
14. K. Anastasiadou, K. Christopoulos, E. Mousios and E. Gidarakos, *J. Hazard. Mater.*, **207-208**, 165 (2012).
15. A. Andres, R. Ibanez, I. Ortiz and J. A. Irabien, *J. Hazard. Mater.*, **57**, 155 (1998).
16. R. Arce, B. Galan, A. Coz, A. Andres and J. R. Viguri, *J. Hazard. Mater.*, **177**, 428 (2010).
17. P. Palfy, E. Vircikova and L. Molnar, *Waste Manage.*, **19**, 55 (1999).
18. C. Roussel, H. Bril and A. Fernandez, *C. R. Acad. Sci., IIa; Earth Plant. Sci.*, **329**, 787 (1999).
19. D. Wang, Y. Zhu, Y. Liang, J. Liu and Z. Jiang, *Energy Environ. Prot.*, 40 (2006).
20. F. Wei, *Water and wastewater monitoring and analysis methods*, China Environmental Science Press, Beijing (2002).
21. H. Nan, J. Zhou, Y. Liu, Q. Pen, D. Pen and J. Zhen, *Environ. Monit. China*, **23**, 49 (2007).
22. V. Schifano, C. MacLeod, N. Hadlow and R. Dudeney, *J. Hazard. Mater.*, **141**, 395 (2007).