Immobilization of high concentrations of soluble Mn(II) from electrolytic manganese solid waste using inorganic chemicals

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Abstract Electrolytic manganese solid waste (EMSW) is a by-product of electrolytic manganese production and generally contains a high concentration of soluble Mn(II) (2000–3000 mg/L). Millions of tons of EMSW are stored in China, and the environmental pollution caused by manganese in this waste product is concerning. Unfortunately, little attention has been paid to the immobilization of manganese from industrial solid waste because manganese is absent from toxicological identification standards, and there is a lack of relevant quality standards in China. The objectives of this study were to immobilize soluble Mn(II) using chemical reagents, to analyze the immobilization mechanism, and to identify the most economical reagents. We investigated the immobilization degrees of soluble Mn(II) achieved by the reagents quicklime (CaO), carbonates (NaHCO₃ and Na₂CO₃), phosphates (Na₃PO₄, Na₂HPO₄, NH₄H₂PO₄, and Ca₁₀(PO₄)₆(OH)₂), and caustic

magnesia (MgO) both individually and in combination. Our results showed that the use of 9 % CaO+ 5 % NaHCO₃, 9 % CaO+ 5 % Na₃PO₄, 10 % MgO alone, or with 1–5 % NaHCO₃ or 1–5 % Na₂CO₃ can reduce the amount of Mn(II) leached to 100 mg/kg when the eluate pH was in the range of 6–9. The most economical reagent treatments were determined using K-means cluster analysis. Analysis of the immobilization mechanism showed that CaO+NaHCO₃ may be favorable for immobilizing soluble Mn(II) as precipitation and oxidation products because the addition of NaHCO₃ releases OH[−] and buffers the system.

Keywords Electrolytic manganese solid waste · Soluble Mn(II) · Immobilization · Carbonates · Oxidation · Mechanism

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Introduction

Manganese metal provides alloy products that are widely used in non-ferrous metallurgy, electronics, chemical processing, and other industries. China is the largest producer, consumer, and exporter of electrolytic manganese metal (EMM) in the world (Du et al. 2014). Currently, about 10 Mt of electrolytic manganese solid waste (EMSW) is discharged each year, and this amount is expected to reach about 50 Mt in the coming years (Zhou et al. 2014).

EMSW is a type of residue produced in the traditional hydrometallurgical process that extracts manganese from rhodochrosite using sulfuric acid. During this process, the majority of MnCO₃ in rhodochrosite is converted to MnSO₄. Even though the separation of EMSW from the aqueous solution of MnSO₄ is conducted via a high-pressure press filter, there is residual MnSO₄ in the EMSW. Duan et al. (2010) determined

that the residual contains 1.5–2.0 % Mn from the raw materials based on an analysis of substance balances of the raw materials, products, and waste. We found that soluble Mn(II) accounted for 60 % of the total manganese in EMSW, and the amounts of other heavy metals, such as Pb, Cd, Zn, and Cu, were far lower than Mn. Hence, soluble Mn(II) is the main pollutant in EMSW that could cause soil, river, or groundwater contamination (Li et al. 2007). It was reported that the Mn content in the river water surrounding a manganese residue landfill was 143.49 times that of the standards for type III groundwater, and the Mn content in residential drinking water in this area exceeded national sanitary standards for living and drinking water (Luo 2012). Analysis of hair, nail, and urine of operators in EMM production showed that they suffered manganese contamination in varying degrees (Wang 2012).

There is current concern about manganese pollution; however, it has not drawn widespread interest. This lack of interest may be because of the common perception that Mn is a relatively non-toxic metal, an attitude that is reflected by the absence of any mention of Mn in many toxicological assessments and by the lack of relevant quality standards in China (Li et al. 2007). However, exposure to excess manganese may cause Parkinson-like symptoms (Erikson and Aschner 2003; Gerber et al. 2002), infertility in mammals, and immune system malfunctions (Vartanian et al. 1999). In light of these negative effects, it is critical to immobilize manganese in EMSW in order to reduce its release into the environment.

Solidification/stabilization (S/S) is a statistically proven “best demonstrated available technology” for the treatment of heavy metal-bearing waste. Stabilization or immobilization results in a reduction of the hazard potentials from a waste by converting the contaminants into their least soluble, mobile, or toxic form (Malviya and Chaudhary 2004). A survey of the literature shows that several technologies have explored the stabilization of waste. These include adsorption, oxidation–reduction, ion-exchange, precipitation, etc. Among these techniques, adsorption is frequently applied because of different adsorbents, such as active carbon (Lata et al. 2008), kaolinite and montmorillonite (Bhattacharyya and Gupta 2007; Ikhsan et al. 1999), zeolite (Qiu and Zheng 2009), and boron waste (Olgun and Atar 2011; Yola et al. 2014a, b). Besides, precipitation or oxidation–reduction technologies are preferred to treat pollutants with high concentrations because of its high efficiency, easy process, and cost-effectiveness as well as availability of different inorganic reagents. Soluble phosphates are the mostly commonly tested additives. In addition, lime or quicklime (Dash and Hussain 2012; Kogbara and Al-Tabbaa 2011; Williford et al. 2007), hydroxyapatite (HA) (Ma et al. 1994; Mavropoulos et al. 2002; Seaman et al. 2001), carbonates (Conner and Hoeffner 1998), and caustic magnesia (Cubukcuoglu and Ouki 2012; Rötting et al. 2008) have also been used. It is common knowledge that applying liming materials can overcome the problems resulting from acidic

conditions, such as stored metals, and release them by dissolution during wetting events. During remedial activities aimed at mitigating metal release from tailings, large quantities of alkaline compounds are often added to the tailings to increase the pH and immobilize the metals. Liming materials are typically additives for decreasing metal mobility and leachability with CaO and Ca(OH)₂ being the most common additives (Catalan and Yin 2003). Several studies (Dutr and Vandecasteele 1998; Guo et al. 2006) have indicated that CaO (quicklime) is a more effective additive because it is readily soluble and available for reactions. However, the high proportion required (15 %) to be added to the waste material results in an unacceptable increase in pH.

Our previous studies (Du et al. 2014; Zhou et al. 2014) have reported that lime-based stabilization can significantly reduce the leachability of soluble Mn(II); however, the pH of the treated EMSW was higher than 10. It is hypothesized that an appropriate reagent or combination of reagents may be used that reduces the leachability of soluble Mn(II), and still results in pH values in the acceptable range of 6–9 (China, 2001). This work examines the validity of this hypothesis by comparing the results of immobilization tests carried out with trisodium phosphate (TP), disodium hydrogen phosphate (DHP), diammonium phosphate (DAP), sodium bicarbonate (SB), sodium carbonate (SC), hydroxyapatite (HA), magnesia oxide (MO), and quicklime (CO) as well as with combinations of these reagents. Moreover, the speciation of manganese and the microstructure of the sample following treatment with different reagents were also determined.

Materials and methods

EMSW samples

Samples of EMSW collected from Tianyuan Manganese Ind. (Ningxia Province, China) were dried at 60 °C continuously for 7 days and then analyzed to determine the chemical compositions of the EMSW. The data in Table 1 shows that sulfur, silica, and calcium oxide were major components of the EMSW, whereas several other minerals were present in trace amounts.

The results of the heavy metal leaching test for EMSW are shown in Table 2. The data revealed that all of the eight metals tested for (Cu, Zn, Cd, Pb, Cr, Ni, As, and Se) were present in the sample in amounts far below the thresholds of the national standards determined by GB 5085.3-2007 (China, 2007). Note, however, that the concentration of Mn was quite high. Although no threshold for Mn is given in GB 5085.3-2007, this concentration is high enough to pose a significant risk to the surrounding environment.

The various forms of manganese detected in the EMSW sample are shown in Table 3. Soluble Mn comprised the main

Table 1 Chemical composition of EMSW samples

Component	SiO ₂	SO ₃	CaO	Al ₂ O ₃	Fe ₂ O ₃	MnO	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅
Mass %	27.93	37.31	15.39	5.78	5.29	5.08	1.14	0.56	0.32	0.06

form of Mn in the EMSW samples—70.83 % of the total Mn. Such a large quantity of soluble Mn poses a serious risk of water and soil pollution.

Sample preparation

The content of soluble Mn(II) in EMSW is generally less than 2 % wt. For this study, target chemicals were added, producing synthetic EMSW, in order to determine the immobilization products (Hills et al. 1999). This synthetic EMSW (SE) was prepared by adding a 0.1-M MnSO₄ solution into the EMSW and adjusting pH to 6.0±0.2, similar to the control EMSW (CE).

Testing chemical additives

For the immobilization of soluble Mn(II), four different types of reagent were tested, whose characteristics are indicated in Table 4. The quantities of these additives added to the samples were selected based on preliminary tests and from the quantities of the additions indicated in the referenced literature (Bone et al. 2004).

The methodology summarized in Fig. 1 was used for the chemical stabilization experiments. The immobilization efficiency (F_{ST}) may be expressed as the percentage of the availability factor (Dell'Orso et al. 2012) through:

$$F_{ST} = \frac{\sqrt{C_{OS}} - \sqrt{C_L \cdot L/S}}{\sqrt{C_{OS}}} \times 100 \% \quad (1)$$

where C_L is the manganese concentration in the leachate (mg/L), L is the volume of leachant (L), S is the sample mass (mg), and C_{OS} is the total concentration of manganese in the sample (mg/kg).

Incubation procedure

The incubation procedure was similar to that previously reported (Rodríguez-Jordá et al. 2010), where a specified

portion of the SE samples was evenly blended with single, double, and triple reagent treatments. In each single treatment, the reagent was added at the quantity given in Table 3. Based on the F_{ST} determined for the single treatment, the worst and the best additives were excluded from the double and triple treatments. SE samples (20 g) were evenly blended with the chemical reagents as single (CO, MO, HA, or TP), double (CO+SB, CO+SC, CO+TP, CO+DAP, CO+DHP, CO+HA, MO+SB, and MO+SC), and triple additive treatments (CO+TP+SB, CO+TP+SC, CO+HA+SB, and CO+HA+SC). For example, the CO₉+SB₅ combination indicates the addition of 9 % CaO (1.8 g) and 5 % NaHCO₃ (1.0 g) to the SE sample. The incubation period was 7 days in a curing box at 35 °C and a relative humidity of 60 %. The sample was then oven-dried (at 60 °C) and homogenized to determine amounts of Mn(II), Mn(III), and Mn(IV) in the sample. The leaching experiments are described below.

Determination of Mn(II), Mn(III) and Mn(IV)

Mn(II) is easily oxidized to form Mn(III) or Mn(IV) especially in alkaline conditions (at pH 8) (Morgan 2005). Mn(II) in aqueous solution reacts with OH[−] to form a precipitate of Mn(OH)₂. Oxidation of Mn(OH)₂(s) by O₂(aq) is very rapid and leads to the formation of Mn₃O₄(s) (Bricker 1965; Morgan 1967), as shown in Eqs. (2)–(4).

Using these reactions, a three-variable linear equation was set up to calculate the contents of Mn(II), Mn(III), and Mn(IV)

Table 2 Heavy metal leaching test results for EMSW samples

Heavy metal	Cu	Zn	Cd	Pb	Cr	Cr(IV)	Ni	As	Se	Mn
Contents (mg/L)	0.062	1.34	0.036	N.D. ^a	0.17	N.D.	4.83	0.024	N.D.	1820
Threshold (mg/L)	100	100	1	5	15	5	5	5	1	— ^b

^a Not detected

^b No threshold has been set for manganese

Table 3 The speciation of manganese in the EMSW samples

Forms	Total Mn	MnCO ₃	Soluble Mn	MnO ₂
Mass %	2.16	2.10	1.53	0.029

in the SE samples. Specified determination steps are shown in the [Supplementary Material](#).

Leaching experiments

Two leaching methods were used to evaluate the leaching behavior and pollution potential of manganese in the untreated and treated SE samples: (1) The Chinese solid waste-extraction procedure for leaching toxicity sulphuric acid and nitric acid (HJ/T 299) and (2) deionized water extraction (HJ/T 577). Both extractions were conducted using 20:1 liquid-to-solid ratio with a contact time of 18 ± 2 h in three replicates. This liquid that passed through the filter was centrifuged for 15 min at 5000 rpm and filtered through a 0.45- μ m membrane filter. This was regarded as the eluate. The eluate was sampled to measure the manganese ion concentration and the sample pH.

Methods of chemical analysis

The manganese ion concentrations were measured by atomic absorption spectroscopy (novAA 350, Germany). The pH was measured with a Ag/AgCl electrode and a Thermo Scientific Orion pH meter. The electrode was calibrated weekly at pH 4.01, 7.00, and 10.01 using fresh buffers. The mineralogical composition evaluation was performed to identify the presence of crystalline using X-ray diffraction (XRD; X' Pert PANalytical, Netherlands) with Cu K α radiation, 2 θ range of 10°–60°, and a scan step size of 0.026°.

Statistical analysis

A one-way analysis of variance (ANOVA) was performed to test the significance of differences in soluble Mn(II)

Fig. 1 Experimental methodology for chemical immobilization of soluble Mn(II)

concentrations among the stabilization treatments. A K-means cluster analysis (KCA) was performed to find the groups of treatment conditions (additive_dose) that showed similar responses to F_{ST} and to determine the most economical reagent treatments. The different additive_dose experimental conditions considered were projected over a two-dimensional plot to identify those additive_dose clusters that improved the stabilization efficiency of soluble Mn(II). All statistical analyses were performed using the statistical package SPSS 21.0 (SPSS, Inc., an IBM Company, Chicago, IL, USA).

Results

Effect of different treatments on soluble Mn(II) stabilization

Single additive treatment

Four chemicals—two phosphates and two alkaline oxides—were used as a stabilizer for the waste samples. Figure 2a–d shows the released amounts of soluble Mn after the treatment with CO, HA, MO, or TP according to the methodology indicated in Fig. 1. Each additive decreased the amount of soluble Mn(II), but to different degrees. For example, when CO was

Table 4 Chemical reagents tested for stabilization of residue with heavy metals

Reagents/supplier	Molecular formula	Notation	Physical state	Tested quantities/20 g S-E
Quicklime/Sinopharm	CaO	CO	Solid	0.6, 1.2, 1.8, 2.4, 3.0 g
Carbonates/Sinopharm	Na ₂ CO ₃	SC	Solid	0.1, 0.3, 0.5 g
	NaHCO ₃	SB		
Soluble phosphates/Sinopharm	Na ₃ PO ₄	TP	Solid	0.1, 0.3, 0.5 g
	Na ₂ HPO ₄	DHP		
	NH ₄ H ₂ PO ₄	DAP		
Hydroxyapatite/Hongxing Reagent	Ca ₁₀ (PO ₄) ₆ (OH) ₂	HA	Solid	1, 2, 3, 4 g
Caustic magnesia/Sinopharm	MgO	MO	Solid	1, 2, 3, 4 g

Fig. 2 Released amounts of soluble Mn after treatment with CO (a), HA (b), MO (c), and TP (d)

added at a concentration of 12 % or higher, the amounts of Mn in the eluate were not detectable. However, the eluate pH for deionized water extraction was higher than 10, which exceeds the pH limit of 9 for landfilling in the Chinese standard for pollution control on the storage and disposal sites for general industrial solid waste (GB 18599–2001) (China, 2001).

When the quantity of the added MO was equal to or greater than 10 %, the amount of soluble Mn(II) in the eluate was less than 100 mg/kg and the pH approached 9.0. These results showed that MO had a good immobilization effect on Mn(II). Cortina et al. (2003) conducted experiments that demonstrated MO could be used to deplete concentrations of 75 mg/L Mn to values below 40 µg/L.

The immobilization effects of adding TP and HA were not as significant as those with CO and MO. The soluble phosphates which effectively immobilize lead and zinc fail to make much of an impact on soluble manganese. Soluble phosphates should not be selected as the primary agent to bring about the required level of manganese immobilization (Bone et al. 2004).

Although MO has good immobilization capacity for Mn(II), its high cost may limit its industrial application. CO would be a preferable additive if the eluate pH was between 6

and 9. Obviously, high pH values may be problematic for the single additive treatment with CO. Therefore, to realize the industrial application of this reagent, it is necessary to add other reagents in addition to CO to retain good Mn(II) immobilization and control the eluate pH values to between 6 and 9.

Double and triple additive treatments

To improve the treated EMSW to be classified as first-class general industrial waste, other additives, such as carbonates and soluble phosphates, were added in addition to CO. Figure 3a–f illustrates the leaching results obtained for soluble Mn and the pH values after stabilization of the EMSW using various treatments of CO, carbonates, and phosphates. CO was combined with carbonates and phosphates; the amount of Mn that could be leached was reduced. Both CO+SB and CO+SC resulted in the eluate pH both in the range 6–9. A lower amount of released Mn was obtained with CO₉+SB₅. As for the soluble phosphates, Fig. 3c–f shows that CO₉+TP₅ and CO₉+HA₁ can lead to a lower amount of released Mn than CO+DAP and CO+DHP, and all the eluate pH values tend to be in the range of 6–9 except when CO+HA was used for water extraction.

Fig. 3 Released amounts of soluble Mn and pH variation after double reagent treatment with CO+SB (a), CO+SC (b), CO+TP (c), CO+HA (d), CO+DAP (e), CO+DHP (f), MO+SB (g), and MO+SC (h)

Figure 3g–h shows the comparison of the amount of released soluble manganese and the pH values after using MO alone, and MO combined with SB and SC. The results showed that a lower amount of manganese was released using MO+SB and MO+SC, whereas the pH was somewhat higher than that obtained when using MO alone.

To decrease the amount of soluble Mn released to a lower level than that achieved by CO+TP and CO+HA, additional reagents were used. The results of the double additive experiments indicated that both SB and SC could reduce leaching and modify the eluate pH. Hence, they were used again in the triple additive experiments. Figure 4a–d presents the amounts of soluble Mn released and pH values. These results revealed that the addition of an appropriate amount of SB or SC could lead to a further reduction of leached soluble manganese while maintaining the pH of the eluate below 9. The optimal amount of added SB is less than 3 % w.t. and for SC is at 1 % w.t. The addition of carbonates did not change the alkalinity of the solution. Furthermore, the results also illustrated that the

addition of carbonates may strengthen the acid neutralization capacity because when the soluble phosphates were added, the pH of the treated waste solution decreased somewhat (depending upon the amount added) (Quina et al. 2010).

Speciation of manganese

Oxidation of Mn(II) to higher oxidation states (Mn(III) and Mn(IV)) by oxygen easily occurs in alkaline conditions. The formation of these various reaction products revealed that a mixed oxidation mechanism might occur in the waste. MnO_x is used to denote the general empirical formula for the oxidation product, and x values of 1, 1.5, and 2.0 correspond to Mn(II), Mn(III), and Mn(IV) oxides, respectively, without concern for the degree of hydration. The fractions of Mn species in EMSW treated with various additives are presented in Table 5.

From the results obtained, x , as an oxidizing product average value, can be calculated from:

$$x = \omega(Mn^{2+})/\omega(Mn^{Total}) \times 1 + \omega(Mn^{3+})/\omega(Mn^{Total}) \times 1.5 + \omega(Mn^{4+})/\omega(Mn^{Total}) \times 2 \quad (5)$$

Fig. 4 Released amounts of soluble Mn and pH variation after triple additive treatment with CO+TP+SB (a), CO+TP+SC (b), CO+HA+SB (c), CO+HA+SC (d)

Table 5 Species concentration fractions of manganese of EMSW treated with different reagents

Reagents	$\omega(\text{Mn}^{2+})$ (mg g ⁻¹)	$\omega(\text{Mn}^{3+})$ (mg g ⁻¹)	$\omega(\text{Mn}^{4+})$ (mg g ⁻¹)	$\omega(\text{Mn}^{\text{Total}})$ (mg g ⁻¹)	MnO _x =	pH
Control	56.32/95 %	0.34/0.6 %	2.23/3.8 %	58.79	1.04	4.84
CO9	38.44/65 %	14.43/25 %	6.02/10 %	58.84	1.22	7.93
CO9+SB5	32.01/54 %	0.36/1 %	26.52/45 %	58.89	1.45	8.66
CO9+TP5	37.77/64 %	1.31/2 %	19.81/34 %	58.56	1.35	8.52
CO9+HA3	52.21/89 %	3.38/6 %	3.30/6 %	58.88	1.08	8.24
MO10	40.09/68 %	2.38/4 %	16.42/28 %	58.42	1.30	8.83
MO10+SC1	36.23/62 %	4.31/7 %	18.35/31 %	58.63	1.35	9.49

where $\omega(\text{Mn}^{2+})$, $\omega(\text{Mn}^{3+})$, and $\omega(\text{Mn}^{4+})$ are the mass concentrations of Mn(II), Mn(III), and Mn(IV), respectively. The x values were calculated to be less than 1.5 after treatment with the different reagents. The conclusion of a previous study (Kessick and Morgan 1975) indicated that this result could be considered as the product of coprecipitation under appropriate conditions with manganese hydroxide or carbonate. The oxidation rate of Mn(II) has been shown to depend on the pressure of oxygen pressure of oxygen and the square of the concentration of OH⁻. MnOOH is thought to be the primary product from Mn(II) autoxidation in aqueous solution and Mn(II) oxidation under solution conditions resulted in the precipitation of Mn(OH)₂, which is oxidized rapidly by oxygen only, and leads to the formation of Mn(III) and Mn(IV) complexes (Morgan 2005). Mn(II) ions are strongly absorbed to the surface of manganese dioxide at high pH, and OH⁻ ions are potential determining factor to determine what happens on this surface (Kessick and Morgan 1975). Thus, manganese dioxide surface may be helpful for stabilization and further oxidation of Mn(II).

The conversion of these various manganese species may be depicted, as shown in Fig. 5, which shows that Mn(III) plays an important part in further oxidation reaction. However, the redox activity and stability of Mn(III) are strongly dependent on the solution pH (Wang et al. 2014). Higher pH values (i.e.,

above 8.5) favor oxidation of Mn(II) and Mn(III), and low pH values (i.e., below 7) can lower the rate of Mn(II) oxidation leading to the release of more soluble manganese species. The effect of carbonates and phosphates on Mn(II) oxidation will be discussed later.

Mineral composition analysis

XRD patterns of the control sample and a sample treated with reagents are presented in Fig. 6. The patterns showed a large number of crystalline phases. The primary mineralogy of the samples was calcium sulfate hydrate and quartz. However, there were substantial changes in the content of the crystalline phases when different additives were used. The intensities of the peaks corresponding to manganese sulfate in the control samples disappeared, while in the sample treated with CO, peaks were observed corresponding to manganese(IV) oxide (MnO₂) in the “e” pattern, manganese oxide-alpha (Mn_{0.98}O₂) and bixbyite (Mn₂O₃) in the “b” pattern, and santaclarite (CaMn₄Si₅O₁₄·2H₂O). Hexahydrite (MgSO₄·6H₂O) and hausmannite (Mn₃O₄) were observed in samples where MO was used as the primary reagent. Using CO alone, MnSO₄ dissolves completely and Mn₂O₃ and Mn_{0.98}O₂ began to appear. When both CO and a carbonate were used, some peaks corresponding to Mn₃O₄ and MnO₂ were found, consistent with the pattern seen when using phosphates. The intensities of specific peaks were very similar between the “c” and “d” patterns. The detailed mineral phases, however, could not be analyzed using XRD. When using MO as the reagent, Mn₃O₄ and MnCO₃ were found, which served as evidence for stabilization of soluble Mn(II) to a higher oxidation state and the formation of insoluble manganese species. This result was consistent with Cortina et al. (2003) who identified Mn₃O₄ water within higher Mn concentrations after treatment with MO.

Identification of the most economical reagent treatments

The most economical reagent treatments are those that not only have a high immobilization rate but also a low cost. The normalized immobilization rates associated with the

Fig. 5 Schematic drawing of conversion of manganese species in this experiment

Fig. 6 XRD patterns of EMSW samples treated with primary reagent CO (a) and MO (b), including the control sample (a) and EMSW treated with CO9 (b), CO9+TP5 (c), CO9+HA3 (d), CO9+SB5 (e), MO10 (f), MO10+SC5 (g), and MO10+SB5 (h). Selected major diffraction lines for the predominant crystalline components are indicated: *Q* quartz [SiO₂], *Ch* calcium sulfate hydrate [CaSO₄·xH₂O], *Cs* calcium sulfate [CaSO₄], *G* gypsum [CaSO₄·2H₂O], *Ms* manganese sulfate [MnSO₄], *Hm* hausmannite [Mn₃O₄], *Mo* manganese(IV) oxide [MnO₂], *S* santaclaraite [CaMn₄Si₅O₁₄·2H₂O], *M9* manganese oxide-alpha [Mn_{0.98}O₂], *B* bixbyite-C [Mn₂O₃], *R* rhodochrosite [MnCO₃], *H* hexahydrite [MgSO₄·6H₂O], *P* pyrochroite [Mn(OH)₂]

different additive_dose experimental conditions and reagent costs were projected over a two-dimensional plot to identify those additive_dose conditions that operate to reduce the HNO₃–H₂SO₄ leachability of manganese. A K-means cluster analysis (KCA) was used to find the groups of treatment conditions that showed similar responses according to the variables. The KCA divides all treatments into three clusters, as shown in Fig. 7. The optimum economical additives for reduction of the extraction of manganese are those located within the top left-hand quadrant on the cluster plots, where the immobilization degree is higher than 90 % and cost is less than \$750/t of EMSW. The reagent treatments that are included in those relative positions are indicated by red dotted circle and are identified as the economical reagent treatments for reducing leachability of manganese. These treatments are CO_9+SB_5, CO_9+TP_5, CO_9+SC_5, and CO_9+TP_5+SC_1, whose treatment costs are \$720, \$545, \$750, and \$641/t of EMSW, respectively. These prices correspond to the reagents used in laboratory scale studies. The reagent prices of CO, SB, SC, TP, MO, DAP, and DHP are \$3, \$9, \$9.6, \$5.5, \$16.3, \$20, and \$6/kg, respectively. It is uneconomical to use HA to treat EMSW at a price of \$420/t.

Discussion

Immobilization of manganese by quicklime and carbonates

Carbonation reactions can occur with an internal carbon source (e.g., Na₂CO₃ and NaHCO₃). Carbonation reactions effectively reduced the leaching of lead and barium, but increased that of antimony and chromium, whereas arsenic, copper, nickel, and most anions are largely unaffected (Chen et al. 2009).

Although the single reagent CO reduced the leaching of manganese, carbonate as an assisting reagent further decreased the leachability of manganese. The pH value of the system gradually reduced around 0.5–0.8 upon the carbonate addition of 1–5 %. This decrease in pH is dependent on the relationship between the rate of dissolution of solid calcium hydroxide and the rate of consumption of OH[−] (Johannesson and Utgenannt 2001). When solid Ca(OH)₂ is consumed by Mn(II) to form precipitations, the consumption rate of OH[−] becomes slower and the pH decreases. The addition of carbonates to the waste has two effects: First, the acid-neutralizing capacity increased under acidic conditions, and second, hydrolysis of carbonates can provide OH[−], which

Alternatively, the high pH promotes the direct oxidation of Mn(II). This oxidation sequence would occur as shown in Eqs. (8)–(10):

The oxidation rate of Mn(II) has been shown to depend on the square of the concentration of OH^- (Kessick and Morgan 1975) and proportional to O_2 concentration (Morgan 2005). Experimental observations of Mn(II) oxidation revealed that the rate of oxidation increased dramatically with increasing pH. The product of reaction is MnOOH in the pH range ca. 8 to 9.5. The observed rate constants for the oxidation of Mn(II) oxidative span almost three orders of magnitude in the pH range 8.03 to 9.30 (Morgan 2005). The oxidation of Mn(II) to Mn(III) species which is intermediate is crucial because it can be progressively transformed to $\text{MnOOH}(\text{s})$ via hydrolysis, nucleation, and precipitation formation (Morgan 2005).

Immobilization of manganese by using caustic magnesia

MO in water can be hydrated causing an increase in pH, as in Eq. (11) (Rocha et al. 2004), and the soluble manganese will participate a precipitation reaction, as in Eqs. (2)–(4) and (12).

MO alone or combined with SB and SC is an attractive reagent for EMSW treatment systems, primarily because of: (1) low solubility: the hydration of MO produces brucite ($\text{Mg}(\text{OH})_2$) which buffers the solution pH to between 8.5 and 10 where the solubility of metal manganese compounds is low (Cortina et al. 2003; Rötting et al. 2008), (2) oxidation and precipitation: dissolution of MO would achieve a high pH (near 10) where Mn(II) is rapidly oxidized and precipitate immediately as manganite (Rötting et al. 2008) and is later transformed to hausmannite which was detected by XRD in the sample treated with caustic magnesia, and (3) cementitious effect: the hydration of MO can cause gelation and formation of compacting clumps. This process is similar to the

solidification of cement used to encapsulate contaminants. As a consequence of all of these characteristics, the immobilization of Mn(II) is a result of physical encapsulation, oxidation, and precipitation.

Conclusion

This work addressed the chemical immobilization treatment of EMSW produced from electrolytic manganese. In order to reduce the amount of soluble Mn(II) that leaches into the environment, eight chemical reagents were tested. $\text{CO}_9 + \text{SB}_5$ and $\text{CO}_9 + \text{TP}_5$ reduced the amount of Mn(II) leached to 100 mg/kg while maintaining the eluate pH in the range of 6–9. Using MO alone and MO+SB/SC also had a positive immobilization effect, and leaching amounts to as low as 0.01 mg/kg of EMSW. The most economical reagent treatments, determined by using K-means cluster analysis, are $\text{CO}_9 + \text{SB}_5$, $\text{CO}_9 + \text{TP}_5$, $\text{CO}_9 + \text{SC}_5$, and $\text{CO}_9 + \text{TP}_5 + \text{SC}_1$, which cost \$720, \$545, \$750, and \$641/t of EMSW, respectively (for analytical grade reagents).

The XRD analysis carried out in this study showed that the mechanism of immobilization of soluble Mn(II) consisted of precipitation and oxidation. A high degree of immobilization and a high oxidation state of manganese were obtained using $\text{CO}_9 + \text{SB}_5$ because the addition of SB causes an increase in OH^- and maintains the alkaline conditions, which are favorable for immobilization and oxidation. Using MO could also effectively immobilized the soluble Mn(II) because of its physical encapsulation properties, the oxidation products such as Mn_3O_4 , and the precipitation of insoluble Mn(II) species.

The additive has a good immobilization on soluble Mn(II) from EMSW in laboratory study. However, study of short- and long-term of immobilization performance is indispensable and we continue to focus on its research.

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