Arsenic release from arsenic-bearing Fe–Mn binary oxide: Effects of E_h condition

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ABSTRACT

Ferric and manganese binary oxide (FMBO) has been successfully used to remediate arsenic-polluted river, but there still lacks sufficient data to evaluate its effects on environments. The release behaviors of iron (Fe), manganese (Mn), and arsenic (As) in different E_h ranges were investigated for As-bearing FMBO sediment after remediating As-polluted DaSha River by FMBO. Under high E_h range (+550 to +400 mV), slight dissolution of Fe and Mn, which corresponded to 12.2% and 25.6%, and less than 5% of As release were observed in 336 h. Under lower E_h range (+50 to –100 mV), elevated extent of the dissolution of Mn and Fe were observed, which corresponded to as high as 61.3% and 70.1%. Under such conditions, the dissolution rate of Mn was higher than that of Fe. Furthermore, from the established relationship of As release and the dissolution of Fe and Mn, the release of As seemed dominated by the dissolution of Fe. X-ray photoelectron spectroscopy (XPS) analysis demonstrated the release of Fe, Mn, As(III), and As(V) after sodium ascorbate-treatment, and the re-adsorption of As(V), as indicated from the increased binding energy of As 3d from 44.78 to 45.83 eV. Surface element composition analysis indicated significant decrease of Mn from 3.22% to 0.54%, slight increase of Fe from 12.45% to 13.67%, and elevated ratio of As from 0.11% to 0.32% accordingly. The main reactions of Fe and Mn dissolution and the pathways of As release under different E_h ranges were also proposed.

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1. Introduction

Surficial sediments in rivers impact water quality and ecology, and show activity towards water pollutants (Dudka and Adriano, 1997). The oxides of iron (Fe) and manganese (Mn) were identified as the most important geochemical components related to their abundance and wide existence in river sediments (Perret et al., 2000). They are crucially important for the mobility and transformation of cationic heavy metals (e.g., Pb, Cd, Cu, and Zn) and anionic species such as arsenic (As) and phosphate (P) (Wang et al., 2005; Bauer and Blodau, 2006; Li et al., 2009). Fe oxide was reported to correlate best with As among other metal oxides (Smedley and Kinniburgh, 2002). The transportation and release behaviors of As was controlled by the dissolution of Fe or Mn oxides, which also affected As concentrations in water environments such as river and groundwater (Matisoff et al., 1982; Keimowitz et al., 2005).

In the past several years, there have occurred several urgent environmental pollution accidents due to the unexpected discharge of high-arsenic wastewater into water environments in China. The DaSha River in HeNan Province in China was seriously polluted in 2008, with arsenic concentrations ranging from 2 to 6 mg L^{–1} along the 100-km river. This river was successfully

remediated by the novel Fe–Mn binary oxide (FMBO) with oxidative and adsorptive activities towards arsenic (Zhang et al., 2007a,b). The As-bearing FMBO after settling in the riverbed may definitely show different leaching and desorption behaviors due to the critically different environmental conditions such as E_h , coexistent ions and bioactivities. E_h condition in sediments of river and lake is normally in the range of +200 to +100 mV (Yin et al., 2008), which could impact the mobilization of arsenic within the As-bearing FMBO in river sediments. Unfortunately, the release behaviors of arsenic from As-bearing FMBO under different E_h conditions have not been well studied, which restrict the evaluation of ecological risks and the promotion of technological strategy for the safe dealing of these sorbents.

On the other hand, arsenic concentrations in drinking water should be controlled as low as 0.01 mg L^{–1}, and adsorption is widely used especially in rural areas. Most spent oxide sorbents are used in a throw-away (non-regenerable) mode (Ghosh et al., 2006), but the As leaching behaviors and the secondary risks of spent sorbents (e.g., As-bearing FMBO) under different environment conditions have not been well studied. Fe and Mn oxides within FMBO exhibit different oxidation potential (Eqs. (1) and (2)) and reductive dissolution of Fe and Mn from As-bearing FMBO possibly show diverse effects on As release under different E_h conditions.

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Table 1
pH and E_h conditions in batch experiments with various reducing agents.

Reducing agents	Concentrations (mg L ⁻¹)	pH	E_h
Sodium citrate	0.05	6.9–8.2	+550 to +400 mV
Sodium ascorbate	0.01	6.7–6.9	+250 to +50 mV
Sodium ascorbate	0.05	6.9–7.1	+100 to –100 mV
Sodium citrate + sodium ascorbate	0.05 + 0.025	7.8–8.0	+50 to –100 mV

The As-bearing FMBO used in this study was collected from the DaSha riverbed. The objectives of this work were: (1) to investigate the release behaviors of As species (As(III) and As(V)), Fe and Mn from As-bearing FMBO under different E_h conditions; (2) to illustrate the relationship between As release and the dissolution of Fe and Mn; (3) to propose the main pathways involved in the release of arsenic under different E_h conditions. E_h were controlled by reducing reactants such as sodium citrate and sodium ascorbate. This study ignored the microorganism activities that occurred in the riverbed in practice, and focused on the release of arsenic from As-bearing FMBO.

2. Materials and methods

2.1. Characterization of As-bearing FMBO

The As-bearing FMBO sludge, collected from riverbed in DaSha River in Shangqiu City, HeNan Province, China, was sealed in nitrogen atmosphere and freeze-dried before analysis and batch

adsorption experiments. The As-bearing FMBO powder was then digested in triplicate by microwave-assisted digestion procedures following EPA method 3051A (USEPA, 2007) for the analysis of main elements therein show in Table S1 (Supporting information).

The analysis of the binding phases of As(III) and As(V) within As-bearing FMBO (i.e., dissolved arsenic, ionically bound arsenic, strongly adsorbed arsenic and arsenic coprecipitated or occluded by amorphous Fe oxides and Mn oxides) followed the methods reported by Keon et al. (2001). The results were presented in Table S2 (Supporting information) (Kien et al., 2009). From the result the main phase of arsenic is strongly adsorbed and occluded by amorphous Fe oxides and Mn oxides.

2.2. Batch experiments

Batch experiments were conducted in sealed 50 ml polypropylene tubes in an end-over-end tumbler for 336 ± 2 h (20 ± 1 °C). The 30 mL reducing agents at designed concentrations (Table 1) were added in tubes with 0.05 g As-bearing FMBO. To avoid the introduction of oxygen during sampling, several sets of tubes were prepared for sampling at intervals with prolonged reaction times. After sampling, each tube used was discarded. pH and E_h were directly and quickly measured after sampling, and the concentrations of As(V), As(III), Fe, and Mn were determined after samples were filtered through 0.45 μm cellulose acetate membrane.

2.3. Analytical methods

pH and E_h were detected after sampling using combination ORP Electrode (HACH Sension 2, America). The measured E values were transformed into E_h values (vs. SHE) (oxidation reduction potential of the sample relative to the standard hydrogen electrode (SHE)) by

Fig. 1. Fe, Mn dissolution and As desorption from As-bearing FMBO by different reducing agents. A: 0.05 M sodium citrate (+550 to +400 mV); B: 0.01 M sodium ascorbate (+250 to +50 mV); C: 0.05 M sodium ascorbate (+100 to –100 mV); D: 0.05 M sodium citrate + 0.025 M Sodium ascorbate (+50 to –100 mV).

addition of the potential developed by the reference electrode portion relative to the SHE.

As(III) and total As analysis were selectively performed using hydride generation-atomic fluorescence spectroscopy (HG-AFS) with an AF-610A instrument (Beijing Ruili Analytical Instrument Co., Ltd., China). The total concentration of Fe and Mn were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (SCIEX Perkin–Elmer Elan mode 5000). Total Carbon, hydrogen and nitrogen were detected by an automated elemental analyzer (Elementar Vario MICRO CUBE, Germany).

Selected samples were freeze-dried for XPS analysis. The chemical analysis on the surfaces of sorbents was conducted by XPS (Kratos AXIS Ultra, UK), with monochromatized AlK α X-ray source (1486.7 eV) working at 150 W, 15 kV, and 10 mA and base pressure of 3×10^{-8} Torr in the analytical chamber. For wide-scan spectra, an energy range of 0–1100 eV was used with pass energy of 160 eV. The high-resolution scans were conducted according to the peak being examined with pass energy of 40 eV. C 1s peaks were used as an inner standard calibration peak at 284.7 eV. The XPS results were collected in binding energy forms and fit using the software of Vision (PR2.1.3) and CasaXPS (2.3.12Dev7).

Electrochemical experiments employed an EG&G model 263A potentiostat system (Princeton Applied Research, USA) connected with a counter electrode (Pt wire, 70 mm in length with a 0.4 mm diameter), a working electrode (Indium Tin Oxides (ITO) electrode (CSEM, Switzerland), active area of 9 cm²) and a reference electrode (a saturated calomel electrode (SCE)). The electrolyte solution of 200 mg L⁻¹ sodium sulfate (Na₂SO₄) was used. The solution was stirred continuously by a magnetic stirring bar. Cycling voltammetry was conducted between –1.0 and 1.0 V with a scan rate of 10 mV s⁻¹.

3. Results and discussion

3.1. As-bearing Fe–Mn binary oxide dissolution and associated-As release

Fig. 1 showed the dissolution behaviors of As(III), As(V), Fe, and Mn from As-bearing FMBO in four E_h ranges of high E_h (+550 to +400 mV, Condition A), medium E_h (+250 to +50 mV, Condition B), low E_h (+100 to –100 mV, Condition C), and strongly reductive E_h (+50 to –100 mV, Condition D). It was observed that the release of both As(III) and As(V) from As-bearing FMBO was much more important under Conditions C and D than that in Conditions A and B.

In high E_h range (Condition A), within the contact time of 336 h, less than 5% of As(V) and 1% of As(III) were released from As-bearing FMBO, and E_h accordingly decreased from +550 mV to +400 mV. Similar trends of arsenic release were observed in medium E_h ranges (Condition B). The release ratios of As(III) (4.1%) and As(V) (13.8%) were slightly higher than those in Condition A. The release of arsenic was significantly increased from As-bearing FMBO in the low E_h ranges. Within the equilibrium contact time of 336 h, the release of 12.9% of As(III) and 69.6% of As(V) in Condition C was determined, which was increased to be 16.0% and 77.5% under strongly reduction condition, respectively. Additionally, as shown in Fig. 1, the critical time to achieve the maximal As(V) release was shortened as 162 h and 72 h in Conditions C and D, respectively. Interestingly, it was also observed that the As(V) concentration decreased whereas As(III) concentration increased with prolonged contact time under these two E_h ranges. This may be ascribed to the combined effects of the reduction of As(V) to As(III) (Eq. (3)) and the re-adsorption

Fig. 2. Apparent desorption rate of As and dissolution rate of Fe and Mn calculated from dissolution or desorption data using Eq. (6). A: 0.05 M sodium citrate (+550 to +400 mV); B: 0.01 M sodium ascorbate (+250 to +50 mV); C: 0.05 M sodium ascorbate (+100 to –100 mV); D: 0.05 M sodium citrate + 0.025 M Sodium ascorbate (+50 to –100 mV).

of As(V) onto the surfaces of As-bearing FMBO ($-S_{Fe-Mn}$) (Eq. (4)).

To check the reduction of As(V) to As(III), blank experiments of reducing As(V) to As(III) by 0.05 M sodium ascorbate were performed. The results (Table S3 (Supporting information)) indicated that 18% of As(V) was reduced to As(III) by sodium ascorbate within 336 h in the absence of As-bearing FMBO. Deuel and Swoboda also reported that the reduction of As(V) to As(III) was insignificant in the release of As from an untreated black clay soil whereas the reduction and dissolution of 'ferric arsenates' dominated the mobility and transportation of As (Deuel and Swoboda, 1972). However, the reduction of FMBO by reductive reagent provided more surface sites available for As(V) adsorption (Zhang et al., 2007a), which favored the re-adsorption of As(V) onto FMBO surfaces.

The reductive dissolution of Fe and Mn in four different E_h ranges (Fig. 1) provided valuable information on the explanation of arsenic release from As-bearing FMBO. In high E_h range, 25.6% of Mn and 12.2% of Fe were dissolved in equilibrium time. The dissolution amount of both Mn and Fe was increased with the E_h decrease, which was determined to be 40.7% and 29.7% respectively in Condition B. And, in strong reductive E_h ranges of Conditions C and D, dissolution amount and rate of Fe and Mn were largely increased.

The reductive dissolution of Mn(IV) oxides by reductive species (i.e., phenols, oxalate) has been well reported before, and the inner electron transfer mechanism was proposed (Xyla et al., 1992).

Mn(IV) oxides exhibit oxidative activities towards sodium citrate, sodium ascorbate, and the organics within As-bearing FMBO Table S1 (Supporting information) (Eq. (5)). These reactions were more acute at lower E_h ranges, leading to more significant and higher rate of Mn(IV) dissolution (Fig. 1). Comparatively, Fe(III) oxides showed lower oxidizing potential than Mn(IV) oxides did (Eqs. (1) and (2)), which led to slower rate and less ratio of Fe release than that of Mn under similar conditions in Conditions A–C. In Condition D, dissolution amount and rate of Fe and Mn were fiercely almost the same.

The above results exhibited that the release of arsenic from As-bearing FMBO was mainly controlled by the dissolution of Fe and Mn oxides. The similar results were also reported (Suter et al., 1991; Deng, 1997; Perret et al., 2000).

3.2. The release rate of As from As-bearing FMBO

To provide insight on the desorption of As from As-bearing FMBO, the apparent release rate of As and dissolution rate of Fe and Mn were calculated by the Eq. (6) as follows:

$$RR_i = \Delta DR_i / \Delta t_i = (DR_{i+1} - DR_i) / (t_{i+1} - t_i) \quad (6)$$

where RR_i represents the apparent release rate of As, Fe, and Mn at a specified interval ($\% h^{-1}$); DR_i represents the desorption ratio of As, Fe, and Mn at a specified interval (%); and t_i represents the specified interval (h).

The variation of RR_i values of As(III), As(V), Fe, and Mn at each interval from 0 to 336 h under different E_h ranges was illustrated in Fig. 2. In low E_h range, not only higher extent of As release

Fig. 3. Correlation between release of As(V) and dissolution of Fe using Linear Fitting to calculate their relativity. Linear relationship equation of dissolution of Fe and release of As in four conditions also shown in this figure. In equation x stands for dissolution of Fe (%) and y stands for release of As (%). A: 0.05 M sodium citrate (+550 to +400 mV); B: 0.01 M sodium ascorbate (+250 to +50 mV); C: 0.05 M sodium ascorbate (+100 to –100 mV); D: 0.05 M sodium citrate +0.025 M sodium ascorbate (+50 to –100 mV).

was observed, but also the dissolution of Fe and Mn were accelerated. The maximal RR_i value for Mn was $1.08\% \text{ h}^{-1}$ in E_h range from +550 mV to +400 mV (Condition A), which increased to $5.31\% \text{ h}^{-1}$ in strong reductive E_h range (Condition D). Additionally, the dissolution rate of Mn was also higher than that of Fe, especially in initial periods, owing to the higher activity of MnO_2 towards reductive species than Fe. In E_h ranges from +550 mV to 50 mV (Conditions A–B), the RR_i values of Mn were 3–10 times higher than those of Fe within 40 h, which remained to be below $1\% \text{ h}^{-1}$ within 336 h. Dissolution rate of Fe increased under stronger reductive conditions (+50 mV to –100 mV), with maximal value of $0.78\% \text{ h}^{-1}$ at the interval from 40 to 52 h and $1.72\% \text{ h}^{-1}$ from 16 to 24 h for Conditions C and D, respectively.

The trends in dissolution rate of Mn and Fe were different within 336 h contact time. Generally, the RR_i values of Mn decreased steadily within 336 h contact time under these four different E_h conditions. However, the variation trends of RR_i values of Fe were observed to be dependent on the E_h conditions. For example, under strong reductive E_h condition from +50 to –100 mV (Condition D), the RR_i values of Fe oxides increased steadily within 24 h, and then began to decrease within 24–336 h after achieving the maximal value of $1.72\% \text{ h}^{-1}$. In E_h ranges from +100 to +400 mV (Conditions A and B), relatively stable RR_i values were observed for Fe. This may be ascribed to the higher oxidative activity of Mn oxides than that of Fe oxides. Reductive species better react with Mn oxides, leading to the decrease of the E_h values accordingly, which accelerated the dissolution of Fe from FMBO, especially under strong reductive E_h conditions (Conditions C and D).

3.3. The correlation of dissolution of Fe and Mn with release of As(V)

The correlation between As(V) release and the dissolution of Fe and Mn was furthermore studied. The release of As(V) was linearly

correlated with that of Fe (Fig. 3). Under four E_h conditions, the slopes of linear relationship equation for release of As and dissolution of Fe were determined to be 0.314, 0.489, 1.296, and 1.167, respectively. It was obvious that the slopes in Conditions C and D were almost four to three times larger than that of Conditions A and B. Sorption of arsenic onto this As-bearing FMBO was not saturated and many ferri-hydroxyl sites the surfaces of this oxide were still vacant (Zhang et al., 2007a). So higher slope in lower E_h condition could be explained by the fact that in Conditions A and B iron(III) in vacant ferri-hydroxyl on the surfaces of As-bearing FMBO was easier to be reduced than iron(III) in arsenic connected ferri-hydroxyl.

The release of As(V) was obviously different from that of Mn. As shown in Fig. 4, two different scenarios could be concluded in the relationship between As(V) release and Mn dissolution in a specified condition: the remarkable Mn dissolution with low extent of As(V) release, and the significant As(V) release with little increase of Mn dissolution. In Condition B, the Mn dissolution ratio of 33% was only followed by 3.7% of As release, whereas slight increase of Mn dissolution ratio from 40.2% to 40.7% was followed by large increase of As release ratio from 5.1% to 13.8%. Similar trends were also observed in other E_h conditions. These results confirmed that the release of As(V) from As-bearing FMBO was controlled by the dissolution of Fe, rather than that of Mn.

3.4. Surface analysis of the Fe–Mn binary oxides by XPS

The XPS spectra of Fe 2p, Mn 2p, and As 3d between the As-bearing FMBO and that after being treated by 0.05 M sodium ascorbate for 100 h was compared in Fig. 5. As shown in Fig. 5, the binding energy of Fe 2p within As-bearing FMBO was 711.8 eV, and the peak shape indicated that the oxidation state of Fe was +III. Change of peak shape and binding energy was not

Fig. 4. Relationship between release of As(V) and dissolution of Mn. A: 0.05 M sodium citrate (+550 to +400 mV); B: 0.01 M sodium ascorbate (+250 to +50 mV); C: 0.05 M sodium ascorbate (+100 to –100 mV); D: 0.05 M sodium citrate + 0.025 M sodium ascorbate (+50 to –100 mV).

observed after reaction with sodium ascorbate. However, decrease of Fe 2p spectra intensity was observed after being treated by sodium ascorbate, showing the occurrence of strong interactions between As(V) and Fe atoms (Zhang et al., 2005).

The Mn 2p spectra of the As-bearing FMBO before and after reaction with sodium ascorbate were illustrated in Fig. 5. The binding energy of original sample was 642.6 eV, which corresponded to the oxidation state of +IV. After being treated by sodium ascorbate, there exhibited slight decrease of binding energy to be 642.2 eV and significant decrease in intensity by 50%. The decrease of binding energy could be ascribed to the reductive dissolution of Mn(IV) and the increased proportion of reduced Mn species (i.e., Mn(II)) on the surface of the FMBO (Zhang et al., 2007a), because Mn(II) was easy to be absorbed by MnO₂ (Petrie et al., 2002). Nesbitt et al. analyzed thoroughly the Mn2p spectra of synthetic birnessite before and after reaction with As(III) (Nesbitt et al., 1998). They found that binding energies of Mn(IV), Mn(III), and Mn(II) species were very close to each other and the binding energy of Mn with low oxidation state was located on the low-energy side (Zhang et al., 2007a). Additionally, the remarkable decrease in intensity of Mn 2p spectrum suggested the release of elemental Mn to solution and the enrichment of reduced forms (i.e., Mn²⁺) relatively to original sample.

The binding energy of As 3d core for As(III) and As(V) within arsenic oxides are commonly 44.3–44.5 eV and 45.3–45.6 eV (Nesbitt et al., 1998; Ouvrard et al., 2005; Zhang et al., 2007a). After being adsorbed onto iron oxides, the binding energy of arsenic anions could be shifted up to 44.6 ± 0.13 eV for As(III) and 46.0 ± 0.17 eV for As(V) (Ding et al., 2000). In this study, fit results (Table S4 (Supporting information)) showed that the As 3d line of the original As-bearing FMBO could be fitted with two components with respective binding energies of 44.34 and 45.52 eV. These two peaks were assigned to As(III) and As(V), and illustrated the co-existence of As(III) and As(V) on the surfaces of As-bearing FMBO (Table S4 (Supporting information)). After sodium ascorbate-treatment, the binding energy of As 3d increased from 44.78 eV to 45.83 eV indicated that the peak of As(III) disappeared and arsenic on treated sample could be attributed to As(V) (Fig. 5). The oxidation of As(III) to As(V) could not occur under this strong reductive conditions (+100 to −100 mV). The shift of binding energy of As 3d was ascribed to the desorption of As(III) and the re-adsorption of As(V) onto the surfaces of As-bearing FMBO after sodium ascorbate-treatment. The non-ionic As(III) was more difficult to be adsorbed onto sorbents than the negatively-charged As(V) (Zhang et al., 2007a), and was thereafter more prone to desorption than As(V) (Dixit and Hering, 2003). Additionally, the formation of more active sites on FMBO surfaces after Na₂SO₃-treatment was confirmed in our previous study (Zhang et al., 2007a), and the re-adsorption of As(V) could be favored by this effect.

Surface composition analysis of As-bearing FMBO before or after treatment from XPS results indicated that Fe atom content increased from 12.45% to 13.67% whereas Mn atom content decreased from 3.22% to 0.54% after sodium ascorbate-treatment. The increase of As atom content from 0.11% to 0.32% also indicated the occurrence of As(V) re-adsorption.

3.5. Proposed pathway of As release under different E_h conditions

Cyclic voltammetry scan also indicated the species transformation under different E_h conditions (Fig. S1 (Supporting Information)). Elemental Mn showed two reductive peaks with the potential decreasing from +600 to 0 mV (Fig. S1a), which was assigned to +550 mV and +50 mV respectively. The cathode reduction peak of As(V), which indicated the reduction of As(V) to As(III), was determined to be −210 mV (Fig. S1c). There showed no remarkable change in the peaks under the simultaneous presence of As and Mn (Fig. S1b).

Fig. 5. Core level photoelectron spectra of Fe 2p, Mn 2p and As 3d. Original Sample stood for untreated Fe–Mn binary oxide. Treated sample stands for As-bearing FMBO treated by 0.05 M sodium ascorbate reacted for 100 h.

From above results, the major pathways involved in the release of arsenic from As-bearing FMBO under different E_h conditions could be concluded in Eqs. (7)–(11) and was presented in Fig. 6. It was noted that the desorption of As(III) within As-bearing FMBO was not taken into account.

- (1) Reductive dissolution of Mn(IV) to Mn²⁺ with limited extent of As release

- (2) Reductive dissolution of Fe(III) to Fe²⁺ with remarkable release of As

Fig. 6. Schematic diagram of main reactions involved in As-bearing FMBO under different E_h conditions.

(3) Re-adsorption of Mn²⁺ onto –SFe–Mn surfaces

(4) Re-adsorption of As(V) on FMBO surface

(5) As(V) reduction to As(III)

where, As(V)–SFe–Mn represents the As-bearing FMBO surfaces; As(V)–S_{Fe-Mn}^{*}, As(V)–S_{Fe-Mn}^{**}, –S_{Fe-Mn}^{*}–Mn(OH)₂, and –S_{Fe-Mn}^{*} represents the reductive products of As(V)–SFe–Mn. The E_h ranges were not concluded from theoretical calculation but from the experiment results in this study.

4. Conclusions

It has been exhibited in this study that the dissolution of Fe, Mn, and the subsequent release of As from As-bearing FMBO were largely controlled by the E_h conditions. In E_h range from +300 to +600 mV, the reduction of Mn(IV) oxide to Mn²⁺ resulted in limited As release. By contrast, the dissolution of Fe mainly occurred in E_h range below +300 mV, which dominated the release and desorption of As. The reduction of Mn(IV) on the surfaces of As-bearing FMBO was beneficial to the re-adsorption of As(V) onto its surfaces. Under strong reductive E_h ranges (below 0 mV), the As species transformation from As(V) to As(III) was observed, which acceler-

ated the release of As from As-bearing FMBO. So the E_h condition should be well considered for the safe disposal of the As-bearing FMBO to avoid secondary pollution.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2011.01.066](https://doi.org/10.1016/j.chemosphere.2011.01.066).

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