ELSEVIER

Sustainability of humic acids in the presence of magnesium oxide

Nathalie A. Wall *, Sara A. Mathews

Sandia National Laboratories, 4100 National Parks Highway, Carlsbad, NM 88220, United States

Abstract

The Waste Isolation Pilot Plant (WIPP) is a U.S. Department of Energy (DOE) repository for the disposal of transuranic waste generated from the U.S. defense program. Humic acids (HA), known to strongly bind to actinides and which may be generated by the degradation of organic materials present in the waste, may influence the performance of the WIPP. This work presents experimental results on the effect of WIPP brines, ERDA-6 and GWB, and of the WIPP engineered barrier, Premier Chemicals magnesium oxide, on the solubility of HA. In the absence of MgO, a portion of HA initially precipitates, but a constant concentration of HA remains in solution: over a 60 day period of time, at least 290 ± 10 mg/L HA can remain soluble in de-ionized (DI) water, 30 ± 4 mg/L in 95% ERDA-6, and 31 ± 4 mg/L in 95% GWB. For solutions initially containing from 0 to 400 mg/L HA, the ratio of the initial HA concentration and the soluble HA concentration is 1.3 in DI water, 13 in 95% ERDA-6, and 11 in 95% GWB. In the presence of MgO, all HA precipitate within 60 days in systems with a high liquid-to-solid ratio (10.0 g/g) or a low ratio (2.4 g/g). This phenomenon is due to HA precipitation and/or sorption on the surface of MgO.
© 2005 Elsevier Ltd. All rights reserved.

1. Introduction

The Waste Isolation Pilot Plant (WIPP) located 42 km east of Carlsbad, New Mexico, is a repository for transuranic waste from U.S. Department of Energy (DOE) defense programs. The WIPP is 655 m below the surface in bedded salts of the Permian Salado Formation, which consists principally of halite, overlaying the Castile Formation, an interbedded halite and anhydrite formation (U.S. DOE, 2004, Chapter 2). The repository will consist of 8 seven-room panels upon completion. Two main access drifts in the waste region will also be available for waste disposal and will consti-

tute two additional panels. The WIPP Performance Assessment (PA) analyzes the consequences of future human intrusions into the repository by inadvertent and intermittent drilling for resources; such intrusions could release radionuclides to the accessible environment before the end of the 10 ka regulatory period. Therefore, the DOE has defined different drilling scenarios, which involve the penetration of the repository by one or more drill holes; the scenarios also involve the possibility of the penetration of a pressurized Castile brine reservoir (U.S. DOE, 2004, Chapter 6).

One of the parameters used in PA is the expected concentration of humic acids (HA), organic compounds well known for their strong complexing ability with actinides (e.g. Bertha and Choppin, 1978; Nash and Choppin, 1980; Minai and Choppin, 1989; Kim et al.,

---
* Corresponding author. Fax: +1 505 238 006.
  E-mail address: nawall@sandia.gov (N.A. Wall).

1991; Moulin et al., 1992a; Kim and Czerwinski, 1996; Labonne-Wall et al., 1999; Seibert et al., 2001; Wall et al., 2002) and their role in the environmental behavior of actinides (Buffle, 1988; Choppin, 1988; Moulin et al., 1992b; Kim et al., 1994; Czerwinski et al., 1996; Labonne-Wall et al., 1997). HA, often found in natural waters as the result of biodegradation of animal and plant matter, may form in situ in the WIPP due to the presence of soils, nutrients, and cellulosic substrates for microbial action in the waste. The current literature data are insufficient to predict the generation rates of HA in WIPP brines, or the solubility in the WIPP. The influence of several parameters relevant for the WIPP on the HA solubility are known. High ionic strengths promote HA coagulation (Tombacz and Meleg, 1990; Grace et al., 1997; Wall and Choppin, 2003). Also, the presence of multivalent cations such as Ca^{2+} and Mg^{2+}, present in significant concentrations in WIPP brines, increase significantly HA coagulation in low-ionic-strength solutions (Pefferkorn, 1997; Ong and Bisque, 1968; Hong and Elimelech, 1997; Römkens and Dolfing, 1998; Tipping and Ohnstad, 1984; Wall and Choppin, 2003). However, an increase of the ionic strength decreases the coagulating efficiency of multivalent cations (Wall and Choppin, 2003), making it difficult to predict the effect of the WIPP brines on the HA solubility. Moreover, MgO, the WIPP engineered barrier, currently mined and processed by Premier Chemicals in Gabbs, Nevada, could affect HA solubility. Magnesium oxide and its hydration and carbonation products could dissolve and release more Mg^{2+} than already present in WIPP brines and/or HA could precipitate at the surface of the minerals.

This paper presents experimental results on the solubility of HA in the brines representative of those found in the Salado and the Castile formations: Generic Weep Brine (GWB) and ERDA-6, respectively. The effect of MgO on HA coagulation in WIPP brines was also studied. The range of HA concentrations studied was larger than that found in most natural systems, to obtain conservative estimates of HA solubilities in WIPP. The authors chose to use purified commercial HA instead of HA extracted from WIPP brines or solid samples, because of the large quantities needed to carry the studies and because HA of various origins and natures have shown similar properties (Labonne-Wall et al., 1999).

2. Experimental

De-ionized (DI) water was obtained from a Nanopure Infinity DI water system. The brines GWB and ERDA-6 were periodically prepared according to Robinson's (1996) procedure, using reagent-grade chemicals and DI water to obtain the concentrations presented in Table 1. HA were purchased from Aldrich Chemicals

and purified. A solution of 1 g/L HA in 0.25 M NaOH was stirred overnight. Then, 12 N HCl was added to the solution (70 mL/g HA) to precipitate HA, and the slurry was stirred overnight. The slurry was centrifuged at 3000 rpm for 0.5 h in a Fisher Scientific Marathon 21K/R centrifuge, the supernatant was discarded, and the slurry was freeze-dried in a Labconco Freeze Dry System Freezone 4.5. The purification procedure was repeated until the ash content (sample heated at 500 °C for 5 h in a Fisher Scientific Isotemp muffle oven) was less than 10%; the ash content of the original Aldrich HA is about 60%. Reagent-grade Fisher Chemicals MgO (Fisher MgO) (containing 97.0% MgO) and the material used as the WIPP engineered barrier, Premier MgO (containing 87–89% MgO (Snider, 2003a,b)), were used without any further preparation. HA solutions were prepared in DI water by dissolving HA in a concentrated NaOH solution and adjusting pH to 9 with concentrated HCl. HA solutions were prepared in GWB or ERDA-6 by adding a 1 g/L HA solution prepared in DI water and at pH 9 to the brine of choice and DI water to obtain 95% brine solutions. When not in use, the HA solutions were kept in a refrigerator, to retard colloidal coagulation.

HA concentration ([HA]) was determined by spectrophotometry at 465 nm. The Varian CARY 300 Conc. spectrophotometer was calibrated by measuring the absorbance at 465 nm (A_{465}) of HA solutions of known concentrations. The pH was measured with an Orion model 900A pH meter and a semicombination Corning electrode.

Spectrophotometry is not always an appropriate technique to quantify the HA concentrations of filtered HA samples. Absorbance measurements fail to provide accurate concentration values if HA solutions are filtered through very small pore size filters, such as 100 kDa (Wall and Choppin, 2003). The authors verified that spectrophotometry is an appropriate technique to measure the concentration of HA solutions filtered with 1.0 μm pore size membranes. The concentration of unfiltered HA solutions and of freshly filtered (over 1.0 μm pore size filter) HA solutions were determined. The total organic C (TOC) of these solutions was measured using a UIC, Inc. CM 5014 CO_2 Coulometer coupled to a UIC, Inc. CM 5120 furnace apparatus. The TOC measurement system was calibrated with standardized sucrose solutions.

Whatman Nucleopore Trach-Etch membranes with a pore size of 1.0 μm were chosen to coincide with the upper limit of colloidal size. New filters were used for each sample filtration. In this document, the HA contained in the filtrate from a 1.0 μm filtration is referred to as "soluble HA", versus "precipitated HA" or "coagulated HA", which describes the fraction of HA removed by 1.0 μm filtration. Freshly prepared HA solutions of various initial concentrations pre-

Table 1
Compositions of in situ GWB (Snider, 2003c, Table 2), synthetic GWB (Snider, 2003c, Table 4) and ERDA-6 (Popielak et al., 1983)

Element or property	In situ GWB	Synthetic GWB	ERDA-6
$B(OH)_x^{3-x}$ (M)	0.157	0.155	0.063
Na^+ (M)	3.53	3.48	4.87
Mg^{2+} (M)	1.02	1.00	0.019
K^+ (M)	0.465	0.458	0.097
Ca^{2+} (M)	0.014	0.014	0.012
SO_4^{2-} (M)	0.177	0.175	0.170
Cl^- (M)	5.87	5.51	4.8
Br^- (M)	0.027	0.026	0.011
Ionic strength (M)	6.4	6.2	5.2

pared in DI water, 95% ERDA-6, or 95% GWB were filtered, to study the initial effect of the medium on the HA coagulation (the time elapsed between the preparation of the HA solutions and the completion of their filtration was about 30 min). Freshly filtered 200 mg/L HA solutions prepared in DI water, 95% ERDA-6, or 95% GWB were added to MgO (Fisher MgO or Premier MgO) at different liquid-to-solid ratios (10.0 and 2.4 g/g), to estimate the effect of MgO on the HA coagulation; samples were also prepared without MgO. The samples were placed in the dark for various periods, the solutions were filtered, and the filtrate HA concentrations were determined. Filtered HA solutions of various initial concentration prepared in 95% ERDA-6 were added to Premier MgO at the liquid-to-solid ratio of 2.4 g/g to study the effect of the initial HA concentration on the kinetics of MgO-induced HA coagulation. After fixed periods during which the samples were kept in the dark, the solutions were filtered and the filtrate HA concentrations were determined. The MgO dissolution was studied by adding Fisher-MgO or Premier-MgO to DI water at different liquid-to-solid ratios and storing these samples in the dark; after fixed periods the samples were filtered and the filtrate Ca^{2+} and Mg^{2+} concentrations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Perkin–Elmer Optima 3300 DV). The ICP-OES was calibrated using Mg and Ca standard solutions, prepared in DI water. The effect of Ca and Mg on HA stability was studied; various Ca and Mg concentrations were added to filtered HA solutions prepared in DI water; the samples were stored in the dark. The solutions were filtered and the filtrate HA concentrations determined. The pH of every sample was measured.

Several of the MgO samples equilibrated with HA solutions were filtered and analyzed with a JEOL 5900LV scanning electron microscope (SEM) equipped with an energy dispersive system (EDS). A Bruker D8 ADVANCE X-ray diffractomer (XRD) was used to obtain the XRD powder patterns.

3. Results and discussion

3.1. Spectrophotometer calibration

The absorbance A_{465} is a linear function of pH, for $4 <$ pH < 12, for fixed HA concentration of 1.0 µm-filtered HA solutions prepared in DI water. Therefore, at fixed HA concentration,

$$A_{465} = \alpha_i \times pH + \beta_i. \qquad (1)$$

Values for α_i and β_i are presented in Table 2. The HA concentration of a given sample is then calculated by a double interpolation using the measured A_{465} and pH of the sample and the parameters of Table 2.

The value of A_{465} is constant with pH for HA solutions prepared in 95% ERDA-6 or 95% GWB. Therefore, at fixed pH,

$$[HA] = \delta \times A_{465}. \qquad (2)$$

Values for δ are presented in Table 3.

Standard deviation calculations are used to estimate the errors for [HA].

Concentration data obtained by spectrophotometry were compared to TOC results for 1.0 µm-filtered HA

Table 2
Eq. (1) parameter values

1.0 µm filtered [HA] (mg/L)	α_i	β_i
20.00	0.0047 ± 0.0006	0.072 ± 0.005
40.00	0.0075 ± 0.0006	0.148 ± 0.005
99.82	0.0184 ± 0.0006	0.367 ± 0.005
200.44	0.038 ± 0.001	0.684 ± 0.008

The errors are reported as one standard deviation.

Table 3
Eq. (2) parameter values ([HA] expressed in mg/L)

Medium	pH	δ
95% ERDA-6	8–12	147 ± 5
95% GWB	7–8.5	194 ± 8

The errors are reported as one standard deviation.

solutions and unfiltered HA solutions prepared in DI water at pH 7. The plots of [HA] vs. TOC, shown in Fig. 1, are approximately linear and identical for both sets of measurements (the filtered and the unfiltered HA samples), demonstrating the validity of using spectrophotometry for concentration determination of 1.0 μm-filtered HA solutions. The ratio [HA]/TOC is 2.2 ± 0.1, where [HA] and TOC are expressed in mg/L.

3.2. Initial effect of the medium on HA solubility

The pH values of HA solutions freshly prepared in 95% ERDA-6 and 95% GWB are 7.9 and 7.1, respectively. Fig. 2 shows the influence of the medium (DI water, 95% ERDA-6, or 95% GWB) on the filtration of freshly prepared HA solutions. The correlations between the initial HA concentration and the soluble HA concentration are linear. The following equations were determined:

$$\text{Water}: \quad [HA]_{soluble} = 0.751 \, (\pm 0.006) \times [HA]_{initial}, \quad (3)$$

$$95\% \, \text{ERDA-6}: \quad [HA]_{soluble} = 0.077 \, (\pm 0.003) \times [HA]_{initial}, \quad (4)$$

$$95\% \, \text{GWB}: \quad [HA]_{soluble} = 0.092 \, (\pm 0.004) \times [HA]_{initial}, \quad (5)$$

in which the values of [HA] are expressed in mg/L.

DI water promotes much less HA coagulation than ERDA-6 or GWB, with GWB inducing slightly less coagulation than ERDA-6. The large difference in coagulating effects of the DI water and the brines is explained by the difference in their ionic strengths and the presence of multivalent cations in the brines. Both parameters have been discussed by Wall and Choppin (2003). GWB exhibits characteristics, which, if considered separately, would be expected to induce more coagulation than ERDA-6. For example, GWB has a higher ionic strength than ERDA-6 and every multivalent cation in the brines has a higher concentration in GWB than in ERDA-6 (e.g., the Ca^{2+} concentration is 14 mM in GWB and 12 mM in ERDA-6 and the Mg^{2+} concentration is 1.02 M in GWB and 19 mM in ERDA-6). However, a higher ionic strength mitigates the coagulating effect of multivalent cations as the cations compete for populating the electrostatic double layer at the HA surface, in GWB (Wall and Choppin, 2003), leading to a higher coagulating efficiency of ERDA-6.

3.3. Effect of MgO on HA solubility

The pH measurements of the HA solutions equilibrated for periods of up to 60 days with Fisher MgO and Premier MgO shows the buffering effect of both
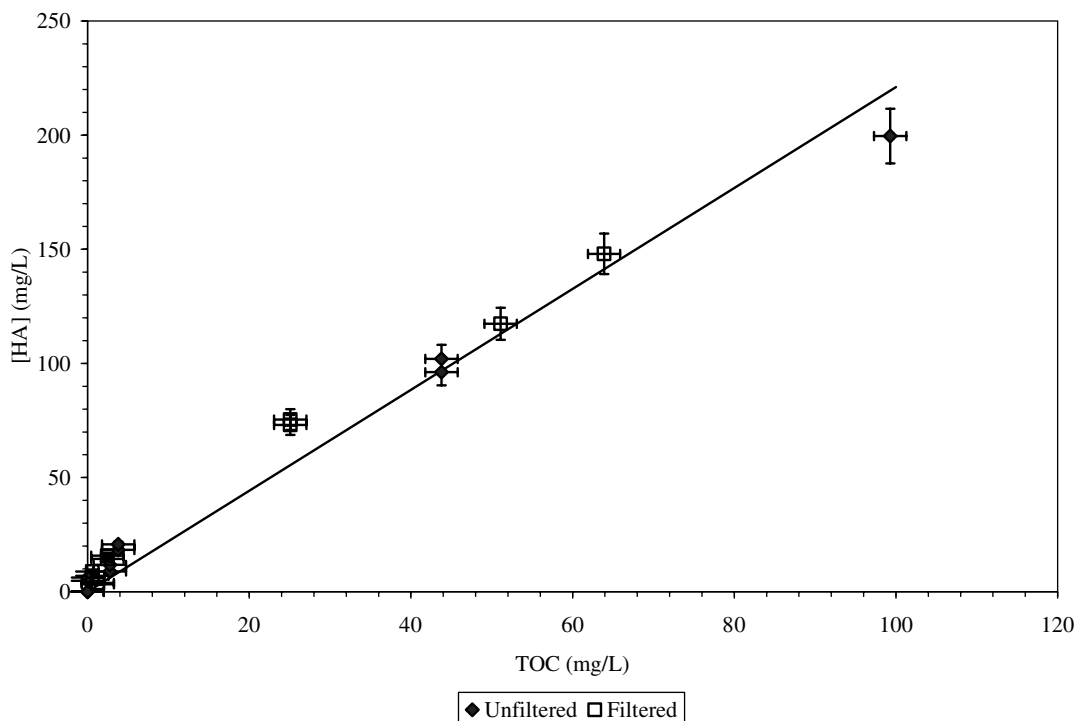

Fig. 1. Absorbance and TOC measurements of unfiltered and 1.0 μm filtered HA solutions, prepared in DI water at pH 7.
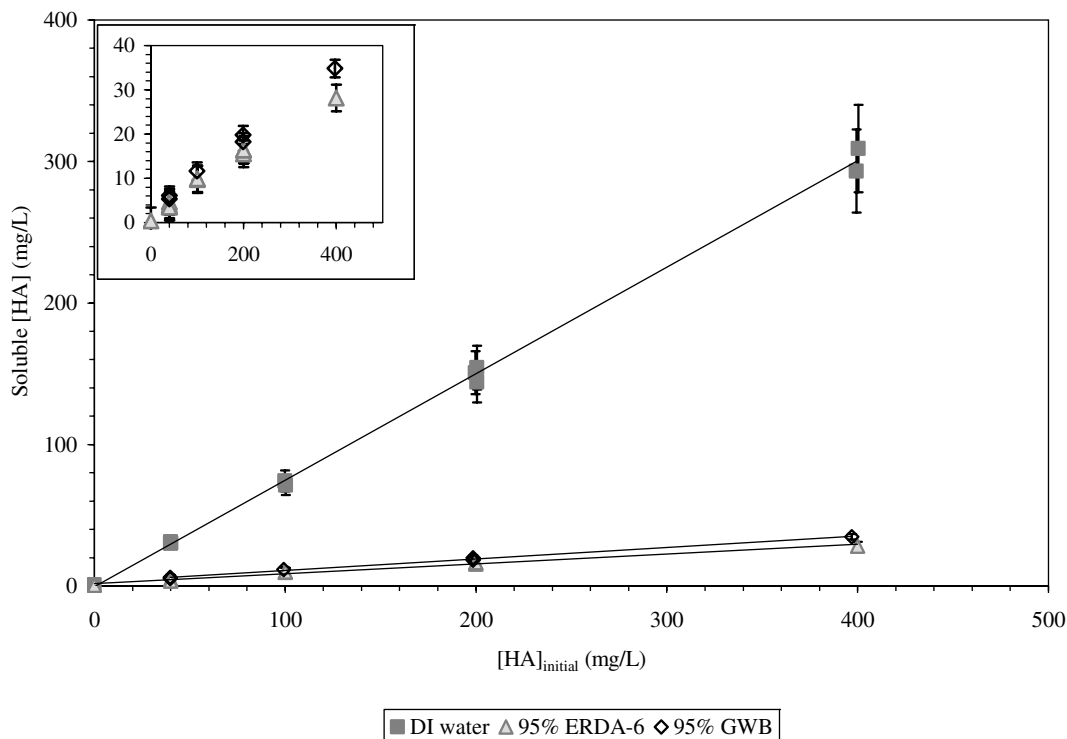
Fig. 2. Initial effect of DI water, 95% ERDA-6, and 95% GWB on the solubility of 200 mg/L HA solutions.

the brines and MgO. The average pH of 2.4 g/g liquid-to-solid samples prepared in DI water is 11.2 ± 0.5 and 12.8 ± 0.1 for Fisher MgO and Premier MgO, respectively. The average pH of the 2.4 g/g samples prepared in 95% ERDA-6 is 10.7 ± 0.1 and 12.1 ± 0.1 for Fisher MgO and Premier MgO, respectively. However, in the absence of MgO, the average pH of the HA solutions in 95% ERDA-6 is 7.92 ± 0.03. In the case of GWB, the average pH of the 2.4 g/g samples is 8.1 ± 0.2 and 8.4 ± 0.1, for Fisher MgO and Premier MgO, respectively. The average pH of HA solutions in 95% GWB and in the absence of MgO is 7.08 ± 0.08.

Figs. 3–5 present the kinetics of the coagulation of filtered 200 mg/L HA solutions in the presence and absence of MgO, in DI water, 95% ERDA-6, and 95% GWB. The soluble [HA] remains constant with time, in the absence of MgO and in any of the media studied; none of the HA remaining after the initial filtration (ca. 150 mg/L in DI water, ca. 15 mg/L in 95% ERDA-6, and ca. 18 mg/L in 95% GWB) coagulates over a 2 month period. Additional data also showed that, in experiments performed with initial [HA] higher than 200 mg/L, HA also remain in solution at constant concentrations. For example, a filtered 400 mg/L HA solution remains at a constant soluble HA concentration of 290 mg/L $\pm$ 10 in DI water, 30 mg/L $\pm$ 4 in 95% ERDA-6, and 31 mg/L $\pm$ 4 in 95% GWB, over a 60-day period of time.

Figs. 3–5 present the kinetics of coagulation when Fisher or Premier MgO is present in filtered 200 mg/L HA solutions prepared in DI water, 95% ERDA-6, and 95% GWB, at different liquid-to-solid ratios (10.0 and 2.4 g/g). The concentration of soluble HA remaining after contact with Fisher MgO for 10 days is below the detection limit of the spectrophotometer, in the case of solutions prepared in DI water, 95% ERDA-6, or 95% GWB. Fisher MgO is a slower coagulating agent in the case of the brines than in DI water. The remaining soluble HA is below the detection limit, at a 95% ERDA-6-to-Fisher MgO ratio of 2.4 g/g and after 1 day, but a small amount of HA remains at 10.0 g/g 95% ERDA-6 to Fisher MgO ratio and at 10.0 and 2.4 g/g of 95% GWB to Fisher MgO. Fisher MgO is more effective in coagulating HA in 95% ERDA-6 than in 95% GWB. This might be due to (1) the greater competition of the multivalent cations to populate the electrostatic double layer at the HA surface in the case of GWB and (2) the different pH values between the two systems (pH 10.7 in ERDA-6 versus pH 8.1 in GWB) affecting the HA surface properties. In 95% GWB and 95% ERDA-6, HA coagulates faster when Fisher MgO is present at a ratio 2.4 g/g than at 10.0 g/g.

The remaining soluble HA concentration is below the detection limit within the first day in samples containing Premier MgO and DI water at liquid-to-solid ratios of 10.0 and 2.4 g/g and for the experiments performed at
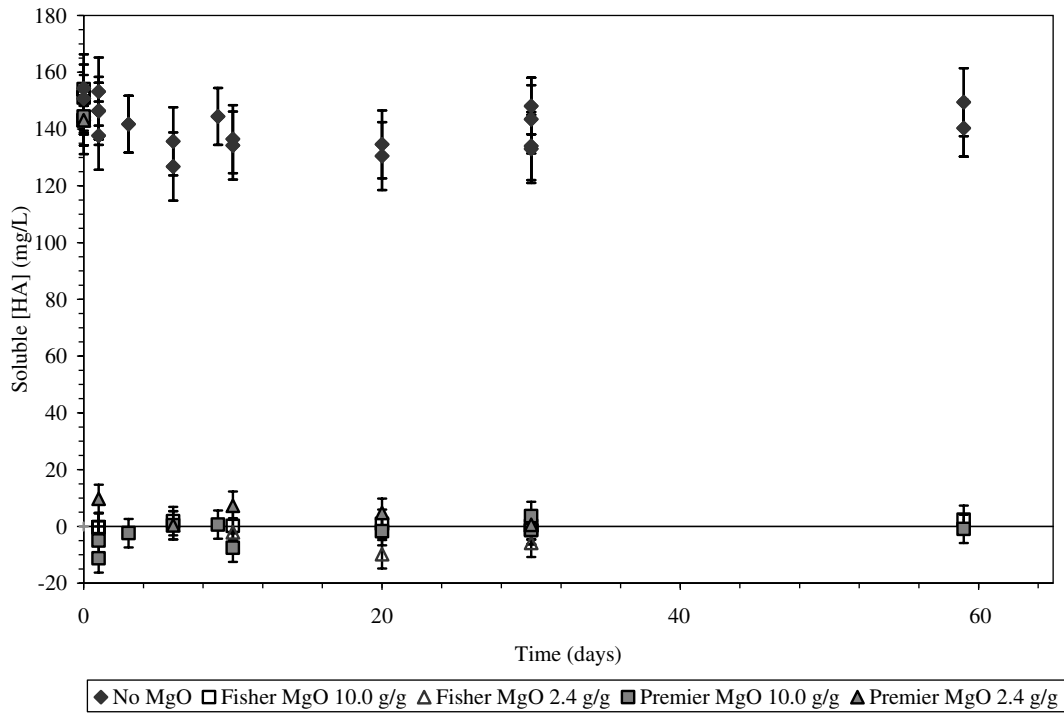
Fig. 3. Influence of Fisher and Premier MgO on the solubility of a filtered 200 mg/L HA solution prepared in DI water.
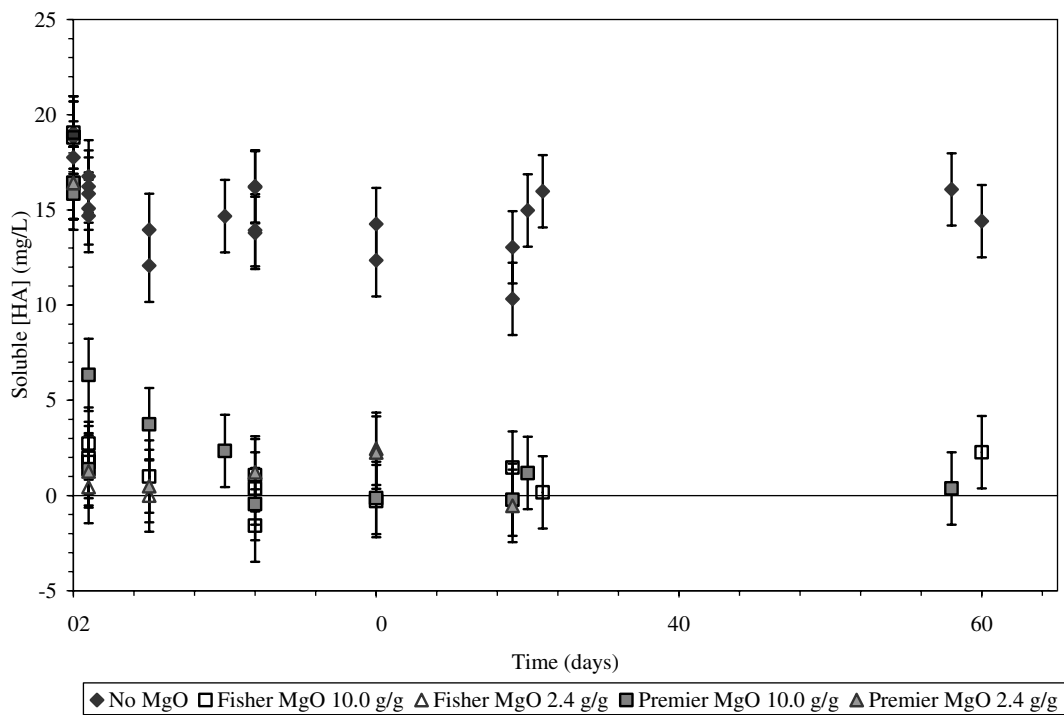

Fig. 4. Influence of Fisher and Premier MgO on the solubility of a filtered 200 mg/L HA solution prepared in 95% ERDA-6.
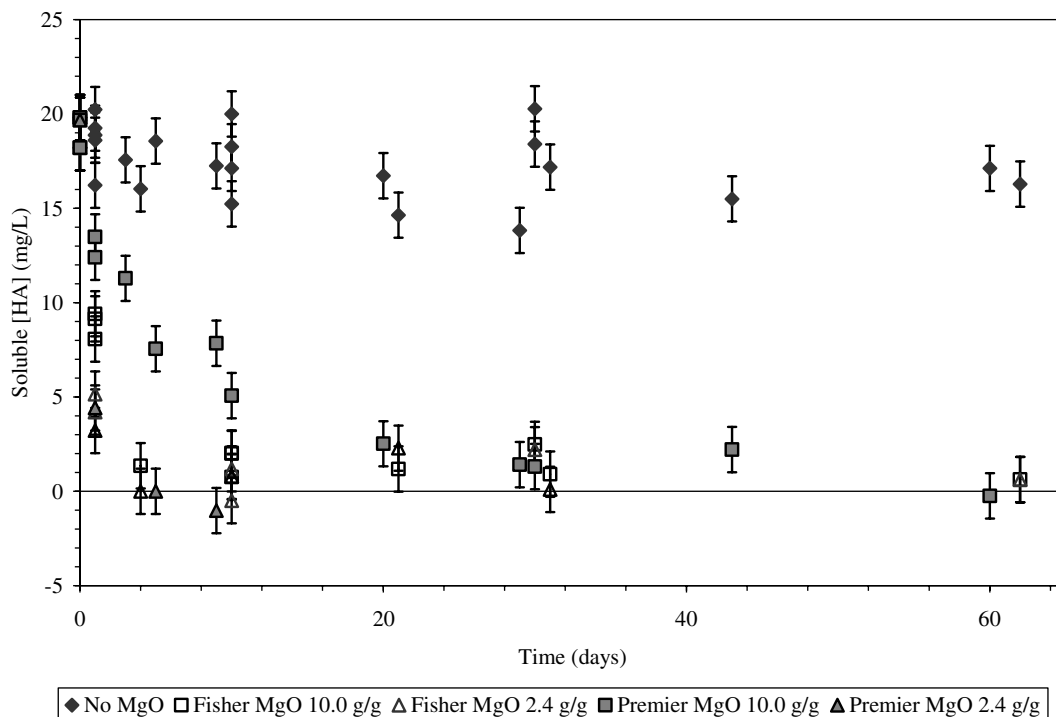
Fig. 5. Influence of Fisher and Premier MgO on the solubility of a filtered 200 mg/L HA solution prepared in 95% GWB.

a 95% ERDA-6-to-Premier MgO ratio of 2.4 g/g. The HA coagulation is slower in the case of the higher 95% ERDA-6-to-Premier MgO ratio and for both 95% GWB-to-Premier MgO ratios, 2.4 and 10.0 g/g. The soluble HA concentration is below the detection limit after 12 days in experiments performed at the 95% ERDA-6-to-MgO ratio of 10.0 g/g. The remaining soluble HA concentration decreases to the instrument detection limit within only a few days in the case of the experiments performed in 95% GWB for a liquid-to-solid ratio of 10.0 g/g; however, for a ratio of 2.4 g/g this phenomenon occurs after 60 days. Comparison of Figs. 4 and 5 shows that ERDA-6 more efficiently coagulates HA than GWB, as observed in the case of Fisher MgO. Comparison of data for Fisher MgO and Premier MgO shows that the Premier MgO is a less efficient HA coagulation agent than Fisher MgO. This variation may be due to the level of impurities between the two MgO products. Premier MgO contains monticellite ($MgCaSiO_4$), forsterite (Mg_2SiO_4), lime (CaO), and spinel ($MgAl_2O_4$), in addition to the 87–89% MgO (periclase) (Snider, 2003b). The experiments presented here were performed using 200 mg/L HA solutions, but additional data showed that Premier MgO is an effective coagulating agent for any other initial HA concentration, from 40 to 400 mg/L. For example, a 95% ERDA-6-to-Premier MgO ratio of 2.0 g/g coagulates all HA solutions of

original concentration varying from 40 to 400 mg/L, resulting in an undetectable soluble HA concentration within the first 2 days (similar results occur in the case of Fisher MgO). Furthermore, while the soluble HA concentration of a filtered 400 mg/L HA solution prepared in 95% GWB remains constant for at least 3 months at 35 mg/L, the addition of Premier MgO leads to an undetectable soluble HA concentration, although such a phenomenon occurs after 60 days.

Fisher MgO and Premier MgO react with DI water and WIPP brines to form hydration and carbonation products such as brucite ($Mg(OH)_2$), sorel cement ($Mg_3(OH)_5Cl\cdot4H_2O$), and hydromagnesite ($Mg_5(CO_3)_4$-$(OH)_2\cdot4H_2O$) (Bryan and Snider, 2001a,b; Snider, 2002, 2003a,b; Snider and Xiong, 2002). The experimental data described so far in the present paper cannot explain the mechanism by which MgO and its products induce HA coagulation. A combination of sorption and precipitation of HA at the surface of MgO and its products can occur or the minerals may dissolve to release enough Mg^{2+} to solution to induce HA precipitation. To test this second hypothesis, the Mg^{2+} and Ca^{2+} concentrations resulting from MgO dissolution in DI water were determined. These results, presented in Table 4, are compared to the data presented in Fig. 3, discussed above, and to the data of Fig. 6, which shows the effect of various concentrations of Ca^{2+} and Mg^{2+} on the HA

coagulation in DI water after 1 and 7 days. Fig. 6 shows that, in DI water, both Ca^{2+} and Mg^{2+} induce HA precipitation, as Wall and Choppin (2003) have observed in 0.1–5.0 m NaCl solutions. HA coagulation occurs in DI water after 1 day when Ca^{2+} and Mg^{2+} are present in concentrations larger than 2 and 5 mM, respectively. Table 4 shows that Fisher MgO suspended in DI water for 60 days at a liquid-to-solid ratio of 10.0 g/g does not release any Mg^{2+} or Ca^{2+}. However, Fig. 3 shows that such conditions induced a maximum HA coagulation within 1 day. Premier MgO, in suspension in DI water at liquid-to-solid ratios of either 10.0 or 2.4 g/g released small amounts of Mg^{2+} and Ca^{2+} (0.2 and 24 mM, respectively) after 9 days, as shown in Table 4; it also leads to a maximum HA precipitation from the first day, as shown in Fig. 3. However, Fig. 6 shows that neither Mg^{2+} present at 0.2 or 24 mM of Ca^{2+} are sufficient to totally coagulate HA within the first week; the result-

ing soluble [HA] of a 200 mg/L HA solution prepared in DI water and containing 0.2 mM Mg^{2+} or 24 mM Ca^{2+} is 125 or 35 mg/L, respectively. Therefore, it can be expected that the HA coagulation is not due to MgO dissolution but is due to a precipitation and/or sorption phenomenon of HA at the surface of MgO. The authors tried to verify this hypothesis by employing SEM to study a fraction of MgO previously equilibrated with a HA solution. SEM observation of the material failed to give relevant information on the system and the amount of the humic C deposited at the MgO surface was below the limit of detection of the EDS, the SEM qualitative tool for elemental analysis. XRD analysis showed the same patterns whether or not MgO was previously equilibrated with WIPP brines containing HA; XRD patterns of MgO after equilibration in WIPP brines are presented elsewhere (Bryan and Snider, 2001a,b; Snider, 2002, 2003a,b; Snider and Xiong, 2002).

Table 4
Mg^{2+} and Ca^{2+} concentrations obtained after MgO dissolution

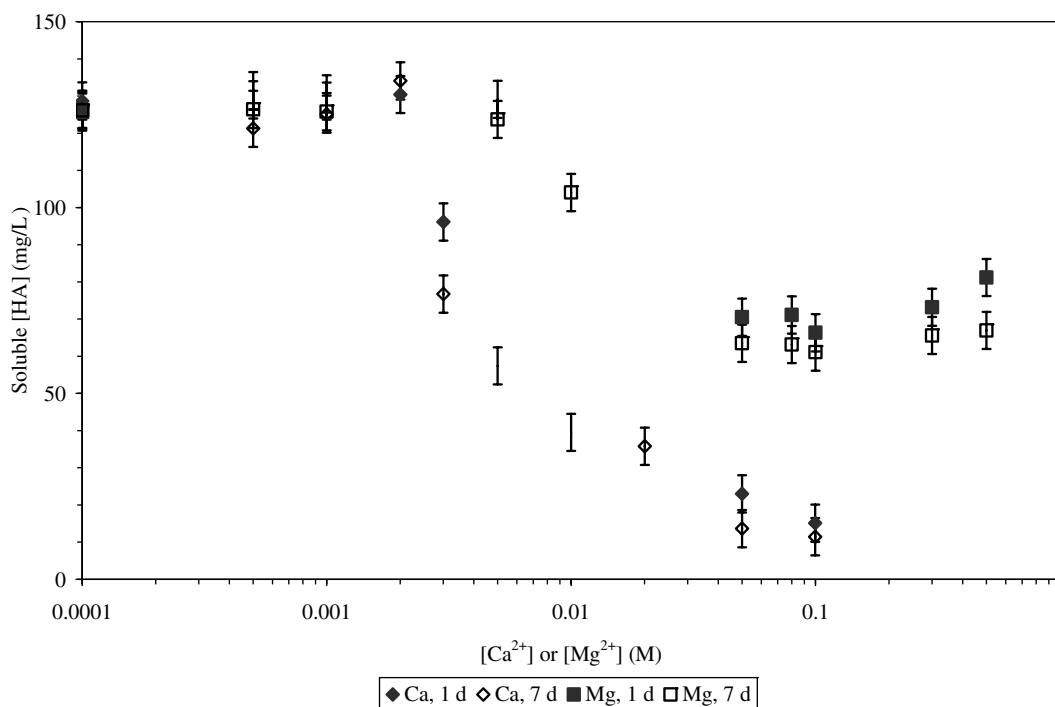| Medium	MgO	Liquid:solid ratio (g/g)	Time (days)	$[Mg^{2+}]$ (M)	$[Ca^{2+}]$ (M)
DI water	Fisher MgO	10.0	60	0.0000	0.000
DI water	Premier MgO	10.0	9	0.0005	0.021
DI water	Premier MgO	2.4	9	0.0002	0.024

Fig. 6. Influence of Ca^{2+} or Mg^{2+} on the solubility of a filtered 200 mg/L HA solution prepared in DI water, after 1 and 7 days.

4. Conclusion

The WIPP brines ERDA-6 and GWB do not lead to a complete HA precipitation in the absence of MgO. The Fisher Chemicals reagent grade MgO or the less pure Premier MgO, used as the WIPP engineered barrier, precipitates HA, resulting in a negligible HA concentration after a relatively short period in systems with a high liquid-to-solid ratio (10.0 g/g) or a low ratio (2.4 g/g). This phenomenon is probably the result of HA precipitation and/or sorption on the surface of MgO or MgO hydration and carbonation products. The HA concentration of solutions initially containing 200 mg/L HA and in contact with Premier MgO at a 2.4 g/g liquid-to-solid ratio stabilizes at 1 ± 8 mg/L for samples prepared in DI water, 0 ± 4 mg/L in 95% ERDA-6, and 0 ± 1 mg/L in 95% GWB. The times necessary to obtain such concentrations are 10 days, 12 days, and 60 days, respectively.

Acknowledgments

References

Bertha, E.L., Choppin, G.R., 1978. Interaction of humic and fulvic acids with Eu(III) and Am(III). J. Inorg. Nucl. Chem. 40, 655–658.

Bryan, C.R., Snider, A.C., 2001a. MgO hydration and carbonation at SNL/Carlsbad. Sandia National Laboratories Technical Baseline Reports, WBS 1.3.5.4, Repository Investigations, Milestone RI010, January 31, 2001. ERMS 516749. Sandia National Laboratories, Carlsbad, NM, pp. 66–83.

Bryan, C.R., Snider, A.C., 2001b. MgO experimental work conducted at SNL/CB: continuing investigations with Premier Chemicals MgO. Sandia National Laboratories Technical Baseline Reports, WBS 1.3.5.4, Repository Investigations, Milestone RI020, July 31, 2001. ERMS 518970. Sandia National Laboratories, Carlsbad, NM, pp. 5-1–5-15.

Buffle, J., 1988. Complexation Reactions in Aquatic Systems: an Analytical Approach. Ellis Horwood, Chichester, UK.

Choppin, G.R., 1988. Humic and radionuclide migration. Radiochim. Acta 44/45, 23–28.

Czerwinski, K.R., Kim, J.I., Rhee, D.S., Buckau, G., 1996. Complexation of trivalent actinide ions (Am^{3+}, Cm^{3+}) with humic acid: the effect of ionic strength. Radiochim. Acta 72, 179–187.

Grace, M.R., Hislop, T.M., Hart, B.T., Beckett, R., 1997. Effect of saline groundwater on the aggregation and settling of suspended particles in a turbid Australian river. Colloid Surf. A 120, 123–141.

Hong, S., Elimelech, M., 1997. Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. J. Membr. Sci. 132, 159–181.

Kim, J.I., Czerwinski, K.R., 1996. Complexation of metal ions with humic acid: metal ion charge neutralization model. Radiochim. Acta 73, 5–10.

Kim, J.I., Rhee, D.S., Buckau, G., 1991. Complexation of Am(III) with humicacids of different origin. Radiochim. Acta 52/53, 49–55.

Kim, J.I., Delakowitz, B., Zeh, P., Klotz, D., Lazik, D., 1994. A column experiment for the study of colloidal radionuclide migration in Gorleben aquifer systems. Radiochim. Acta 66/67, 165–171.

Labonne-Wall, N., Moulin, V., Vilarem, J.-P., 1997. Retention properties of humic substances onto amorphous silica: consequences for the sorption of cations. Radiochim. Acta 79, 37–49.

Labonne-Wall, N., Choppin, G.R., Lopez, C., Monsallier, J.-M., 1999. Interaction of uranyl with humic and fulvic acids at high ionic strength. In: Reed, D.T., Clark, S.B., Rao, L. (Eds.), Actinide Speciation in High Ionic Strength Media. Kluwer Academic/Plenum Publishers, New York, pp. 199–211.

Minai, Y., Choppin, G.R., 1989. Interaction of americium (III) with humic acids and two synthetic analogues. In: Proc. Internat. Symp. Advanced Nuclear Energy Research, Oarai, Japan, February 15–16, 1989. CONF-8902166. Japan Atomic Energy Research Institute, Tokyo, pp. 224–233.

Moulin, V., Tits, J., Ouzounian, G., 1992b. Actinide speciation in the presence of humic substances in natural water conditions. Radiochim. Acta 58/59, 179–190.

Moulin, V., Tits, J., Moulin, C., Decambox, P., Mauchien, P., de Ruty, O., 1992a. Complexation behaviour of humic substances towards actinides and lanthanides studied by time-resolved laser-induced spectrofluorometry. Radiochim. Acta 58/59, 121–128.

Nash, K.L., Choppin, G.R., 1980. Interaction of humic and fulvic acids with Th(IV). J. Inorg. Nucl. Chem. 42, 1045–1050.

Ong, H.L., Bisque, R.E., 1968. Coagulation of humic colloids by metal ions. Soil Sci. 106, 220–224.

Pefferkorn, E., 1997. Structure and stability of natural organic matter/soil complexes and related synthetic and mixed analogues. Adv. Colloid Interface Sci. 73, 127–200.

Popielak, R.S., Beauheim, R.L., Black, S.R., Coons, W.E., Ellingson, C.T., Olsen, R.L., 1983. Brine reservoirs in the Castile Formation, Waste Isolation Pilot Plant Project, Southeastern New Mexico. TME 3153. U.S. Department of Energy, Waste Isolation Pilot Plant, Albuquerque, NM.

Robinson, K.L., 1996. Preparing synthetic brines for chemical retardation and transport experiments. Technical operating procedure. TOP-544. ERMS 415562. Sandia National Laboratories, Albuquerque, NM.

Römkens, P., Dolfing, J., 1998. Effect of Ca on the solubility and molecular size distribution of DOC and Cu binding in soil solution samples. Environ. Sci. Technol. 32, 363–369.

Seibert, A., Mansel, A., Marquardt, C.M., Keller, E., Kratz, J.V., Tratmann, N., 2001. Complexation behaviour of neptunium with humic acid. Radiochim. Acta 89, 505–510.

Snider, A.C., 2002. MgO studies: experimental work conducted at SNL/Carlsbad. Efficacy of Premier Chemicals MgO as an engineered barrier. Sandia National Laboratories Technical Baseline Reports, WBS 1.3.5.3, Compliance Monitoring; WBS 1.3.5.4, Repository Investigations, Milestone RI110, January 31, 2002. ERMS 520467. Sandia National Laboratories, Carlsbad, NM, pp. 3.1-1–3.1-18.

Snider, A.C., 2003a. Hydration of magnesium oxide in the Waste Isolation Pilot Plant. Sandia National Laboratories Technical Baseline Reports, WBS 1.3.5.3, Compliance Monitoring; WBS 1.3.5.4, Repository Investigations, Milestone RI 03-210, January 31, 2003. ERMS 526049. Sandia National Laboratories, Carlsbad, NM, pp. 4.2-1–4.2-6.

Snider, A.C., 2003b. Hydration of magnesium oxide in the Waste Isolation Pilot Plant. In: Finch, R.J., Bullen, D.B. (Eds.), Materials Research Society Symp. Proc., Scientific Basis for Nuclear Waste Management XXVI, December 2–5, 2002, Boston, Massachusetts, USA, Vol. 757. Materials Research Society, Warrendale, PA, pp. 665–670.

Snider, A.C., 2003c. Verification of the definition of generic weep brine and the development of a recipe for this brine. Unpublished analysis report, April 8, 2003. ERMS 527505. Sandia National Laboratories, Carlsbad, NM.

Snider, A.C., Xiong, Y.-L., 2002. Carbonation of magnesium oxide. Sandia National Laboratories Technical Baseline Reports, WBS 1.3.5.3, Compliance Monitoring; WBS 1.3.5.4, Repository Investigations, Milestone RI130, July 31, 2002. ERMS 523189. Sandia National Laboratories, Carlsbad, NM, pp. 4.1-1–4.1-28.

Tipping, E., Ohnstad, M., 1984. Aggregation of aquatic humic substances. Chem. Geol. 44, 349–357.

Tombacz, E., Meleg, E., 1990. A theoritical explanation of the aggregation of humic substances as a function of pH and electrolyte concentration. Org. Geochem. 15, 375–381.

U.S. DOE, 2004. Title 40 CFR Part 191 Compliance Recertification Application for the Waste Isolation Pilot Plant, Vol. 1–8. DOE/WIPP 2004-3231. U.S. Department of Energy, Carlsbad Field Office, Carlsbad, NM.

Wall, N.A., Choppin, G.R., 2003. Humic acids coagulation: influence of divalentcations. Appl. Geochem. 18, 1573–1582.

Wall, N., Borkowski, M., Chen, J., Choppin, G., 2002. Complexation of americium with humic, fulvic, and citric acids at high ionic strength. Radiochim. Acta 90, 563–568.