



SPE 106802

Barium Sulfate: A Protocol for Determining Higher Site-Specific Barium Cleanup Levels

Jim McGinty, Halliburton; Thomas E. McHugh, D.A.B.T.; and Elaine A. Higgins, Groundwater Services, Inc.

Copyright 2007, Society of Petroleum Engineers

This paper was prepared for presentation at the 2007 SPE E&P Environmental and Safety Conference held in Galveston, Texas, U.S.A., 5–7 March 2007.

This paper was selected for presentation by an SPE Program Committee following review of information contained in an abstract submitted by the author(s). Contents of the paper, as presented, have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material, as presented, does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Papers presented at SPE meetings are subject to publication review by Editorial Committees of the Society of Petroleum Engineers. Electronic reproduction, distribution, or storage of any part of this paper for commercial purposes without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of where and by whom the paper was presented. Write Librarian, SPE, P.O. Box 833836, Richardson, Texas 75083-3836 U.S.A., fax 01-972-952-9435.

Abstract

Although different barium compounds are known to exhibit vastly different toxicities, cleanup standards for barium in soil or sediment at environmental corrective action sites are typically based on total barium concentration without regard for the specific barium compounds present. However, the Texas Commission on Environmental Quality (TCEQ) has recently agreed that the insoluble barium compound barium sulfate (i.e., barite) is not a compound of concern with regard to human health, thereby eliminating the need for cleanup standards or site remediation for this compound. The TCEQ still requires that their barium cleanup standards be applied to any soluble barium compounds that may be present at a site. To allow the application of barium cleanup standards to soluble barium compounds while excluding barium sulfate, we have developed a protocol to measure the concentration of soluble barium in soil or sediment samples that may contain both barium sulfate and soluble barium compounds. In this paper, we present (1) a review of the toxicity and regulation of soluble barium compounds and insoluble barium sulfate, and (2) a description of our protocol to measure the concentration of soluble barium compounds in soil and sediment samples and the validation of this protocol.

Introduction

Barite, the mineral form of barium sulfate, has been used for years throughout the oil and gas industry as a weighing agent during drilling. Barite, which has a density more than four times that of water, is mixed with water, mineral oil, or diesel oil, and other materials to form drilling mud, a fluid solution used to control downhole pressures while drilling. In addition to its high density, barite is insoluble and thus provides stability for the drilling mud. Other uses of barium sulfate include filler material in products such as golf balls and automotive interiors and as a whitener for paints. Barium sulfate is also used in medical testing procedures.

Oil services companies that sell and store barite along with drilling mud and additives at their facilities often have areas of the facility where barite may have been spilled or released into the environment. Typical site assessments at these facilities conducted under a state voluntary cleanup program will show elevated levels of barium in the soil, which may require response actions. We have developed a protocol to identify barium sulfate in the environment and to differentiate it from other barium compounds with specific laboratory methods.

Toxicity and Regulation of Barium Compounds

Toxicity of Barium Compounds

The key physical and chemical properties of barium compounds are summarized in **Table 1**. Barium toxicity is mediated through the free barium ion.¹ Exposure to insoluble barium sulfate does not cause significant toxicity because barium sulfate does not release free barium ions that can be absorbed into the lungs or intestine. The available human and animal data²⁻⁴ indicate that barium sulfate is poorly absorbed from the gastrointestinal tract with an absorption efficiency of 10^{-4} to 10^{-6} . This compares to an absorption efficiency for soluble barium compounds of 0.03 to 0.95. This difference in absorption efficiency provides a clear mechanistic explanation for the observed difference in toxicity between barium sulfate and soluble barium compounds. For example, barium sulfate is a radio-opaque agent that is administered orally as a medical diagnostic at doses of >200 g to increase contrast during x-rays of the digestive system. Although this dose is approximately 100 times the acutely lethal dose of soluble barium, diagnostic barium sulfate typically causes only minor side effects of constipation or diarrhea. In addition, occupational exposure to high levels of barium sulfate dust can result in benign pneumoconiosis (baritosis) that usually resolves following termination of exposure. In contrast to barium sulfate, soluble barium compounds dissociate in water, releasing barium ions and corresponding anions. As a result, soluble barium compounds are readily absorbed by the lungs or intestines and have a much higher toxicity than barium sulfate. Soluble barium doses of 0.2 to 0.5 grams have been found to cause acute toxic effects in humans; in the absence of treatment, the lethal dose of soluble barium for adults is 3 to 5 grams.⁵

Regulatory Standards for Barium Sulfate

In 1993, the United States Environmental Protection Agency (USEPA) exempted barium sulfate from the reporting requirements under Section 313 of the Emergency Planning

and Community Right-to-Know Act of 1986.⁶ In other words, barium sulfate is not covered by the rules requiring the reporting of releases of toxic chemicals. Other barium compounds are covered by these reporting requirements. In explaining the decision to exempt barium sulfate, the USEPA concluded that:

Human and animal data show that barium sulfate is essentially non-toxic to humans or other mammalian species. This is attributable to the very low solubility of the compound in water. Barium sulfate is not expected to be absorbed through the skin and is expected to be only minimally absorbed through the lung and gastrointestinal tract. . . . Barium sulfate cannot reasonably be anticipated to cause acute or chronic toxicity in humans or adverse effects in the environment.

Both NIOSH and OSHA have established separate occupational exposure limits for barium sulfate and soluble barium compounds.⁷ NIOSH and OSHA have established a time weighted average (TWA) exposure limit for soluble barium compounds of 0.5 mg/m³ to protect against acute and chronic toxicity associated with the barium ion. In contrast, NIOSH has established a TWA exposure limit for barium sulfate of 10 mg/m³ to protect against benign pneumoconiosis. OSHA applies the general particulate dust standard of 15 mg/m³ to barium sulfate.⁷

The USEPA has established an oral reference dose (RfD) for barium and barium compounds of 0.2 mg/kg-day based on human and laboratory rodent studies of barium chloride,⁸ a value increased from 0.07 mg/kg-day in 2005 based on newer rodent toxicity studies using barium chloride. In addition, the USEPA has established an MCL of 2 mg/L for drinking water. The USEPA regional and state corrective action programs have used these standards to develop cleanup goals for corrective action sites.

In contrast to the approach adopted by NIOSH and OSHA, the USEPA and state regulatory agencies have applied the soil and sediment cleanup goals developed based on barium chloride toxicity to all barium compounds without consideration of how differences in solubility and other chemical properties influence the potential for these compounds to cause toxicity. However, based on the lack of toxicity associated with oral exposure to barium sulfate, it is appropriate to apply barium cleanup standards only to soluble barium compounds that may be present at corrective action sites. In 2004, the TCEQ became the first state environmental regulatory agency to find that barium sulfate is not a compound of concern in soil or sediment. Based on this finding, they have agreed to apply barium cleanup standards only to soluble barium compounds.

Development and Validation of Protocol to Measure Soluble Barium in Soil and Sediment

The standard analytical method used to extract barium from soil or sediment samples (i.e., USEPA Method 3050B) uses a strong acid digestion to remove the barium and, as a result, does not distinguish between soluble and insoluble barium compounds. In order to allow the application of barium cleanup standards to only the soluble barium present, we have developed and validated a protocol using standard laboratory methods to measure the soluble barium concentration in soil and sediment samples. This protocol uses two separate

laboratory analyses to evaluate (1) the potential for leaching of soluble barium resulting in unacceptable concentrations of barium in groundwater and (2) the concentration of soluble barium for the evaluation of risk associated with direct exposure to affected soil or sediment.

Laboratory Study Details

Objectives. To evaluate the capability of existing laboratory analytical methods to distinguish between soluble and insoluble barium compounds, we conducted a laboratory study to determine whether USEPA leaching procedures could be used to accurately measure the concentration of soluble barium in an environmental sample containing a mixture of soluble and insoluble barium compounds. For the study, we evaluated the performance of three leaching procedures: (1) toxicity characteristic leaching procedure (TCLP), (2) synthetic precipitation leaching procedure (SPLP), and (3) a modified SPLP using deionized water in place of the standard SPLP leaching fluid.

Procedures. We analyzed two test mixtures to evaluate the accuracy of these leaching procedures: (1) drilling-grade barite (i.e., a fine powder typically containing >95% barium sulfate and <0.01% soluble barium compounds) and (2) drilling-grade barite with 0.3% laboratory-grade barium chloride by weight (i.e., 3000 mg/kg barium chloride or 2000 mg/kg barium chloride as barium). The barite was obtained from Halliburton Energy Services, Inc. (Product No. HM000105), and the barium chloride was obtained from Mallinckrodt Chemicals in Phillipsburg, New Jersey. The barium sulfate and barium chloride were mixed in the laboratory to obtain the second test mixture.

Sample Preparation. To ensure that the barium sulfate and barium sulfate/barium chloride materials were well mixed and homogenized, the laboratory coned and quartered the materials a minimum of three times before weighing out the aliquots for each test. No grinding was required to meet the particle size limits for SPLP or TCLP because of the fine-grained nature of the test materials (barium sulfate and barium chloride). Sample materials were dried before weighing out the aliquot for each test.

Analytical Methods. The USEPA has published two primary methods for the preparation of extracts by leaching: TCLP (SW-846 method 1311) and SPLP (SW-846 method 1312). TCLP was developed to simulate leaching of toxics from materials in a landfill while SPLP was developed to simulate leaching of toxics from soil under typical environmental conditions. For this study, however, we simply evaluated the capability of these leaching procedures to extract soluble barium from a mixture of soluble and insoluble barium compounds. Both SPLP and TCLP use a 20:1 ratio of extraction fluid to solid material. The primary difference between the two leaching methods is the extraction fluid, which is based on dilute acetic acid for TCLP and dilute sulfuric/nitric acid for SPLP. In addition, we evaluated the SPLP procedure using deionized water as the extractant.

For each evaluation, the test material (i.e., barium sulfate or barium sulfate/barium chloride) was extracted using one of the three extraction fluids. Resulting leachate samples were digested in accordance with USEPA method 3010A, and barium concentrations of the resulting leachates were

quantified using USEPA method 6010B. Analyses for the laboratory study were completed by STL Inc., Houston, Texas.

Program Summary. All tests were conducted in triplicate, resulting in a total of 18 leachate analyses, as indicated in **Table 2**. The analyses were conducted in accordance with quality control procedures specified in SW-846, including calibration standards that bracketed the range of concentrations analyzed.⁹

Laboratory Study Results. The TCLP method was shown to provide the most accurate measurement of soluble barium concentration in the test materials. Results are summarized in **Table 3**. The average concentration of barium in the TCLP leachate from the barium sulfate alone was 18.8 mg/L, only 0.06% of the total barium present in the sample. The average concentration of barium in the TCLP leachate from the barium sulfate/barium chloride mixture was 132 mg/L, indicating 113% recovery of the barium chloride. Therefore, our results indicate that TCLP is suitable for quantifying the concentration of soluble barium in samples containing a mixture of barite and soluble barium compounds. In contrast to TCLP, the SPLP method and the modified SPLP with deionized water both resulted in an under-measurement of soluble barium in the barium sulfate/barium chloride test material. These methods yielded barium chloride recoveries of 38% and 32%, respectively, from the barium sulfate/barium chloride test material, indicating that these two test methods are not suitable for accurately measuring the concentration of soluble barium in barium mixture.

In addition to the leaching analyses, we measured the total barium concentrations in both the barium sulfate and barium sulfate/barium chloride samples using USEPA methods 3050B for extraction and 6010B for quantitation. The average total barium concentrations reported in the barium sulfate and the barium sulfate/barium chloride materials were 3800 mg/L and 6900 mg/kg, respectively. These values are far less than the theoretical concentration of barium in the two test materials of approximately 600 000 mg/kg. Even when barium specific digestion procedures specified in USEPA method 3050B were used on subsequent samples, no significant improvement in recovery of total barium was obtained. These results suggest that these methods may underestimate the total barium concentration in soil or sediment samples containing barium sulfate.

Application of TCLP to Barium-Containing Soil Samples. Results of the laboratory study indicate that the TCLP method may be employed to accurately determine the concentration of soluble barium in a sample containing both insoluble barium sulfate and soluble barium compounds. Based on this finding, we worked with the TCEQ to develop a protocol to measure soluble barium concentrations in soil and sediment samples. This protocol may be used as an alternative to the traditional approach of comparing the total barium concentration in samples to the published barium cleanup standard. [In Texas, risk-based cleanup levels for each environmental medium and exposure pathway are designated protective concentration levels (PCLs).]

The alternative protocol employs TCLP to measure the concentration of soluble barium in the sample for comparison to the direct contact cleanup standard, but also requires the use

of SPLP for evaluation of leaching from soil to groundwater. Although our laboratory study indicated that SPLP recovers less than 100% of soluble barium, the procedure is still appropriate for the evaluation of leaching to groundwater, the original purpose of the analytical method.

In Texas, the following procedure can be used to compare laboratory results for soluble and insoluble barium to the cleanup standards for barium.

(1) **Initial Screening.**: Collect and analyze soil samples for total barium and compare to the groundwater protection standard (i.e., the ^{GW}Soil PCL) This standard is 440 mg/kg for a <0.5 acre soil area over a drinking water quality aquifer. If all concentrations are less than 440 mg/kg, then no further work is required to address barium as a chemical of concern (COC) at the site.

(2) **Leachate Analysis.** If the screening concentration is exceeded, prepare soil sample leachate by SPLP and TCLP in accordance USEPA SW-846 methods 1312 and 1312, respectively. Quantitatively analyze the leachate for barium in accordance with USEPA method SW-846 method 6010 or 6020.

(3) **Soil Leaching to Groundwater (^{GW}Soil).** Compare results from SPLP testing directly to the PCL for groundwater (i.e., 2 mg/L for drinking water aquifers, based on the federal MCL). A maximum SPLP concentration of <2 mg/L indicates that the concentration of barium in soil is protective of groundwater.

(4) **Soil Direct Contact (^{Tot}Soil_{Comb}).** Multiply the results from the TCLP testing by a factor of 40 to calculate the concentration of soluble barium in the soil sample. Multiplying the leachate concentration by 20 accounts for the dilution that occurs in the leaching procedure. This is based on the fact that Method 1311 calls for extracting the solid phase with an amount of extraction fluid equal to 20 times the weight of the solid phase. The additional factor of 2 was requested by the TCEQ as a conservative to ensure protectiveness even of the TCLP leaching procedure recovers only 50% of the soluble barium in the sample. This assumption ensures that the procedure yields a conservative over-estimate of the soluble barium concentration in the sample.

Compare the calculated soluble barium concentration to the PCL for direct soil contact (i.e., 8,000 mg/kg for residential land use). A maximum soluble barium concentration in soil of less than the ^{Tot}Soil_{Comb} PCL indicates that the barium in soil is protective for direct contact with the soil.

(5) **Data Evaluation.** If all SPLP results are below the ^{GW}GW_{Ing} PCL and all calculated soluble barium concentrations (based on the TCLP results) are below the ^{Tot}Soil_{Comb} PCL, then no response action is necessary to address barium.

Case Study

In June 2005, soil samples were collected from a drilling mud storage site in Tyler, Texas. Based on the historic use of the property, these samples were expected to contain elevated concentrations of barium sulfate but no soluble barium compounds. In samples analyzed for both total barium and TCLP barium, total barium concentrations ranged from 1,200

mg/kg to 7,950 mg/kg, while TCLP leachate barium concentrations ranged from 2.13 mg/L to 24.0 mg/L (**Table 4**). These results indicate that even weathered barium sulfate will not be recovered in significant quantities by TCLP.

The data available for the case study represent the conditions for a site which is the first to be evaluated using the protocol described herein. Although the dataset encompasses a limited number of samples, the analytical results are useful for demonstrating the application of the protocol to a site in Texas. As required under state standards, the groundwater at the site is assumed to be drinking water quality for this evaluation. The data were subjected to the protocol and yielded the following results:

(1) *Site Investigation*. Soil samples were collected and analyzed for total barium and concentrations ranged from 15 mg/kg to 14,300 mg/L total barium. The majority of samples collected exceeded the $^{GW}Soil_{Ing}$ PCL of 440 mg/kg. Therefore, additional samples were analyzed in accordance with our protocol.

(2) *Leachate Analysis*. Samples collected and analyzed during Step 1 were further analyzed for barium concentration in the SPLP and TCLP leachate. Results of soil sample leaching and analyses are as follows:

3) *Soil Leaching to Groundwater*. Results from SPLP testing were compared directly to the PCL for groundwater ingestion ($^{GW}GW_{Ing}$). For residential land use the $^{GW}GW_{Ing}$ PCL is 2.0 mg/L. At this site, several results exceed the $^{GW}GW_{Ing}$ PCL.

(4) *Soil Direct Contact*. Results from the TCLP testing are multiplied by a factor of 40 to find the corresponding concentration in the soil samples. Results of the calculated soluble barium concentrations in the solid phase are compared to the PCL for direct soil contact ($^{Tot}Soil_{Comb}$). For residential land use the $^{Tot}Soil_{Comb}$ PCL is 8,000 mg/kg. For this site all soluble barium results are less than the $^{Tot}Soil_{Comb}$ PCL.

(5) *Data Evaluation*. For this site, all soluble barium results are below the $^{Tot}Soil_{Comb}$ PCL; however, several SPLP results exceed the groundwater ingestion PCL ($^{GW}GW_{Ing}$). Therefore, no response action is required to address direct contact with soils. However, additional evaluation will be required to determine to address the soil leaching to groundwater pathway. This evaluation could involve direct testing of groundwater to determine if unacceptable leaching of barium has occurred at the site.

Conclusion

A protocol has been developed to distinguish between soluble and insoluble barium compounds that may be present in soil

and sediment at a site. Quantifying the concentration of soluble barium allows response actions to target the barium compounds which have the potential to impact human health. Conversely, cleanup efforts need not be directed toward insoluble barium sulfate which is not a human health concern. A case study for an actual drilling mud storage site in Tyler, Texas, was presented to demonstrate the utility of the protocol.

References

1. ATSDR: Toxicological Profile for Barium and Compounds, Agency for Toxic Substances and Disease Registry, Washington, D. C. (July 1992).
2. Seife, B.: "Radioactive Inert-Indicator Method for Intestinal Absorption Utilizing Differential Counting," *Journal of Laboratory and Clinical Medicine* (1962) 59, No. 3, 513-519.
3. Mauras, Y., Allain, P., and Roque, M. A.: "Etude De L'absorption Digestive Du Baryum Apres L'administration Orale Du Sulfate De Baryum Pour Exploration Radiologique," *Therapie* (1983) 38, 109-111.
4. Clavel, J. P., Lorillot, M.L., Buthiau, D., Gerbet, D., Heitz, F., and Galli, A.: "Absorption Intestinale Du Baryum Lors D'explorations Radiologiques," *Therapie* (1987) 42, 239-243.
5. Barium Health and Safety Guide, Health and Safety Guide No. 46, IPCS International Programme on Chemical Safety, World Health Organization, Geneva, <http://www.inchem.org/documents/hsg/hsg/hsg046.htm> (1991).
6. "Barium Sulfate; Toxic Chemical Release Reporting Community Right-to-Know," 40 CFR Part 372, Federal Register, (June 10, 1993) 58, No. 111, 32622-32628.
7. NIOSH: Pocket Guide to Chemical Hazards, Department of Health and Human Services, National Institute for Occupational Safety and Health, Washington, D.C. (2003).
8. USEPA: Integrated Risk Information System (IRIS) Database, <http://www.epa.gov/iris/index.html> (2006).
9. USEPA: Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846, 3rd ed., as updated (January 2005).
10. Chemfinder: <http://chemfinder.cambridgesoft.com/> (May 2004).
11. CRC Handbook of Chemistry and Physics, 57ed., D.R. Lide (ed), CRC Press, Boca Raton (1994).
12. Stumm, W. and Morgan, J.J.: *Aquatic Chemistry*, 3rd ed., John Wiley & Sons, New York City (1996).

Table 1—Key Physical and Chemical Properties of Barium Compounds

Compound	CAS No. ¹⁰	Chemical Formula	Mineral Name	Molecular Weight ¹⁰	Water Solubility at 18–26°C, g/L ¹¹	Solubility Product at 25°C, Ksp ¹²	Density ¹¹ at 18–26°C, g/cm ³
Barium sulfate	7727-43-7	BaSO ₄	Barite	233.3876	0.00222	1.10E-10	4.5
Barium carbonate	513-77-9	BaCO ₃	Witherite	197.3392	0.022	2.74E-09	4.43
Barium sulfite	7787-39-5	BaSO ₃	—	217.3882	0.2	8.00E-07	—
Barium fluoride	7787-32-8	BaF ₂	—	175.3268	1.2	1.00E-06	4.89
Barium hydroxide	17194-00-2	Ba(OH) ₂	—	171.3446	56	5.00E-03	2.18
Barium nitrate	10022-31-8	BaN ₂ O ₆	—	261.3398	87	—	3.23
Barium chloride	10361-37-2	BaCl ₂	—	208.236	375	—	3.86

Table 2—Summary of Test Program

	Test Material/ Extraction Fluid	Analytical Methods (USEPA SW-846)			Number of Tests
		Extraction	Digestion	Quantitation	
Drilling-Grade Barium Sulfate	SPLP extraction fluid	1312	3010A	6010B	3
	TCLP extraction fluid	1311	3010A	6010B	3
	Deionized water	1312	3010A	6010B	3
Drilling-Grade Barium Sulfate with 0.3% Barium Chloride	SPLP extraction fluid	1312	3010A	6010B	3
	TCLP extraction fluid	1311	3010A	6010B	3
	Deionized water	1312	3010A	6010B	3

Table 3—Results of Test Program*

Extraction Fluid	Average Barium Conc. in Leachate, mg/L		Concentration of Soluble Barium in Test Material, mg/kg		BaCl ₂ Recovery, %
	Barite	Barite + 0.3% BaCl ₂	Barite	Barite + 0.3% BaCl ₂	
TCLP Leachate	18.8 (+/- 0.40)	132 (+/- 3.6)	376	2640	113
SPLP Leachate	0.204 (+/- 0.005)	37.9 (+/- 0.57)	4.08	758	38
Deionized water	0.198 (+/- 0.002)	32.3 (+/- 0.35)	3.96	646	32

*Standard deviation = +/-0.40

Table 4—Results of Case Study

Applicable PCL	Barium Concentration			
	Total, mg/kg ^{GW} Soil _{Ing} 440 mg/kg	SPLP, mg/L ^{GW} Soil 2 mg/L	TCLP, mg/L —	Soluble, mg/kg ^{Tot} Soil _{Comb} 8,000 mg/kg
HA-12-1 ft	2,310	NA	2.7	54
HA-12-1 ft (dup)	1,570	NA	3.72	74
HA-12-5 ft	2,740*	3.04**	3.54	71
HA-18-2 ft	2,830*	1.03	2.76	55
HA-18-2 ft (dup)	3,810*	2.91**	3.28	66
HA-23-2 ft	3,640	NA	3.45	69
HA-23-2 ft (dup)	3,630	NA	3.34	67
HA-23-5 ft	3,620*	2.22**	3.25	65
HA-25-1 ft	4,840	NA	4.2	84
HA-25-1 ft (dup)	7,950	NA	24	480
HA-25-5 ft	1,200*	NA	3.27	65
HA-38-1 ft	7,280	NA	2.66	53
HA-38-1 ft	6,980	NA	2.56	51
HA-87-0.5 ft	1,900*	0.56	2.13	43

NA = Not analyzed

*Barium analyzed by method 6020A after sample digestion by method 3050B (standard digestion). Samples not denoted by an * were digested using barium-specific digestion specified in 3050B Section 7.5

**exceeds the applicable PCL