
Barium in Produced Water: Fate and Effects in the Marine Environment

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EXECUTIVE SUMMARY

This review provides a summary of what is currently known about the physical/chemical behavior of barium in produced water and in the ocean and discusses the factors that may influence the rate of precipitation of barium as barite. The toxicity of barium to marine and freshwater organisms and humans also is discussed in relation to the concentrations and forms in which barium may occur in the marine and aquatic environment.

The concentration of dissolved barium in oil well produced water ranges from less than 100 to more than 2,000,000 $\mu\text{g/L}$ (parts per billion). The concentration of dissolved barium in the ocean is in the range of 4 to about 20 $\mu\text{g/L}$ and is controlled by the high concentration of sulfate in sea water. Barium sulfate (barite) has a low aqueous solubility, reflected by its molal solubility product of approximately 1.05×10^{-10} at 25°C. The saturation concentration of barium in equilibrium with barite in sea water is approximately 37 $\mu\text{g/L}$. Consequently, it is expected that when produced water containing a high concentration of dissolved barium is discharged to the ocean, the barium will precipitate rapidly as barite. However, organic acid anions, sometimes present in produced water at concentrations as high as 10,000,000 $\mu\text{g/L}$, may complex with barium and slow its precipitation upon mixing of produced water with seawater.

Barium concentrations in produced water are roughly inversely proportional to concentrations of sulfate, indicating that the barium is in equilibrium with barite in the formation. If saline water is injected into the fossil fuel reservoir to enhance secondary production and some of the injection water mixes with the formation water, the concentration of sulfate in the produced water may cause supersaturation with respect to barite.

The rate of precipitation of barium from produced water in the ocean has not been measured directly. Upon discharge of produced water to the ocean, precipitation of barium as barite may be slow unless the produced water/sea water mixture is several-fold supersaturated with respect to free, ionic Ba^{+2} and SO_4^{-2} . After initial barite crystal nuclei are formed, precipitation may be rapid. Produced water containing more than about 100 $\mu\text{g/L}$ dissolved barium will produce, upon discharge, a produced water/sea water mixture that is supersaturated with respect to barite in the presence of a typical concentration of sulfate in sea water (0.028 M).

A typical Gulf of Mexico produced water contains about 50,000 $\mu\text{g/L}$ (0.000364 M) dissolved barium; Gulf of Mexico sea water contains about 0.029 M sulfate. Assuming an apparent activity coefficient of 0.2 for barium in produced water and an apparent activity coefficient of 0.17 for sulfate in sea water, a 99:1 sea water:produced water mixture is about 30 times supersaturated with respect to barite. The rate of precipitation of barite from such a highly supersaturated mixture is diffusion-rate limited, so precipitation will be very rapid in a well-mixed receiving water environment.

If a scale inhibitor is used in the production stream or produced water treatment system, it may appear in the treated produced water that is discharged to the ocean and may inhibit the initiation or slow the rate of precipitation of barium. In addition, organic acid anions, sometimes present at high concentrations in produced water, may complex with dissolved barium, reducing its apparent activity coefficient and reducing the rate of barium precipitation in the ocean.

Solid barite and dissolved barium in sea water are not very toxic to marine and freshwater organisms. In sea water, toxic concentrations of barium ion are in excess of barium solubility and are only observed in bioassays with embryos and larvae of marine invertebrates during exposure to fine suspended barite particles or

barium-organic acid complexes. In fresh water, barium solubility is controlled by sulfate; barium can only reach toxic concentrations if the water contains a low concentration of sulfate. Barium in drinking water has a low toxicity to humans. Thus, dissolved barium at concentrations that are stable in the sea water and fresh water is not likely to be toxic to marine, freshwater, or terrestrial organisms.

Section 1

INTRODUCTION

The two most important (in terms of volumes generated and regulatory concern) waste products sometimes permitted for discharge from offshore exploration and production platforms are drilling fluids and produced water (Neff *et al.*, 1987). Both wastes are complex mixtures of water-soluble and insoluble, inorganic and organic chemicals in water. Barium is one of the most abundant inorganic chemicals (other than the dominant seawater ions) in both drilling fluids and produced water from some locations. Barium is added intentionally, as the mineral barium sulfate (BaSO_4), to most drilling fluids as a weighting agent because of its high density and low aqueous solubility. Barium is a natural ingredient of produced water.

Studies of barite in drilling fluids generally have shown that this dense, insoluble mineral is virtually nontoxic to marine organisms (National Research Council, 1983). The low toxicity of barite to marine organisms usually is attributed to its low solubility in seawater (high in sulfate). However, most of the barium in produced water is present in a dissolved form. Concern has been expressed and some circumstantial evidence published (Higashi *et al.*, 1992; Raimondi and Schmitt, 1992; Cherr and Fan, 1993) that dissolved or colloidal barium discharged to the sea in produced water may be toxic to sensitive life stages of marine organisms. The kinetics of precipitation of soluble barium as barite upon mixing of produced water with sea water is not understood; therefore, the persistence of dissolved barium in a diluting produced water plume at concentrations significantly higher than natural background is not known.

The objectives of this review are to summarize the scientific literature on the concentrations and behavior of barium in produced water and its behavior and

toxicity upon discharge to saline receiving waters. The concentrations and chemical speciation of barium in natural marine and fresh water and in produced water are discussed first. This section will include a discussion of the effects of various physical and chemical parameters on the solubility product of barite and the solubility of barium. Our current understanding of the physical chemistry of precipitation of barium upon mixing of produced water with sea water is described next. There is a discussion of the factors that may affect the rate of barium precipitation following discharge of produced water to the ocean. Finally, the toxicity of barium and barium sulfate to freshwater and marine organisms and humans is discussed in relation to the predicted precipitation kinetics of barium plus sulfate in the receiving water environment.

Section 2

PHYSICAL CHEMICAL PROPERTIES OF BARIUM

Barium is an alkaline earth element (Group IIA of the periodic table). There are four alkaline earths with lower molecular weights than barium. These are beryllium (MW 9.01), magnesium (MW 24.32), calcium (MW 40.08), and strontium (MW 87.63). There is one alkaline earth element with a higher molecular weight, radium (MW 226.05) (Table 2-1). Barium, with a molecular weight of 137.36, shares many physical/chemical properties with the other alkaline earth elements. Beryllium, with a charge density more than twice that of the other Group IIA elements, has different chemical properties than the other elements in the group.

Table 2-1. Physical/Chemical Properties of the Alkaline Earth Elements (Group IIA). From Snavey (1989).

Ion	Molecular Weight	Crystal Radius (Å)	Hydrated Radius (Å)	Charge Density	K_{sp} [M][SO ₄] @ 25°C
Be ⁺⁺	9.01	0.31	4.59	6.45	--
Mg ⁺⁺	24.32	0.65	4.28	3.01	--
Ca ⁺⁺	40.08	0.99	4.12	2.02	3.75X10 ⁻⁵
Sr ⁺⁺	87.63	1.13	4.12	1.77	3.42X10 ⁻⁷
Ba ⁺⁺	137.36	1.35	4.04	1.48	1.05X10 ⁻¹⁰
Ra ⁺⁺	226.05	1.52	3.98	1.32	4.30X10 ⁻¹¹

Like all the alkaline earth elements, barium readily loses its outer two electrons, forming the divalent cation (Ba⁺²). Barium is a stronger reducing agent and more readily forms bases than the other alkaline earths, except radium. Because barium has a relatively low ionic potential, it goes into aqueous solution as the hydrated ion. Adsorption of ionic barium to clay particles and organic matter is stronger

than adsorption of lower molecular weight earths, because of its smaller hydrated ionic radius (Lagas *et al.*, 1984).

All the alkaline earth elements readily form oxides, hydroxides, carbonates, and sulfates. However, because its crystal radius (1.35 Å) is larger than that of lower molecular weight alkaline earths, Ba^{+2} does not readily substitute for other alkaline earths in various crystal matrices, such as calcium carbonate. Barium is incorporated more readily into precipitating calcite than aragonite (Kitano *et al.*, 1971); it also tends to inhibit incorporation of strontium into these two crystal forms of calcium carbonate (Morse and Bender, 1990). The most abundant naturally occurring barium minerals are barite (BaSO_4 ; also called barytes), witherite (BaCO_3), barytoangelsite ($[\text{Ba,Pb}]\text{SO}_4$), and bromlite ($\text{CaBa}[\text{CO}_3]$) (Pilkey, 1972).

Barium, like the other alkaline earth elements, forms soluble salts with chloride, bromide, and nitrate, and relatively insoluble salts with sulfate, carbonate, phosphate, and acid phosphate. The least soluble barium salt is barite with a solubility product (K_{sp}) of approximately 1.05×10^{-10} at atmospheric pressure and a temperature of 25°C (Table 2-1). Barite has a low solubility in fresh water and sea water of 2,300 µg/L (1,360 µg Ba/L) and 81 µg/L (48 µg Ba/L), respectively, at 20°C (Burton *et al.*, 1968). The solubility product increases with temperature, resulting in barite solubilities in distilled water ranging from 1,746 µg/L (1,027 µg Ba/L) at 0°C to 3,946 µg/L (2,320 µg Ba/L) at 100°C (Haarberg *et al.*, 1992). The solubility product of barite also increases with increasing ionic strength of the water. At 25°C, the solubility of barite increases from approximately 2,450 µg/L (1,441 µg Ba/L) in deionized water to 25,680 µg/L (15,100 µg Ba/L) in water with an ionic strength of 1.4 molal as various inorganic chlorides (Haarberg *et al.*, 1992). At the ionic strength of sea water (≈ 0.66 M with respect to NaCl), barite would have a solubility of 15,400 µg/L (9,060 µg Ba/L) in the absence of sulfate. However, the high concentration of inorganic sulfate in sea water controls the solubility of barite and the saturation concentration of dissolved barium at a much lower level.

Section 3

BARIUM IN PRODUCED WATER AND NATURAL WATERS

BARIUM IN PRODUCED WATER

Water may be trapped with liquid and gaseous petroleum during millions of years of geologic time in porous sediments sandwiched between layers of impermeable rock deep within the earth. This water, called formation water or produced water, may be generated with the fossil fuels. Freshwater or seawater may be injected into the hydrocarbon reservoir to increase production of fossil fuels. Some of this injected water may mix with and be produced with the formation water. Water generated during fossil fuel production from offshore oil and gas reservoirs often is treated to remove as much oil as possible and discharged to the sea.

Large amounts of treated produced water are discharged to the ocean each year.

Table 3-1 summarizes the volumes discharged in several major offshore oil and gas production areas world-wide.

Table 3-1. Estimated Average Volumes in Millions of Liters/Day (Millions of Barrels/Day in Parentheses) of Treated Produced Water Discharged to Coastal and Offshore Waters of the Gulf of Mexico, California, Cook Inlet, Alaska, the North Sea, and Australia.

Location	Average Daily Discharge	Reference
Gulf of Mexico	547 (3.44)	Boesch and Rabalais, 1989a
California	140 (0.88)	Hudgins, 1992
Cook Inlet, AK	15 (0.09)	Neff, 1991
North Sea	450 (2.83)	Bedborough <i>et al.</i> , 1987
Australia	100 (0.63)	Black <i>et al.</i> , 1994

Most discharges of treated produced water from individual oil/water separator or production platforms to nearshore waters of the northwestern Gulf of Mexico are less than about 80,000 L/d (500 bbl/d) (Boesch and Rabalais, 1989a). Large production or treatment facilities may discharge much larger volumes of treated produced water. The Grand Isle treatment facility, which no longer discharges produced water, received produced water from several offshore fields in the northern Gulf of Mexico and discharged about 16.6 million L/d (104,000 bbl/d) of treated produced water to Bayou Rigaud, Louisiana in 1989 (Boesch and Rabalais, 1989a). In 1992, the Statfjord oil field, the largest offshore oil field in the world, discharged 30.9 million L/d (195,000 bbl/d) of treated produced water to the Norwegian sector of the North Sea (Ynnesdal and Furuholt, 1994).

Over the life of a well, the amount of water produced with the oil or gas often increases as the amount of fossil fuels produced decreases (Read, 1978). In older fields and stripper wells, the water fraction may be 90 percent or more. For example, produced water discharges to the Norwegian sector of the North Sea are expected to increase nearly six-fold from 43.8 million L/d in 1990 to 246.6 million L/d in the year 2000 (Brendehaug *et al.*, 1993).

Produced water is a complex mixture of a great many chemicals that have been dissolved or dispersed from the geologic formation in which the produced water resided for millions of years (Table 3-2). The most abundant organic chemicals in produced water are low molecular weight organic acids and saturated and aromatic hydrocarbons. Hydrocarbons and organic acids usually represent more than 90 percent of the organic compounds in produced water. In the United States, the current standard for total petroleum hydrocarbons (oil and grease) in treated oil well produced water destined for ocean disposal is 42 mg/L (parts per million: ppm)

Table 3-2. Typical concentration ranges of several classes of organic compounds and inorganic ions in produced water. Concentrations are in $\mu\text{g/L}$ (Parts per Billion). Data are from Kharaka *et al.*, (1978), Grahl-Nielsen (1987), McGowan and Surdam (1988), Boesch *et al.*, (1989a,b), Macpherson (1989), Barth (1991), Stueber and Walter (1991), Jacobs *et al.*, (1992), Neff *et al.*, (1992), Stephenson (1991, 1992), and Tibbetts *et al.*, (1992).

Compound Class	Concentration Range
<u>Organic Compounds</u>	
Total Organic Carbon	< 100 - 1,500,000
Total Saturated Hydrocarbons	17,000 - 30,000
Total BTEX	300 - 93,000
Total PAH	80 - 1,700
Steranes/Triterpanes	140 - 175
Ketones	1,000 - 2,000
Phenols	600 - 2,900
Organic Acids	500 - 10,000,000
<u>Inorganic Ions</u>	
Sulfate	< 1,000 - 8,000,000
Arsenic	5 - 300
Barium	< 100 - 2,000,000
Cadmium	0.1 - 200
Chromium	0.7 - 1,100
Copper	0.4 - 1,500
Lead	1.5 - 8,800
Mercury	0.05 - 2.0
Nickel	0.4 - 1,700
Silver	12 - 152
Zinc	100 - 69,000

daily maximum and 29 ppm monthly average. Oil/water separators on offshore platforms generally are able to remove dispersed oil droplets from produced water to attain oil concentrations in the discharged produced water that are below the current standards.

Organic acid anions may be present in produced water at non-detectable concentrations ranging from zero to as high as 10,000,000 $\mu\text{g/L}$ (parts per billion) (McGowan and Surdam, 1988; Barth, 1991; Helgeson *et al.*, 1993). Most of the organic acids in produced water are short-chain aliphatic mono- and di-carboxylic acids. They are thought to have been produced by hydrous pyrolysis of hydrocarbons in the hydrocarbon-bearing formation (Borgund and Barth, 1994). The most abundant acid usually is acetic acid, though, in some coal-associated waters, propionic acid may be most abundant (Fisher, 1987).

If heavy use is made of water-soluble organic additives (e.g., biocides, scale inhibitors, anti-corrosion chemicals, flocculents) in the production stream or produced water treatment system, small amounts of them may also be present in the produced water discharged over board (Hudgins, 1989, 1991, 1992). An estimated 0.4 to 4 percent of the corrosion inhibitors, 50 to 80 percent of the flocculents, and less than 1 percent of the biocides used on production platforms in the Norwegian sector of the North Sea are discharged to the North Sea in produced water (Ynnesdal and Furuholt, 1994).

The concentration of total dissolved solids (salinity) in produced water varies widely from essentially fresh water (less than 3 ‰) to a saturated brine with a concentration of about 300 ‰ (Rittenhouse *et al.*, 1969; Large, 1990). Low salinity produced waters may have been derived from ancient freshwater lakes. However, most produced waters have salinities similar to or greater than that of sea water (salinity, about 35 ‰) and are thought to have been derived from ancient seawater (Collins, 1975). As in sea water, the dominant inorganic ions are sodium and chloride. The other abundant inorganic ions in sea water usually are present at high concentrations in saline produced waters; however, ion ratios in produced water may be different from those in modern sea water, possibly reflecting ion ratios of ancient seas.

All the alkaline earth elements, including barium, are present in most saline produced waters at much higher concentrations than in modern seawater. The concentration of barium in produced water varies from less than 100 $\mu\text{g/L}$ (Barth, 1991; Stueber and Walter, 1991) to approximately 2,000,000 $\mu\text{g/L}$ (Barth *et al.*, 1989; Macpherson, 1989). Most formation waters contain no or low concentrations of sulfur, most of it in the form of reduced sulfur species such as sulfide (Shock and Koretsky, 1993). Often, when high concentrations of sulfate are present, it is an indication of contamination of formation water with saline injection water (Barth *et al.*, 1989; Tibbetts, 1991). When both barium and sulfate are present in produced water, they may precipitate on the walls of production pipe as barium scale (barite). Therefore, concentrations of barium in the produced water in the formation may be higher than concentrations in the water that is produced, treated, and discharged to the ocean (Rollheim *et al.*, 1993).

There is a roughly inverse relationship between the concentrations of barium and sulfate in produced water (Figure 3-1). Produced waters with very high barium concentrations nearly always contain undetectable or trace concentrations of sulfate (Barth *et al.*, 1989). However, the correlation is not good, particularly for waters with low concentrations of barium. Treated produced water often contains water from other sources than the fossil formation water (e.g., saline injection water) that may contain elevated concentrations of sulfate (McCort and Peers, 1987). Barium may precipitate in water-flooded formations or in the production stream as the sulfate, so that the concentrations of barium and sulfate in such produced waters do not reflect the concentrations in the original formation water before saline water injection. However, most data fall near the $\text{Ba}^{+2}/\text{SO}_4^{-2}$ regression line for equilibrium with barite at 100°C, a typical temperature for produced water coming from a geologic formation (Macpherson, 1989). The barium in produced water probably is derived from dissolution of potassium feldspars (containing up to about 1 weight percent barium), plagioclase, and biotite

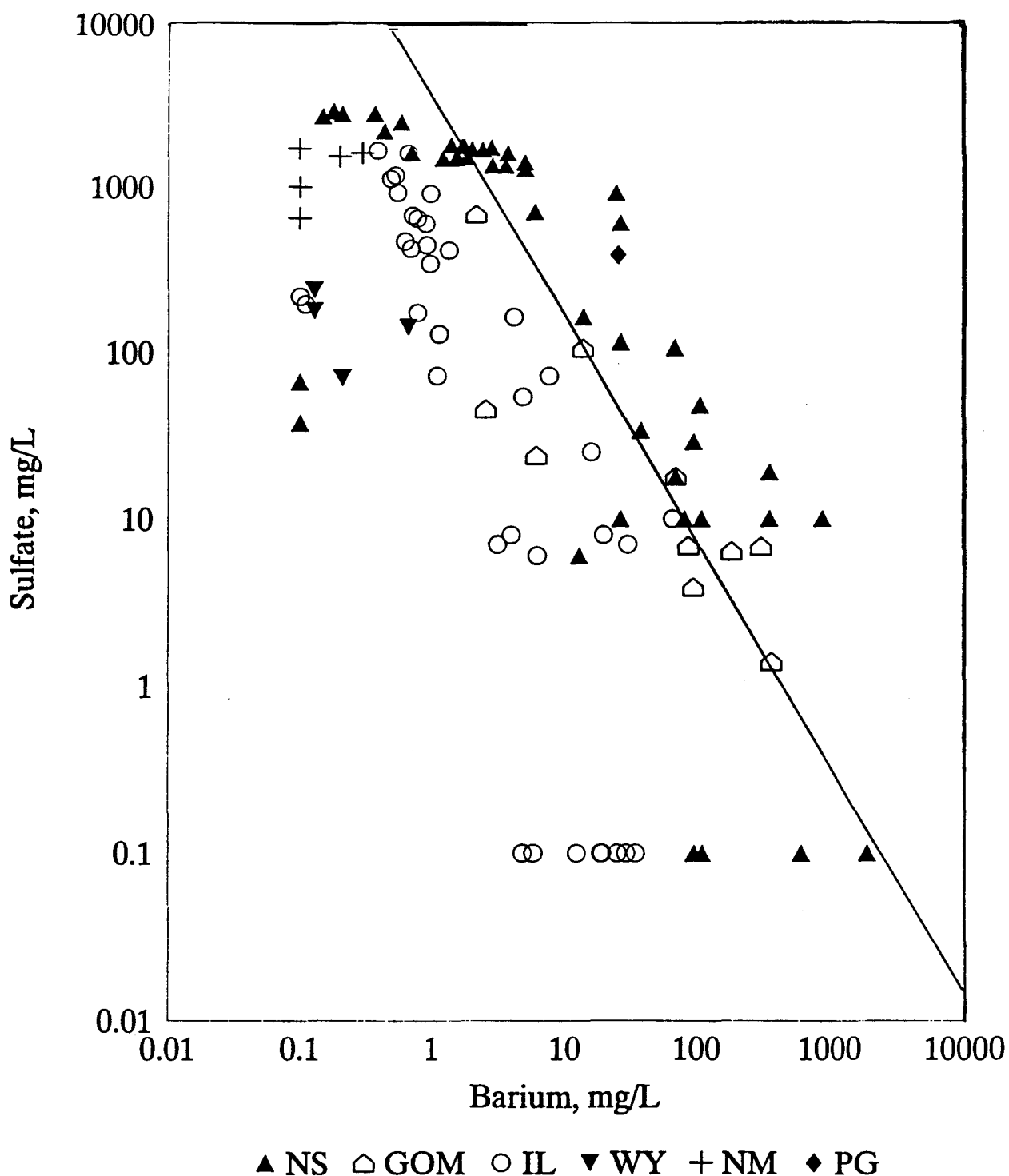


Figure 3-1. The relationship between the concentrations of barium and sulfate in produced waters from different sources. The solid line is the approximate solubility product for barite at 1000°C. NS, North Sea; GOM, Gulf of Mexico; IL, Illinois; WY, Wyoming; NM, New Mexico; PG, Persian Gulf.