

Geochemical signature of formation waters associated with coalbed methane

Wayne A. Van Voast

ABSTRACT

Formation waters associated with coalbed methane have a common chemical character that can be an exploration tool, regardless of formation lithology or age. Effectively devoid of sulfate, calcium, and magnesium, the waters contain primarily sodium and bicarbonate and, where influenced by water of marine association, also contain chloride. The distinct geochemical signature evolves through the processes of biochemical reduction of sulfate, enrichment of bicarbonate, and precipitation of calcium and magnesium. Cation exchange with clays may also deplete the dissolved calcium and magnesium, but is not prerequisite. Low sulfate/bicarbonate ratios characterize these waters and are also common but less pronounced with occurrences of conventional oil and gas. Waters rich in sulfate, calcium, and magnesium occur in many coalbed aquifers but are not found in association with methane.

Users of total dissolved solids data should ensure that the values reflect adjustments of bicarbonate concentrations to simulate evaporation residues. Results that erroneously sum the entire bicarbonate content can be far too high in these bicarbonate-rich waters, thereby exacerbating the issues of disposal.

Evaluations of prospects and choices of exploration targets can be enhanced by an added focus on the geochemical signature that should be expected in association with methane. Knowledge of the geochemical signature may also be useful in the commonly protracted testing of wells. The appearance of high sulfate concentrations in water analyses can justify early curtailment of test pumping and can prompt the siting of subsequent drill holes farther from areas of recharge.

INTRODUCTION

Almost all commercial production of methane from coalbeds in the United States occurs in six geologic basins (Figure 1). At the time of writing (2001), methane produced from coal in these basins

AUTHOR

WAYNE A. VAN VOAST ~ *Montana Bureau of Mines and Geology, Montana Tech of the University of Montana, 1300 West Park Street, Butte, Montana, 59701-8997; wvanvoast@mtech.edu*

Wayne A. Van Voast has worked as a well-site geologist in the United States and Canada, as a hydrologist with the U.S. Geological Survey in Minnesota, and as a mineral fuels geologist and a hydrogeologist with the Montana Bureau of Mines and Geology. He has published numerous technical reports on coal and ground water and is currently researching the aspects of the occurrence of methane with coal.

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Figure 1. Principal coalbed-methane-producing basins in the United States, 2001.

is approaching 8% of the United States's total natural gas production, and new development will occur in numerous other coal-bearing basins as exploration expands and the techniques of this young industry are refined. Disposal of water produced with the gas will be an issue almost everywhere because of the quantities necessary to achieve gas production and because of the chemical quality of production water in contrast to that of potential disposal options. Interest in water quality has thus far focused overly on the issue of disposal, in large part overlooking its application for exploration. In this article, the terms "ground water," "formation water," and "production water" are chosen to represent ground water in the general sense, its occurrence with oil or gas, and its production with oil or gas, respectively.

The purposes of this article are to identify the specific chemical character common to all coalbed waters associated with methane and to dramatize its value as an exploration tool. The chemical character has been noted before (Decker et al., 1987) for three of the producing basins (Piceance, San Juan, and Black Warrior) in Figure 1. This article underscores some of those conclusions and adds interpretations from additional basins and different data. Of the numerous commonly used diagrams for showing water quality, the semilog milliequivalent diagram introduced by Schoeller (Freeze and Cherry, 1979) was chosen here. The Schoeller diagram allows quantitative as well as comparative perspectives, both judged useful for this topic. Water-quality conditions for the six producing basins are described, with emphasis on the similarities of relative chemical concentrations in both marine and nonmarine depositional environments. Discussion of the geochemical processes in the evolution of these conditions is presented, together with sidebars on water quality associated with conventional oil and gas, cautions in the use of total

dissolved solids (TDS) values, and suggestions for using the geochemical signature during methane exploration, testing, and development.

BASIN DEVELOPMENTS

Although methane from coal has been a source of energy for many decades, the first significant commercial production of methane from coal in the United States was in the Black Warrior basin of Alabama (Figure 1). The coalbed-methane industry had a somewhat serendipitous beginning there from research designed to reduce the amount of gas infiltrating the underground mines. The degassing for safety purposes ultimately proved profitable for the sale of the gas, and the first United States coalbed-methane field was subsequently defined in 1980 as the Black Warrior basin (Pashin and Hinkle, 1997). Large-scale commercial development in the San Juan basin, Colorado and New Mexico, closely followed the developments in Alabama, and as of 2001, production (mostly in New Mexico) far exceeds all other United States coalbed-methane production combined (Colorado Oil and Gas Conservation Commission statistics; Energy Information Administration, 2001). Other Rocky Mountain basins with substantial production are the Raton basin, which also spans the Colorado/New Mexico border, the Piceance basin in Colorado, which is one of the deepest structural basins in the Rocky Mountain region, the Uinta basin in western Utah, and the Powder River basin, which is geographically the largest of all United States producing basins although methane production there is geologically the shallowest.

Ages of the producing coals range from Pennsylvanian to Tertiary (Table 1), and coal rank varies from subbituminous to bituminous. In all basins, except the Powder River, marine or marine-transitional environment accompanied deposition. The coals and associated beds in the Powder River basin are entirely continental and are deposited in a freshwater environment. The chemical quality of the coalbed water can, in large part, reflect depositional environment, but wherever produced with methane, the water carries an additional chemical signature from diagenetic (postdepositional) geochemical processes.

PRODUCTION-WATER QUALITY

Production waters in the six producing basins (Table 1; Figure 2a–f) have chemical similarities despite the long

Table 1. Summary Information on United States Coalbed-Methane-Producing Basins Identified in Figures 1 and 2a–f

Basin	Formation	Depositional Environment(s)	Coal Rank	Production-Water Type and Source of Data
Black Warrior basin, Alabama	Pennsylvanian Pottsville Formation	marine/continental	bituminous	sodium bicarbonate/chloride (Figure 2a); O'Neil et al. (1989) and Pashin et al. (1990)
San Juan basin, Colorado and New Mexico	Upper Cretaceous Fruitland Formation	continental to marine-transitional	subbituminous to bituminous	sodium bicarbonate/chloride (Figure 2b); Kaiser et al. (1991) and Colorado Oil and Gas Conservation Commission files
Raton basin, Colorado and New Mexico	Upper Cretaceous Vermejo Formation, and Upper Cretaceous to Paleocene Raton Formation	continental, marine, and marine-transitional	bituminous	sodium bicarbonate/minor chloride (Figure 2c); Colorado Department of Public Health and Environment files
Piceance basin, Colorado	Upper Cretaceous Cameo zone of the Mesa Verde Formation	marine-transitional	subbituminous to bituminous	sodium bicarbonate/chloride (Figure 2d); Colorado Department of Public Health and Environment files
Uinta basin, Utah	Upper Cretaceous Ferron Sandstone Member of the Mancos Shale	marine-transitional	bituminous	sodium bicarbonate/chloride (Figure 2e); Utah Division of Oil, Gas, and Mining files
Powder River basin, Wyoming and Montana	Paleocene Tongue River Member of the Fort Union Formation	continental	subbituminous	sodium bicarbonate (Figure 2f); Rice et al. (2000) and Montana Bureau of Mines and Geology files

geographic distances between basins and the disparities of stratigraphy and geologic age for the producing formations. The very low concentrations of calcium and magnesium, the almost total absence of sulfate, and the predominance of sodium, bicarbonate, and sometimes chloride are clearly evident for each producing basin and typify ground-water quality associated with coalbed-methane occurrence and production.

In most basins, the ionic concentrations reflect the processes of recharge, flow, flushing, and discharge. In those basins where flow conditions have been determined, concentrations nearer the recharge areas are generally lower for sodium and chloride and somewhat greater for calcium and magnesium than they are nearer the discharge areas.

The San Juan basin's hydrogeology, for example, has been extensively studied and modeled by Kaiser et al. (1991), who related the conditions of ground-water flow, hydrostatic pressure gradients, and water quality. They demonstrated the sodium bicarbonate-chloride chemical type of coproduced ground water (Figure 2b) and showed that concentrations are lowest in the Colorado part of the basin due to the recharging fresh water there. Downgradient concentrations of all three constituents in the New Mexico part of the basin increase dramatically.

The hydrogeology of the Raton basin is also well known through studies by McLaughlin (1966) and Hemborg (1998). Concentrations of all dissolved constituents increase along the downgradient flow path toward the center of the basin (Figure 2c). The only significant concentrations in the produced water are those of sodium, bicarbonate, and chloride, whereas other ions common to ground water (calcium, magnesium, and sulfate) are nearly absent.

In the Piceance basin, water produced with coalbed methane at the southeast end of the basin is the same sodium bicarbonate-chloride-type water (Figure 2d) found with coalbed-methane production elsewhere.

Sodium and bicarbonate are the principal constituents in the Powder River basin production waters (Figure 2f) as well as in all others. Along the recharging eastern side (Daddow, 1986), there are somewhat higher concentrations of calcium and magnesium and lower sodium contents than elsewhere. Deeper in the basin and toward the distal northern end, calcium and magnesium contents are substantially lower, and sodium is about doubled from that in the recharge area. Throughout this and all other coalbed-methane-producing basins however, the predominance of sodium and bicarbonate (and chloride in marine associations) defines the chemical

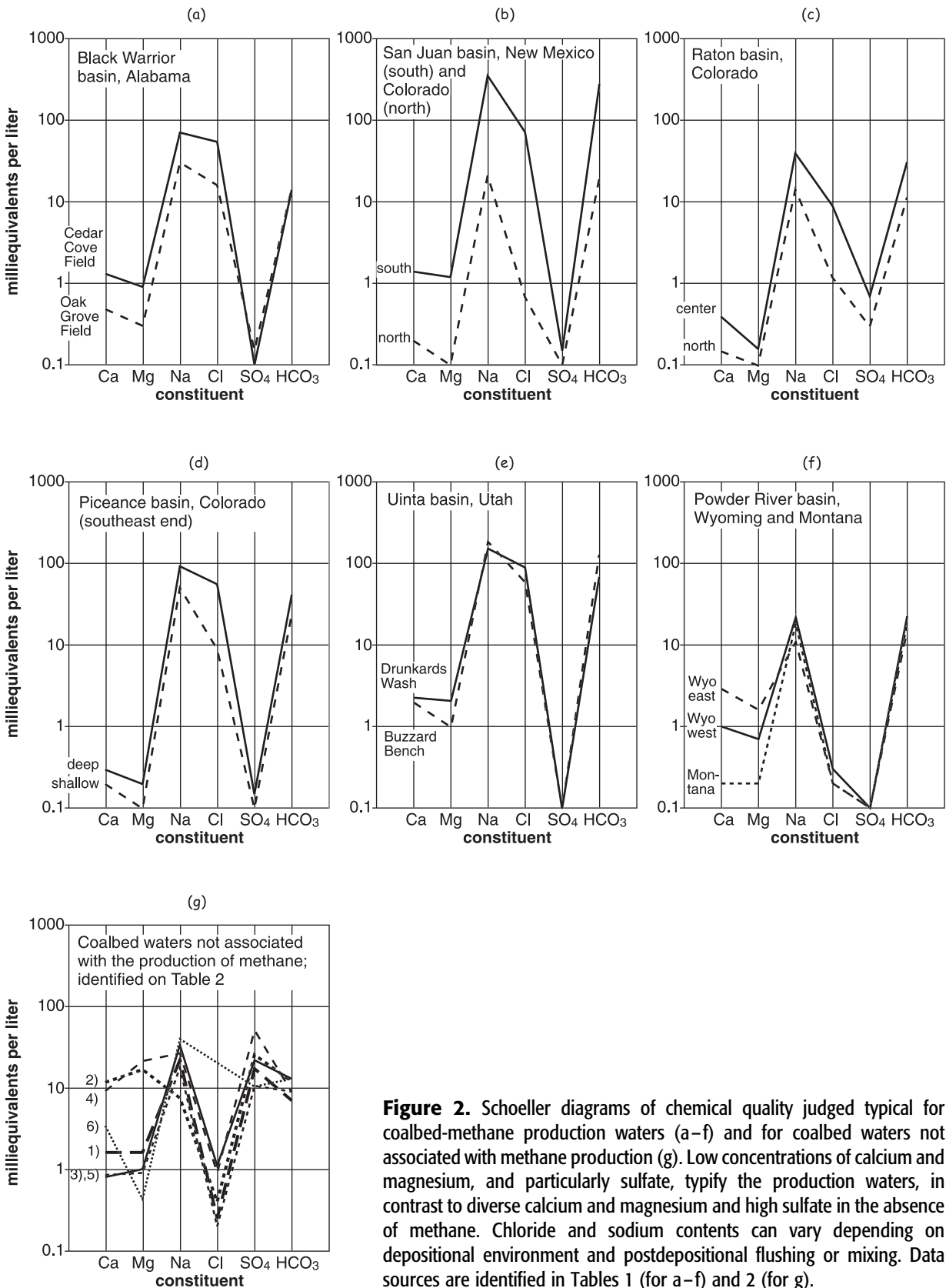


Figure 2. Schoeller diagrams of chemical quality judged typical for coalbed-methane production waters (a–f) and for coalbed waters not associated with methane production (g). Low concentrations of calcium and magnesium, and particularly sulfate, typify the production waters, in contrast to diverse calcium and magnesium and high sulfate in the absence of methane. Chloride and sodium contents can vary depending on depositional environment and postdepositional flushing or mixing. Data sources are identified in Tables 1 (for a–f) and 2 (for g).

Table 2. Summary Information on Examples of Coalbed Waters Not Productive of Methane Identified in Figure 2g

Setting	Formation	Depositional Environment(s)	Coal Rank	Formation-Water Type and Source of Data
Northernmost Powder River basin, Montana	Paleocene Tongue River Member, Robinson Coal	continental	subbituminous	sodium sulfate/bicarbonate (Figure 2g[1]); Van Voast and Hedges (1980, well 2-C)
Northernmost Powder River basin, Montana	Paleocene Tongue River Member, Rosebud Coal	continental	subbituminous	sodium sulfate/bicarbonate (Figure 2g[2]); Ferreira et al (1989, well WR-125)
Bull Mountain basin, Montana	Paleocene Tongue River Member, Mammoth Coal	continental	subbituminous	sodium sulfate/bicarbonate (Figure 2g[3]); Thompson (1982, well BM-3A)
Williston basin, North Dakota	Paleocene Tongue River Member, Harmon bed	continental	lignite	sodium sulfate/bicarbonate (Figure 2g[4]); Horak (1983, well 141-105-36AAA3)
Alberta plains, Wabamun area	Upper Cretaceous – Tertiary Paskapoo Formation, Ardley Coal, seam #6	continental	subbituminous	sodium sulfate/bicarbonate (Figure 2g[5]); Trudell and Faught (1987, well HV-19)
Alberta plains	not specified	not specified	not specified	sodium sulfate/chloride/bicarbonate (Figure 2g[6]); Alberta Geological Survey (unpublished information)

character of formation water predictable with the occurrence of methane.

COALBED-WATER QUALITY NOT ASSOCIATED WITH METHANE PRODUCTION

Methane is not being produced with coalbed waters that contain substantial concentrations of sulfate. In the examples of this type of water (Figure 2g) and the comparisons with production-water quality (Figure 2a–f), high sulfate concentrations and diverse concentrations of calcium and magnesium characterize coalbed water in the nonmethane settings. Particularly evident are the sulfate concentrations greater than about 10 meq/L (~500 mg/L) in the non-methane-producing wells. The examples in Figure 2g are from wells in a variety of coals and settings in Montana, North Dakota, and Alberta (Table 2). In all of these general areas, there may be ground waters having favorable chemical quality for methane occurrence, but there is no evidence of natural gas at these particular locations where sulfate is a predominant anion.

DISCUSSION

The chemical similarities of known coalbed-methane production waters demonstrate a standard chemical type that can be expected in future coalbed-methane developments, without respect to formation lithology or age. The waters are typified not so much by their dissolved constituents but by the specific absences of some of these constituents. Knowledge of this standard chemical signature should have a primary use in methane exploration, testing, and development. It is proposed here that coalbed methane will be found exclusively with formation waters of this specific chemical type. It does not follow, however, that methane will be found wherever these waters occur. Although comparatively uncommon in the Earth's ground-water regime, they do occur in some settings that are not productive of methane, such as in sediments of the San Joaquin basin in California, in the Fox Hills-Hell Creek aquifer in Montana, and in Cretaceous aquifers beneath the Atlantic and Gulf Coastal plains. The common geochemical nature of all waters of this type reflects a background of chloride and sodium (in marine associations) and a succession of the processes of microbial sulfate reduction, bicarbonate enrichment, and calcium and magnesium depletion.

Marine Influence

In all of the basins where the coals are in stratigraphic association with marine or marine-transitional beds, chloride and sodium are the substantial components in the production waters (Figure 2a–e). Variations in concentrations within the basins have been shown to relate to mixing with, or flushing by, ground water. In the San Juan basin, for example, concentrations along the recharging north end of the basin are about a tenth of those in the downgradient southern part of the basin (Figure 2b). Similar mixing or flushing is evident in the upgradient or near-surface parts of the Raton and Piceance basins (Figure 2c–d). Insignificant concentrations of chloride in the Wyoming and Montana production waters (Figure 2f) reflect the nonmarine character of the Powder River basin sediments, a condition different from that of the other geologically older basins. Whether influenced by chloride and sodium from marine sources, the chemical signature of the production waters demonstrate at least three geochemical processes. The first of these, sulfate reduction, is a prerequisite reaction for the biogenesis of methane, is an attendant condition in its thermogenesis, and enhances the enrichment of dissolved bicarbonate that in turn results in the depletion of calcium and magnesium.

Microbial Sulfate Reduction

Most ground waters encounter and dissolve sulfate minerals along the paths of flow. In recharge areas of sulfide-common terranes such as those associated with coal, high concentrations of dissolved sulfate result from weathering and oxidation of pyrite and marcasite. As the coalbed waters enter deeper, oxygen-poor parts of flow systems, biochemical reduction of the dissolved sulfate reprecipitates the sulfides, thereby depleting the sulfate content of the waters. Given the presence of an anoxic environment, low sulfate concentrations, organic matter such as coal, methanogenic bacteria, and optimum conditions of temperature and in-situ space (Rice and Claypool, 1981), biogenic methane is produced. Some research suggests that the generation of methane occurs concurrently with the sulfate-reduction process, depending on the methanogenic species present (Oremland et al., 1982).

Coalbed methane in basins described by Rice (1993), other than the Powder River basin, is chiefly but not exclusively of thermogenic origin. Coalification is essentially a reduction process, biologically driven in its first stages such as in Tertiary coals of the Powder River basin

and ultimately as metamorphism by pressure and heat of burial in the deeper basins. The attendant chemical reduction of dissolved sulfate is evidenced by the sulfide minerals pervasive in and near the coal and by the absence of sulfate in formation waters produced with the methane. Whether reduced by the original microbial activity or later by advanced coalification, the sulfate content in coalbed-methane production water is negligible, regardless of the methane's origin.

Bicarbonate Enrichment

Waters produced with coalbed methane are rich in dissolved bicarbonate, which is a direct product of carbonate dissolution by oxygenated recharge waters and of both the sulfate-reduction and methane-fermentation processes (Freeze and Cherry, 1979) deeper in the basins. It is not a coproduct in the biochemical process of carbon dioxide reduction however, which is considered the preferred pathway for methanogenesis. Beyond the influence of recharge, the universal presence of elevated bicarbonate with coalbed methane, regardless of methane origin, suggests that biochemical reduction of sulfate is the primary bicarbonate producer in the formation waters.

Calcium and Magnesium Depletion

The production waters are almost devoid of the divalent cations, calcium and magnesium, but contain high concentrations of sodium. The predominant process for calcium and magnesium depletion is likely the inorganic precipitation of calcite and dolomite due to reduced solubility in the presence of the elevated concentrations of bicarbonate. Probably, the first field example of calcium and magnesium precipitation associated with sulfate reduction was described by Eaton (1935) for ground water of the San Joaquin Valley, California. Diagenetic precipitation is also attributed to clay, carbonate, and other precipitates identified on cleat surfaces of coals in the Black Warrior and San Juan basins by Fowler and Nick (1997). Carbonate precipitation occurred in the laboratory during an injection compatibility test by Decker et al. (1987), during which the experimental mixing of high-bicarbonate production water from the Piceance basin with low-bicarbonate water created insoluble precipitates of calcium, magnesium, barium, and strontium carbonates. Solubility limitations for calcite are well known and predictable (Drever, 1997), but are less certain for dolomite. An assumption of dolomite in equilibrium with calcite produces the relationship in Figure 3, which

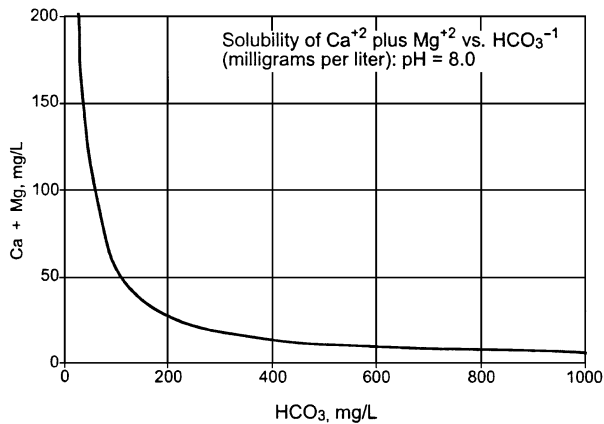


Figure 3. Solubility of calcium plus magnesium in waters containing dissolved bicarbonate. As concentrations of dissolved bicarbonate (HCO_3) increase, the solubilities of calcium and magnesium (Ca and Mg) decrease, causing precipitation of calcite and dolomite. This relationship explains the low concentrations of calcium and magnesium in the high-bicarbonate-production waters. Calculated from equilibrium constants (Freeze and Cherry, 1979), assuming that calcium is in equilibrium with magnesium and concentrations are equivalent to activities.

although not rigorous, demonstrates the reason for low calcium and magnesium concentrations found in produced coalbed-methane formation waters. Bicarbonate enrichment inherent with the sulfate-reduction process causes precipitation of calcite and dolomite, producing the high-bicarbonate, low-calcium, and low-magnesium character of the formation waters.

Augmenting the precipitation, but not prerequisite, may be the exchange of sodium from clays for calcium and magnesium in solution. Cation exchange is considered the principal process for calcium and magnesium depletion in terrains of reactive, volcanically derived clay minerals such as in the Powder River and Williston basins. Although not necessarily related by cause and effect to the generation or presence of methane, cation exchange is a process commonly attributed to the evolution of sodium-rich waters (Lee, 1981). In recharge areas, infiltrating waters readily dissolve available salts, building commonly high concentrations of calcium, magnesium, and sodium. Progressively along the flow paths and the water's contact with reactive clay minerals, the calcium and magnesium ions adsorb to the clay and are replaced in the water solution by equivalent molar concentrations of sodium previously adsorbed on the clay.

Evolution of the overall chemical quality proceeds sequentially by dissolution of inorganic ions in recharging waters, dilution of marine-associated waters where present, biochemical sulfate reduction directly enrich-

ing bicarbonate, and depletion of calcium and magnesium through cation exchange and/or bicarbonate-driven precipitation of calcite and dolomite. The final product develops through several relatively simple geochemical processes and is not difficult to recognize because of the simple content of two or three major constituents as in Figure 2a–f, rather than the six or more ions that are commonly predominant. However, not all coals contain water of this type (Figure 2g). Waters rich in sulfate, calcium, and magnesium are found in many coalbed aquifers, and in these cases, the coals should not be considered likely sources of methane.

Applications for Exploration and Development

The geochemical signature of coalbed-methane production water can be a useful criterion in the preliminary evaluations of prospects when broad assemblages of data are reviewed. It may be more important, however, in the design and duration of test pumping and in the selection of subsequent drilling sites. Where coalbeds are aquifers, such as in the Powder River and Williston basins, test pumping for many weeks may be required before indications of gas productivity are evident. In these cases, an early water-quality analysis can indicate whether the expense of prolonged pumping is warranted. If dissolved sulfate content exceeds 10 meq/L (~ 500 mg/L), the well is an unlikely producer of methane. Moving the next drilling site(s) farther from the outcrop may avoid the influence of recharge and any associated sulfate.

Conventional Oil and Gas

Aqueous chemical processes associated with conventional occurrences of oil and gas may include all of those ascribed for coalbed methane, but the processes must occur under conditions far beyond the scope of this article. Inherently complicating all evaluations are the diverse testing and completion practices and the dynamic near-well oil/gas/water regimen induced by production (Hanor, 1999). Consideration must also be given that formation-water quality, particularly having reduced sulfate, is in large part a prerequisite in the genesis of biogenic and thermogenic coalbed methane, whereas reduced sulfate content associated with conventional hydrocarbon occurrences probably relates to sulfate instability in the hydrocarbon environment. Sulfate reduction in coalbeds precedes or is concurrent with hydrocarbon genesis, but in the conventional case, it may be a result.

Microbial reduction of sulfate and associated enrichment of bicarbonate, here deemed axiomatic for formation waters associated with coalbed methane, had long been thought to modify the chemistry of formation waters associated with conventional occurrences of oil and gas; that record, however, is less clear and the evidence less compelling. Russian and Canadian scientists have actively sought hydrochemical associations with petroleum occurrences for purposes of exploration. In the United States, formation-water chemistry has been of keenest interest because of problems of production and disposal.

Vel'kov (1960) related sulfate/bicarbonate ratios in formation waters to the presence or proximity of oil and gas occurrences in several areas of western Russia. In that work, ratios less than about 3 (not specified, but presumed to be based on milligrams per liter) were characteristically found within about 1500 m (presumed laterally) of an oil pool, and ratios less than unity were common in waters in contact with the oil itself. High contents of gas shown on gas logs were also distinctive of waters with low ratios (<3). Early evaluations of Devonian formation waters in western Canada did not yield succinct relationships between dissolved sulfate and bicarbonate (van Everdingen, 1968). It was concluded at that time that no clear-cut case for acceptance or rejection of sulfate reduction had thus far been presented.

For the United States, Daly et al. (1995, their table 3-2) list production-water quality for 42 conventional onshore gas basins in the conterminous states for 1990. In a simplistic statistical overview of sulfate and bicarbonate concentrations (Figure 4) for the 42 basins, about 70% of the ratios of average concentrations (milligrams per liter) are less than about 3, the limit claimed by Vel'kov for western Russia. Although not rigorous, this may reflect a broad association between conventional natural gas and the chemical quality of formation water. The larger picture, along with the demonstrated instability of sulfate in the presence of petroleum, underscores the merit of research into applications of formation-water chemistry for petroleum exploration.

Know Your Total Dissolved Solids

In the review of laboratory analyses for this article, it was evident that all labs do not use the same criteria in calculating and reporting TDS. In water-disposal issues such as surface discharge or subsurface injection, TDS is a governing parameter for mixing with any surface or ground water. For many decades, TDS was determined

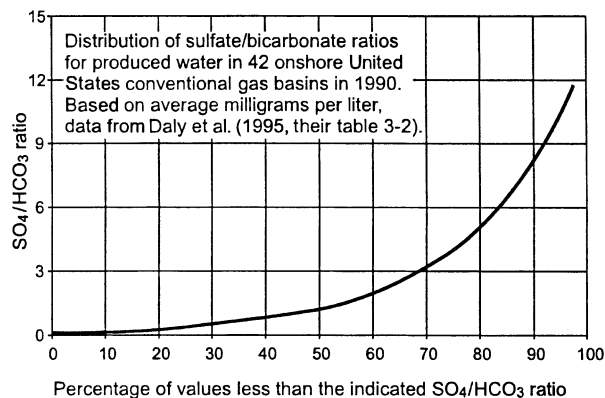


Figure 4. Statistical distribution of average sulfate/bicarbonate ratios (mg/L per mg/L) for waters coproduced with conventional oil and gas. Seventy percent of the reported values were less than 3.0, indicating that reduced sulfate and/or elevated bicarbonate concentrations are common but not pervasive in these waters. A maximum ratio of 3.0 was suggested as an indicator of oil or gas association by Vel'kov (1960) in early studies in western Russia.

only by weighing the residue on evaporation of the water. In that procedure, about half the bicarbonate in the water is volatilized and lost from the solution and residue. The remainder is converted to carbonate and weighed in the residue. With modern analytical techniques (particularly for sodium and potassium), TDS became directly calculable, but the method of calculation has not been consistent.

For water-resources purposes, temporal continuity of data is needed for historical reference and for determining and projecting trends. For consistency with the many decades of historical residue-on-evaporation data, calculated TDS values are adjusted to include only about half (0.4917) the bicarbonate content; the results may be thought of as calculated as residue on evaporation. Not all labs follow this convention, erroneously adding the entire bicarbonate value; the errors can be very large for coalbed-methane and other high-bicarbonate waters. For example, a typical TDS for the southern San Juan basin (Figure 2b) might be about 19,000 mg/L, including about 17,000 mg/L bicarbonate; erroneously reported, the TDS would exceed 27,000 mg/L. Similarly, a typical TDS content in the central Raton basin would be about 2200 mg/L with about 1900 mg/L bicarbonate; erroneously reported, the TDS would exceed 3100 mg/L. In the western Powder River basin (Figure 2f), TDS values are typically about 1200 mg/L, but could be reported erroneously at 1900 mg/L because of the 1400 mg/L bicarbonate in the produced water. From the discrepancies that have been noted, it

is clear that operators can benefit if they and the regulators ensure that they are working with properly reported TDS concentrations.

Data Sources in the Public Sector

Producers and explorationists may be pleasantly surprised at the amount of coal-related data available through the public sector. For most coal basins, data needed to address mining issues such as those of water discharge or injection have already been collected and summarized, as have geologic and ground-water-quality information that can be useful for exploration.

In response to the Surface Mining Control and Reclamation Act of 1977, the U.S. Geological Survey conducted a program of hydrologic study of United States coal basins. It produced a series of more than 60 open-file reports, each one covering an area of known coal resources, and in total covering all areas of minable coal in the conterminous United States. These reports contain general geologic and hydrologic interpretations (e.g., Chaney et al., 1987), along with extensive bibliographies of more detailed data and studies for each area. The bibliographies are highly useful, citing federal, state, and private sources otherwise locatable only by extensive literature study. State geological surveys provide another source of useful information, particularly geologic and hydrologic. Many analyses of ground-water quality, the focus of this article, are publicly available in state files of water wells and oil and gas drillstem and production tests. As an early step in the exploration process, these files can be searched for coalbed water analyses having the geochemical character known to be associated with methane, specifically the relative absences of dissolved calcium, magnesium, and sulfate.

CONCLUSIONS

Coalbed methane is a fast-developing energy resource in the United States, with production from six coal basins thus far approaching 8% of the total natural gas production. Production of the methane entails the coproduction of large volumes of formation water having a common chemical character, regardless of formation lithology or age. Geochemical processes inherent with the conditions of methane occurrence and generation modify ground-water quality to a distinctive type that is easily recognized. Most ground water contains at least six major inorganic constituents: calcium,

magnesium, sodium, bicarbonate, chloride, and sulfate. Waters associated with coalbed methane have been geochemically modified by processes of sulfate reduction, bicarbonate enrichment, and calcium and magnesium depletion to contain primarily sodium and bicarbonate and chloride where influenced by water of marine association.

Microbial reduction of dissolved sulfate seems to drive the sequence of processes that modify the water quality. Bicarbonate is a product of the reduction, and with increased dissolved concentrations, calcite and dolomite precipitate because of reduced solubilities of calcium and magnesium. Cation exchange with clays may also deplete the dissolved calcium and magnesium, but is probably not necessary to arrive at the final chemical character. Low sulfate/bicarbonate ratios invariably occur with coalbed methane, but commonly relate to occurrences of conventional oil and gas. A statistical analysis of water quality in 42 conventional onshore gas basins suggests that low (<3 mg/L per mg/L) sulfate/bicarbonate ratios do characterize most production, but the relationship appears far less rigorous than that for water produced with coalbed methane.

Users of TDS data in addressing environmental issues should be sure of the way the numbers are calculated. Adjustment of the bicarbonate values for evaporation conversion to carbonate and carbon dioxide is the convention, but some laboratories directly sum the bicarbonate. Those results for high-bicarbonate waters can be much too high, thereby exacerbating the problems of disposal.

Exploration and testing for coalbed methane can be enhanced by an added focus on ground waters that are nearly devoid of calcium, magnesium, and sulfate. For reconnaissance-level exploration, a surprising wealth of water-quality and associated geologic data is available in the public sector. The U.S. Geological Survey, for example, has conducted and published hydrologic studies of all known coal basins in the conterminous states. Most states can provide additional data and reports through their geological surveys or other appropriate agencies. Operators can sample formation water during the drilling and testing of prospects and during field development, and the analyses can be used in decisions on duration of test pumping, likelihood of methane production, and siting of locations. An approximate limit of 10 meq/L (~500 mg/L) of dissolved sulfate is suggested by the available data as a maximum concentration to be associated with coalbed methane. When coalbed waters are encountered with sulfate concentrations approaching or exceeding that level, extensive

and unnecessary test pumping to induce gas production can be avoided and subsequent drill sites can be staked at increased distances from outcrops or other sources of recharge.

REFERENCES CITED

- Chaney, T. H., G. Kuhn, and T. Brooks, 1987, Hydrology of area 58, Northern Great Plains and Rocky Mountain coal provinces, Colorado and Utah: U.S. Geological Survey Water-Resources Investigations Open-File Report 85-479, 103 p.
- Daddow, P. B., 1986, Potentiometric-surface map of the Wyodak-Anderson coal bed, Powder River structural basin, Wyoming, 1973–84: U.S. Geological Survey Water-Resources Investigations Report 85-4305, scale 1:250,000, 1 sheet.
- Daly, D. J., R. S. Stoa, J. A. Sorensen, S. A. Bassingthwaite, G. E. Mesing, J. P. Fillo, S. Pemmaraju, K. D. Martz, and J. T. Tallon, 1995, Atlas of gas-related produced water for 1990 (table 3-2): Gas Research Institute Topical Report GRI-95/0016, p. 39.
- Decker, A. D., R. Klusman, and D. M. Horner, 1987, Geochemical techniques applied to the identification and disposal of connate coal water: Proceedings of the 1987 Coalbed Methane Symposium, Tuscaloosa, Alabama, p. 229–242.
- Drever, J. I., 1997, The geochemistry of natural water, surface and groundwater environments, 3d ed.: Upper Saddle River, New Jersey, Prentice Hall, 436 p.
- Eaton, F. A., 1935, Changes in the composition of ground waters resultant to anaerobic sulfate decomposition and the attendant precipitation of calcium and magnesium: Transactions American Geophysical Union 16th Annual Meeting, April 1935, p. 512–516.
- Energy Information Administration, 2001, U.S. Crude Oil, Natural Gas, and Natural Gas Liquids Reserves 2000 Report: DOE/EIA-0216(2000) December 2001, 160 p.
- Ferreira, R. F., J. H. Lambing, and R. E. Davis, 1989, Chemical characteristics, including stable-isotope ratios, of surface water and ground water from selected sources in and near East Fork Armells Creek basin, southeastern Montana, 1985: U.S. Geological Survey Water-Resources Investigations Report 89-4024, 32 p.
- Fowler, K. S., and K. E. Nick, 1997, Diagenetic clays as pore-lining minerals in coalbed methane reservoirs (abs.): AAPG Bulletin, v. 81, no. 8, p. 1350.
- Freeze, R. A., and J. A. Cherry, 1979, Groundwater: Englewood Cliffs, New Jersey, Prentice Hall, 604 p.
- Hanor, J. S., 1999, Effects of subsurface advection and dispersion during hydrocarbon production on the composition of produced waters (abs.): AAPG Annual Meeting Abstracts, v. 8, p. A54.
- Hemborg, H. T., 1998, Spanish Peak field, Las Animas County, Colorado: geologic setting and early development of a coalbed methane reservoir in the central Raton basin: Colorado Geological Survey Resource Series 33, 34 p.
- Horak, W. F., 1983, Hydrology of the Wibaux-Beach lignite deposit area, eastern Montana and western North Dakota: U.S. Geological Survey Water-Resources Investigations Report 83-41570, 89 p.
- Kaiser, W. R., T. E. Swartz, and G. J. Hawkins, 1991, Hydrology of the Fruitland Formation, San Juan basin, in Geologic and hydrologic controls on the occurrence and productivity of coalbed methane, Fruitland Formation, San Juan basin: Gas Research Institute Topical Report GRI-91/0072, p. 195–241.
- Lee, R. W., 1981, Geochemistry of water in the Fort Union Formation of the Powder River basin, southeastern Montana: U.S. Geological Survey Water-Supply Paper 2076, 17 p.
- McLaughlin, T. G., 1966, Ground water in Huerfano County, Colorado: U.S. Geological Survey Water-Supply Paper 1805, 91 p.
- O'Neil, P. E., S. C. Harris, K. R. Drottar, D. R. Mount, J. P. Fillo, and M. F. Mettee, 1989, Biomonitoring of a produced water discharge from the Cedar Cove degasification field, Alabama (table 5.1): Geological Survey of Alabama, Biological Resources Division Bulletin, v. 135, p. 29.
- Oremland, R. S., L. M. March, and S. Polcim, 1982, Methane production and simultaneous sulfate reduction in anoxic, salt marsh sediments: Nature, v. 296, p. 143–145.
- Pashin, J. C., and F. Hinkle, 1997, Coalbed methane in Alabama: Geological Survey of Alabama, Economic Geology Division Circular 192, 71 p.
- Pashin, J. C., W. E. Ward II, R. B. Winston, R. V. Chandler, D. E. Bolin, R. P. Hamilton, and R. M. Mink, 1990, Geologic evaluation of critical production parameters for coalbed methane resources: part II: Black Warrior basin: Gas Research Institute Annual Report GRI-90/0014.2, 190 p.
- Rice, D. D., 1993, Composition and origins of coalbed gas, in B. E. Law and D. D. Rice, eds., Hydrocarbons from coal: AAPG Studies in Geology 38, p. 159–184.
- Rice, D. D., and G. E. Claypool, 1981, Generation, accumulation, and resource potential of biogenic gas: AAPG Bulletin, v. 65, p. 5–25.
- Rice, C. A., M. S. Ellis, and J. H. Bullock Jr., 2000, Water co-produced with coalbed methane in the Powder River basin, Wyoming: preliminary compositional data (tables 1 and 2): U.S. Geological Survey Open-File Report 00-372, 22 p.
- Thompson, K. S., 1982, Ground water and potential coal mining in the Bull Mountains, south-central Montana: Montana Bureau of Mines and Geology Open-File Report 100, 51 p.
- Trudell, M. R., and R. Faight, 1987, Premining groundwater conditions at the Highvale site: Alberta Land Conservation and Reclamation Council Report RRTAC 87-12, 83 p.
- van Everdingen, R. O., 1968, Studies of formation waters in western Canada: Geochemistry and hydrodynamics: Canadian Journal of Earth Sciences, v. 3, p. 523–543.
- Van Voast, W. A., and R. B. Hedges, 1980, Hydrology of the area of Westmoreland Resources, tract 3 coal reserves near Sarpy Creek, southeastern Montana (appendix): Montana Bureau of Mines and Geology Open-File Report 54, 50 p.
- Vel'kov, A. M., 1960, Hydrochemical indicators of gas and oil productivity: Petroleum Geology, v. 4, p. 539–541.