Benzene content of subsurface brines can indicate proximity of oil, gas

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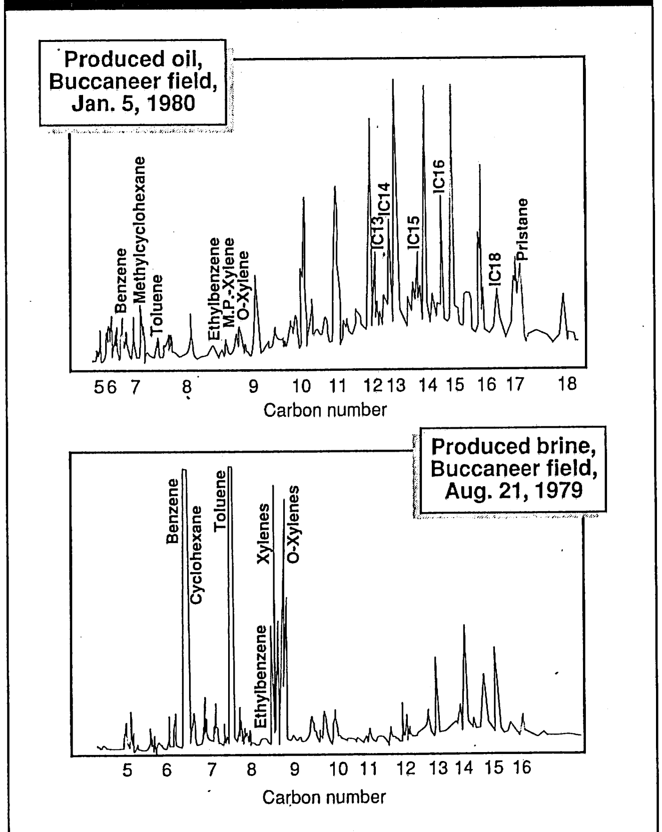
Over the years geochemists have explored the application of brine benzene analysis as a proximity indicator of petroleum deposits.[1] Such studies have been shown to be highly effective in confirming the approximate distance from a dry hole to a reservoir in the same hydrogeologic system by mapping the plume of dissolved petroleum constituents emanating from the nearby accumulation.[2]

Major sources of error in these initial studies were due to the difficulty in storing, handling, and analyzing brine samples without loss or fractionation of volatile constituents. With the advent of standardized environmental sampling and analytical techniques, brine analysis for benzene as well as ethylbenzene, toluene, and xylene (BTEX) aromatics is now routine and reliable. This relatively low cost environmental analytical method, assisted by next-day air courier service, can now be effectively applied to domestic and international petroleum exploration drilling pro-

Fig. 1

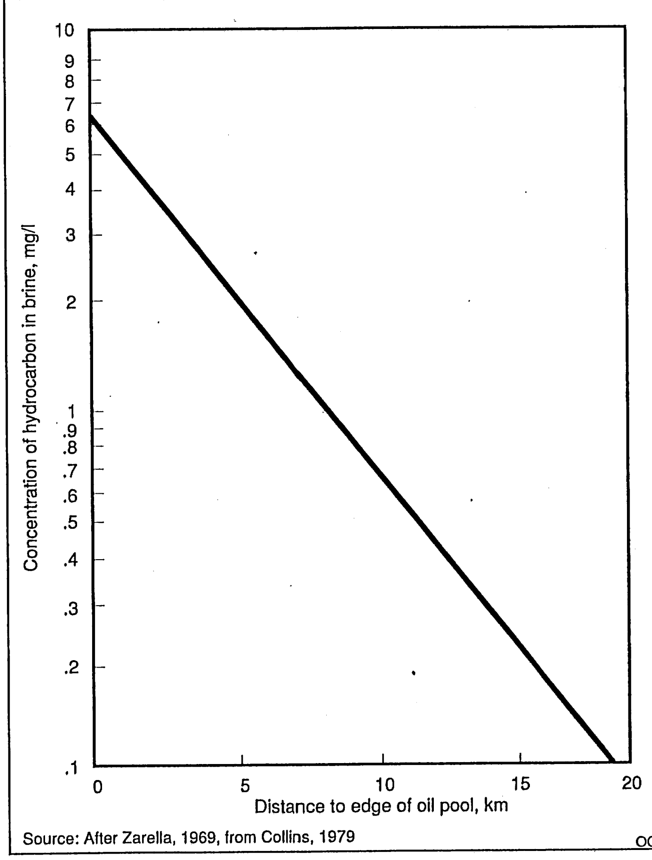
BUCCANEER FIELD OIL, BRINE GAS CHROMATOGRAMS



Source: From Weisenburg et al., 1981 OGJ

Fig. 2

HOW BRINE BENZENE RELATES TO OIL PROXIMITY



Source: After Zarella, 1969, from Collins, 1979 OGJ grams as an economical formation evaluation tool.

Background

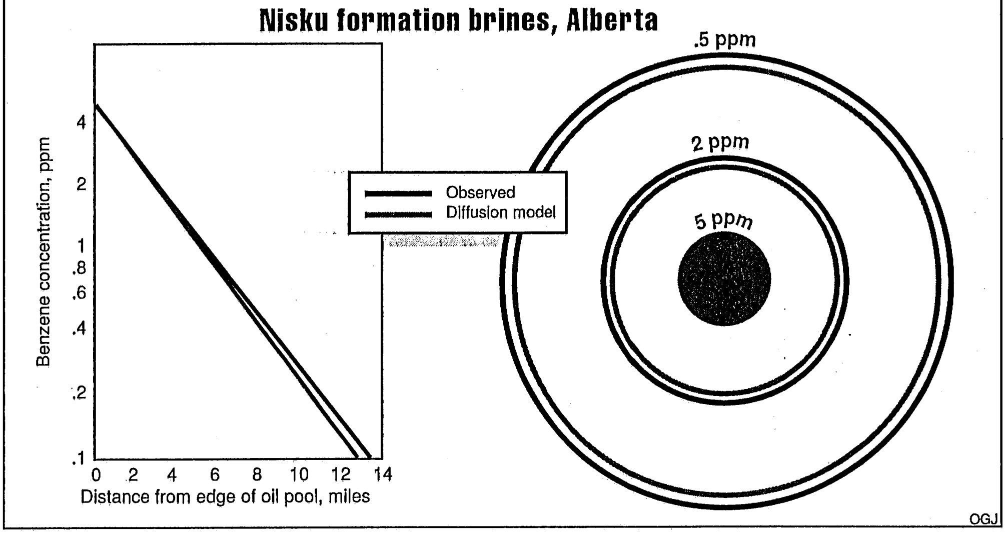
Extensive reservoir fluid compositional studies and research have shown that soluble aromatic hydrocarbons, such as, benzene, toluene, and xylenes make up a large proportion of the dissolved hydrocarbons found in brines associated with oil reservoirs.[3]

Fig. 1 and Table 1 show a comparison of oil and co-produced brine from Buccaneer oil and gas field on Galveston Blocks 288 and 296 in the Gulf of Mexico. As can be seen from these illustrations, BTEX aromatic hydrocarbons are the primary volatile liquid hydrocarbons dissolved in the brines due to their high solubility in water. As summarized in Table 2, empirical studies by Zarrella et al.[2] indicate that the benzene content of brines from typical oil reservoirs ranges from about 5 to 20 ppm depending on oil composition and source.

Benzene and related aromatic constituents, which are in chemical equilibrium with adjacent oil accumulations, emanate from the vicinity of the reservoirs, forming a plume of decreasing magnitude with increased distance from the reservoir edge. Research by Zarrella et al.[2] has confirmed that the distance to an oil reservoir is directly proportional to the log of the benzene concentration of the adjacent brines. This relationship, as plotted on Fig. 2, is due to solubility and diffusion factors.

Fig. 3

RELATIONSHIP BETWEEN CALCULATED, OBSERVED BENZENE CONTENT



Analyses of benzene concentrations in brine samples from non-productive exploration wells can therefore be used to predict the distance to a nearby petroleum accumulation with a reasonable level of confidence. With tests from the same formation, in two or more nearby wells, results can often be used to provide a much more accurate prediction of the distance and direction to potential undiscovered reservoirs within the stratigraphic horizon tested.

As a data base of local wells is developed, the benzene magnitude to distance relationship can be further refined for a specific basin or formation of interest, improving the quality of the distance predictions.

This exploration method was used extensively by the Gulf Oil Corp. in the late 1960s and 1970s and has been discussed in several books on petroleum geochemistry including Hunt[4] and Collins.[1]

Applications

Brine analysis for dissolved aromatic hydrocarbons can be applied in new field exploration programs, development drilling, and predicting extensions of existing fields.

New field exploration. Brine sample analysis can be used to confirm if, despite an apparent dry hole, the formation has an oil accumulation within a radius of up to about 12 miles (20 km).

This information is extremely valuable when assessing the results of rank wildcat areas and international concessions, when decisions must be made with respect to the general prospectiveness of a lease position, in addition to its obvious use in selecting step-out locations and for evaluation of similar structures in the basin. Results provide a lease evaluation tool by predicting the presence or absence of petroleum within a known radius of an exploration well location.

Development drilling. During development and step-out drilling, brine analyses can be used to help confirm

Table 1

VOLATILE LIQUID HYDROCARBONS IN BUCCANEER FIELD OIL AND DISCHARGE BRINE

Compound	Oil, µg/g (ppm) Jan. 5, 1980	Oil, µg/g (ppm) Apr. 8, 1980	Brine, µg/l (ppb) Aug. 21, 1979	Brine, µg/l (ppb) Jan. 8, 1980
n-Pentane	580	4,600	—	—
n-Hexane	1,700	6,100	20	30
n-Heptane	3,900	10,000	21	39
n-Octane	3,700	14,000	19	130
n-Nonane	10,000	16,000	16	200
n-Decane	17,000	18,000	39	400
n-Undecane	20,000	19,000	18	880
n-Dodecane	22,000	17,000	35	1,000
n-Tridecane	26,000	19,000	77	1,050
n-Tetradecane	36,000	25,000	180	1,410
Benzene	2,200	6,000	6,200	17,700
Methylcyclohexane	6,800	15,000	62	340
Toluene	2,700	6,800	2,600	8,500
Ethylbenzene	3,500	5,500	220	1,100
m, p-Xylene	7,200	12,000	500	1,900
o-Xylene	7,060	11,000	480	1,800
Total n-C5-C14	140,000	150,000	420	5,100
Total aromatic	23,000	41,000	10,000	31,000
Total VLH	420,000	490,000	11,300	44,400
% n-C5-C14	33.3	30.6	3.7	16.4
% aromatics	5.5	8.4	88.5	70.0

From Weisenberg et al., 1981

the location of a well with respect to the edge of the reservoir zone. If samples are collected from each well during initial production and testing it may be possible to reduce the number of dry holes by helping to vector step-outs toward areas of higher magnitude benzene content, which would be indicative of more economical reservoir zones.

Field extensions. Extensions to existing fields may be predicted by comparing brine samples from groups of producing wells. As fluids are extracted, formation waters from adjacent areas are drawn to the producing wells. If the brine is drawn from barren areas, the benzene content will continue to decrease over the life of the well.

Wells that draw brine from beneath adjacent, undrained accumulations or untested extension areas in the field often show consistently higher benzene content, since produced brines from these wells were in contact with fresh, unproduced petroleum deposits. This technique is also useful to confirm whether individual wells are influenced by water injection or other secondary and tertiary recovery operations that would alter the magnitude and composition of indigenous formation brines.

Sample collection

Brine samples from drill stem tests, flow tests, or repeat formation testers can be acquired using standard environmental sampling methods by collecting duplicate 1.35 oz (40 ml VOA) sample jars from each test interval.

Samples are collected with no headspace and stored on ice or refrigerated to a temperature of about 5° C. Care should be taken to obtain samples with minimal drilling fluid dilution or contamination from petroleum products used during the drilling operation.

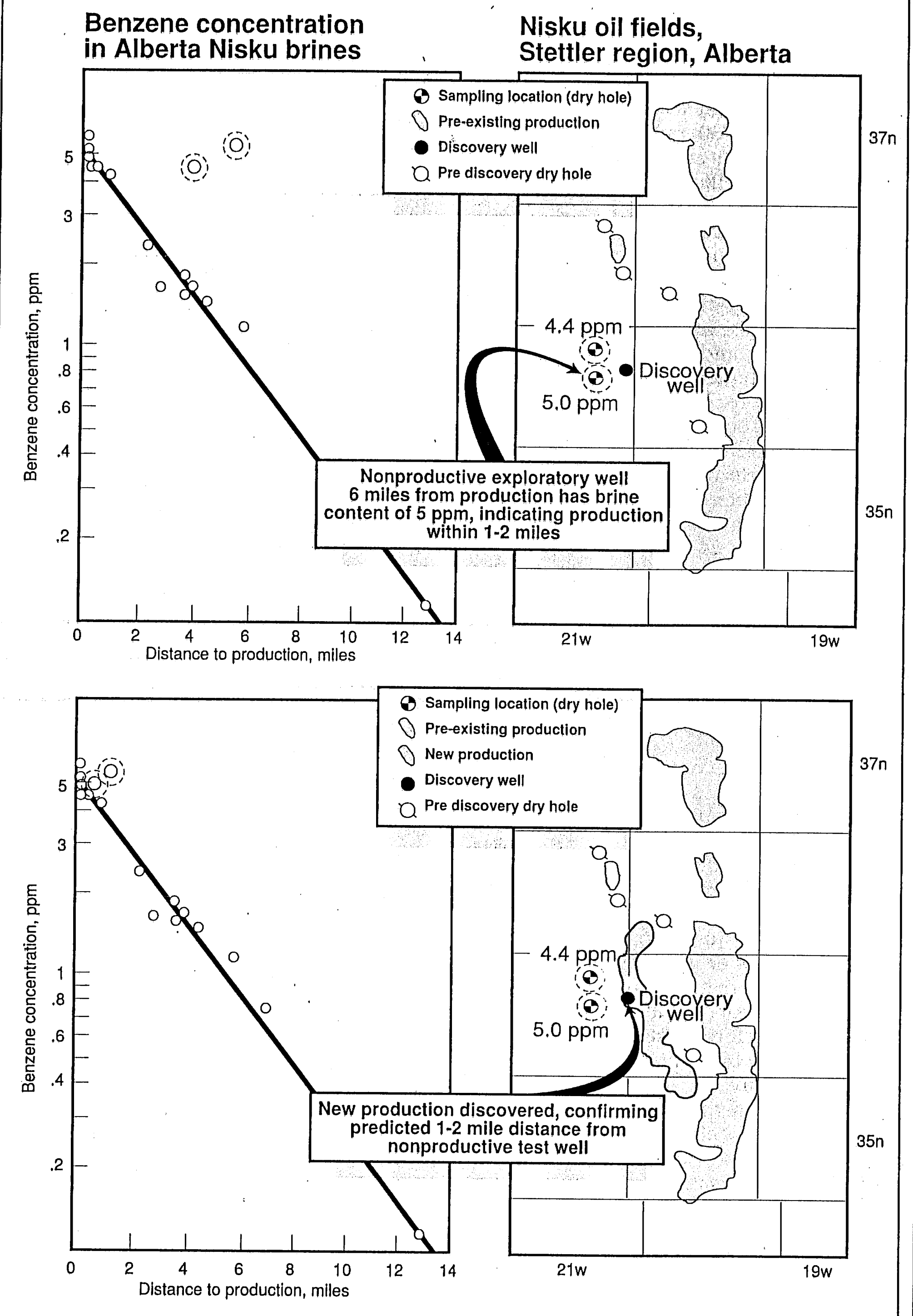
In existing wells on production it is better to obtain a sample, if possible, from the flow line close to the pump rather than from the stand tank. Well fluid samples should be collected into a clean separation funnel and allowed to phase separate for about 5 min. Water samples for analysis are then drawn from the bottom of the funnel and placed into sample jars.

It is very important that good quality brine samples, without appreciable free oil, be collected to reduce the possibility of alteration during sample handling and transport.

Samples can be delivered directly to the laboratory in coolers or sent by air courier on ice in insulated shipping containers. With proper planning and documentation,

Fig. 4

HOW NISKU DISCOVERY FOLLOWED BRINE ANALYSIS



Source: After Jones, 1984

OGJ

samples can easily be shipped or hand carried from international locations without significant reduction in sample quality.

Analytical approach

Samples are extracted by US-EPA method 5030, purge and trap followed by analysis using US-EPA method 602, by photoionization detector (PID) gas chromatography for benzene, toluene, ethylbenzene, and xylene content. This standard analytical method, which is routinely applied for ground water contamination studies, can be performed by most environmental testing laboratories.

Typically the method has an analytical detection limit of about 1 microliter per liter (ppb). Samples can often be analyzed within 24 hr of receipt in the laboratory and results sent by fax or e-mail immediately after analysis. Confirmation samples from each interval are recommended to help insure reliable results and interpretation.

If properly preserved during transport and storage, samples can be analyzed up to 14 days from the date of collection with little or no loss of volatile components. Due to loss of volatiles with time, samples stored for extended periods or at room temperature cannot generally be analyzed for reliable results and therefore must be interpreted with caution.

Total dissolved solids (TDS) are also measured on brine samples to help determine solubility factors of organics in the formation fluids. Additional analyses for iodine and other commonly used proximity indicators can also be completed as available sample volume allows.

Data interpretation

As documented by Zarrella et al.[2] dissolved benzene magnitudes, when plotted versus distance from oil accumulations, plot as a straight line on a semi-log scale (Fig. 2). Test results are posted onto this line to provide an estimate of the distance to an adjacent reservoir.

As a data base is developed for a specific geographical area more precise predictions of distance may be possible. Once a prediction is made it is up to the exploration team to evaluate the results in light of their knowledge of the area's local geologic framework, nearby production, and other exploration test results. Depending on the availability of detailed geologic control from surrounding areas it may be possible to further reduce the area to be searched by eliminating areas around the well that have been previously tested.

Analytical results for benzene can also be compared and confirmed by toluene, ethylbenzene, and xylene data. These compounds, which also have appreciable solubilities in oil field brines (Fig. 1 and Table 1), occur in varying proportions in different reservoirs and can therefore serve as independent parameters for evaluation. As noted by Collins[1] typically a benzene to toluene ratio of greater than 1 can be expected for brines adjacent to petroleum accumulations.

While toluene may be present in greater quantities than benzene in the oil (Table 1), benzene is approximately three times more soluble in water or brine as toluene.[5] Therefore due to diffusion factors the ratio of benzene to toluene in brine adjacent to a reservoir should increase from 1 with distance from the reservoir. The presence and concentration of the other alkylbenzenes further con-

Table 2

BENZENE CONTENT OF BRINES CO-PRODUCED WITH CRUDE OIL

Field	Area	Formation	Type of production	Benzene content of brine, ppm
Gwinville	Mississippi	Eagle Ford	Condensate	18.6
Bough	Lea Co., N.M.	Pennsylvanian	Crude oil	10.7
Golden Spike	Alberta	Basal Quartz	Crude oil	7.1
Lampman	Saskatchewan	Frobisher-Alida	Crude oil	7.0
Keystone	Crane Co, Tex.	Holt	Crude oil	5.6-4.7
Stettler	Alberta	Leduc	Crude oil	6.0-4.8
Stettler	Alberta	Nisku	Crude oil	6.0-4.9
Darst Creek	Texas	Edwards ls	Crude oil	0.21
Braeburn	Alberta	Permo Penn	Gas	0.0
Hereford	Alberta	Viking	Gas	0.0

Source: From Zarrella et al., 1967

Table 3

DOCUMENTED PETROLEUM DISCOVERIES NEAR BENZENE ANOMALIES

Test well	Formation	Distance to production, miles	Estimated distance to new pool, miles	Distance to discovery, miles
West Texas				
W.N. Waddel 542C	Holt	13	3-5	3
McElroy J. 1	Clearfork	>25	4-6	5.5
McElroy Ranch G-2	Pennsylvanian	>25	2-4	1
U.S. Smelting 1	Wolfcamp	15	4-6	5
W.N. Waddell 589	Wolfcamp	20	2-4	1
W.N. Waddel 522	Silurian	17	2-4	4
McPowell B. 1	Devonian	5	2-3	0.75
M.B. Simpson A1	Ellenburger	11	1-2	1
O.N. Beer 1	Ellenburger	22	6-8	6
Oklahoma				
Osborne Dotter 1	Morrow	16	2-3	1.5
Am. Climax 1 Bill	Tyler	8	2-3	4
Rusch B1	Mission Canyon		1-2	0.5
New Mexico				
O.L. Cryer 1	San Andres	7	1-2	4
Skelly Blue Quail 1	San Andres	17	1	4
1-Navajo-107	Paradox B	.	2-3	0.5
Seven Rivers Unit 1	Pennsylvanian	>25	5-6	8
Mississippi				
Gwinville Unit 1, Well 1	Sligo	18	1	1.5
Gulf of Mexico				
Gulf 1 Block 772	Frio		1 (condensate)	*2 (condensate)
Alberta				
Gulf Kerbes 6-23	Nisku	6	1	1
Gulf Snipe Lake 4-22	Beaverhill Lake	20	1-2	4
Gulf Little Bow 6-18	Glauconite	6	1-3	*4
Gulf Ardley 8-19	Nisku	15	1	3
Gulf Ardley 8-19	Leduc	15	2-3	3
Gulf Strachan 12-31A	Leduc	40	1 (condensate)	0.5 (condensate)

*Anomaly partially confirmed.

Source: From Jones, 1984

firms the proximity to a potential reservoir.

Limitations

The benzene content of a brine versus the distance to a potential reservoir is dependent on a number of factors that may limit application of the tool to specific geologic environments. Therefore the following limitations must be considered when applying this method:

The amount of benzene in a particular oil and the associated brines may vary significantly from about 5 ppm to 20 ppm depending on oil composition, salinity, temperature, pressure, and hydrogeologic environment.[6-7] Therefore it is important that these factors be considered when making a prediction of distance to a potential reservoir. As data are accumulated for a specific basin or formation, a more precise proximity curve can be calculated to replace the generalized curve used in Fig. 2.

Samples must be reasonably fresh and collected and stored properly to help insure reliable results. Therefore older samples from plugged and abandoned wells are probably not useful for re-evaluation.

The use of the method may be limited in areas where oil pools may be hydraulically isolated by lithologic changes or other permeability barriers. In such cases results can only be applied to the immediate area with hydraulic communication.

Case studies

Summaries of several case studies performed by Gulf Oil were presented by Gulf Research & Development Co. scientists Pirkle, Hager, and Jones[8] and Jones.[9] Over a period of years various Gulf Oil divisions kept records of the predicted distances to petroleum reservoirs and actual distance to subsequent discoveries.

Table 3 includes a list of petroleum discoveries near to 24 benzene anomalies from West Texas, Oklahoma, New Mexico, Mississippi, Gulf of Mexico, and Alberta. As can be seen from these results, the distance to a potential new field discovery can be reliably predicted from benzene analysis in a wide variety of environments, reservoir types and basins.

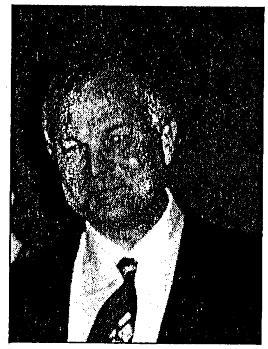
In the Alberta basin of Canada, where this tool was applied extensively for many years, records of the benzene content of Nisku and Leduc formation brines in exploration wells versus the distance to production proved very useful. As summarized in Fig. 3, this observed relationship correlates extremely well with predicted benzene magnitudes as calculated using a diffusion model for benzene migration from typical Nisku reservoirs.

This model for the Nisku formation was tested in the Stettlers region of Alberta, where anomalous benzene magnitudes were identified in two non-productive exploration wells located about 4 and 5 miles from the nearest known Nisku production. Brine benzene contents for these wells of 4.4 and 5.0 ppm plot well off the calculated magnitude to distance correlation line (Fig. 4).

These results were used to predict the presence of an undiscovered accumulation at a radius of 1 to 2 miles from the dry holes. Later drilling confirmed this prediction with the discovery of a new Nisku field a distance of about 2 miles from the test wells. This field has an area of about 12 sq miles with a 20 ft thick oil pay. Fig. 4 shows the new field boundaries with respect to the original test wells and confirms the dissolved brine benzene content in these wells now plot near to the predicted correlation line.

The Authors

Burtell



Jones

Stephen G. Burtell re-joined Exploration Technologies Inc. in September 1995 as manager of exploration services after five years with Fugro companies based in Houston, Malaysia, and Singapore. He has worked in a variety of countries including China, Indonesia, Brunei, Malaysia, Singapore, Thailand, Italy, and Yemen and many U.S. basins including several areas of Alaska. He began his career working for Gulf Oil Corp. and later worked for Exploration Technologies Inc. from 1984-90. His interests include onshore and marine surface geochemical studies and the application of proximity indicators to exploration programs and environmental investigations. He has a BS degree in geology and an MS degree in geology/geochemistry from the University of Pittsburgh.

Dr. Victor T. Jones III, president, Exploration Technologies Inc., has been involved in the application of surface geochemical techniques to both exploration and environmental studies for more than 25 years, initially at Superior and Gulf Oil, then at Woodward Clyde Oceaneering, and finally at ETI. Since founding ETI, he and his staff have further refined and applied exploration and geochemical methods to numerous environmental assessments and surface geochemical studies. He has a BS degree in physics from University of Southwestern Louisiana and MS and Ph.D degrees in physics from Texas A&M University.

Conclusions

Analysis of dissolved benzene and BTEX hydrocarbons in formation water samples from exploration and development wells provides a reliable means of predicting the presence of and distance to petroleum deposits in adjacent, hydrologically equivalent areas.

When evaluated in light of prevailing geologic conditions, this information is invaluable in both frontier and development areas, since the results can not only reduce the area to be searched but can significantly increase the information gained from an exploration test.

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8. Pirkle, R.J., Hager, R.N., and Jones, V.T., Second derivative absorption spectroscopic determination of benzene and toluene at the wellsite, presented at the 187th ACS national meeting, St. Louis, April 1984.
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PUBLICATIONS

Geological Aspects of Coalbed Methane in the Northern Appalachian Coal Basin, Southwestern Pennsylvania and North-Central West Virginia, *available from National Technical Information Service, 5285 Port Royal Rd., Springfield, Va. 22161. 72 p., $19.50 plus shipping.*

This report is based on geological investigations conducted in seven counties in southwestern Pennsylvania and eight counties in West Virginia in 1991-93 by the respective state geological surveys.

Areas where repeated intervals of coal and intervening sandstones are stacked are the best target areas for exploratory drilling and production, mainly because coal rank is higher in these areas.

Sequence Stratigraphy in Offshore South African Divergent Basins, An Atlas on Exploration for Cretaceous Lowstand Traps by Soekor (Pty.) Ltd., *by L.F. Brown Jr. and others, published by American Association of Petroleum Geologists, P.O. Box 979, Tulsa, Okla. 74101-0979. 184 p., $89 plus shipping.*

This heavily illustrated, spiral bound, 11 by 24 in. atlas provides the results of a seven year exploration program for stratigraphic traps within lowstand systems tracts. The program covered about 175,000 sq km in the Bredasdorp, Pletmos, and Orange basins and used only sequence stratigraphic concepts and methods.

Unconformities and Porosity in Carbonate Strata, AAPG Memoir 63, *edited by David A. Budd, Arthur H. Saller, and Paul M. Harris, published by American Association of Petroleum Geologists, P.O. Box 979, Tulsa, Okla. 74101-0979. 313 p., $119 plus shipping.*

Memoir 63 contains papers derived from 15 presentations made at a July 1993 AAPG Hedberg Research Conference in Vail, Colo.

Dissolution associated with subaerial exposure is thought to be responsible for many large oil and gas fields, but subaerial exposure is not always present as predicted and subsurface porosity is not always associated with it.

PHILIPPINES

Labrador Oil Co., Dallas, plans to move a 20,000 ft capacity land rig to explore GSEC 85 surrounding Manila Bay, where flow tests of an indicated gas discovery were to start last week.

About 500 km of aeromagnetic and gravity surveys started in late May with emphasis on potential prospects in southern GSEC 85 close to Manila Bay. The area is on the west flank of the Central Luzon Valley near power stations considered gas markets.

Coplex Energy Corp. (Coenco), owned 72.4% by Coplex Resources NL, Hobart, Tasmania, is farming out to Labrador an 18.75% interest initially. That could rise to 45%.

MANITOBA

The province asked operators to apply by Sept. 1 for funds to conduct field projects under its Petroleum Exploration Assistance Program.

Manitoba Energy & Mines said some of the 12 companies that qualified in February for $1 million in assistance may not spend their total allocation (OGJ, Apr. 1, p. 81).

U.S. GULF

Norcen Explorer Inc. plans to start a second well near a Miocene discovery on Eugene Island Block 107, from which sales are to start in August.

The 1 EI-107 well, drilled to 17,800 ft in 35 ft of water, encountered 153 ft of Miocene pay sands.

Working interests are Norcen 49%, Enserch Exploration Inc. and Global Natural Resources 24.5% each, and Case-Pomeroy Oil Corp. 2%.

The well is in a joint development area that covers blocks 107, 118, and part of Block 108. Norcen, Enserch, and Global acquired rights to Block 117 at the last federal offshore lease sale.

ARKANSAS

Keith F. Walker Oil & Gas Co. LLC, Ardmore, Okla., staked a rank Arkoma basin wildcat in Conway County.

The 1 Alpine, in 31-8n-15w, 2 miles north of an abandoned gas discovery well, is projected to 4,200 ft or Pennsylvanian Barton and Hale.

CALIFORNIA

Santa Fe Energy Resources, Houston, plans to drill eight to 10 more horizontal wells in giant Midway-Sunset field in the next 18 months.

Production at Santa Fe's first horizontal well in the field climbed to 250 b/d of 11° gravity oil recently from 50 b/d upon completion in May 1995.

The 1H well produces from a 1,865 ft lateral at 1,465 ft TVD. Nearby vertical wells yield 20-25 b/d. Drilling costs are $350,000 for a horizontal well and $150,000 for a typical vertical well.

The company's 2H and 3H wells, drilled in April 1996, produced an initial 100 b/d/well from 1,685 ft and 2,030 ft laterals.

FLORIDA

Plains Resources Inc., Houston, is gathering more seismic data in South Florida's Cretaceous Sunniland Trend after plugging its first wildcat there.

Plains' Calumet Florida Inc. affiliate plugged the 4 Duda, in 26-44s-28e, Hendry County, 4½ miles north of Felda oil field, to 11,620 ft. It had good oil shows in Sunniland.

N. DAKOTA

Cedar Hills field in Bowman County has grown rapidly since discovery two years ago, PI reported.

Completion by Meridian Oil Inc. and Continental Resources Inc. of 16 more horizontal wells producing oil from Ordovician Red River bring the field to 50 wells.

March sales were 50,187 bbl from Meridian's nine new producers and 45,868 bbl from Continental's seven new wells.

The field's 50 wells sold 267,839 bbl of oil during March, state figures showed.

WYOMING

Conley P. Smith, Denver, will attempt completion at an indicated Pennsylvanian Minnelusa discovery in Campbell County.

The independent reversed out 6,205 ft of 20° gravity oil on a Minnslusa B sand drillstem test at 8,054-74 ft at the 32-3 Charlotte, in 32-51n-69w, PI reported. The wellsite is between Windmill and Hamm fields.