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Trace and Precious Metal Content of Mississippi
Oil Field Brines

James A. Saunders
1989

The Mississippi Mineral Resources Institute
University, Mississippi 38677

FINAL REPORT

TRACE AND PRECIOUS METAL CONTENT OF MISSISSIPPI OIL FIELD BRINES
(U.S. Bureau of Mines Grant No. G1184128)
MMRI No. 89-8F

by

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ABSTRACT

Lead- and zinc-rich oil field brines from central Mississippi contain geochemically significant levels of other trace and precious metals, but do not appear to be potential economic sources of these metals at the present time. However, if a low-cost extraction process could be developed, it is possible that the aggregate value of all of the base and precious metals might make their extraction economic as a byproduct to oil production. Existing technology for the removal of metals from waste waters (industrial, municipal, etc.) by electrochemical reduction potentially could be employed to extract metals from Mississippi oil field brines.

Copper content of brine samples from Lower Cretaceous formations ranges from <0.015 mg/l to 13.5 mg/l, and silver was detected in 3 samples with a maximum value of 0.062 mg/l. Cobalt values range from <0.04 mg/l to 2.2 mg/l, and molybdenum is present in the range of <0.03 mg/l to 0.055 mg/l. Gold, platinum, and palladium are present at levels below their respective lower detection limits of 0.0001 mg/l, 0.003 mg/l, and 0.002 mg/l for the graphite furnace AA procedure used. Formation waters in lowermost Cretaceous units attained a temperature of 100°C approximately 100 million years ago, and published geologic and geochemical evidence indicates that significant vertical migration of brines has occurred. The composite effects of the reduced sulfur content and salinity of the brines, formation mineralogy, and migration history apparently control the observed present-day concentrations of trace and precious metals in Mississippi oil field brines.

INTRODUCTION

Mississippi oil field brines contain levels of zinc and lead (Carpenter et al., 1974; Kharaka et al., 1987; this study) that make them some of the most metal-enriched natural waters yet documented. The concept that these fluids are analogs to the ore-forming solutions that precipitated the Mississippi Valley Type (MVT) Pb-Zn deposits of the mid-continent region of the United States is now widely accepted. Sverjensky (1984), using thermochemical modeling, demonstrated that a fluid with the initial composition of a Mississippi oil field brine could evolve to a MVT-forming solution by water-rock reactions as it moves toward the basin margin. Similarly, Sverjensky (1987) demonstrated that reduced Pb-Zn rich brines could evolve to more oxidized, copper-rich fluids capable of producing sediment-hosted copper deposits by migrating through and equilibrating with evaporites.

Data of Carpenter et al. (1974) and Kharaka et al. (1987) indicate that zinc- and lead-rich brines are present throughout a large area in central Mississippi, suggesting that the processes that produced the metal-rich waters operated on a regional scale. Diagenetic reactions that accompany the evolution of a sedimentary basin under typical geothermal gradients appear capable of producing metal-rich fluids with the aid of evaporite-derived high salinities (Manor, 1979).

The highest values for lead and zinc come from Lower Cretaceous formations, where several hundred mg/l Pb+Zn are not uncommon (Carpenter et al., 1974; Kharaka et al., 1987). These brines have high salinities, locally greater than 300,000 mg/l total dissolved solids (TDS), and temperatures in the range of about 90-130°C. Kharaka et al. (1987) found that the most metal-rich

formation waters have very low concentrations of reduced sulfur, which causes brines with high Fe, Pb, and Zn concentrations to be undersaturated with respect to their sulfide minerals. The general physicochemical characteristics of these brines suggest that they could potentially contain elevated concentration of other metals.

There are few data available on the metal content of Gulf Coast oil field brines other than that for iron, manganese, zinc, lead, cadmium, and copper published by Carpenter et al. (1974) and Kharaka et al. (1987). Indirect evidence of significant concentrations of other metals come from MVT style deposits themselves, which locally contain cobalt and nickel minerals, minor amounts of silver in sphalerite and galena, and trace amounts of gold (Heyl, 1988; Snyder and Gerdemann, 1988). In addition, zinc-lead mineralization hosted by salt dome caprocks and deep formations in the Gulf Coast region locally contain more than 100 ppm silver (Kyle and Price, 1986; Kyle et al., 1988). Hanna and Wolf (1941) report trace amounts of gold in mineralized salt dome caprocks, verified by more recent work at Hockley dome, Texas, where gold is present in amounts up to 0.1 ppm (P.E. Price, pers. commun., 1988). In addition, lead- and zinc-rich barite scale from oil wells in Mississippi contain up to 110 ppm silver and 21 ppb gold. This study presents geochemical data from 7 oil fields from central Mississippi not sampled by earlier workers and includes the first analyses of a number of trace metals in Mississippi oil field brines.

GEOLOGIC SETTING

Oil fields included in this study are located within the Mississippi

Interior Salt Basin (Figure 1), which contains approximately 60 documented piercement salt domes at shallow to intermediate depths (Halbouty, 1979; Mississippi State Oil and Gas Board, 1986). The basin extends from north Louisiana, through Mississippi, and into southwest Alabama. Within Mississippi, the salt basin is bounded to the north by the Pickens-Gilberton fault zone and on the south by the Wiggins Arch. Salt domes are the primary structures in the basin and are rooted in the mid Jurassic Louann Salt, which contains up to 5000 feet of massive halite and minor amounts of disseminated anhydrite. However, two of the larger dome features in the basin, the Jackson dome and the Sharkey Platform, are cored by Cretaceous igneous intrusions.

Hydrocarbon accumulations in the basin are primarily controlled by salt structures or their associated faults (Davis and Lambert, 1963; Evans, 1987) as evidenced by the fields included in this study. For example, Overt, Glazier, and Kola fields lie directly above or adjacent to recognized intermediate-depth salt domes (Figure 1). Production from the Summerland and MaGee fields comes from faulted anticlinal structures that apparently overlie deeper salt structures (Davis and Lambert, 1963), and Boykin Church field is localized by a faulted anticline directly over a deep salt dome (confirmed by drilling). Producing formations within these fields range from the Upper Jurassic Smackover Formation to the Upper Cretaceous Eutaw Group. The Mesozoic stratigraphy in Mississippi has been compiled by Carpenter et al. (1974) and Kharaka et al. (1987), and can be subdivided into two principal lithologic groupings for the stratigraphic interval of interest: Jurassic carbonates (e.g. Smackover Formation) and Cretaceous siliciclastics, typically alternating red and gray shales with varicolored sands. Brine samples collected for this study come from the Jurassic Smackover Formation, the Lower Cretaceous Hosston,

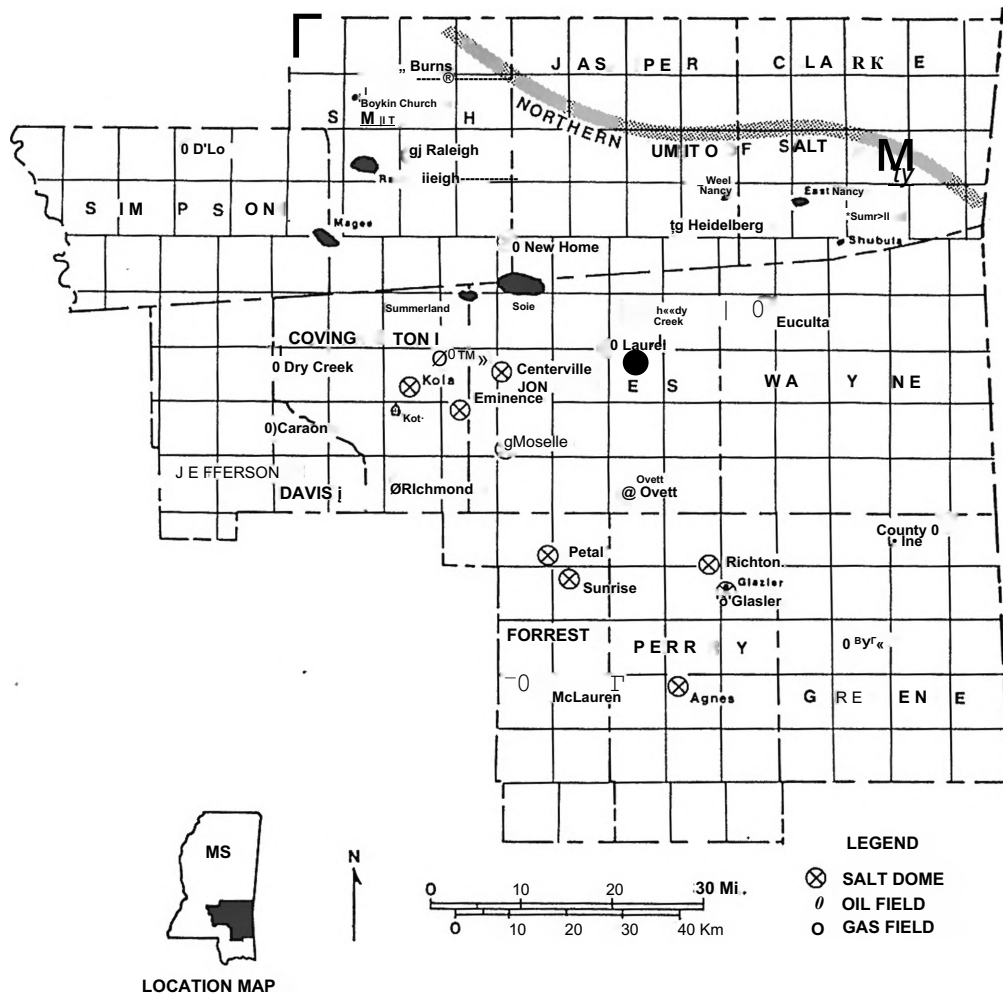


Figure 1. Map showing the locations of oil or gas fields from which brine samples were obtained. Also shown are the location of known salt domes.

Sligo, Rodessa, Haluxy Formations, the Washita-Fredricksburg Groups (undifferentiated) Formations, and zones within the Upper Cretaceous Tuscaloosa and Eutaw Groups (Table 1).

METHODS OF STUDY

Brine samples from twenty wells were collected as close to the well head as the plumbing arrangement would allow, although most often were collected from the separator tank where the oil is isolated from the brine. Samples were then coarse-filtered to remove suspended material and droplets of crude oil, and then filtered using disposable nylon syringe filters with a pore diameter of 0.22 μm . The samples were also acidified to a pH of approximately 1 with concentrated reagent grade nitric acid. Density was measured by weighing known volumes of the brine. TDS was measured using the residue method modified from Collins (1975), where a known volume of brine is evaporated as much as possible in an oven at 90°C, and then for several hours at 190°C to remove all hygroscopic water. The mass of the residue is determined while it is still hot, and TDS can then be calculated. The residue was analyzed commercially for a number of elements by instrumental neutron activation analysis (INAA; Table 2).

In addition to the 20 samples collected as part of this study, 11 splits of brine samples from other wells from central Mississippi were provided by Y.K. Kharaka. These samples were filtered and acidified in a similar fashion (see Kharaka et al., 1987). Residue from these 11 samples, and 7 of the samples analyzed by neutron activation, were analyzed commercially using a

TABLE 1. LOCATION AND PHYSICAL CHARACTERISTICS OF BRINE SAMPLES

Sample	Field	Well	Formation	Depth (m)	Temp. (°C)	Density
1	Glazier	S.F. Hinton-2	Eutaw	2285	77	1.113
2	Glazier	Stevens 9-14	Eutaw-Tusc.	2435	80	1.116
3	Ovett	Carter-3	Tuscaloosa	2360	80	1.118
4	Ovett	McClellan-1	Eutaw	2360	80	1.116
5	Ovett	Majors-16	Tuscaloosa	3055	93	1.145
6	Ovett	Vickers-2	Eutaw	2750	87	1.122
7	Boykin Ch.	Bd. Sup 16-6-1	Paluxy	3740	98	1.162
8	Boykin Ch.	Bd. Sup 16-10-3	Paluxy	3575	93	1.166
9	Shubuta	Barlow 7-2	Smackover	4190	136	1.187
10	MaGee	Keyes 1-6	Hosston	4300	139	1.149
12	MaGee	Magnum 2-1	Rodessa	3920	128	1.145
13	MaGee	V. Womack 1-3	Rodessa	3960	129	1.154
16	Kola	A.O. Meyers-1	Sligo	4385	140	1.131
17	Summerland	Gambrell-3	L.Wash./Fred	2990	87	1.170
18	Summerland	Gambrell-8	L. Tusc.	2650	84	1.144
19	Summerland	Laird-1	Paluxy	3650	95	1.173
20	Summer land	Laird-Gambrell-3	U. Paluxy	3225	90	1.166
21	Summer land	Easterling-1	Wash./Fred.	3000	88	1.155
22	Summer land	Laird-Central-2	Tusc./Wash.	2880	91	1.137
23	Summerland	Laird-2	Wash./Fred.	3100	93	1.155
84-1	Soso	28-7-2	Paluxy	2875	89	1.15
84-4	Raleigh	Central 5-6	Hosston	3715	107	1.18
84-5	Raleigh	T.H. Lucky 1	Hosston	3760	108	1.19
84-6	Raleigh	H. Currie 6	Sligo	3660	105	1.15
84-7	Reedy Creek	Geiger Cupp 9-13-1	Wash./Fred.	2835	88	1.17
84-8	Reedy Creek	Sara Bemis 10	Paluxy	2840	88	1.17
84-11	Reedy Creek	Geiger 2-1	Rodessa	3485	102	1.22
84-14	Sumral	Tony 2	U. Smackover	4370	121	1.19
84-15	E. Nancy	J. Allen 1-N	Norphlet	4350	121	1.22
84-16	E. Nancy	Allen Est. 20-7	Smackover	4135	116	1.18
84-20	W. Nancy	West 6-6-1	Smackover	4235	118	1.18

Note: Data for ČM series of samples is from Kharaka et al. (1987)

combination of TCP and graphite furnace AA (Table 3). In this procedure, 5 grams of residue was treated with a strong organic solution that selectively-extracted metals from the salt, in an attempt to mitigate against analytical interference problems.

The analytical scheme employed in this study was not designed to provide complete chemical analyses of all major and minor elements in solution. Instead, the procedure allowed the determination of several metals of interest that are virtually impossible to analyze by standard wet chemical techniques directly on brine samples because of either the relatively high lower detection limits of those procedures, or more typically, interference problems caused by major ions in solution (Na, Ca, Cl, Br). The weight percent (ppm) for a number of elements was determined on the residue, and then back calculated to mg/l of the original brine. Instrumental neutron activation analyses were conducted by Nuclear Activation Services, Hamilton, Ontario, and ICP-AA analyses were by Geochemical Services Inc., Rocklin, California.

RESULTS

Salinities of brines sampled as part of this study are similar to those reported in previous studies, ranging from 174,000 mg/l to 288,000 mg/l TDS (Table 2). There is a general trend of increasing TDS with depth (and temperature) as noted by Kharaka et al. (1987). The concentrations of cesium, strontium, manganese, iron, cadmium, and bromide are similar to those reported by Carpenter et al. (1974) or Kharaka et al. (1987).

Lead and zinc: Both lead and zinc levels are consistent with those found in the previous studies of Mississippi oil field brines, with lead and zinc

TABLE 3. BRINE ANALYSES (ICP-AA)

Sample	Ag	As	Cu	Mo	Pb	Tl	Zn	Cd
5	0.009	<0.3	0.153	<0.03	4.02	0.213	21.9	0.193
7	<0.004	<0.3	0.226	0.036	6.23	0.150	118	0.549
17	<0.004	0.346	0.370	0.045	17.5	<0.15	118	0.615
19	<0.004	<0.3	<0.015	0.041	31.4	<0.15	174	0.819
20	0.062	0.303	13.5	0.055	95.3	<0.15	129	0.951
21	<0.004	<0.3	0.202	0.040	18.7	<0.15	109	0.553
22	<0.004	<0.3	0.144	0.039	5.96	<0.15	47.0	0.288
84-1	<0.004	<0.3	<0.015	<0.03	6.55	<0.15	56.4	0.452
84-4	<0.004	<0.3	<0.015	0.034	48.9	0.339	241	0.833
84-5	0.021	0.311	0.024	0.034	57.4	0.340	251	0.834
84-6	<0.004	<0.3	<0.015	0.039	23.3	<0.15	113	0.636
84-7	<0.004	<0.3	<0.015	0.038	30.8	<0.15	192	0.861
84-8	<0.004	<0.3	<0.015	0.038	19.7	<0.15	124	0.650
84-11	<0.004	<0.3	<0.015	0.041	71.5	0.486	279	1.05
84-14	<0.004	<0.3	<0.015	<0.30	<0.075	<0.15	<0.3	<0.03
84-15	<0.004	<0.3	<0.015	0.034	1.02	<0.15	4.76	0.038
84-16	<0.004	<0.3	0.138	<0.03	<0.075	<0.15	<0.3	<0.03
84-20	<0.004	<0.3	<0.015	<0.03	<0.075	<0.15	<0.3	<0.03

Note: All values in mg/l .

content of up to 95 mg/l and 279 mg/l respectively. ICP values for lead and zinc obtained from the residue extraction technique used in this study are generally within 10% of values reported for the same samples by Kharaka et al. (1987). Kharaka et al. (1987) used both graphite furnace AA and ICP on unevaporated brine samples, and results from both their techniques were within 5%. Zinc values from INAA are consistently lower than the ICP values (Tables 2 and 3) for the same samples.

Copper : In general, copper values obtained in this study appear to be higher than those reported by Kharaka et al. (1987), with a maximum value of 13.5 mg/l (Table 3). This appears to be the result of local variations in copper content between separate fields or formations as opposed to different results from the varying analytical procedures employed. For example, the copper values from this study are generally in good agreement with the values reported by Kharaka et al. (1987) for the same samples. The elevated levels of copper obtained in this study indicate that Mississippi oil field brines locally may have considerably more copper than previously thought (see Sverjensky, 1987). Another indication of this comes from barite-rich scale from the well that yielded Sample 7 (Table 3). The well scale contains 910 ppm Cu compared to the brine that has 0.226 mg/l Cu. The local elevated copper contents in some of the formation waters could represent the early stage of a change from reducing, Pb- and Zn-rich brines to more oxidizing, Cu-rich fluids along the evolution path proposed by Sverjensky (1987), or due to local copper sources in the host formations.

Silver: Three samples analyzed by graphite furnace AA had silver levels in excess of the 0.004 mg/l lower detection limit, with the highest value of 0.082 mg/l in the sample with the highest copper content (Table 3). This is

the first direct data on the silver content of brines from the Gulf Coast region yet documented, and the silver content at this level implies that formation fluids may locally evolve into potential ore-forming solutions with respect to silver, as suggested by Kyle et al. (1988).

Boron: The boron content of the samples range from 21 to 180 mg/l. The highest value is from the Smackover Formation, which is consistent with the data of Kharaka et al. (1987). Boron is concentrated in the bitterns remaining during evaporite formation, and the breakdown of marine organisms also releases boron (Collins, 1975). Boron minerals are present in the Louann Salt and the overlying Norphlet Formation and probably precipitated from boron-enriched fluids released from the Louann during diagenesis (Simmons, 1988). The boron enrichment of brines of the Smackover Formation, which immediately overlies the Norphlet Formation, could be related to this event. However, the breakdown of marine organisms within the Smackover Formation, or a boron contribution from the original bittern brines formed during the deposition of the Louann Salt, cannot be ruled out.

Cobalt and molybdenum: Cobalt contents range from <0.04 mg/l to 2.2 mg/l (Table 2) and molybdenum ranges from <0.03 mg/l to 0.055 mg/l (Table 3). Lindgren (1933) proposed that the presence of minor amounts of cobalt minerals in MVT deposits is consistent with a sedimentary origin for the element, and the cobalt content observed in this study appears to confirm Lindgren's hypothesis. In addition, sedimentary formation waters appear capable of carrying levels of molybdenum sufficient to account for its association in MVT deposits as well.

Arsenic and antimony: Arsenic concentration in the brines is generally less than the lower detection limit of the analytical procedure, which varied

from 0.5 mg/l to 1 mg/l depending on the sample composition for INAA, and 0.3 mg/l for ICP. However, 3 samples contain arsenic levels slightly above the 0.3 mg/l detection limit (Table 3). Antimony is present at levels less than the lower detection limit of 0.075 mg/l for ICP, although INAA indicates levels as high as 1 mg/l in a few samples.

Gold: Gold was detected in 8 of the samples analyzed by INAA (Table 2). However, analytical interference problems caused by Na, Cl, and Br and the relatively high values for gold compared to other natural waters (McHugh, 1988) suggests that these values are suspect, for these reasons, 7 of the samples with reported gold were included in the group of samples analyzed using graphite furnace AA on the organic extract. All 18 samples analyzed by this procedure had gold contents below the detection limit of 0.1 ug/l, suggesting that the higher levels from INAA were an artifact of the interference problems. In addition, the values obtained from the graphite furnace AA are consistent with an average value of 0.022 parts per billion reported by McHugh (1988) for 4 brine samples from southern California.

Other metals: A series of other metals are present at levels below the lower detection limit of the procedures employed. These include (with lower detection limits shown): platinum (0.003 mg/l), palladium (0.002 mg/l), mercury (0.03 mg/l), gallium (0.15 mg/l), selenium (0.3 mg/l), and tellurium (0.15 mg/l). In addition, bismuth was generally below 0.075 mg/l with the exception of 1 sample containing 0.077 mg/l.

DISCUSSION AND CONCLUSIONS

Diagenetic processes associated with the evolution of a sedimentary

basin appear capable of releasing a variety trace metals to deep formation waters, even under normal geothermal gradients. A number of possible metal-producing processes have been proposed, such as the dewatering and recrystallization of clays, membrane filtration, destruction of detrital feldspars, and dissolution of other detrital minerals such as iron oxides. However, the involvement of evaporites in the process appears to be essential in producing the high salinities necessary for enhanced metal solubilities. The elevated salinities of Gulf Coast formation waters are interpreted to be derived either from residual bittern brines remaining from the deposition of the mid-Jurassic Louann Salt (Carpenter et al., 1974) or from the dissolution of evaporites (e.g., Land and Prezbindowski, 1981). Isotopic evidence of Kharaka et al. (1987) indicates that Mississippi oil field brines are primarily a mixture of mid-Jurassic bittern brines and meteoric water. This indicates that inter-formational brine movement has been significant sometime since the Jurassic. Light et al. (1987) suggest that salt dome flanks provide a good vertical brine migration path, and supra-domal faults might provide further vertical migration capability.

The timing of the onset of metal release by diagenetic reactions, and the length of time over which the processes have operated, are poorly understood. For example, Nunn and Sassen (1986) estimate that the lowermost Cretaceous formations in the Mississippi Interior Salt basin reached a temperature of 100°C approximately 100 million years ago, which probably represents a minimum age for the onset of diagenetic processes capable of releasing metals to formation waters. Indirect evidence suggests that the release of metals by diagenetic processes appears to be ongoing at the present. For example, barite-rich scale precipitated from brines in producing oil wells

in central Mississippi locally is very radioactive, primarily due to the presence of ^{228}Ra in the barite (E.S. Fuente, Mississippi State Department of Health, pers. commun., 1989). This isotope has a half life of approximately 1600 years, indicating it was contributed to the brine in the relatively recent past.

Kharaka et al. (1987) showed that there is an inverse relationship between lead and zinc and the amount of reduced sulfur in solution due to the low solubility of the respective sulfide minerals. In general, the reduced sulfur content is greatest in the deeper formations (i.e. Smackover) and very low in the Lower Cretaceous siliciclastic units (Kharaka et al., 1987). In the Lower Cretaceous formations, high metal contents are possible because of the high brine salinities, which generally increases with depth and temperature (Carpenter et al., 1974; Kharaka et al., 1987). Figure 2 is a plot of TDS versus Zn and Fe content for brines from the Lower Cretaceous formations sampled as part of this study. There appears to be a rough correlation between Zn and Fe and TDS, indicating that salinity may be an important control on metal solubility in brines with low reduced sulfur content. In addition, local sources of iron and zinc in the host formations may explain much of the variability of the data.

Variations in host formation mineralogy or varying redox conditions may be as important as salinity for increasing the concentration of other metals such as silver and copper. For example, published descriptions of Lower Cretaceous formations from central Mississippi indicate the red sand horizons are locally present in the units that are typically composed of alternating sands and shales (Moore, 1963). Red beds are generally considered the source of copper in sediment-hosted stratiform copper deposits, which also typically

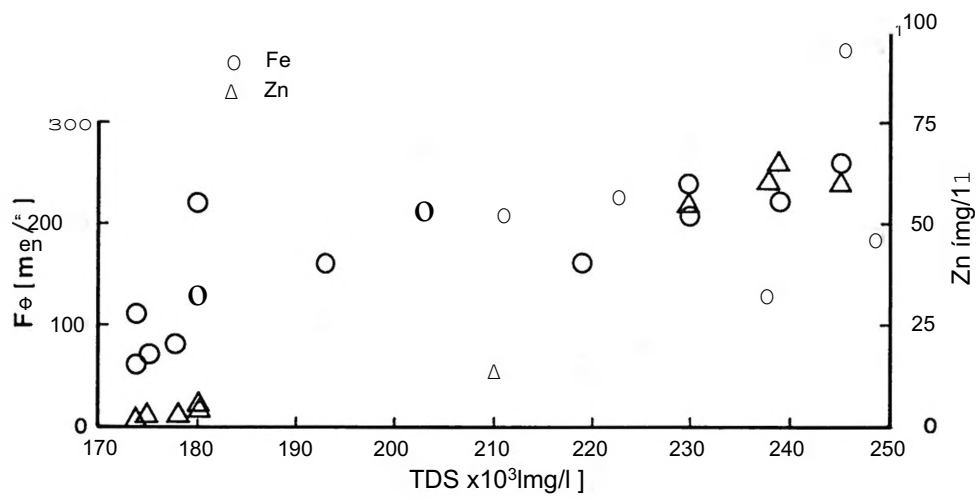


Figure 2. Plot of Fe and Zn content versus TDS in brine samples collected as part of this study from Cretaceous units.

contain significant levels of silver and cobalt (Gustafson and Williams, 1981). In addition, Zielinski et al. (1983) found that Cu and Co were two of the metals most effectively released using various leach solutions on secondary iron oxy-hydroxides from a geologically young red bed sequence.

Given the history of extensive inter-formational brine movement, the present-day metal content of Mississippi oil field brines probably reflects the composite metal contribution of the present and past host formations along the brine migration route. If so, then the order of encounter of host formations, and their respective mineralogy, should control the availability of the various metals and impact the ultimate metal composition. In addition, the formation mineralogy will also affect the prevailing redox state of the contained brine, locally enhancing the copper content, which is more soluble under more oxidizing conditions (Sverjensky, 1987).

Given the general low levels of the metals with the highest intrinsic values, such as gold, silver, and Platinum Group Elements, the Mississippi oil field brines do not appear to be a potential economic source of these metals. However, the chemical nature of these brines is such that much higher concentrations of these metals appears possible, given a source rock with elevated metal contents. Additional analyses would be required to address which formations have the most potential and what is the extent of regional variations within particular formations.

It is possible that the aggregate values of all of the metals in the brine could make their extraction economically viable if a low-cost extraction process could be developed. Existing technology employed to remove metals from waste water (industrial, municipal, etc.) using electrochemical reduction might be adaptable to brine metal extraction.

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