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Hydrogeochemical Indices for the Prospecting of Hydrocarbon and Native Sulphur Deposits

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ABSTRACT

Two hydrogeochemical indices are presented namely: the balance of sulfate (B.S) and the index of aeration (I.A) and may be used as geochemical tools to give important information that indicate the presence of good prospects of oil and native sulphur deposits. The B.S and I.A are calculated from the hydrochemical data of natural waters (formation waters, oil field brines, sulphurous springs, …etc) that are associated with these deposits. For hydrocarbon deposits the B.S values were negative and ranged from few to several thousands, while I.A values were positive and ranged from zero to 10 for excellent prospects to 100 or to 1000 for less important prospects. For native sulphur deposits, both the B.S and I.A values were positive and ranged from few hundreds to thousands. Many examples of oil field waters and sulphurous springs from Iraq were examined and gave results of high positive significance.

معاملات هيدروجيوكيميائية للتحري عن التوضعات الهيدروكربونية والكبريت الحر

الملخص

يقدم البحث اثنين من المعاملات الهيدروجيوكيميائية وهما: معامل توازن الكبريتات (B.S) ومعامل التهوية (I.A) واللذان يمكن ان يستخدما كأداتين جيوكيميائيتين لاعطاء معلومات مهمة تشير الى وجـود التوضعات الهيدروكربونية والكبريت الحر. ويحسب كل من B.S و I.A من المعلومات الهيدروكيميائيـة للمياه الطبيعية (مياه تكوينية ومياه مرافقة للنفط ومياه كبريتيـة و...الـخ) المرافقـة لهـذه التوضـعات. فللتوضعات الهيدروكربونية كانت قيمة B.S سالبة وتراوحت بين اثني عشر الف الى عشرين الف، بينما كانت قيمة I.A موجبة وتراوحت من صفر الى عشرة للتوضعات المهمة والـى مائـة او حتـى الـف للتوضعات الاقل اهمية. اما لتوضعات الكبريت الحر فإن قيمـة كـل مـن B.S و I.A كانـت موجبـة وتراوحت من بضعة مئات الى بضعة الوف. كما تضمن البحث امثلة عديدة لمياه مرافقـة للـنفط وميـاه عيون كبريتية من العراق والتي عند تطبيق هذه المعاملات عليها اعطت نتائج ايجابية معتبرة جدا.

INTRODUCTION

The hydrochemical composition of subsurface waters are used by the petroleum industry as a criterion for subsurface exploration (oil and natural gas) deposits, and the hydrochemical features of a basin may reflect the hydrodynamics of petroleum accumulation. Similarly, in the geochemical exploration of subsurface ore deposits.

As for oil field waters, several classification systems were proposed such as those of Sulin (1946), Chebotarev (1955), Bojarski`s (1970) modification of Sulin`s system and Dabrowski (1972) where hydrochemical ratios such as Na/Cl, expressed in milligram-equivalents, were used as hydrochemical indicators of hydrocarbons. Oil field brines with Na/Cl equal to 0.75-0.65, 0.65-0.50 and less than 0.5 characterizes favorable conditions for the preservation of hydrocarbon deposits, in particular those of less than 0.5 which are considered one of the most likely areas where hydrocarbons are accumulated (Collins, 1975).

Moreover, according to Buljan (1962 and 1963), every natural water, including contact waters (oil field brines), can be characterized by two important properties, namely:

1.The balance of sulphate (B.S) which equals the loss of sulphate during the diagenesis of water.

2.The index of aeration (I.A) which indicates the degree of aeration of the water.

These two indices have numerical values which can be calculated for every water from the results of a routine chemical analysis.

The aim of this paper is to introduce these two indices, their method of calculation and to examine and test their application on various natural waters in Iraq that are associated with hydrocarbon and native sulphur deposits.

CALCULATION OF (B.S) AND (I.A)

For natural waters Cl^{-1} and SO_4^{-2} are perhaps the most important pair of ions. The chloride ion is the least affected ion by geochemical processes while the sulphate is the most affected.

Regarding sea water for each quantity of 19.010 $gm.Kgm^{-1}$ Cl^{-1} there is a corresponding quantity of 2.649 $gm.Kgm^{-1}$ SO_4^{-2}. In any type of water, the chloride content will therefore permit the calculation of the theoretical content of sulphate, $(SO_4^{-2})_t$ that corresponds the quantity of chloride (+bromide) in that water (Buljan, 1963).

For sea water (S.W): $$\frac{SO_4}{Cl} = \frac{2.649}{19.010} = 0.1394$$

For natural waters: $$\frac{(SO_4)_{S.W}}{(Cl)_{S.W}} = \frac{(SO_4)_t}{(Cl)_{water}}$$

Therefore, the theoretical sulphate content for natural waters equals to:

$$(SO_4)_t = 0.1394x(Cl)_{water}$$

And:

$$B.S = (SO_4)_{water} - (SO_4)_t$$

$$I.A = \frac{(SO_4)_{water}}{(SO_4)_t} x100$$

From these two equations it is evident that for sea water: B.S=zero and I.A=100.

HYDROCHEMICAL DATA

To fulfill the aim of this paper, hydochemical data were selected from the geochemical literature, which included (Fig.1):

1.Oil field waters from oil fields in Iraq, very well known for their superior reserves and production of oil, namely Zubair reservoir (Cretaceous) of Zubair (Zb), South Rumaila (Ru) and North Rumaila (R) oil fields (Table 1).

2.Natural sulphurous springs at Mishraq sulphur mine, North Iraq, well known for its high reserve and production of native sulphur (Table 2).

3.Oil field waters from not yet developed oil fields in Iraq of different reservoirs, namely: Luhais (LU), Suba (SU), West Qurna (WQ), Nasiriyah (NS), Hemrin (HM) and Jabal Qand (JQ) (Table 3).

4.Sulphurous springs at Qiyara, Fat`ha, Hit, Kubisa and Mosul (Ain Kibrit and Hammam Al-Alil) (Table 4).

Fig. 1: location map of examined oil fields and natural springs.

Table 1: Hydrochemical data of Zubair reservoir (Cretaceous), S. Rumaila and N. Rumaila oil fields (Ref.: Jamil, 1975, 1978).

Field, Well No.	**Salinity gm.L^{-1}**	**Cl^{-1} ppm**	**SO_4^{-2} ppm**	**$(SO_4^{-2})_t$ ppm**	**B.S**	**I.A**
Zb-11	191.80	116939	547	16301	-15754	3.35
Zb-14	192.56	115200	303	16058	-15755	1.88
Zb-15	177.30	105800	405	14748	-14343	2.82
Zb-17	169.80	97628	463	13609	-13146	3.40
Zb-18	196.40	118000	196	16449	-16253	1.20
Zb-23	196.00	120220	320	16758	-16438	1.90
RU-7	----	128868	216	17964	-17748	1.20
RU-8	218.00	133465	268	18605	-18337	1.44
RU-9	209.00	125000	458	17425	-16697	2.26
RU-13	230.00	128912	322	17970	-17648	1.79
RU-29	210.00	130028	335	18125	-17790	1.84
RU-36	274.30	15789	350	21967	-21617	1.59
R-29	226.00	110370	390	15385	-14995	2.5
RU-34	209.91	125850	280	17543	-17263	1.6
R-63	216.21	122710	480	17105	-16625	2.8
R-85	209.36	127419	250	17705	-17476	1.4
R-95	181.72	109697	250	15291	-15041	1.6
R-127	202.75	124500	370	17355	-16985	2.1

Table 2: Hydrochemical data of Mishraq natural springs (Ref.: Miscony, 1988).

Field, Well No.	**Salinity gm.L^{-1}**	**Cl^{-1} ppm**	**SO_4^{-2} ppm**	**$(SO_4^{-2})_t$ ppm**	**B.S**	**I.A**
1	1.99	266	960	133.8	826	717
2	2.82	177	1609	224	1385	718
3	2.73	354	1489	207.4	1282	717
4	5.22	709	2498	348	2150	717
5	2.86	354	1465	204	1261	718
6	1.38	177	756	106	650	713
7	1.31	354	480	67	413	716
8	2.51	266	865	121	744	714
9	3.00	177	1777	248	1529	716

For every water analysis, $(SO_4)_t$ was calculated from its Cl^{-1} value in parts per million (ppm) and then its B.S and I.A as shown in Tables (1 to 4). Plots of log (SO_4) versus log (Cl) and B.S versus log (I.A) of the data are shown in figures (2 to 4).

Table 3: Hydrochemical data of selected reservoirs fromm different oil fields (Ref.: Oil Exploration Company-Private Communication).

Field, Well No.	Salinity gm.L^{-1}	Cl^{-1} ppm	SO_4^{-2} ppm	$(SO_4^{-2})_t$ ppm	B.S	I.A
Mishrif Formation						
Zb-55	216.6	143234	120	19984	-19864	0.6
Zb-36	210.7	123700	340	17243	-16903	1.97
NS-1	203.9	95158	2585	13265	-10680	19.48
NS-2	190.8	116814	868	16283	-15415	5.34
HR-12	160.3	100615	510	14025	-13515	3.63
Yamama Formation						
SU-7	174.4	104128	3021	14515	-11494	20.81
Zb-49	206.0	127556	401	17781	-17380	2.25
LU-2	190.1	116480	370	16237	-15867	2.27
NS-3	209.3	127125	1079	17712	-16642	6.07
NS-4	84.0	483397	1598	6746	-5148	23.68
Nahar Umar Formation						
SU-1	180.7	108190	350	15081	-14731	2.32
SU-9	202.0	121252	237	16902	-16665	1.40
Zb-1	206.5	108940	436	15186	-14750	2.97
Sargwlu Formation (M. Jurassic)						
JQ-1	103.7	57841	2360	8063	-5703	29.27
Qurra China (U. Triassic)						
JQ-1	270.9	138480	7059	19304	-12245	36.56
	189.0	109658	1930	15265	-13335	12.68
Gerli Khana Formation (M. Triassic)						
JQ-1	49.7	27614	1071	3849	-2778	27.08
Euphrates Formation						
HR-9	15.0	7458	700	1039	-339	67.0
HR-13	33.4	17404	734	2426	-1692	30.2
HR-8	98.9	56725	3404	7907	-4503	43.0

Shuaiba Formation						
HR-12	164.9	100052	576	13947	-13371	4.13

Table 4: Hydrochemical data of selected natural sulphuroys springs (Ref.: Jamil et al., 1984, Jamil and Al-Aani, 1986).

Spring	**Salinity gm.L^{-1}**	**Cl^{-1} ppm**	**SO$_4^{-2}$ ppm**	**(SO$_4^{-2}$)$_t$ ppm**	**B.S**	**I.A**
Ain Kibrit	5499	855	1708	119	+1589	1435
Hammam Al-Alil	872	141	214	20	+194	1070
Qiyara-1	16.45	236	4620	33	+4587	1400
Qiyara-2	6.48	1164	4718	162	+4556	2912
Qiyara-3	7.56	437	6494	61	+6433	10645
Qiyara-4	12.37	937	5445	131	+5314	4156
Qiyara-5	11.51	480	2346	67	+2279	3501
Fat`ha-1	23.42	1162	4973	162	+4811	3069
Fat`ha-2	29.87	1241	9351	173	+9178	5405
Fat`ha-3	35.69	306	5977	43	+5934	13900
Fat`ha-4	29.78	283	7263	39	+7224	18623
Fat`ha-5	36.32	206	2101	29	+2072	7244
Fat`ha-6	39.93	356	7179	50	+7129	14358
Fat`ha-7	40.70	6324	6014	881	+5133	682
Fat`ha-8	23.60	7397	5900	1031	+4869	572
Fat`ha-9	29.37	1828	7840	255	+7585	309
Fat`ha-10	21.54	5510	5612	768	+4844	730
Hit-1	31.07	16100	403	2244	-1841	17.9
Hit-2	18.20	7350	681	1052	-344	66.4
Hit-3	12.33	5950	186	829	-643	22.4

Hit-4	11.64	5600	199	781	-583	25.4
Hit-5	5.64	2400	438	335	+103	130.7
Hit-6	5.85	2240	421	312	+109	134.9
Hit-7	5.36	2170	403	303	+100	133.0
Kubaisa-8	2.62	1155	202	161	+41	125.5
Kubaisa-9	3.17	1372	127	191	-64	66.5
Kubaisa-10	3.66	1505	126	210	-84	60
Kubaisa-11	3.05	1487	90	207	-117	43.5
Kubaisa-12	2.97	1365	125	190	-66	65.8
Kubaisa-13	3.20	1477	196	206	-10	95

Fig. 2: Plots of log Cl^{-1} vs log SO_4^{-2} in ppm for natural waters associated with hydrocarbon and native sulphur deposits in Iraq.

Fig. 3: Plots of BS vs log (IA) for some natural waters associated with hydrocarbon and native sulphur deposits in Iraq.

Fig. 4: Plots of log Cl^{-1} vs SO_4^{-2} in ppm for some reservoirs and oil fields in Iraq.

RESULTS, PRESENTATION AND DISCUSSION

For the examined oil field waters, the B.S values were highly negative and ranged from over –13000 (Zb-17) to more than –21000 (RU-36), while their I.A values were positive and low, less than 10 or even less than 5. Such criteria are excellent indicative for the presence of hydrocarbons. The position of the data on the log Cl versus log SO_4 (Fig.2) fall for below and far away to the right from sea water and its line, while they fall to the left below sea water on the log I.A versus B.S plot (Fig.3).

For the natural sulphurous springs of Mishraq sulphur deposits, their B.S values were positive in the low range 413 to 1529 and their I.A values were positive and ranged between 713-718 which meant that these sulphurous waters are of good aeration. In fact, they represent waters associated with gypsum or gypsum waters (Fig.2). Similarly, for Ain Kibrit (Mosul) and Mammam Al-Alil.

Applying the above criteria to other oil fields or reservoirs, particularly those that have not yet developed (Table 3 and Fig.4), it was evident that they were divided into two groups:

Group 1: Those with I.A values less than 10 and high negative B.S values, more than –13000. They represented reservoirs of high potential of oil and their data on the same position of the known giant oil fields.

Group 2: Those with I.A values between 12-67 and B.S values less than =12000, represented reservoirs of less oil potential and their data fall parallel to the sea water line.

For Hit and Kubisa natural sulphurous springs, the B.S values were low and ranged between –1841 to +109 and I.A values roughed between 17.9 to 134.9 indicating waters associated with oil fields of very poor potential (Table 4, Figs.2 and 3).

For Qiyara and Fat`ha natural springs, their B.S values were positively high and ranged between 2072 to more than 9000 and their I.A values were also very high, mostly more than 1000 (Table 4, Fig.2). Such criteria indicate that these sulphurous waters are associated with poor deposits of native sulphur except probably the last four springs at Fat`ha with I.A values less than 1000, but their high B.S values make them less promising. It is of interest to note that Qiyara natural springs were thought for a long time associated with an oil field, which is evident now is not true.

CONCLUSIONS

Oil field water associated with superior potential oil fields gave high negative values for the balance of sulphate (B.S) and very low values for the index of aeration (I.A), usually less than 10.

Natural waters associated with native sulphur deposits are usually gypsum waters, have high positive B,S values and high I.A values.

The B.S and I.A may be considered very useful geochemical indicators for future explorations of hydrocarbon and native sulphur deposits.

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