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A Chemical Characterization of Geothermal Waters from West Field of Romania. II. Geothermal Waters from Felix Spa.

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ABSTRACT

Chemical characterization of geothermal waters of Cretaceous System from region Felix Spa is presented here. Both the constituent like (Cl^-, NO_2^-, NO_3^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, Ca^{2+}, Mg^{2+}, Na^+, K^+ etc) and microelements were found in these waters using various methods. On the basis of these facts those can be classified in category of bicarbonate – sulfate – calcium – magnezic waters. The work is a comparative study with waters from Oradea region to prove their common origin.

INTRODUCTION

The study involves the geothermal waters from an aquifer localized in a fissured system with karstic parts [1], formed in cretaceous age. The surface is presented in fig. 1

These waters were studied time ago because of both balneologique and therapeutic proprieties. As Tenu describe, the hydro geologic feature of the collector, must be regarded from structural and karsto genetic point of view, which confers a lot of benefit

The reservoir is placed in a tectonic compartment on the largest branch of the "Padurea Craiului" mountains. Tectonic fractures and fissures are the ascending pathways for the deep warm waters and form's lot of cavities and caves in the superior floor, being the ideal structure for stoking and preserving the energetic potential of the reservoir.

The origin of the geothermal waters is at a depth between 60 and 120 meters, and the temperature at the surface opening is between 29 and 47 Celsius degrees. The flow capacity is high 120 l/sec.

The chemical and physical characterization of the waters from reservoir was made by investigation of the following natural springs: "Ochiu Mare"(OM), "Ochiu Pompei"(OP), "Ochiu Tiganului" (OT), "Frederic" (F) which are supplying a lake in a natural park with a unique species of plant "Nimphaea Lotus var Thermalis", and drillings: "Izbuc" (I), Rontau (F2), Cordau (402) and Felix (4003, 4011, 4012) Balint (B), Vila (V4).

METHODS OF WORK

To establish the content of the major elements of the geothermal waters studied it has been determined the following: the pH (with pH-meter MV-85), the conductivity (with Radelkis conductometer), the total residue (to be obtained during evaporation of 100 cm^3 water at 105°), oxidable organic compounds (permanganate method), the harness of water (complexometric titration with EDTA) [2], the soluble silicate (colorimetric determination as silicomolibdenic acid) [3], the phenols (colorimetric determination with diazotization sufanilic acid) [2], the nitric ion ((colorimetric determination with phenyl disulfonic acid in ammonium hydroxide medium) [3], the nitrite ion (colorimetric determination as azo compound of β-naphtol), the carbonate and bicarbonate ions (acid titration) [2], the sulfate ion (gravimetric determination as barium sulfate), the phosphate ion (colorimetric determination as ammonium phosphowolframate) [β], the ammonium ion (colorimetric determination with Nessler reaction), the natrium and the kalium ions (with phlamphotometer Phlapho-4), the calcium and magnesium ions (complexometric titration) and iron ion (colorimetric determination with o-phenantrolyne). [4]

The microelements were determination from the residue by evaporate through gamma spectroscopy and emission spectroscopy.

The probes were harvesting at head of the well and transported in the laboratory. The analyses had been done during 8 years every 3 months. The results represent an average of the obtained values.

RESULTS AND DISSCUTIONS

The experimental results are presented in table no. 1 - 3

For the clasification of these waters table no. 4 presents the compozition in meq percentage of the major chemical ions.

Figure no. 2 and 3 represents the triangle and Schoeller – Bercaloff diagram from Felix reservoir (cretaceous colector)

Basicly we can see that the geothermal waters from this cretacic reservoir are bicarbo-sulphatic-calcic-magnezic, with allmost the same compozition as the the waters from triasic reservoir (Oradea 4), but the balance between sulphate and bicarbonate is reversed.

Studying each source we saw that:

- the waters from (I),(F),(OM),(OP),(402) and (4003) are high bicarbonate, low sulphate, high calcic and low magnezic with formula $C^hS^lCa^hMg^l$.
- the waters from (4011),(B) and (V4) are moderate bicarbonate and sulphate, high calcic and low magnezic with formula $C^mS^mCa^hMg^l$
- waters from (4012) are very high carbonate, high sulphate and low magnezic with formula $C^{vh}Ca^hMg^l$
- waters from (4087) are very high carbonate, low sulphate, high calcic and low magnezic with formula $C^{vh}S^lCa^hMg^l$.

Regarding positive ions we saw that waters from all sources are Ca^hMg^l

Regarding negative ions there are some differences (4011), (B), (V4), (F2) and (OT) are C^hS^m or C^mS^m, (I), (402), (4003), (4087), (F), (OM), (OP) are C^hS^l, and (4012) is C^{vh}.

Comparing the chemical caracteristics of the waters from the cretacic reservoir four groups can be discribe.

First group from (4011), (B), (V4), (F2) and (OT) have the ratio of echivalent-grams $\frac{[HCO_3^-]}{[SO_4^{-2}]}$ is between 1 and 1,3. These waters have the highest temperature and probable their origin is in depth of the reservoir.

The second group from (I) and (4003) have the ratio between equivalents-gram $\frac{[HCO_3^-]}{[SO_4^{-2}]}$ between 1,5 şi 2,0. These waters are probably more far away from the main source and suplyed with phreatic waters. This waters are colder.

The third group is formed by the rest of the reservoir suplying the (4087) and (402) drillings with the ratio between the echivalenții $\frac{[HCO_3^-]}{[SO_4^{-2}]}$ is between 2,8 și 3.

The fourth group is the water from (4012) drilling with the ratio $\frac{[HCO_3^-]}{[SO_4^{-2}]}$ more than 5 is much diferent from the general characteristics of the cretacic colector.

Elements in traces were determined by emision spectroscopy and are presented in table no. 5

Time to time we could trace also nitrate and phosphate ions.

Using gamma emision spectroscopy were identified traces of many microelements as hafniu, scandiu, bariu, crom, tantal, promețiu, stronțiu, cesiu, silver, platină, gold, europiu și neptuniu.?

The gases discovered in these geothermal waters were insignificant, carbon dioxide is present in very low concentration in the waters from (4012), (4011), (4003) and (OM).

We chose Izbuc (I) and Balint (B) drilings made in 1886 and 1887, too follow the changes in time of the phisical and chemical caracteristics. The results are presented in table no. 6 and 7.

This data is presented in figures 4 and 5

Following the chemical changes in time of the geothermal waters from Izbuc and Balint drillings in a long period, we desoovered several interesting things

In the Izbuc driling waters there was a decreasing of the calcium and sulphate ions concentration and in minerals that shows a low contribution of the deep waters.

In the Balint driling waters the changes are even more interesting. In the beginning of the XX century, the waters were sulphatic-bicarbonate (analises made in 1887, 1926 and 1951), in the seventh decade the ratio between the ions is 1 (analise made in 1960, 1966 și 1969), and after few years the waters became bicarbonato-sulphatic.

The reversig between sulphate and bicarbonate can be explaned because an intensly drenaje of the waters causing a smole contribution of deep suphate containing waters.

REFERENCES

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2. A Tenu, Studii de Hidrologie, Ac. XII.2. p.59. 1975.
3. L. Gilau, C. T. Hozan, A. M. Maghiar, T. T. Maghiar and O. Straciuc Twenty-Third Workshop Geothermal Reservoir Engineering, Jan. 26-28, 1998, Stanford.
4. C. Liteanu "Chimie Analitica Cantitativa" Ed. Did. Ped. Bucuresti 1985
5. J. Rodier "L'analyse de L'eau" Ed. Dumond, Paris 1975.

Table no. 1

The chemical characterization of geothermal waters from Felix Spa

Sources	pH	Conduct.	Total residue	Minera-lisations	Harness	Oxyd. organic comp.	SiO2
		(μS/cm)	(mg/l)	(mg/l)	(oG)	(mg/l KmnO4)	(mg/l)
Izbuc	6,88	950	492	708,66	21,50	0,64	21,00
Frederic	7,05	799	620	799,62	25,84	2,05	25,84
O.M.	6,30	630	609	793,20	25,40	7,43	18,00
O.P.	6,30		490	763,20	23,80	5,26	23,30
O.Ţ.	7,05	840	519	881,89	17,63	0,92	16,50
F-2	6,85	1060	605	769,35	25,25	0,35	25,00
402	6,80	1090	606	817,04	23,50	0,32	23,50
4003	6,80	1050	640	811,70	26,30	0,32	24,10
4011	6,60	1200	621	881,90	32,39	0,42	28,50
4012	7,21	700	381	548,26	19,60	4,68	16,00
4087	7,00	1050	476	702,50	23,32	0,48	21,10
Balint	6,80	1290	715	924,88	33,06	0,32	31,00
Vila-4	6,80	1310	766	937,67	33,06	0,64	33,33

Table no. 2.

The distribution in anion of geothermal waters from Felix Spa

Sources	$[Cl^-]$		$[HCO_3^-]$		$[SO_4^{-2}]$		Total
	(mg/l)	(meq/l)	(mg/l)	(meq/l)	(mg/l)	(meq/l)	(meq/l)
Izbuc	14,18	0,399	332,58	5,452	146,06	3,043	8,894
Frederic	20,63	0,582	393,11	6,444	165,12	3,440	10,466
O.M.	14,20	0,400	439,30	7,197	88,30	1,839	9,436
O.P.	21,30	0,601	457,60	7,501	51,80	1,126	9,240
O.Ţ.	7,09	0,200	324,21	5,315	301,62	5,315	11,809
F-2	14,18	0,399	340,50	5,582	290,52	3,969	9,950
402	17,37	0,489	444,15	7,281	120,15	2,503	10,273
4003	17,73	0,500	436,33	7,153	133,04	2,772	10,425
4011	14,18	0,340	355,31	5,825	245,19	5,066	11,231
4012	6,73	0,185	343,84	5,637	53,06	1,105	6,952
4087	14,18	0,340	379,00	6,213	112,75	2,349	8,902
Balint	17,37	0,490	384,92	6,310	245,25	5,109	11,909
Vila 4	17,73	0,500	384,94	6,310	259,69	5,409	12,213

Table no. 3

The distribution in cations of geothermal waters from Felix Spa

Sources		$[NH_4^+]$	$[Na^+]$	$[K^+]$	$[Ca^{+2}]$	$[Mg^{+2}]$	$[Fe^{+2}]$	Total
Izbuc	(mg/l)	2,56	20,00	5,00	157,15	9,12	0,46	
	(meq/l)	0,142	0,870	0,128	7,842	0,751	0,017	9,730
Frederic	(mg/l)	4,03	31,00	6,10	125,58	28,05	0,16	
	(meq/l)	0,224	1,348	0,156	6,266	2,307	0,006	10,307
O.M.	(mg/l)	few	3,70	5,40	137,80	26,70	0,10	
	(meq/l)	-	0,161	0,138	6,876	2,196	0,003	9,374
O.P.	(mg/l)	few	1,70	3,80	120,20	36,00	0,10	
	(meq/l)	-	0,074	0,097	5,998	2,960	0,003	9,200
O.Ţ.	(mg/l)	0,66	40,00	5,00	136,91	24,80	0,03	
	(meq/l)	0,048	1,739	0,129	7,830	2,041	0,001	11,777
F-2	(mg/l)	1,74	19,00	8,00	153,08	16,79	0,55	
	(meq/l)	0,094	0,826	0,203	7,639	1,381	0,020	10,108
402	(mg/l)	1,44	18,00	6,00	171,64	14,04	1,155	
	(meq/l)	0,080	0,783	0,153	8,565	1,155	0,027	10,763
4003	(mg/l)	1,50	18,00	7,00	150,70	22,70	1,20	
	(meq/l)	0,083	0,783	0,179	7,520	1,867	0,043	10,475
4011	(mg/l)	1,51	19,50	6,00	185,57	28,09	0,05	
	(meq/l)	0,084	0,848	0,153	9,260	2,310	0,002	12,657
4012	(mg/l)	1,42	10,50	2,50	71,84	41,53	0,07	
	(meq/l)	0,079	0,456	0,064	3,585	3,418	0,002	7,604
4087	(mg/l)	1,28	14,00	4,00	139,18	16,84	0,17	
	(meq/l)	0,071	0,609	0,102	6,945	1,385	0,006	9,118
Balint	(mg/l)	1,27	22,00	8,20	180,92	33,83	0,12	
	(meq/l)	0,070	0,956	0,210	9,028	2,782	0,004	12,050
Vila 4	(mg/l)	1,36	20,00	7,00	185,57	31,01	0,05	
	(meq/l)	0,077	0,859	0,179	9,260	2,550	0,020	12,937

Table no. 4

The percent distribution in major ions of geothermal waters

Sources	$[Cl^-]$	$[HCO_3^-]$	$[SO_4^{-2}]$	$[Na^+ + K^+]$	$[Ca^{+2}]$	$[Mg^{+2}]$
Izbuc	1,99	33,21	14,80	2,68	30,08	16,85
Frederic	2,19	36,33	11,14	- -	33,70	13,31
O. M.	3,39	34,98	11,33	4,86	27,75	21,82
O. P.	2,09	36,28	11,56	2,73	31,41	13,54
O. Ţ.	0,85	22,50	22,50	7,92	33,24	8,66
F-2	2,11	30,90	16,99	-	32,68	16,43
402	1,81	37,56	10,38	3,19	33,94	12,64
4003	2,07	28,98	18,95	3,56	36,51	9,55
4011	2,07	25,33	23,13	4,42	32,08	13,23
4012	2,73	42,63	5,62	-	28,86	21,71
4087	1,95	38,96	9,09	2,53	33,76	13,41
Balint	2,06	26,49	21,45	4,84	37,46	11,54
Vila –4	1,98	27,02	21,00	4,37	35,16	10,03

Table no. 5.

The microelements composition of the geothermal waters from cretacic reservoir mesured by emision spectroscopy

Sources	$[V]10^4(mg/l)$	$[Co]10^4(mg/l)$	$[Ni]10^3(mg/l)$
Balint	9	5	-
4003	25	5	23
402	4	-	1,2
Izbuc	16	-	1,6
4012	1,1	-	-
4087	4	-	-
4011	13	-	-
F-2	13	-	2,7

Table no. 6.

Concentration of major elements. IZBUC drilling. [19, 20, 60 – 69, 155]

Data	$[Cl^-]$ (meq/l)	$[HCO_3^-]$ (meq/l)	$[SO_4^{-2}]$ (meq/l)	$([Na^+]+[K^+])$ (meq/l)	$([Ca^{+2}]+[Mg^{+2}])$ (meq/l)
1886	0,68	1,57	0,94	2,37	10,97
1922	0,26	5,81	5,16	0,96	10,25
1951	0,29	5,63	5,25	0,90	9,95
1960	0,45	5,42	4,83	0,69	9,97
1966	0,45	5,61	5,31	0,90	9,43
1969	0,45	5,61	5,31	0,90	9,48
1976	0,29	6,48	3,80	1,06	9,48
1977	0,40	5,54	4,13	0,85	9,18
1978	0,31	5,75	3,64	0,86	8,84
1980	0,34	5,68	3,43	1,09	8,13
1981	0,33	6,10	2,86	1,00	7,88

Tabel no. 7.

Concentration of majbr elements. BALINT driling. [19, 20, 60 – 69, 155]

Data	$[Cl^-]$ (meq/l)	$[HCO_3^-]$ (meq/l)	$[SO_4^{-2}]$ (meq/l)	$([Na^+]+[K^+])$ (meq/l)	$([Ca^{+2}]+[Mg^{+2}])$ (meq/l)
1887	0,34	3,19	5,18	1,15	10,67
1926	0,57	3,11	5,99	1,15	11,43
1951	0,38	6,39	6,36	1,20	11,67
1960	0,60	5,80	6,18	1,35	11,16
1966	0,51	5,74	6,74	1,48	11,46
1976	0,36	7,76	2,77	0,98	9,91
1977	0,49	6,15	5,98	1,52	11,01
1981	0,41	6,13	5,43	1,14	11,46

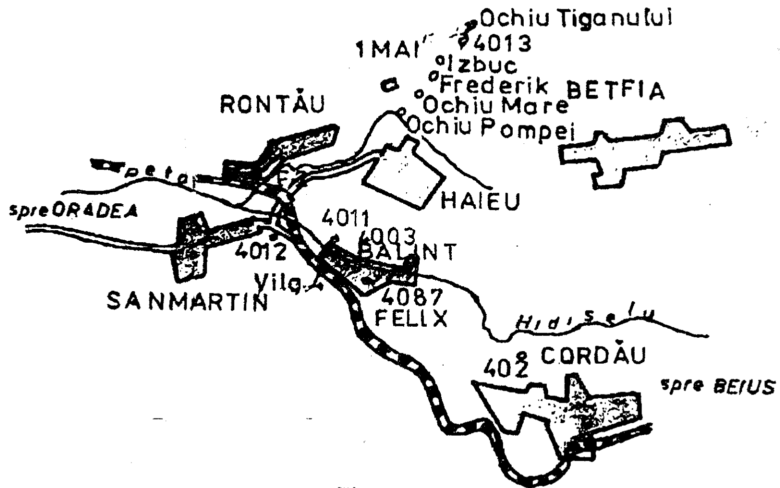

Figure no. 1
Repartition of geothermal water sources map

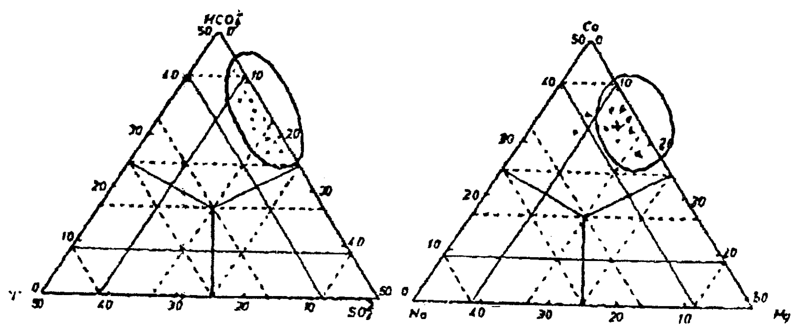

Figure no. 2
Triangle diagram of the chemical composition

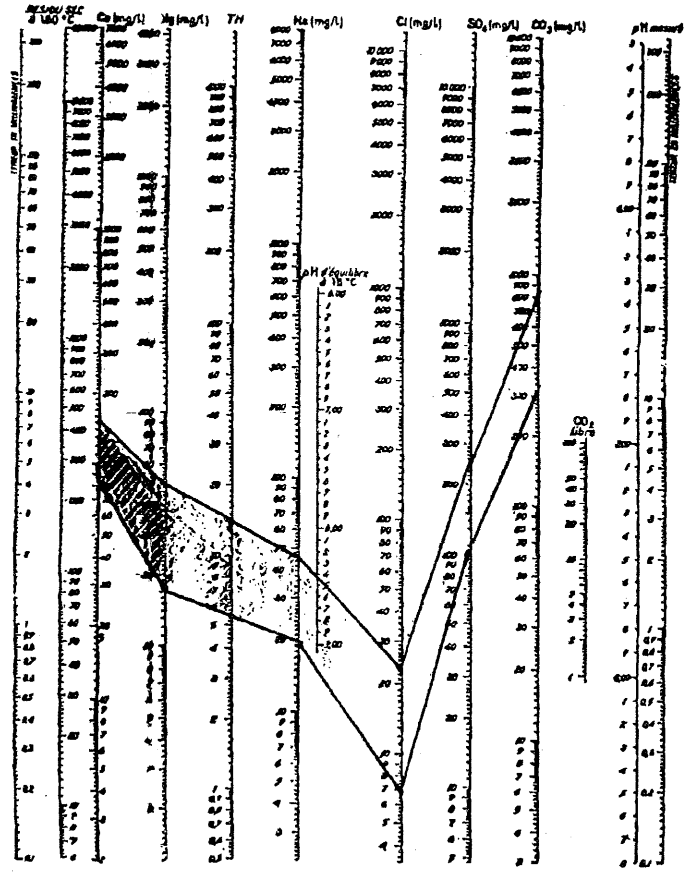

Figure no. 3
Schoeller – Bercaloff diagram from Felix reservoir (cretaceous colector)

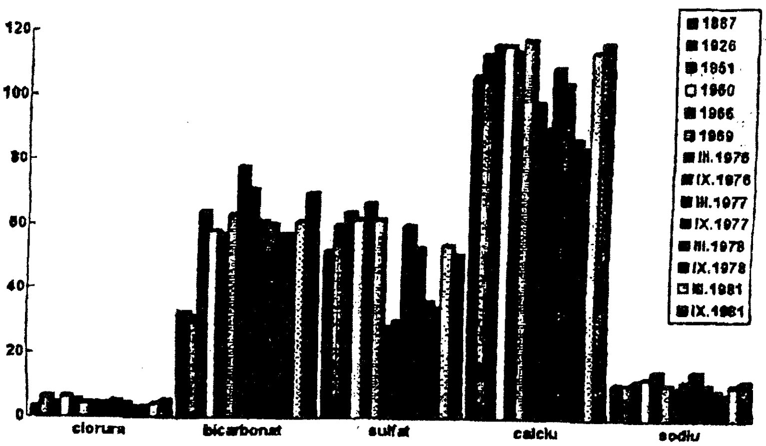

Figure no. 4
Changes in time of the chemical composition – waters from Izbuc drilling

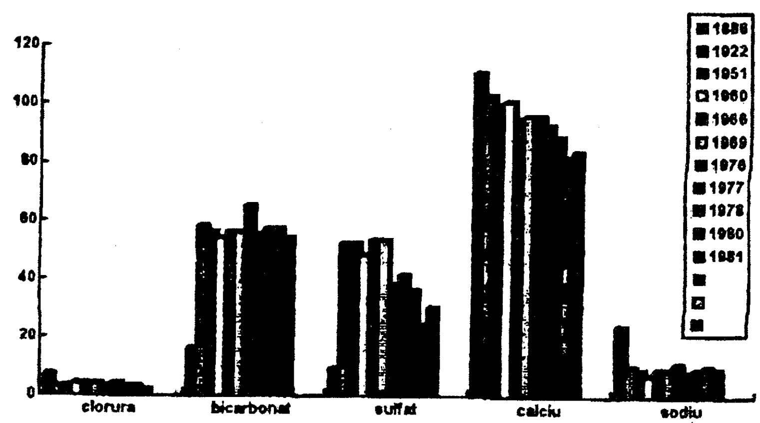

Figure no. 5
Changes in time of the chemical composition – waters from Balint drilling