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CONTRIBUTIONS TO THE STUDY OF THE REPARTITION OF SOME CHEMICAL COMPONENTS FROM THE WATERS IN THE BURDIGALIAN OF THE PETROLIFEROUS GETIC DEPRESSION

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Abstract *To determine the impact of the oil on the waters chemical composition, the authors examined a few chemical elements (SO_4, HCO_3, iodine, and Na/Cl) from the Burdigalian waters of the X and Y structures, which are petroliferous at the X structure and non-petroliferous at the Y structure. Both the correlations between the indicators in the pairings and the spatial distribution of each indicator have been researched. A sufficient association between SO_4 and HCO_3 and lower Na/Cl levels than the other waters are found in the waters in contact with the oil (structure X) according to the study's research (structure Y). However, the levels of iodine and SO_4 are comparable in the two types of water.*
Keywords: *chemical components, iodine, repartition, correlation, water.*

1. INTRODUCTION

Hydrogeological research is an important factor in the complex of projects for the discovery of hydrocarbon accumulations. The water associated with oil and gas reservoirs is a component of the environment in which bituminization processes previously took place, one of the byproducts of the transformation of organic substances, and a significant element of a complex of reservoir conditions, according to the theoretical underpinnings of the hydrogeological study of hydrocarbons.

Even if the waters associated with oil reservoirs are not always primary (in the sense attributed by L. Mrazec), they still have particularities which differentiate them from foreign waters, derived from their contact with hydrocarbon accumulations.

Both theoretical and practical hydrogeological studies are of interest for both chemical indices, which highlight the contemporaneity of water and oil, and chemical indices, which were formed as a result of the interactions between water and hydrocarbons, after the formation of oil and gas reservoirs. The selection and evaluation of their importance are problems that have found satisfactory solutions in the literature [1].

The authors of this paper studied the chemical composition of Burdigalian waters in an area of the Getic Depression located south of Târgu Jiu, according to laboratory analyses, to assess the correlation between some hydrodynamic indices and the presence of oil, as are their variations in the waters accompanying or not accompanying oil accumulations.

The examined region is composed structurally of two Miocene anticlinals, faults that are roughly west-to-east orientated, and discordantly covered by a monoclinal Pliocene cover.

Petroleum is found in structure X and aquifers are found at structure Y in the Burdigalian reservoirs, which have a thickness of over 1000 m. They are represented by sandy sandstones, sands, and occasionally weakly cemented microconglomerates that are divided from one another by marly intercalations in both structure X and structure Y [3]. The terrigenous deposits of the Burdigalian are discordantly covered by a weakly undulating (much thinner) Sarmatian series, oil in both anticlines, and this in turn by a Pliocene monoclinal cover.

Several 70 samples at structure X and 140 samples at structure Y were used to analyze the chemical composition of the water saturating the Burdigalian reservoirs. The analyses were limited to substances other than hydrocarbons (also dissociate to iodine). As a result, there are just a few domains in which we can incorporate the hydrochemical investigation of the Burdigalian of the research region. The authors chose the concentrations of sulfates (SO-4), bicarbonates (HCO-3), iodine, and the Na/Cl ratio from the restricted options provided by the analyses carried out, which were evaluated from the points of view of correlation and surface variation of their values [2].

2. CORRELATIONS BETWEEN HYDROCHEMICAL INDICES

The Na/Cl ratio in Burdigalian waters fluctuates typically between 0.65 and 1 on Structure X and 0.44 and 0.96 on Structure Y, corresponding to hard waters (with Cl_2Mg and CaCl2) that have undergone an extensive metamorphosis. Iodine content ranges from 0 to 18.66 mg/l on structure X and 0 and 37.33 mg/l on structure Y, which is normally low. Advanced dilutions of primary reservoir waters from both buildings are used to determine such modest and very small values. The absence of a correlation between the two indices (figures 1 and 2) shows that the reasons for their fluctuations are distinct.

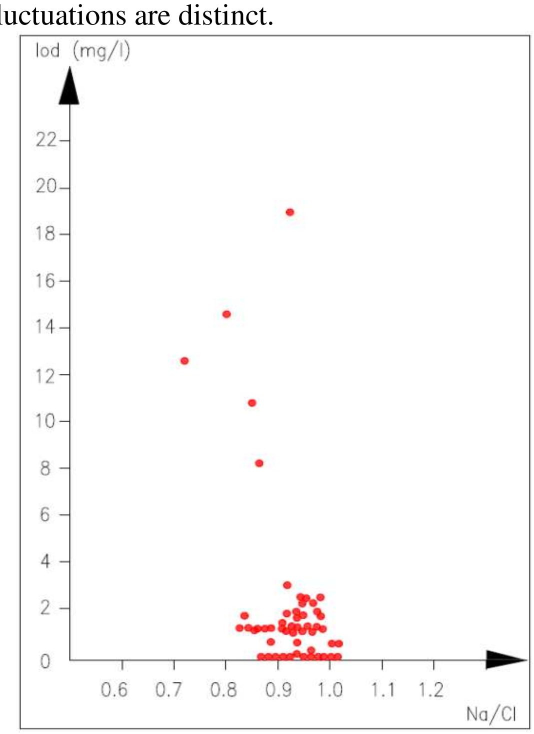

Figure 1 – Correlation between Na/Cl and iodine ratio in Burdigalian waters – structure X

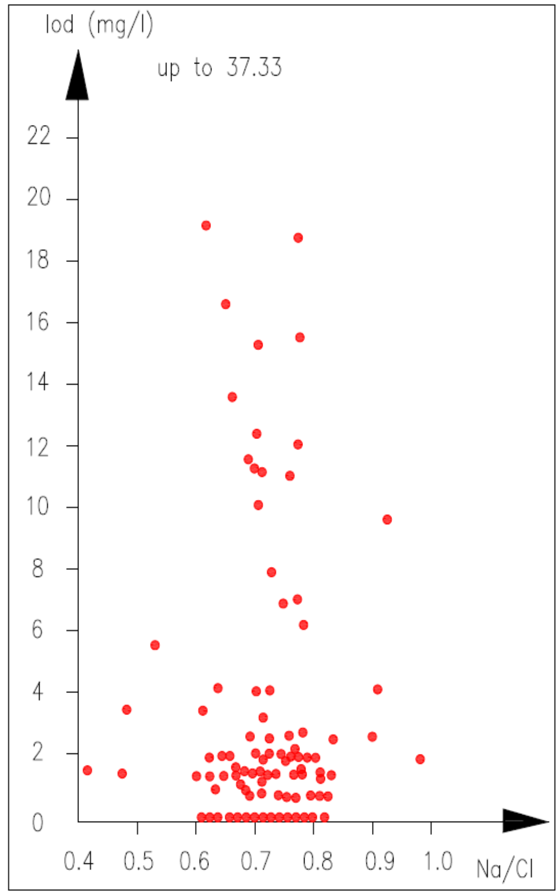

Figure 2 – Correlation between Na/Cl and iodine ratio in Burdigalian waters – structure Y

Burdigalian waters typically have high sulfate concentrations on both structures, which is typical of both related waters and foreign reservoir waters. On structure X, the range of variation of this index is typically between 0 and 450 mg/l, and on structure Y, between 0 and 860 mg/l. These indices are not correlated on structure X, but on structure Y, an inverse variation in their values is seen as a trend [4]. (figures 3 and 4).

However, it is also noted that while the sulfate content is relatively low (below 360 mg/l) at high iodine concentrations (above 10 mg/l), at low iodine contents (below 3 mg/l), highly high sulfate contents of various kinds arise.

This finding shows that, under the open hydrogeological regime, the Burdibalian waters on structures X and Y are secondary and originate from a complex blend of primary reservoir waters and sulfated waters.

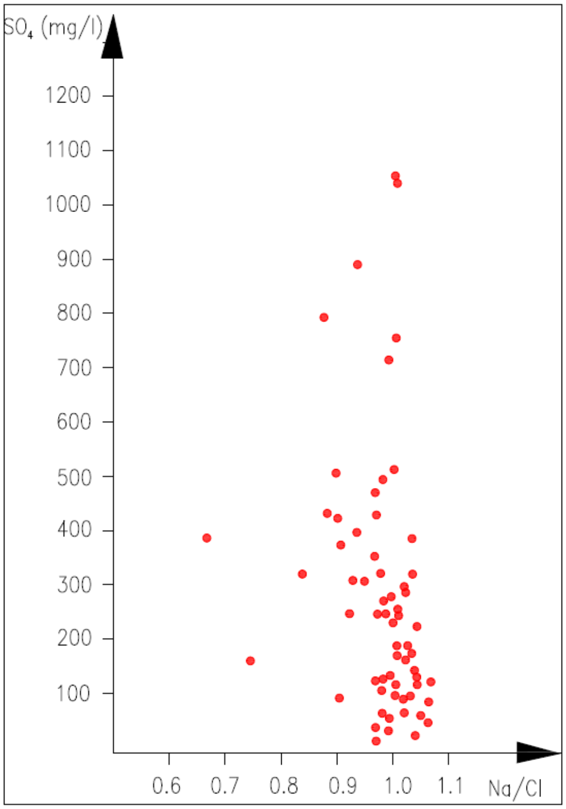

Figure 3 – Correlation of Na/Cl and SO_4 ratio in Burdigalian waters – structure X

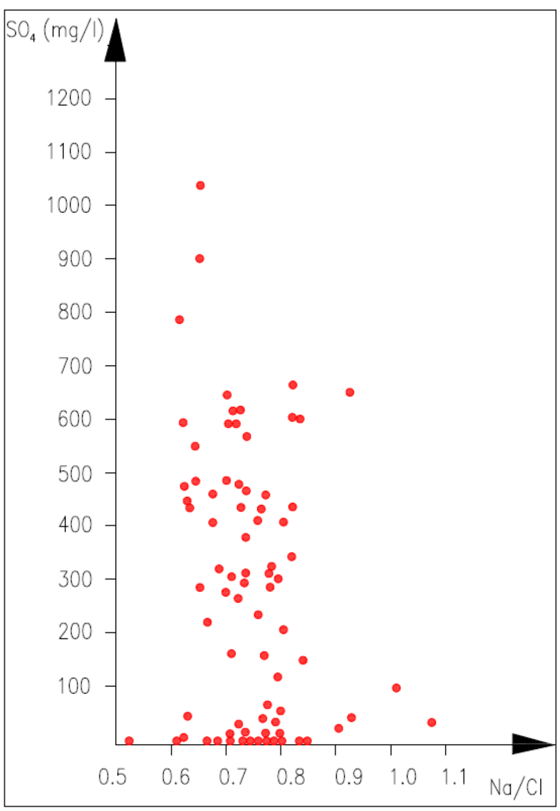

Figure 4 – Correlation of Na/Cl and SO_4 ratio in Burdigalian waters – structure X

Both on structure X and structure Y it is noted (figure 5 and figure 6) the lack of any connection between the content of iodine and sulfates, the components being determined by different causes.

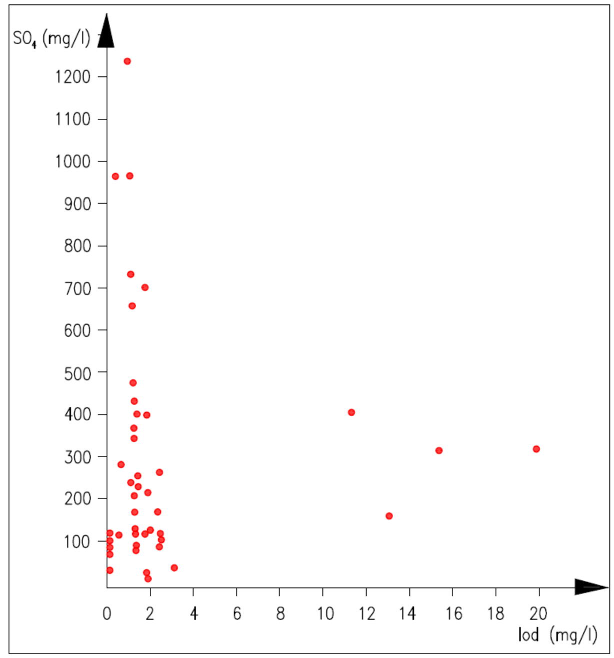

Figure 5 – The correlation between iodine and SO_4 in Burdigalian waters – structure Y

The waters of Burdigalian on structure X contain bicarbonates, expressed by the HCO_3 ion between 30 and 1526.22 mg/l and those on structure Y between 7 and 530 mg/l.

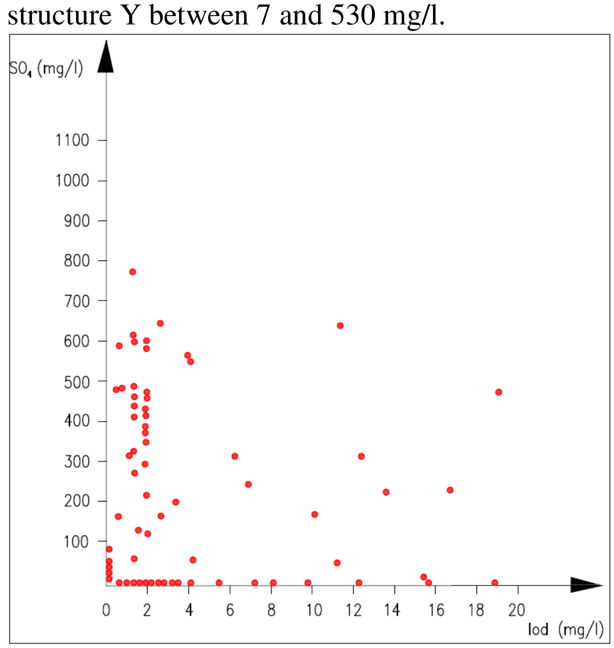

Figure 6 – The correlation between iodine and SO_4 in Burdigalian waters – structure X

The connections between the sulfates content and the bicarbonates is weak and inverse (figure 7 and 8), expressing the dependence of the two indices on a common cause, which we consider in the water desulphurization processes.

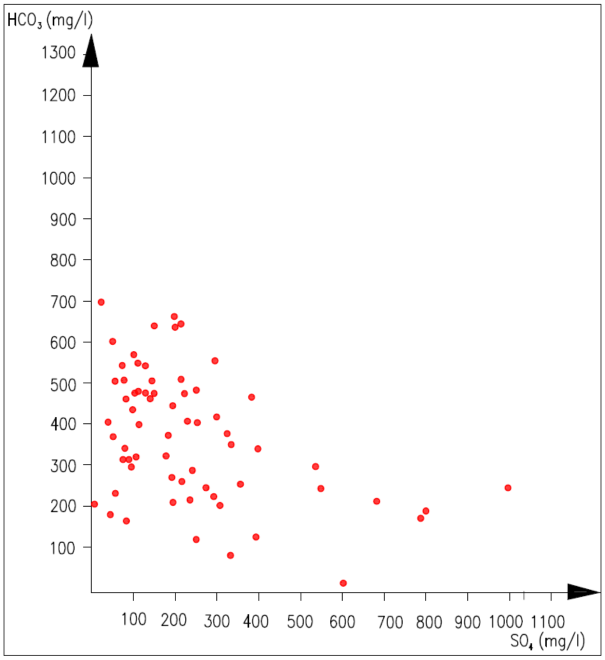

Figure 7 – The correlation between SO_4 and HCO_3 in Burdigalian waters – structure X

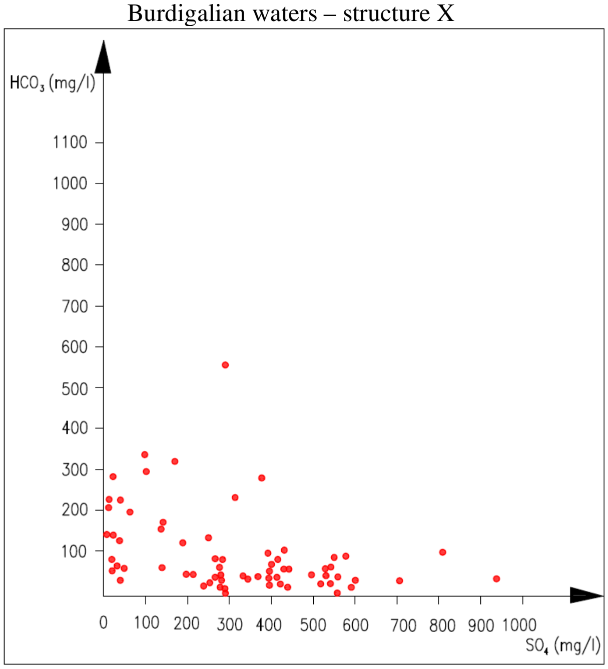

Figure 8 – The correlation between SO_4 and HCO_3 in Burdigalian waters – structure Y

3. SURFACE DISTRIBUTION OF HYDROCHEMICAL INDICES VALUES

3.1 Experimental results

The average values per well for the Na/Cl ratio, iodine, SO^-_4, and HCO^-_3 were taken into consideration for the examination of the surface distribution of the values of the hydrodynamic indices. For structure X, the Na/Cl ratio values range between 0 and 1; for structure Y, where the waters are more extensively metamorphosed, the values range between 0 and 0.96 [5].

The X structure distribution of high values suggests an open hydrogeological regime in the anticline's center, which is supported by the anticline's flanks where they gradually diminish (figures 9 and 10).

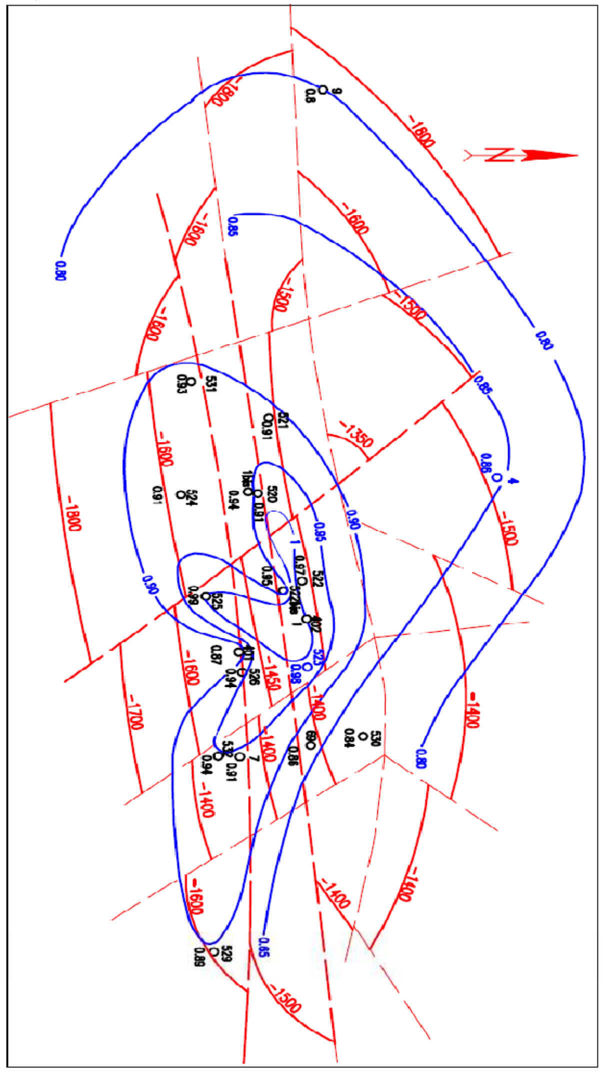

Figure 9 – Simulation of the distribution of the average values of the Na/Cl ratio in Burdigalian waters – structure X

The Burdigalian contain more intensively metamorphosed waters for the Y structure in the center of the anticline compared to the flanks of the structure, which is consistent with the occurrence of oil in the region of highest structural uplift, where the hydrogeological regime is closed. Burdigalian waters on structures X and Y typically have low iodine concentrations, which is unusual for waters near hydrocarbon sources.

The hydrochemical map of structure X shows a general increase in iodine values from SE to NW, where the wells discovered minor oil with a minor anomaly, closed in the eastern pericline zone.

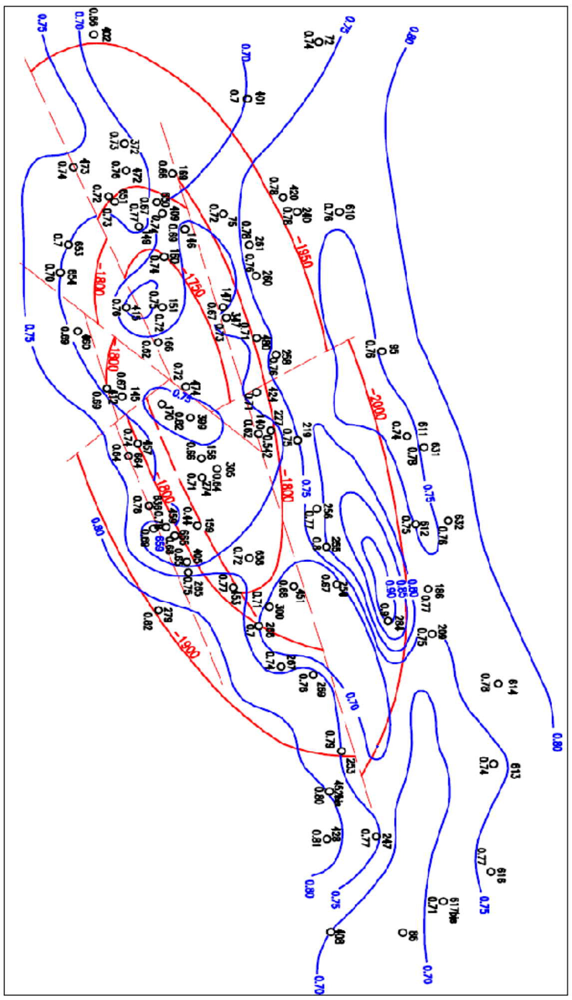

Figure 10 – Simulation of the distribution of the average values of the Na / Cl ratio in Burdigalian waters – structure Y

The surface distribution of the iodine content in the Y structure shows that the lowest values are found in the anticline's middle, from which point they increase toward the flanks, particularly the northern flank and the western pericline. However, there is a maximum concentration anomaly in the structure's central-western region (figures 11 and 12).

The map's look contradicts the presence of oil in the structure's center, which would cause the waters to have higher iodine concentrations. With noticeable differences, the average sulfates concentration of the waters of Burdigalian in both buildings ranges from 6.12 to 880.6 mg/l. Sulfates are present in very small amounts in structure X center region of the anticline, but they gradually rise on the sides and towards the periclinal terminations, particularly to the west.

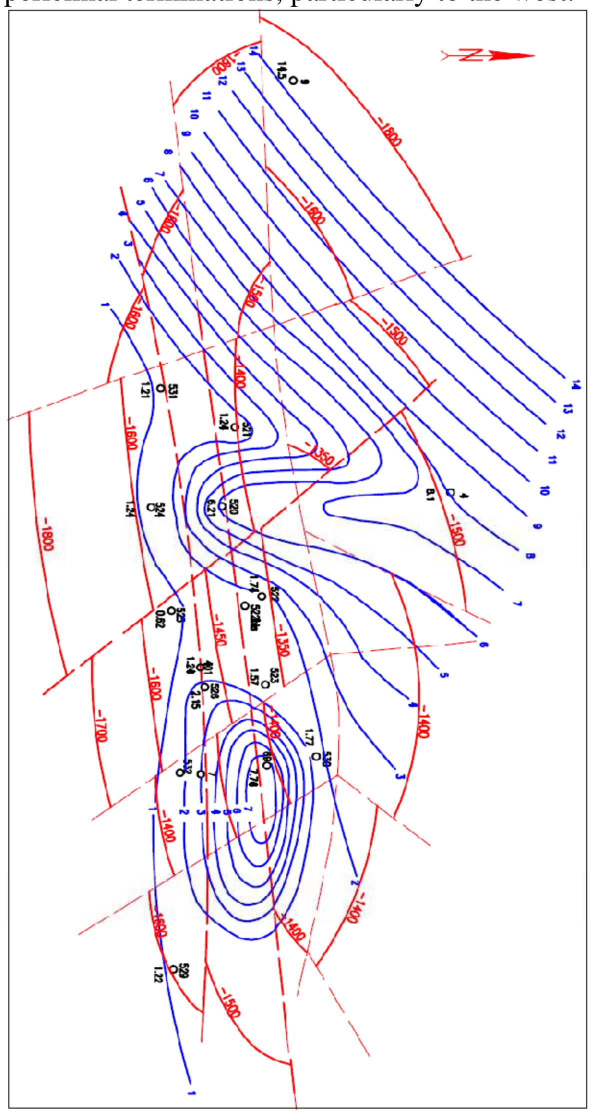

Figure 11 – Simulation of the distribution of average values of iodine content in Burdigalian waters – structure X

This distribution suggests that there are decreasing conditions, which are more clearly displayed at the center of the structure (figures 13 and 14).

The maximum values are collected in the middle of the anticline, with gradual declines in all directions, but more pronounced on the northern side. This is because the surface distribution of the sulfate content is inverse on the Y structure.

This is in contrast to the Burdigalian aquifer's closed or semi-closed hydrogeological character, which is better shown in the core portion of the anticline than on the periphery.

The average bicarbonates content in Burdigalian waters is also high and varies widely.

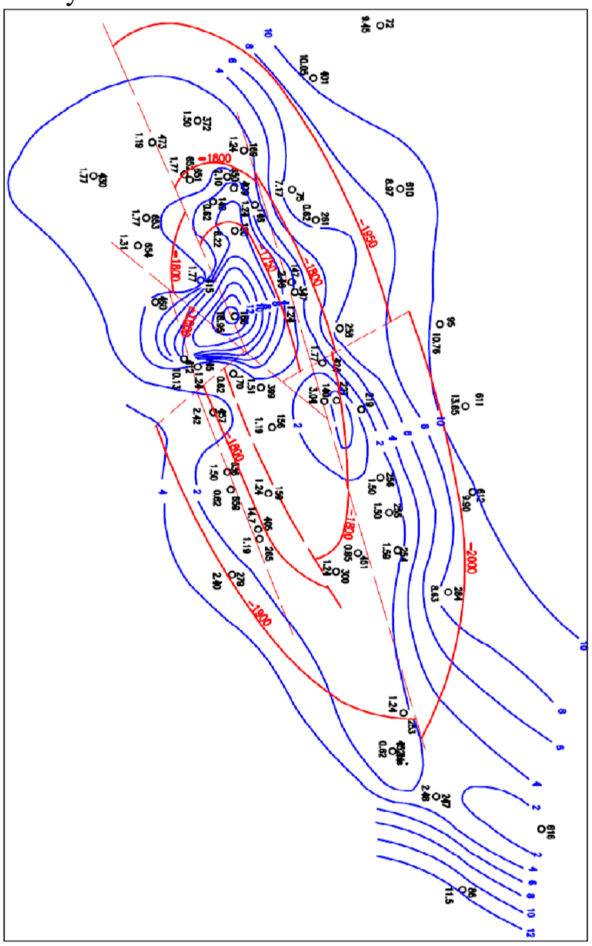

Figure 12 – Simulation of the distribution of average values of iodine content in Burdigalian waters – structure Y

On the X structure (figures 15 and 16) the highest values appear in the central part of the anticline, from where they decrease progressively on the flanks, the variation being inverse about to the SO^{-}_4 content.

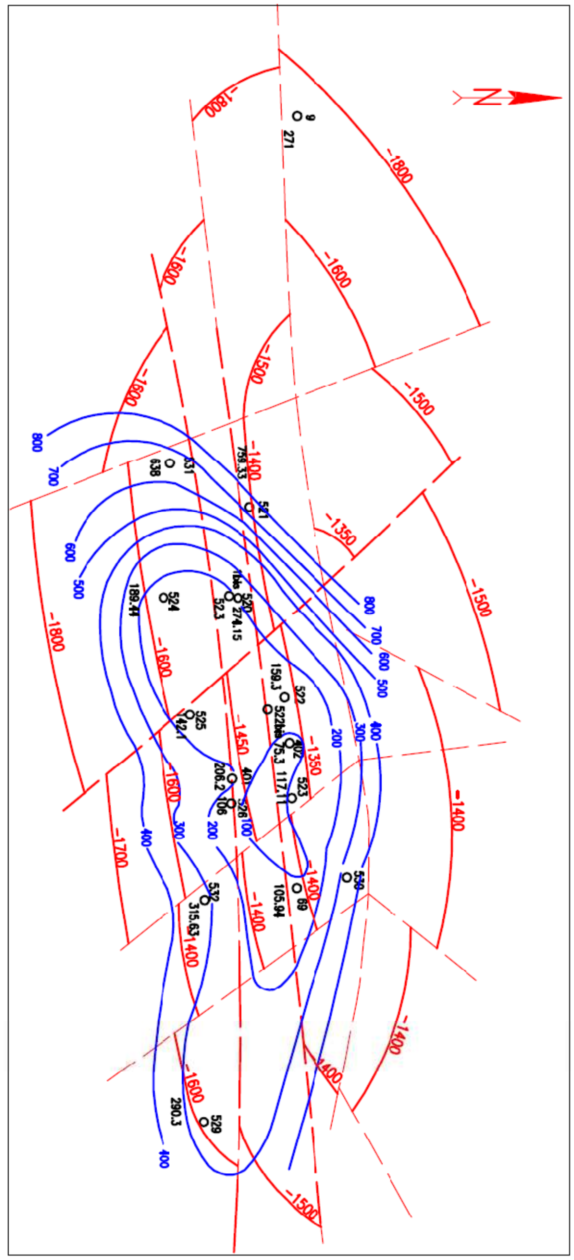

Figure 13 – Simulation of the distribution of average values of SO_4 content in Burdigalian waters – structure X

In the anticline on structure X, the distribution of HCO^{-}_3 ion values is inverse, the central part of the structure being characterized by minimum concentrations (below 50 mg/l), where the values increase progressively on the flanks.

This distribution can be explained by the precipitation in the central area of a part of $CaCO_3$ formed as a result of the interaction between calcium sulfate and hydrocarbons.

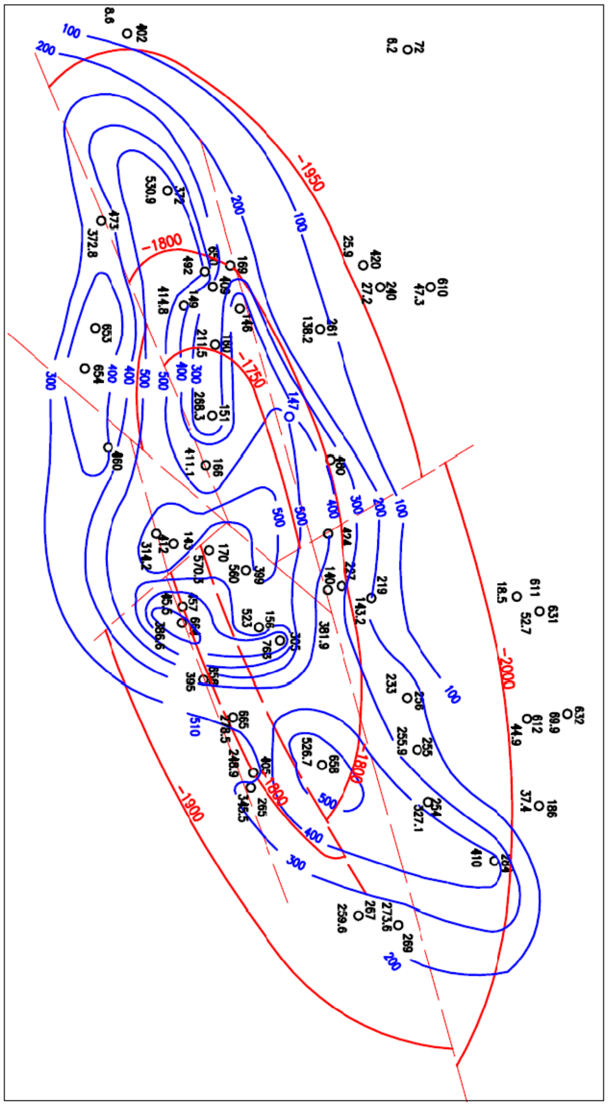

Figure 14 – Simulation of the distribution of average values of SO_4 content in Burdigalian waters – structure X

4. CORRELATION OF HYDROCHEMICAL DATA AND INTERPRETATION OF RESULTS

Summarizing the information provided above, some broad generalizations regarding the distribution of the studied indices and their interdependencies can be drawn.

The Burdigalian waters of structure X exhibit a less severe degree of alteration because there is no oil in this stratigraphic stratum, therefore they are not technically waters connected to oil reservoirs. The iodine concentration is typically quite low and increases to a region in the north-west where wells have found trace amounts of oil.

The SO^-_4 content is often very high, decreasing from the flanks to the central part of the anticline, and the sometimes very high HCO^-_3 content varies inversely with the decrease from the center of the anticline to the axes of the adjacent synclines.

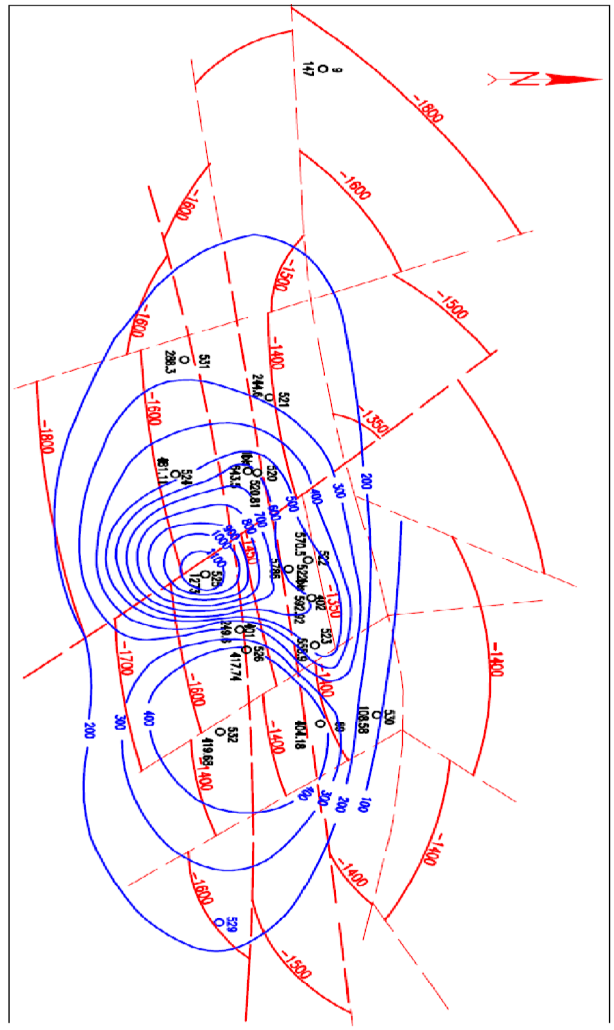

Figure 15 – Simulation of the distribution of average values of HCO^-_3 content in Burdigalian waters – structure X

At most correlation trends, only secure and acceptable correlations between these hydrochemical indices may be created, examined in pairs. Inverse correlations between the Na/Cl ratio and SO^-_4, the range of higher iodine values and SO^-_4, and the relationship between SO^-_4 and HCO^-_3 all show such patterns (inverse correlation).

The Burdigalian waters of the Y structure, such as marginal waters or groundwater, that come into contact with the oil accumulations in each complex are distinguished by a more advanced degree of metamorphosis that is well represented in the center of the anticline and attenuated on the flanks. Their near-water-like iodine concentration is lower in the anticline's center but higher on the flanks, whereas the SO_4^- content declines from the anticline's center to the nearby synclines and the HCO_3^- content increases. decreased compared to the X structure, increasing from the anticline's center to its neighboring synclines.

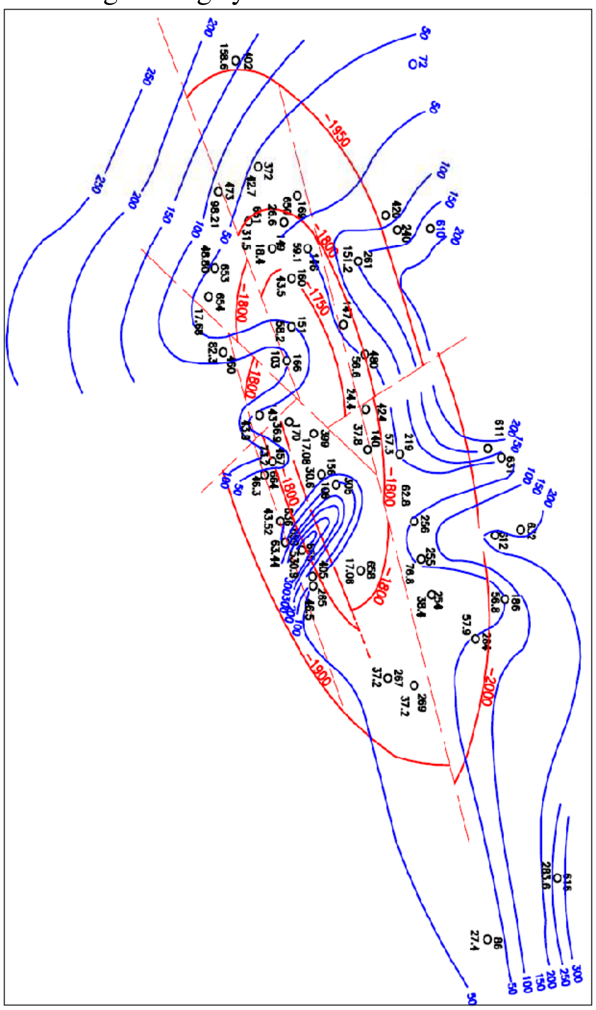

Figure 16 – Simulation of the distribution of average values of HCO_3^- content in Burdigalian waters – structure Y

The correlations between these parameters, considered in pairs, are absent or manifest, as in the X structure, in the form of trends. Such trends occur between Na/Cl ratio and iodine, in the range of higher iodine values (inverse correlation) and between SO_4^- and HCO_3^- (inverse correlation).

From the presented observations are found correspondences, but also non-correspondences between the variation and interdependence of the studied parameters, whose interpretation is not easy on the usual theoretical and practical bases of hydrochemistry.

As it is known, the variation of the global chemical composition of water, as well as of some components considered separately, as well as the relationships that are established between the hydrochemical components, are conditioned by a large number of physical and chemical factors, among which the most important are: the chemical-mineralogical composition of the aquifer, the static or dynamic regime of the water, the degree of mixing of the waters with different chemical compositions, the geochemical conditions of the aquifers and the presence or absence of oil accumulations in contact with groundwater.

These factors facilitate the exchange of bases, dilutions, or concentrations in salts, the reduction reactions of some oxygenated compounds, and the transfers of elements or compounds, respectively, which sometimes fundamentally change the primary properties of water.

Regarding the chemical-mineralogical composition of the aquifer, in the investigated cases there are no differences from one structure to another, everywhere the aquifers are of detric-terigene type, but probably in their composition are present some residual salts (NaCl, $CaSO_4$). The presence of the latter could at least partially explain the high water content of the SO_4^- ion, which is also due to the dissolution of calcium sulfate from rocks.

In both structures, the geological considerations lead to the opinion that the waters of Burdigalian have a closed regime, especially in the central parts of the anticlinals, conditioned by the intense fracturing of the structures and the isolation of the blocks by numerous tight faults.

This stagnant and closed regime facilitates the chemical exchanges between water and the solid environment and between water and hydrocarbons, which explains the advanced degree of water transformation. If on structure X the water metamorphosis is the result almost exclusively of the interaction between water and rock, on structure Y it is the result of two interactions, water-rock and water-oil, the cause of which results in more accentuated transformations. This explains the lower value of the Na/Cl coefficient in Burdigalian waters on the Y structure, compared to that on the X structure.

It is practically impossible to assess the extent to which the waters of structures X and Y have mixed with foreign waters reservoirs, but on the one hand the relatively low and moderate iodine content and on the other hand the moderate or high sulfate content (although they may have other origins), suggests the possibility of mixing primary waters with iodine-free waters, but rich in sulfates (infiltration waters).

The presence of oil in contact with Burdigalian waters in the Y structure weakly influenced the composition of the water in the sense of accentuating its metamorphosis, compared to the X structure, in which Burdigalian is not petroliferous.

There are obvious differences between these two structures in the distribution of SO^{-}_{4} and HCO^{-}_{3} ions, conditioned to some extent by the presence or absence of oil. Thus in structure X, the SO^{-}_{4} content decreases from the periphery to the center of the anticline, and the HCO^{-}_{3} content varies in the opposite direction.

This distribution is in agreement with the current hypothesis that HCO^{-}_{3} is thought to be caused by desulfurate reactions, which are more intense in the central parts of the anticlines than on their flanks.

However, on the Y structure, the SO^{-}_{4} content decreases from the center of the anticline to its periphery, and the HCO^{-}_{3} content varies inversely. This situation could be interpreted as the result of either sulfate-reducing reactions, which are more active on the flanks and in the synclines than in the anticline vault, which is difficult to explain, or by the contamination of Burdigalian's water with foreign sulfide-rich waters.

5. CONCLUSIONS AND PROPOSALS

The following conclusions can be drawn from the presentation and analysis of hydrochemical data:

1. The waters of the Burdigalian deposits in the anticlines of structures X and Y have the chemical characteristics of secondary groundwater, but only on structure Y do they come into contact with oil accumulations.

2. The metamorphosis of these waters is more accentuated when oil is also present (structure Y), but it can be quite advanced even independently of the presence of oil (structure X).

3. The proportion of iodine and SO^{-}_{4} is independent of the presence or absence of oil. In both structures, the Burgigalian waters likely mingled with meteoric fluids during migration or after their replacement, which determined the increase in sulfate content and decrease in iodine proportion.

4. Na/Cl ratio and SO^{-}_{4}, iodine and SO^{-}_{4}, and Na/Cl ratio and SO^{-}_{4} do not have any satisfying relationships, as each of the indices under study is determined not only by common general reasons but also by specific factors that are significant. In contrast, when hydrocarbons are present, the association between SO^{-}_{4} and HCO^{-}_{3} is better and more significant.

5. Sulfates' origins in these fluids are linked to both their dissolution in rocks and their mixing with meteoric waters, but carbonates are primarily produced by sulfate's biogenic breakdown processes, most likely in the presence of hydrocarbons.

6. Only the SO^{-}_{4} – HCO^{-}_{3} dependence of the studied hydrochemical indices is significant for the presence or absence of oil, according to the correlative analysis of the studied hydrochemical indices, with the exception of Na/Cl ratio. None of

the examined indices, taken in isolation, are manifested, in the investigated cases, as reliable indices to establish the reservoir relationship between water and hydrocarbon accumulations.

6. REFERENCES

[1].Altovski M. E. – *On hydrochemical indices and some other indices of petroleum perspectives*, M.I.P.C. – "*News in Geology and geophysics*", Technical Publishing.

[2].The Institute of Oil and Gas and Geology Bulletin – Volume XX – *Drilling of wells and exploitation of oil and gas fields – site dates*.

[3].Mutihac G. – *Romania's geology in the Central-Eastern European geostructural context*, Didactic and Pedagogical Publishing, 2010.

[4].Vasiliu V. E. – *Geochemistry*, Publishing Petroleum and Gas University of Ploiesti, 2018.

[5].Reservoir's studies, 2014 – 2020.

Contribuții la studiul repartiției unor componenți chimici ai apelor Burdigalianul zonei petrolifere din Depresiunea Getică

Rezumat Autorii au studiat unele componente chimice (SO_4, HCO_3, iod) și Na/Cl din apele Burdigalianului din structura X și Y, care este petroliferă la structura X și nepetroliferă la structura Y, pentru a stabili influența țițeiului asupra compoziției chimice a apelor. Ei au studiat atât corelațiile dintre acești indicatori în perechi, cât și repartiția arială a fiecărui indicator.

Din acest studiu rezultă că apele care se află în contact cu țițeiul (structura X), comparativ cu celelalte (structura Y), au mai puține valori pentru Na/Cl și o corelație suficient de bună între SO_4 și HCO^{-}_3 Pe de altă parte, conținutul de iod și SO_4 este similar în cele două tipuri de apă.

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