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THE ORIGIN OF GASES EXPLORED WITHIN THE INERT GAS ZONE, HUNGARIAN GREAT PLAIN, HUNGARY

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I. Introduction

The purpose of this thesis was to find an answer to the origin of high "inert-content" (CO_2, N_2) gases, explored in the "Szolnok Flis Area" and it's direct geological surroundings, with special attention paid to the gases explored within the TNFK Zone (Tiszapüspöki – Nagykörű – Fegyvernek – Kisújszállás), named after the sites providing most of the gas reserves, or with other name the Inert Gas Zone of the Hungarian Great Plain. During the development of the project several problems occurred concerning the maturity of the organic matter and, related to this, geothermal circumstances of the given area, and concerning the genetical relationship between the explored natural gases. However, there were not predetermined, replying to the following questions – i.e. reliability of vitinite reflectance parameter (R_o) in case of small sample sized DOM (Disperse Organic Matter) samples; depth dependence of this parameter and estimation them for unexplored areas (R_{o-sz}); estimation of vertical migration of natural gases on the basis of assumed relationship between R_o and $\delta^{13}C_{CH4}$; modification of TTI calculation (TTI_{Pa-mi} value) and applying them for estimation of maturity of the organic matter; possibility of examination of the relationship between different natural gases by correlation analysis – effectively contributed to solve the original problem. Results, regarding their uncertainty, i. e. every different area requires different interpretation, give a chance for geochemical revaluation of the area, and, therewith, modification of presumed hydrocarbon potential.

On the basis of available analyses results – gas analyses, carbon isotope ratio, e.t.c. –the local and regional hydrocarbon-genetical, geological interrelation between different gas pools at the given area and its environs could be interpreted, and thus, the origin of gases could be answered. However, recognition of these relationships requires studying many times as large area as the original was. Thus, the size of the larger area was around 8800 km^2, which is equal practically with the middle range of Trans-Tisa and its environs. The NE and SW cornerpoints of the area in EOV system are $Y = 844100$, $X = 247300$ and $Y = 715600$, $X = 182500$, respectively. However, there are many new and more reliable analysis – compound specific carbon isotope ratio of methane homologues in the gas components and gases came from artificially pyrolized kerogene of source rocks (HC-IR-MS, Py-HC-IR-MS) - whose applying had to be put aside during this work because of financial and sampling problems, i.e. a few sampling possibilities, non-representative samples, costs of sampling, e.t.c.

II. Database management and the reliability of data

The first step in the examination of the broader area was collecting and cataloguing the related information and data and handling the arising data uncertainties.

In the beginning it was practical to select those drillings of the area from the many thousands, which were deeper than 500 m, as the significant gas pools of the area are below that depth. Then a digital database had to be created from the geological and fluidum composition data found in the drilling records of the selected drillings – gas and oil composition, the measurement of the gases' carbon-isotope ratio (CH_4, homologues and CO_2), the top and bottom depth of the opened reservoir, the name of the pool (if it had any), the geological age and the rock of the reservoir, the testing method, the time and place of sampling, the result of the well flow test, the type of the choke, the H_2S content, the time, place and type (HBM, Engel, Hempel) of taking the oil sample, the oil's quantity, paraffin, naftain and sulphur content of the oil, the result of the aromatic analysis and the gas-chromatographic oil analysis, - the information regarding the dissolved gas content of water wells - GVVSz, MVVSz, dissolved CH_4, CO_2, N_2, O_2 content, the geothermic gradient value in the well, – the data gained from temperature measurements – place and type of the measurement (bottom hole temperature (BHT) measured during well-flow test in closed system, the BHT calculated during geophysical measurements, formation temperature measured during drill strem test, the static formation temperature), – and the Rock Eval and vitrinite reflectance data from the boreholes. The database also had to be complemented with the most essential basic data (drill hole ID, documentation number, character of the drilling, date of the drilling, the bottom hole depth, co-ordinates, abbreviated lithological column data, footwall data and other important notes). This raw "database", built on the information that was found in drilling records owned mainly by Hungarian Geological Survey and Hungarian Oil Co., could be related to the databases containing gas, oil and isotope composition data prepared earlier by ISTVÁN VETŐ, MRS. JÓZSEFNÉ TÖRÖK and ISTVÁN KONCZ, and the data of articles and other summarising works about the area. The variety of the area's geology required that the descriptions of the core samples taken from the "Pre-Neogenic formations" (middle-Miocene formations including the lower-Miocene base conglomerate) would also be computerized. Although, water composition data has also been noted in parts, these data were incomplete, thus they have not been integrated in the database.

The following step was to form a real, uniformed database from the introductory, raw "database", to enable both the representation of values and parameters in various ways (on contour maps, graphs or diagrams) and effective data search. Based on the above, the final structure of the database is as follows:

- Geological and basic data: data of 1168 drilling (8 only denoted), their abbreviated lithological column (68 missing), their footwall rock (47 missing), core sample data of basement (from 234 drillings);
- Vitrinite reflectance: 81 samples from 25 pieces of core were taken (24 data-series and 57 values), the vitrinite reflectance data from 153 rockchip samples from 6 drill holes;
- Temperature data: BHT from 1206 well-flow test, 712 hole-geophysical temperature data (calculated), 28 static formation temperature data (measured), temperature-data measured during 244 drill strem test, geothermic gradient data calculated in 115 water wells;
- Oil and gas data: 2473 gas-compositions (42 incomplete, fully reliable: 231), 888 oil-compositions (22 Hempel, 305 HBM, 156 Engler, 405 HBM+Engler), 388 H_2S data, 31 gas-chromatographic oil-analyses, 18 aromatic analyses, the carbon atom distribution of 15 crude oil and condensates, and the biomarker analysis from 8 crude oil samples;
- Carbon isotope ratio data: 139 pieces of $\delta^{13}C_{CH4}$, 3 pieces of $\delta^{13}C_{C2H6}$, 3 pieces of $\delta^{13}C_{C3H8}$, 1 piece of $\delta^{13}C_{iC4}$, 1 piece of $\delta^{13}C_{nC4}$, 5 pieces of δ^2D (from water), 88 pieces of $\delta^{13}C_{CO2}$, 11 isotope analyses from oil remaining after distillation;
- Water compositions analyses of water samples taken from drillings and Rock Eval data are under processing.

As pointed out by TÖRÖK (1979), the reliability of the data show great differences, since during the 110 years of exploration activities the analysis methods and the supplementary data changed significantly, and the accuracy of the analyses has also gone through a considerable improvement. Following TÖRÖK's suggestions, the selection of the most reliable data had to solved first. The selection, where possible, was carried out based on the industrially accepted principles, but in some cases these principles were not applicable. The gas composition analyses have been categorized into four groups according to their reliability level - unreliable, poorly reliable, fairly reliable and reliable. The categories are shown in Table 1. In terms of data reliability the subjective order of importance between the table elements was:

place of sampling > method of opening the reservoir > composition > O_2 quantity (M+K) > gas flow rate. Although, in some cases there may be significant differences due to the gas analyses' level of technical development, these could be not taken into consideration. Regarding the O_2 content, the analytically only fairly reliable evaluations can also be considered acceptable (MRS. JÓZSEFNÉ TÖRÖK, 1989), and the consideration of the gas flow rate values is less significant, if the sampling is otherwise appropriate. Based on the above, 231 gas analyses could be selected as fully reliable, while based on the O_2 content 351 and based on the gas flow rate 253 gas analyses could be accepted. Neglecting the gas flow rates and accepting the values of the fairly reliable O_2 quantities, the data of altogether 589 analyses were acceptable based on the reliability conditions. This amount of data is statistically sufficient for the recognition of the correlations characteristic for the area. In terms of data reliability, a different category was formed by the analyses gained from the drillings deepened after 1974 in the Hajdúszoboszló area. After this date the Szoboszló-III reservoir has been used for storing gases, therefore the gas samples taken during formation tests may have been contaminated through mixing or penetration. The results of the carbon-isotope-level measurements can also be considered unreliable for the period after 1974.

Reliability	Place of sampling	Method of opening the reservoir	Point of difference between composition in % and 100 %	O_2 content*	Result of gas flow test** [m3 a day]
reliable	separator	perforating, bottom hole sampling	+ / - 0.02 %	< 1 V%	> 1000
fairly reliable	tubing	-	-	1-5 V%	1000-10000
poorly reliable	any other place	formation treatment, casing formation testing	-	unknown	< 1000
unreliable	unknown	unknown	under or over this value	> 5 V%	unknown

*   it was given only for results in volume percent (V%)
**   depends also on the diameter of choke, the limits in table are given for 10 mm size choke

Table 1

The reliability of the gas compound analyses

Among the temperature measurements, the BHT values values measured in closed wells during well flow tests proved to be the most reliable ones. However, sometimes there were significant differences between temperature values measured during certain measurements. Only in these cases the highest temperature value was marked but this value in most cases agreed with the BHT value measured in the closed well. As the quantity of these measurements were adequate also from statistical point of view, only these temperature values

were taken into consideration when the geothermal gradient "gg" and its inverse "gl" values relating to the area were calculated and contour maps - made based on the values of "gg" and "gl" - were created. So, the reliability of the maps practically depend on the reliability of these temperature values and the same mistake occurs in all cases. It is important to note that in drillings where were measured both static formation temperature and BHT (20 drillings), there were significant differences between the "gl" values calculated from these measurements.

The last step of preparing the database was the "encryption" of the data. It means the drillings had to be given arbitrary and unified codes, which codes depend mostly on the drilling signs used in any case, and they had to be transformed into a particular co-ordinate system.

Afterwards, the geological structure of the area had to be surveyed in order to mark the possible source rocks and make a survey of their stratigraphic situation and spatial expansion. Then the results of the geochemical analyses having been done until nowadays on the area had to be surveyed.

On the basis of the results of previous exploration activity basically there were three problems to look into: the maturity of the organic matter and, related to this, the vertical migration of the gases, the composition - in-homogeneity of the gas-pools and the relationships between them.

III. Results, theses

The most accurate evaluation of the maturity of organic matter is essential to the calculation of both the role of the organic matter content of the source rock in the hydrocarbon generation and the minimum and maximum depth of hydrocarbon generation. The thesis is focused on minimising the uncertainty of two parameters: vitrinite reflectance (R_o) and TTI.

The statistical analysis of vitrinite reflectance data partly confirm the practice have used in measurement and interpretation for a long time, and partly conduce to new results:

- On the basis of statistical analysis of large sample sized coal samples the distribution of R_o values is GAUSSIAN or near GAUSSIAN.

- Generally, depending on the experience of operator the measurements contain varying numbers of outliers, i.e. synsedimental, but not syngenetical vitrinite particles, e.t.c. It is presumed that samples without outliers cannot be measured because of the semisubjective nature of the measurements.

- The uncertainty of R_o parameter, calculated as an average value, increases with decreasing sample size, increasing number of outliers and maturity. This difference is a few per hundredths in the case of less mature samples and increases to a few tenths with increasing maturity.

- **I. Thesis: Based on the statistical analysis of the R_o parameter, the standard parameter calculation (ISO, ASTM) needs to be corrected. The mean calculation needs to be changed to median calculation in the case of small sample sized DOM samples (n < 50).**

In some cases the maturity of the organic matter needs to be estimated in areas where the vitrinite reflectance has not been measured. There are two ways to do this: either to find an experimental formula, which gets closest to the measured R_o values (R_{o-sz}), or to find a maturity parameter which can be calculated at any point of the given area (TTI). Both methods raise several questions concerning the given parameters' dependence on depth, temperature and time. On the basis of new results, the answers have given to that questions before were highly unreliable. Decreasing the uncertainty, the following theoretical possibilities are given:

- The area's map of inverse geothermic gradient (gl) at Jászság Basin and its environs can be drawn based on the most reliable temperature data acceptable in industrial practices, which are measured during well-flow test in closed system. Thus, the temperature can be inter- or extrapolated within the unknown areas. On the basis of the estimation of temperatures, the sediments are especially heated, i.e. the "gl" value is the least, where the thickness of Pannonian sediments is the least. It can be observed that the traps above the deep basins, i.e. specifically less heated areas, generally contain crude oils and condensates, gas cap oil pools, while the traps in more heated areas contain natural gases associated in some places with oil traces. This trend is very well outlined within "Szolnok Flish Area".

- The sedimentation period of each layer can be calculated considering the "almost regular" sedimentation of the deeper parts of the Pannon-basin and the estimated time

frames of the ages. The calculated ages of sedimentation of a given layer is in good correlation with R_o values measured from organic matter of younger sediments. In case of presumed sedimentary cyclicism, the ages might be calculated more precise. Hovewer, this latter should be studied in more detail in the future.

On the basis of the extent of correlation between the measured R_o values and the depth, estimated temperature and sedimentation time, the following observations can be found:

- **II. Thesis: Based on the given data set and calculations, the values of R_o, measured from the Pannonian sediments of the Jászság basin, can be estimated significantly more accurately according to the $R_{o-sz} = 0.0387 \cdot e^{0.1572 \cdot \lg(t) \cdot gl}$ (if $R_o \leq 0.7$ %) and $R_{o-sz} = 10^{1.469 \cdot 10^{-9} \cdot z^2 \cdot T^{0.5} - 0.1862}$ (if $R_o > 0.7$ %) calculations than on the basis of the linear relations between R_o and the depth, which had been assumed earlier.**

Based on the more recent research results (KONCZ, LOPATIN) regarding TTI calculations, if the activation energy is regarded as constant, the speed of reaction decreases with the growth of the temperature. Given this, it was advisable to modify Lopatin's TTI calculation:

- **III. Thesis: $TTI_{Pa-mi} = \sum_{i=n_{min}}^{n_{max}} \left(\left(10^{c-1} \int_{T_i}^{T_{i+1}} T^{1.746 \cdot \lg T - 3.4048} dT \right) \cdot \Delta t_i \right)$ to a general formula, where "c" is a constant of $n = 0$ point, and if $T = 105$ ^{o}C, then it's value is -0.25104.**
- Based on the calculations above, and using sedimentation times and estimated temperatures from "gl" values specified before, it has become possible to calculate the values of R_{o-sz} and TTI_{Pa-mi} for the bottom of Pannonian sediments of Jászság sedimentary basin, and can be compare their values.

Considering those gases of the area, that are probably homogeneous and are more matured than katagenetical, the migration distance of these gases could be estimated, using the relations between $\delta^{13}C_{CH4}$ and R_o coming from other fields and the relation between R_o and Z that had been supposed within the area ($Z = \left(\dfrac{\lg(10^b \cdot R_{o-sz})}{c} \right)^{0.4}$).

- **IV. Thesis: Considering the information available from source rocks which compliments the new calculations regarding the maturity of the organic matter and vertical migration of natural gases, it could be stated that the organic matter of Pannonian and Miocene sediments could generate a high quantity of early katagenetical and katagenetical natural gases – with a small quantity of liquid hydrocarbons generated from III and II-III type kerogen – even in the deepest parts of the Jászság basin and it's geological environments. The organic matter of the Mesozoic source rocks, particularly the Liassic coals, could generate a high quantity of late katagenetic natural gases and condensates as well as metagenetic gases (N_2, CO_2). The major part of the CO_2 content of the gas pools is of the inorganic type, originating from the thermal degradation of Mezozoic carbonates.**

- There are less information from paleogene source rocks, but it is just possible that they could generate less amount of catagenetic, late catagenetic gases, subordinately condensates.

The compositional inhomoguenity of gas pools within TNFK Zone has indicated migration and filling up of pools from more than one source rock. Gases coming from same source rock, if the gas generation was from a relatively short maturity interval and during migration the composition of gases couldn't change so much, i.e. only compositional differentiation had been, have same character. On the basis of correlation between gas compounds within the area, and, in case of suffcient quantity of data locally to the drill holes, in connection with origin of natural gases the following observations can be found:

- **V. Thesis: Based on the correlation-analyses between the gas compositions claimed reliable, it could be stated that the gases in the gas-pools of the area originates from the mixing of three basic gases:**
  - **late-katagenetic, metagenetic gas; originating from coal-type organic matter, with high N_2 and probably high CO_2 content, and a CH_4 content that is supposedly below its N_2 (gas "A"). This has come from the so far unexplored, but supposedly existing, Liassic coal seam inside the basement of the Jászság basin in the direction of N-NW from the Fegyvernek – Nagykörű pools;**

- o **early-katagenetic, katagenetic and liquid hydrocarbon-assimilated gas with an origin of mainly coal-type organic matter (gas "B"), which has come from source rocks of the Miocene and Lower Pannonian ages, lying S-SE-E direction of the Kisújszállás – Törökszentmiklós area;**
  - o **CO_2 (gas "C") released during the thermal degradation of Triassic and Jurassic carbonates at great depths of the Jászság basin basement.**
- On the basis of correlation analysis the composition of the gas-pools could also be influenced by the bacterial degradation of the liquid hydrocarbons within them.
- The gas-pool compositions, CH_4 / N_2 rates, $\delta^{13}C_{CH4}$ and $\delta^{13}C_{CO2}$ values refer to that the late katagenetic, metagenetic gas and the CO_2 of non-organic origin have probably mixed through migration, and following this, the early-katagenetic, katagenetic gas has displaced CO_2 from the pools.

Several questions arose during the examinations that cannot be answered in the framework of the present work. At a later date it should be aimed to reduce the uncertainty at the estimation of temperature and the time of sedimentation, and the estimated time must be compared to ages developed by chronostratigraphical methods. The periodicity of the Pannonian sedimentation and the more general estimation of vitrinite reflectance demands further examination towards a more general method, to make it usable for a broader audience. The examination of the relation between the calculations of $TTI_{Pa\text{-}mi}$ for different $n = 0$ points and the measured R_o values could also be interesting as it might help the choice of the most characteristic "0" point, and thus the determination of the most characteristic activation energy value of a certain area. Research is on going but there are only preliminary results available even for modelling the mixing ratio of gases within the area.

Beside all of these, the researches can be completed by studying formation waters and fluid hydrocarbons explored in the given area and its wider surroundings, whose database has been partly made. Though there has been no possibility in this thesis, but more reliable information could be gained from compound specific isotop analysis of methane homologues explored in this area and its environs and gas components came from artificially pyrolized kerogene of possible source rocks, as well as from the comparison of these data.

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