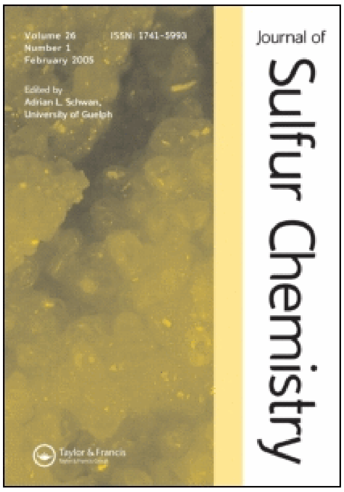

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REVIEW ARTICLE

Interaction of endogenic methane and sulfur: a possible initial stage of condensation conversion and abiogenic genesis of oil

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On the basis of data on the occurrence of methane and sulfur in the Earth's interior as well as reactive potential of the alkane–sulfur system, it has been suggested that geosphere degassing might involve the condensative conversion of hydrocarbon fractions of fluids. The condensation effect of sulfur on methane and products of its condensation may be considered as the initial stage of abiogenic oil formation. It has been revealed that the reactivity of the alkane–sulfur system and regularities of its evolution were in good agreement with the characteristics of real oils, such as hydrocarbon-type content, condensation degree, sulfur content, fraction distribution of sulfur and sulfur-containing compounds. Also discovered was a direct relationship among sulfur concentration in oil, scale of oil fields and reserves of oil and gas. The present review deals mainly with contributions published in Russian journals.

Keywords: Endogenic fluids; Alkane-sulfide transformations; Mercaptans; Sulfides; Thiophenes; Condensation; Oil genesis

1. Introduction

The discussion on biogenic and abiogenic generation of oil and gas has been repeatedly noted over many years. The biogenic theory has gained a wide recognition in the scientific community. Nevertheless, for the last 50 years, much information has been gathered, indicating inconsistencies in some of the fundamental concepts of this theory with actual data on occurrence conditions of oil composition, properties, migration, deposits and the balance of carbon in the Earth's crust. At the moment, the results of geological observations as well as geochemical, geophysical and thermodynamic studies cast some doubt on the assumption that the biomaterials of sedimentary rocks are the only starting materials of oil and gas systems formation. Hydrocarbon reserves resupply takes place on some exploitation of oil deposits over a long period of time. Shortcomings of the biogenic theory have been thoroughly described in many works [1–5]. The chief drawback of the theory is a lack of a distinct relationship between compositions of real oil and organic matter (OM) of rocks surrounding oils. The oils contain

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aromatic and naphthalene hydrocarbons and heterocompounds with a high concentration of $–CH_2–$ and $–CH_3–$ groups, which are absent in living OM. However, there is a lack of a clear idea on how the oil components are formed.

Sulfur is a basic heteroelement of oil systems. Note that most of crude oils throughout the world contain from 10–30 to 120 atoms of sulfur per 1000 C atoms, whereas the living matter has only from 0,5 to 3–4 sulfur atoms [3, 6, 7]. Within the framework of biogenic theory, it is difficult to explain why the content of S atoms in oil is by order higher than that of N atoms, whereas in biomaterials the opposite picture is observed [7]. Sulfur is contained only in two amino acids from the 20 constituting biological systems. This brings up the question—can this ratio be changed so drastically (by two orders) during the process of oil generation? It is known from theory and the practice of processing oil products that elimination of nitrogen from hydrocarbon systems is significantly more difficult than that of sulfur.

According to the biogenic theory of oil generation [8], sulfur as a minor component of biomolecules finds its way into organic matter due to the influence of H_2S and S, which are formed due to sulfate-reducing bacteria. Connecting the presence of sulfur in oils with the activity of the aforementioned bacteria, one should bear in mind that these bacteria are strictly anaerobic, and at 70–80 °C they seem to decrease considerably their activity. It is pertinent to note that in stratal waters of some oil pools (Western Siberia) sulfates are absent [9].

The notions on oil sulfuration, caused by the secondary process, leave unexplained the availability of direct correlations between sulfur concentration and contents of nitrogen, aromatic, highly molecular compounds, bituminous pitch in oils and their fractions, as well as the relationship between density and viscosity of oil. The regularity given above is observed independently on the type of oil and its locality.

A sufficiently reliable basis for rigorous scientific analysis of information concerning the problem of the oil and gas generation is the abiogenic concept that considers the genesis of fossil fuels as a part of global evolution processes of the differentiation of Earth's matter and the outflow of this matter and energy from the interior of the planet to its periphery and beyond. Abiogenic formation of natural hydrocarbons related to general processes of geospheres development was even suggested by Mendeleyev [10] who put forward the idea on mantle genesis of oil. This suggestion was further developed in Kropotkin's hypothesis [11] on the existence of hydrocarbons branch of deep-seated fluids and was supported by the results of geological investigations of many authors. It remains to be established that which chemical reactions are key (starting) in the process of abiogenic oil formation. The most likely route of this process proceeding is believed to be catalytic synthesis from H_2 and carbon oxides. This point of view is based on the presence of these gases in certain amounts in fluids arriving from the Earth's interior. The possibility of various hydrocarbons preparation, which has been proved experimentally, also speaks in favor of the above suggestion. This approach was reported in detail previously [12]. At the same time, there are some factors [4] that do not permit the hydrogenation of the oxide form of carbon to be considered as the only possible initial stage of abiogenic oil formation. The reducing character of deep-seated gaseous fluids, composed mainly of CH_4 [13] and containing in some cases S and H_2S (acting as poisons) [14, 15], which inhibit the reactions of carbon oxides with H_2 [16, 17], should be assumed as the main reason that prevents these reactions proceeding in the Earth's crust and mantle.

As far as the sulfur-free fluids are concerned [18], the reactions between H_2 and carbon oxides may be realized. Nevertheless, in this case primarily CH_4 will be formed. This fact is defined by the abundance of metals catalysts in the Earth's crust ($Fe \gg Ni > Co$) as well as by catalyst influence on the selectivity of the reaction [17, 19]. The results of a chemomathematical study on natural hydrocarbons [20], whose compositions are characterized by the signs of incompleteness of conversions, show that there are no traces of CO and H_2 in naturally occurring mixtures when the starting material is always CH_4.

An analysis of the reactions of hydrocarbon synthesis from H_2 and carbon oxides for the comprehension of oil generation process does not explain the complex heterocomponents (and first of all, sulfur) present oils. The advocates of 'oxidative' abiogenic genesis concepts as well as the authors of biogenic theory of oil generation regard oil sulfuration as the result of secondary processes. The investigations of possible routes of oil hydrocarbon fraction formation are insufficient as they fail to reveal the reasons for and mechanisms of integration of all the components into unified stable system. To this point, it has not been established what causes the observed association of elements. The question is as follows: are sulfur and other heterocomponents the 'satellites' arriving in oil due to differences in time and natural secondary processes that do not significantly affect the hydrocarbon generation process or do the heterocomponents play crucial role in oil genesis even on the initial stage? By now none of the research dedicated to oil genesis provide convincing answers to this question. The necessity of a close look at this problem stems from the availability of the stable regularities of sulfur distribution in oil systems as well as direct correlations between its concentration with other characteristics of oil.

2. Methane and sulfur: components of deep gaseous fluids

From deep high-temperature Earth zones, carbon is primarily carried away as CH_4 [21, 22]. Altogether with other gaseous components (H_2, N, C and S), it arrives with ascending fluxes to upper layers [23]. Owing to the distribution of deep fluids on the degassing channels, a large body of CH_4 is supplied to the hydro- and atmospheres. Annually $2 \times 10^{12}\,m^3$ of CH_4 enters the Earth' atmosphere as a result of the degassing process [24]. Over 500 millions of years, 2.5×10^{22} g of hydrocarbons were moved to the surface of the Earth [25], whereas oil reserves are 2×10^{17} g. Some part of endogenic CH_4 remains in the Earth's crust as gaseous hydrates.

All these findings suggest that CH_4, not carbon oxides, plays a substantial role in the oil generation process. Methane serves also as a starting material for condensation conversion. Moreover, CH_4 is a good solvent for hydrocarbons, and thus, along with water can serve a successful transporting function in oil accumulation.

Sulfur is also one of the main fluid-forming elements [26–28]. Its mass in global geospheres of the Earth (core, lower and upper mantles) is even somewhat greater than that of carbon and hydrogen [27, 28]. The content of sulfur in the whole core reaches to 1.8% [27] and in the liquid core is up to 12% [23] and the ascending gas fluxes 'primordially specialize in C and S transport' [14]. The critical parameters of sulfur ($T = 1040\,°C$, $P = 18.2\,MPa$) are such that it can exist in liquid or gaseous state through the entire routs of the deep fluids migration [15, 26]. Metals occurring on the surface of fluid-way channels as well as gas-transported fluxes are presented in S-containing fluids as sulfides.

The sulfur flows occurring in many volcanoes throughout the world are indicative of the participation of elemental sulfur in magmatic processes. The reaction $2H_2S + O_2 \rightarrow 2H_2O + 2S$ seems to be a possible theoretical explanation of this phenomenon. This reaction is highly improbable because it requires a huge amount of free oxygen. Kinetics of sulfur formation in this case would correspond to powerful chemical explosion. Thus, S^0 can exist during the movement of volcanic gases and be involved in the volcanic process [26]. Being diluted, S^0 along with other fluid volatile components [H_2O, Cl, F, H_2 and CH_4] is contained in sulfide melts [29].

Owing to its origin and physical and chemical properties, sulfur is an active participant of geochemical processes, which is manifested, for example, in the formation of sulfide ores [14, 26]. The sulfur deposits often contain metal sulfides [26].

It should be emphasized that high-carbon fluid systems contain along with S^0 such 'mantle marks' as V, Ni, Co, Fe and Cr [14, 30]. These metals, possessing a well-pronounced catalytic activity in different reactions, are the main microcomponents of oil.

3. Reactive potential of the methane–sulfur system

Elemental sulfur occurs in a reactive radical state at a temperature of >160 °C. It exists primarily as a highly reactive diatomic species at >500 °C and decays at >1500 °C into free atoms-radicals. Under thermal effects, CH_4 may also exist in an active radical state.

The thermodynamic analysis of the reaction of CH_4 with S (molar ratio $S/C = 0 - 0.5 : 1.0$, temperature 430−1330 °C, pressure 0.01–10 MPa) shows that the oxidation of methane with sulfur at >530 °C can afford hydrocarbons, C_2, propylene, aliphatic and cyclic mercaptans [31].

It should be pointed out that the insertion of sulfur into hydrocarbon structure results in polarity reversal as well as increase in acidity of the C−H neighboring bonds [32] and a significant decrease (by 13–22 KJ/mol) of their strength. At the same time attack of the radicals at the S−H bond proceeds by fout to five orders faster than that of at the C−H bond [33].

It has been found [31, 34] that the reaction of sulfur with CH_4 yields CH_3SH, H_2S, dimethylmono- and disulfides, CS_2, C_2H_6, C_3H_6, H_2 and elemental sulfur. Moreover, an increase in the molecular mass of alkane facilitates a considerable increase in the rate of sulfuration reactions. So, for example, *n*-butane is converted at 570 °C into thiophene in 70% yield, while a mixture of sulfides in 72% yield is formed from dimethylpentanes at 160–180 °C, and heptane and octane form mercaptans and disulfides at 60–90 °C [34]. The sulfur compounds formed, in turn, can produce different highly reactive intermediates whose further transformation leads to the appearance of a number of high-molecular products [34, 35]. Since the mantle fluids always contain water, which is capable of suppressing the formation of CS_2, it is unlikely that the 'S-oxidation' reaction will proceed as follows:

$$CH_4 + 4S + 2H_2O \longrightarrow 4H_2S + CO_2$$

Thus, experimental data [31, 34, 36] show that the reaction of CH_4 or other alkanes with S (500–1000 °C, pressure up to 40 MPa) in the presence or in the absence of catalysts involves oxidative condensation that results in a variety of more high-molecular products, including thiols, sulfides, polysulfides, sulfur heterocycles, alkanes, olefins, aromatic hydrocarbons, polymerization products and asphaltic-resinous compounds. Olefins, H_2S and thiols resulting from these sulfur reaction with alkanes may be the primary products [34]. It is apparent that the rate ratio of these competitive reactions depends on relative concentrations of the starting reagents in the reaction medium, thermobaric conditions as well as catalytic effects.

The reaction of sulfur with thiols affords sulfides, which further on are transformed into polysulfides and thiophenes [34]. Hydrocarbons thus formed must not hinder these oxidative processes. It is known, in particular, that thiols are oxidized to disulfides by the action of sulfur in a hydrocarbon medium [37]. The interaction of aromatic hydrocarbons with sulfur leads to a condensation degree increase as well as to the formation of sulfur-containing cyclic compounds [34].

According to the thermodynamic calculations [31], the yield of ethylene in the reaction of CH_4 with sulfur (10 MPa, 1300 °C) must be 0.2 M/M CH_4, while the increase in pressure should result in higher yield. It has been found [34] that ethane and propane are converted to the corresponding alkenes in the yield of 65–95% at 650–750 °C for 0.004–0.1 s. In the case of transition from ethane to *n*-butane, S-dehydrogenation rate increases by 400 times. The rate becomes even higher for iso-structural hydrocarbons, which are also formed during the reaction.

Olefins, formed on the first stage of the reaction of sulfur with alkanes or from disulfides, react further with S and H_2S can produce all kinds of sulfur-containing compounds as well as high-carbon structures. The reactions of unsaturated hydrocarbons with sulfur proceed rather vigorously. For example, in the case of *n*-pentene (160–220 °C), thiol is formed in the yield of up to 40%. *n*-Hexene is completely involved in the addition reaction through the double bond at 210 °C, and at 270–280 °C resulting sulfides, disulfides and an asphalt-like residue [34]. Apart from this fact, olefins are likely to be polymerized and under the corresponding thermobaric conditions and in the presence of H_2 in fluids, they can enter the hydrogenation reaction.

Despite the thermodynamic feasibility of CH_4 condensation under the action of H_2S (700–1000 °C, 0.1–10 MPa, molar ratio of H_2S/CH_4 0–0.5:1), all the attempts to accomplish this reaction have failed [38]. Unlike sulfur, which reacts with all components of the reaction mixture, H_2S interacts only with olefins [34] and transition of sulfur into this less-active state should lead to retarded condensation.

Sulfur is to be considered not only as stoichiometric reagent, but mainly as an initiator of all the reactions as it is known than that sulfur performs catalytic functions. At the same time, the reactions with hydrocarbons proceed, as a rule, according to radical-chain mechanism [34]. Acting as a dehydrogenating and condensing agent, sulfur does not have to be take part in the reaction products. The reactions of sulfur with alkanes, with successful formation of compounds with all kinds of C—H—S bonds (thiols → sulfides → thiophenes) and hydrocarbons of different molecular weight as well as asphaltic-resinous compounds, can be regarded as ‘cascade’ (‘domino’) [39, 40], which lead to the formation of new bonds (C—C basically) without any other reagents or catalysts.

Condensation of CH_4 also occurs in the presence of sulfides of different metals even without introduction of elemental sulfur in the system. Ethylene, propylene and H_2S are formed at 700–900 °C [41]. This phenomenon appears to be caused by the high mobility of sulfur in metal sulfides. Their real surface is usually characterized by the deficiency of metals as well as the availability of the S—S bonds. In this non-stoichiometric layer, sulfur is presented in dimeric and polymeric forms. Properties of sulfur on the surface of metal sulfides are probably close to those of elemental sulfur. In geochemical systems, Me—S constituting sulfide ores, the fugitivity of sulfur is rather high. At 900 °C, the fugitivity of sulfur (S dimer) in the system Fe—FeS—NiS—Ni can be altered by seven orders depending on composition of this mixture [42]. This suggests that the genesis of sulfide ores and oil systems are interrelated.

The condensation ability of sulfur makes itself evident not only in its intramolecular insertion followed by chain of transformations, but also in formation of intermolecular bonds and the generation of supramolecular structures. The ‘cross-linking’ capacity of sulfur is successfully used for the change of reological properties of residual fractions (tars) to prepare road bitumen. Sulfur addition under forcing conditions leads to dehydrocondensation and oxidative effects that result in supplementary associations, change of disperse phase and disperse media ratio and enhancement of intermolecular interactions. For example, thermal treatment (200–250 °C) of tar obtained from low-sulfur East Siberian oil with elemental sulfur, leads to the increase of molecular weight and content of asphaltenes from 813 to 950 and from 6.8 to 11.5%, respectively [43]. At the same time, increase of thermal treatment time involves the growth of sulfur insertion degree into asphaltene structures.

Reaction in the form of radicals, sulfur acts as an initiator of radical transformations of hydrocarbons (dehydrogenation, sulfurization and condensation) yielding some products in the radical state [34]. Hydrocarbon radicals [44] including those containing heteroatoms exist for a sufficiently long time in a medium of diamagnetic molecules and form via exchange interactions, associated entities and large aggregates. Thus, paramagnetics are responsible for the paramagnetism of oil systems.

Oil exists mainly in the form of kinetically stable colloid particles of different size, the nucleus of which contain basically asphaltenes and porphyrins surrounded by the layer after layer of aromatic, resin, naphthene and paraffin structures. The internal nuclear part plays the role of solvent shell. The investigations of absorption electronic spectra of oil and oil products have shown [45] that asphaltenes are unique donors and acceptors of electrons, having no analogs in Nature. The asphaltenes so formed can, in turn, be active and initiate the charge-transfer processes that should result in ionization and acceleration of the transformations. Asphaltenes and porphyrins are capable of acting in intensive intermolecular interactions and forming supramolecular fractal structures [46].

The possibility of the interaction between deep CH_4 and S^0 leading to different hydrocarbons and S-containing compounds is in a good agreement with the results of thermodynamic modeling of the C−H and C−H−S−N−O systems under equilibrium and metastable conditions of mantle fluid movement towards the Earth's surface. The calculations of equilibrium (temperature, $\leq 2330\,^\circ\mathrm{C}$ and pressure, ≤ 2280 MPa) indicate the stability of heavy hydrocarbons and C−H−S−N−O and organometallic compounds under thermobaric conditions (PT) of the upper mantle [22, 47–52].

Oxidative S-dehydrogenation of hydrocarbons and condensation interaction of sulfur resulting in its introduction into hydrocarbon structures are the realized processes of the formation of aromatic polymer backbones containing condensed polythienethiophene, polybenzthiophene, polysulfide and related structures [53–55].

4. Regularities of sulfur and sulfur-containing compounds distribution in oils

The paragenetic connection of brimstone with oil hydrocarbons was discovered more than one hundred years ago [56]. The amount of elemental sulfur in oil can be as high as 0.13% [57]. Chemically bound sulfur is distributed in all oil fields throughout the world as sulfur-containing organic compounds.

On the basis of properties of the hydrocarbon–S system and transformations of sulfur compounds (mercaptans → sulfides → thiophenes), it is assumed that the higher the sulfur concentration in the system, the higher rate of these transformations, their depth, the share of thiophene compounds and, hence, the condensation of the whole system. Indeed, oils and their fractions are observed by direct correlations between sulfur content and concentration of aromatic structures, asphaltic-resinous components and other heteroatoms as well as density and viscosity. At the same time neither the geological age of oil nor the presence of various biomaterials (humus, sapropel) alters the universal pattern of this dependence. Thus, the properties of the C−H−S system determine the oil genesis process.

Depending on the predominance of one or another type of sulfur compounds (mercaptan, sulfide and thiophene), oils differ essentially in condensation degree and fraction composition [58].

In all types of oils, mercaptans occur in light fractions ($<200^\circ$C). Mercaptan oils contain the greatest amount of light fractions and they are characterized by low content of sulfur and asphaltic-resinous compounds as well as by low density. Light fractions of this type of oil incorporate a significant part of total amount of sulfur (higher by order than other oil distillates). So, gasoline distillates of mercaptan oil hold sulfur amounts 50–70 times higher than the corresponding fractions of other types of oils. Mercaptan oils are less thermostable; in some cases they contain H_2S and elemental sulfur [58].

Thiophene oils do not contain gasoline fractions and 'aggressive' sulfur, they are the most thermostable. In the middle and highly boiling distillates of these oils, 85% of sulfur compounds consist of thiophene derivatives [58].

Sulfide oils occupy an intermediate position. As a whole, all oils containing heavy fractions are characterized by increased amounts of thiophenes and a decrease of mercaptan content. In addition, the content of thiophene sulfur increases with the increasing total amount of sulfur in oil [59, 60], which can be explained by the growth of condensation rate and its intensification due to the enhancement of sulfur concentration in the reaction mixture.

The investigation of sulfur compounds' composition in different oils has shown [61] that the set of structural moieties of mercaptan, sulfide, thiophene, sulfoxide and sulfone molecules is identical. The type of oil determines only the quantitative amount of every class of the compounds.

Crude oils of various ages differ in the distribution of sulfur over the fractions [62]. In 'ancient' oils, one observes lower sulfur content in light fractions but a dramatic increase with increasing the boiling temperature of the fraction accompanied by the absence of H_2S and relatively high thermal stability of sulfur compounds. The 'juvenile' oils are characterized by instability and intense evolution of H_2S upon heating.

A certain trend in the change of oil composition with the occurrence depth is also observed. The closer the oil to the Earth's surface, the higher, as a rule, is the concentration of sulfur, aromatic high molecular and asphaltic-resinous compounds [63–65]. Using the methods of statistical and cluster analysis applied to a large number of oil fields, it has been shown that in large depths are located the oils with low content of sulfur and resins [66] but a high content of mercaptan [67].

Elemental sulfur and H_2S, which are normally the constituents of more light and deeper-seated oils, may serve as a source for the formation of additional amounts of organosulfur compounds during the movement of oil fluid towards the Earth's surface [58]. An increase in H_2S concentration with the increase of occurrence depth is observed, in particular, in gaseous condensates. For example, in Astrakhan field, the content of H_2S at the depth of 3–4 km reaches 24% [68]. Other resources of active sulfur may involve labile sulfur of metal sulfides, which react with hydrocarbons leading to sulfuriztion.

The variety of natural hydrocarbons is obviously connected with the heterogeneity of deep fluid systems. There are many qualitative and quantitative methods for the analysis of composition, which can establish geochemical specialization, physical and chemical properties including those specifically intended for carbon and sulfur transfer [14]. Reduced high carbon fluid systems contain specific mantle 'marks' (Ni, V, Co, Cr, etc.) [30], which are contained in the oil composition.

The character of the target hydrocarbon product is likely to be depend on the composition of endogenous fluid, and primarily on ratio of CH_4, H_2, sulfur and metals.

According to our notions on the role of sulfur in the initiation of condensation processes, the methane in sulfur-free fluid has not to be transformed into higher molecular compounds, but it is either evolved in the atmosphere or forms deposits of methane hydrates. Total reserves of methane hydrates are abundant ($1.5 - 2.0 \times 10^{16}$ m^3 CH_4) [25, 69]. As already demonstrated [70], methane hydrates of only the world oceans contain no less than 10^{19} m^3 of methane, whereas the content of carbon in them is three orders higher than the total reserves of oil carbon, natural gas, peat, coal, soil, marine and land biotic substances. Evidence indicative of deep genesis of gaseous hydrates includes scales of methane reserves in the Earth's crust, geological regularities in the distribution of methane hydrates as well as abnormalities of gaseous hydrate water (in particularly, its desalting) [70, 71].

Thus, one should not expect the presence of sulfur in the deposits of methane hydrates. For example, the investigations of composition of the stratum gases and waters in the largest methane hydrate deposit (Messoyakhskoye) [72] have shown that the gases include no sulfur components and water in 30% of wells do not contain sulfate-anion while in other wells its content is lower than 1% of all anions. Although gaseous hydrates have been found in many regions of the world's ocean, the lack of oil deposits [68] is obviously explained by the absence of sulfur in local fluids.

The deficit of sulfur in the fluid flows is one of the reasons for the formation of light oils and gaseous condensates. Another reason for low condensation systems generation may be the enhanced content of H_2S. The presence of H_2S in the reaction mixture does not favor the occurrence of condensation processes (see above). Therefore, it is no surprise that gaseous condensates (in particular, in Astrakhan and Orenburg fields) contain high amounts of H_2S (up to 24%), while in some natural gases (Texas) this value is even higher (more than 80%) [73]. Light oils with low content of sulfur hold also H_2S (Iran, Libya, etc.), and heavy high sulfur oil (Mississippi, California, Mexico, Venezuela, etc.) do not contain it [58].

A high content of sulfur and metals (V mainly) in fluid facilitates the formation of high-viscous oils, bitumen and asphaltites. Specific features of their composition include low content of light fractions and high content of heteroatoms. A typical example is an asphaltite from the Orenburg region [74]. Practically, it has no admixtures of sedimentary rocks and contains high amount of sulfur (7–8%) and 0.6% of vanadium (four to five times higher than the most enriched V-containing ores). It is noteworthy that the content of V is six to seven times higher than that of Ni. Accumulation of bitumen, V and Ni occurs also in sulfuric ores [56]. Total reserves of bitumen with high content of asphaltous-resin components exceed even the total reserves of oils.

Differentiation in distribution of accumulation of hydrocarbon systems with various composition and phase state is a general regularity. One can distinguish either gas-bearing or oil-bearing fields, which, in many cases, are separated from each other [75, 76]. They determine the basic explored reserves of oil and gas. At the same time there are no differences in age and composition of sedimentary rocks, content of organic matter in them, condensation degree of this matter as well as in temperatures and pressure of rock mass [75] that does not correlate with biogenic conception of hydrocarbons system genesis.

The point of view of the authors suggests that the qualitative indices of endogenic oils and scale of its generation are determined by capacity and composition of the deep fluid and, primarily, by the content of sulfur within it. The growth of sulfur content in the fluid must be attended with an increase in the probability of its evolution towards the growth of sulfur content in oil, enhancement of oil condensability and the increase of the reserves formation. As a result one should expect the decrease in gaseous component content in the system. The assumed regularities are really observed when sulfur content is compared with reserves of oil and gas in oil and gas fields. Figure 1A shows the correlations of the indices mentioned for some countries and continents. It should be noted that the decrease of the part of gas is not caused by the drastic drop of the absolute value of its reserves. So, in Australia they are six times lower than in Saudi Arabia and Kuwait [77] and the value gas/oil (G/O) is 17 times greater (figure 1A). Total amount of carbon in oil and gas are approximately equal in Libya and Nigeria [77]. The oil reserves in the former are 1.5 times higher, while the part of gas is two times lower, which can be explained by higher concentration of sulfur in the system. Thus, the concentration of sulfur in deep fluids of one or another region is obviously a crucial factor of the relative rates of oil and gas formation.

The direct correlation between sulfur content in oil and oil reserves is observed not only on a continental level (figure 1A). The similar picture can be demonstrated on a local level, as in studies of the indices of oil from the fields of Western Siberia [9].

On the basis of organic theory, which considers the oil sulfurization as a result of secondary processes, one should expect the opposite phenomenon, namely the decrease of sulfur content

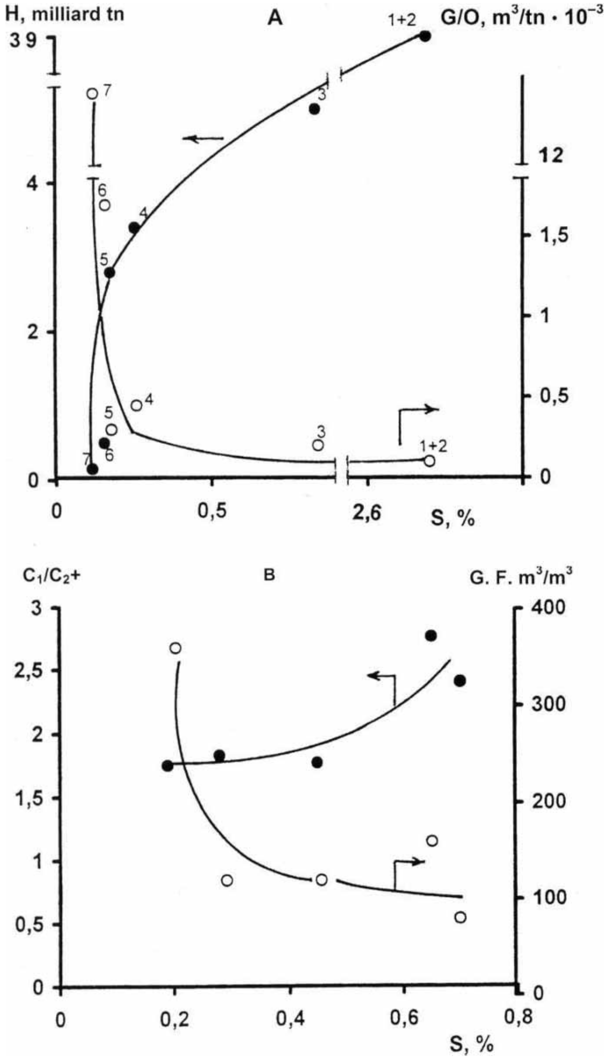

Figure 1. The influence of the concentration of S in oil. (A) On its reserves (H) and the correlation between the reserves of gas and oil (G/O). (1) Saudi Arabis, (2) Kuwait, (3) Libya, (4) Nigeria, (5) Indonesia, (6) Australia, and (7) New Zealand. (B) On the value of gas factor (GF) and the part of methane in the gases, dissolved in West Siberia oil (C_1/C_{2+}).

in oil with the increase of its reserves. Indeed, the growth of sediment accumulation and an increase of the organic matter mass leads, in one degree or another, to the separation of organic matter from sulfate-containing water. Therefore, the access of the latter to organic matter should be hindered or even stopped. Connecting the sulfur content in oil with the activity of sulfate-reducing bacteria, one should bear in mind that the occurrence of this process is limited by some factors. Such bacteria are strictly anaerobic, and under higher temperatures the bacterial activity can be ceased. At the same time, the presence of sulfur in the hydrosphere in the form of readily soluble sulfates and H_2SO_4 is caused by the transformation of sulfides of mountain rocks, *i.e.* this process occurs later than the endogenic interactions of sulfur with ore and hydrocarbon components of the fluids.

The condensation influence of sulfur, which reveals itself in the values of oil and gas reserves and their correlation, should also be manifested in the indices of gases dissolved in oils. Really, the statistical processing of the data related to the oils from all region of Russia [9] has shown the availability of high correlation coefficients between the sulfur content and the amount of accompanying gases (gas factor). The latter, like the G/O index, decreases with the increase of sulfur concentration. Figure 1B shows the data for one of the oils from Western Siberia [9].

The composition of gases dissolved in oil is of special interest. It is characterized by the domination of CH_4 over C_2-C_5 components, specifically in the relative sequence $C_2 > C_3 > C_4 > C_5$ [9, 78]. Figure 1B demonstrated that the quantity of CH_4 not only exceeds the total amount of the homologues, but also its share increases with the growth of sulfur content. These phenomena can be explained taking into account the rates of hydrocarbon transformation under the action of sulfur. As it is known [34] the increase of hydrocarbon molecular weight involves the dramatic acceleration of their reactions with sulfur, which should lead to the enrichment of gaseous fraction by lower molecular components. In addition, one should take into consideration the probable inflow of CH_4 from the depths of the Earth.

The presence of the regularities, shown in the figure, allows one to draw the conclusion that the influence of such factor as the sulfur content of the fluid on some characteristics of oil and gas system is crucial.

One of the most decisive arguments in favor of one or another opinion concerning the source of sulfur in oils may be the comparison of isotopic composition of sulfur of mantle, sea, oceanic and sediment origin. Sulfur of mantle origin contains $0 \pm 3‰$ of the ^{34}S isotope. In oceans and seas the sulfate S content of this isotope is about $+20‰$, whereas modern sea sediment hold to $+30‰$ of the isotope [79]. It is also known that bacterial reduction of sulfates in the hydrosphere leads to significant loss of the ^{34}S isotope (up to -10 to $-40‰$) [79]. The value $\delta^{34}S$, in particular, for most oils of Western Siberia is from $+0.4$ to $+4.3‰$, a value comparable to that of mantle origin sulfur and only two from these oils have lower values of $\delta^{34}S$ (-3.5 and $-7.4‰$) [9]. In stratum, waters of oil fields of this region, sulfates are absent. Thus, isotopic composition of different types of sulfur allows one to suggest that the mantle sulfur can be directly contained in oils. To some extent, an 'admixture' of sulfate form due to the sulfate-reduction is possible.

5. On the relationship of oil and sulfide ores genesis

In some works [80–82], the general fluid-dynamic concept of the mineral fields formation is elaborated. It is based on the notion of the relationship of ore and oil generation with global processes of energy redistribution between geospheres, differentiation of the Earth's matter and deep degassing. The localization of ore and oil bodies in common transglobal systems of deep-seated faults and intensive manifestation of sulfide mineralization in the regions of commercial oil fields are considered as evidences of obeisance to the common laws [81]. The interrelation between oil and gas fields generation and the formation of deposits of wide groups of metals–chalcophiles (Pb, Zn, Cu, Fe, Ni and Co) with the same fluid-dynamic systems has been reported [80].

The transportation and deposition of ore matter can be carried out with active participation of organometallic compounds, which are formed by the reaction of metals with hydrocarbons in the reductive zone, followed with the further decay during the evacuation of deep fluids [29]. The decomposition of deep fluids, containing the greater part of metals as elementoorganic compounds, gives rise to different hydrocarbon systems (from hard bitumen to liquid and gaseous hydrocarbons) as well as to formation of ore-naphtide fields [83, 84].

The extraction of bitumen compounds and n-alkanes from sulfide ores of black smokers containing no residual deposits is indicative of the relationship between sulfide mineralization and naphtidogenesis. Some sulfide structures of oceanic ridges contain oils with high concentrations of asphaltenes and resins [85]. Alkanes and polycyclic aromatic hydrocarbons occur in sulfide ores at the places where sedimentary mantle is absent [86]. The investigations of the sulfide ores composition [56] have shown that they contain, along with gaseous hydrocarbons, oily and asphalt-resin components, which accumulate V and Ni. These metals are 'mantle marks' [14, 30] and they belong to the 'transit' group. These metals are more mobile during different geological processes; they occur in oils mainly as metal porphyrins.

Much evidence of the presence of metal sulfides in oil rocks has been reported [81]. Abnormal high concentrations of heavy metals are observed near the oil pools, whereas close-to-oil waters are enriched with V, Ni, Co, etc. [87].

Despite the convincing proof of the generality of sulfide ore genesis and hydrocarbon systems formation, there is not evidence of chemical substantiation of this process in the literature. Summing up all the aforementioned, one can suppose that it is just sulfur that is responsible for oil generation, by saturating primary magmas and interacting with ore-bearing components of the fluids during their evacuation to give sulfide ores [14, 26] and reacting, at the same time, with hydrocarbon compounds. This is a possible explanation of genetic relationship of these mineral products and the processes of their formation. The participation of sulfur in the process of ore and oil generations makes the latter, to some extent, interrelated.

The reaction of sulfur with hydrocarbon or ore-bearing components of the fluids seems to be a peculiar kind of interactive processes. However, the type of this interaction is not clear. Do these reactions intensify or weaken each other? How are the intensities of the reactions changed in the direction to the Earth's surface and under different physico-chemical and thermodynamic conditions?

The investigations of the reasons of the metals presence in oil as well as the stable correlations between V and Ni concentration and other characteristics of oils are of crucial importance for the understanding the oil genesis.

The advocates of the biogenic concept believe that metal-containing oil compounds are formed from tetrapyrrole structures of the biomaterial on one or another stage of its metamorphism [88, 89]. For example, it is suggested that Cu-complexes are substituted for Ni and VO-porphyrins at late stages [89]. Nevertheless, such an approach is insufficient for comprehension of all the facts related to the metals presence in oils.

On the basis of concept of oil mantle origin, one can assume that the presence of metals in oil, including, first of all, V and Ni, can be explained by their content, along with CH_4, S and N, in the mantle fluids [14, 30, 52]. Thermodynamic studies have shown that metals can be presented in oil as organometallic compounds [52], which are stable in upper mantle. Vanadium is found in the content of porphyrin complexes at a depth of 3500–4500 m in volcanogenic sedimentary structures and is likely to be the product of intense magmatism [90]. Total content of Ni and V in oils monotonically increases with the increasing sulfur concentration [6, 59]. The direct correlation between sulfur content and relative amounts of V (V/Ni) is also observed [6, 20, 59, 60]. Vanadium prevails in oils of thiophene types [60]. Its presence determines the density and viscosity of oils.

Vanadium ($V > Ni$) and nickel ($Ni > V$) types of oils are distinguished. The former, occurring at small and middle depths (1–3 km), are heavy and they have high sulfur and resin content. On the contrary, nickel oils, occurring at a high depth, are light and they contain small amount of sulfur, resins and asphaltenes [91].

Possessing paramagnetic and catalytic properties, vanadium may be a constituent of different chemical compounds and complicate macromolecular complexes. In oils it is presented as a part of porphyrin structures, mineral salts and π-complexes [92].

To now, numerous catalytic processes involving porphyrins are known. Their properties are determined in large extent by the ability of complex formation with various ligands and participation in intermolecular interactions. In particular, properties of VO–porphyrins can be connected with the peculiarities of the V=O moiety, which is out the porphyrin complex plain, and has an ability of donor–acceptor interaction with both acidic and alkaline structures [93].

Probably metal porphyrins, being formed (like asphaltenes) on a certain stage of naphtidogenesis, can be involved in further generation of oil system. For example, the role of vanadium complexes in polymerization processes and oil systems carbonization has been discovered [45]. It must be emphasized that vanadium sulfide possesses very low activity in the reactions of the C−S bond cleavage (two orders lower than Ni and Co) [94]. It is not improbable that Ni activity in the reactions of hydrogenation and the C−S bonds cleavage (when H_2S is evolved) in the case of high (with respect to V) concentration of Ni in the fluid flow causes the decrease of sulfur content and system condensation.

6. Conclusions

It is clear that the multiplicity of oils requires the interplay and participation of sulfur, sulfur-containing compounds, hydrocarbons, metals and their interaction products. All these occur during the migration of S-containing hydrocarbon reaction mixture along the evacuation channels of endogenic fluid flow through different thermobaric barriers. The whole package comes together as one of the explanations for the self-organization and stabilization of the system.

Explicit stable correlations between the content of S and metals (V and Ni) and other parameters of oils' composition allow their classification as genetic characteristics. It may be assumed that sulfur and these metals have a system-forming function at the very early oil formation stages.

The available data on the reactivity of the hydrocarbon–sulfur system correspond to the regularities of S distribution in oil and oil fractions as well as to the character of effects of sulfur concentration on some physico-chemical indices of oil and its reserves.

The current notions on the evolution of initially reduced mantle fluids on the whole as the process of their oxidative transformation [95] and the possibility of hydrocarbon condensation transformation under the oxidizing influence of sulfur allow us to conclude that the generation of abiogenic oil is a part of complex series of oxidative transformations of endogenic fluids.

It can be assumed that the role of endogenic sulfur in the processes of the Earth's matter differentiation is not limited by the formation of sulfide ores and abiogenic oils. New concepts of life origin (such as thioether and pyrite) formulated during the last 15–20 years [96] suggest also the key role of sulfur and are based on evolution of S compounds. Significant attention is paid to organic sulfides and sulfides of iron and nickel, on which surface can occur the processes of polymerization and formation of cellular structures from simple molecules (carbon oxides and methanethiol).

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