

POTENTIALLY TOXIC CHEMICAL ELEMENTS OF SHALE PLAYS – ECOLOGICAL THREAT TO THE ENVIRONMENT

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ABSTRACT

This research considered the content of trace elements (TE), including potentially toxic elements (PTE) in shale plays and deposits in various regions of the world. Their comparative analysis was carried out and the highest concentrations of PTE in the shales of some regions were revealed. The author notes that the destruction of organometallic compounds occurs during the development of shale hydrocarbon (HC) using horizontal drilling with hydraulic fracturing – injecting large volumes of chemicals while increasing the temperature. During such destruction processes, PTE can escape into the environment: into groundwater, soil layers, and other objects of economic use, and also deteriorate well equipment. In connection with the noted environmental hazards present during the development of shale HC, this paper proposes to monitor the content of TE in both shale rocks as well as in extracted shale oil in order to mitigate the risks of their release into the environment. In addition, developers and scientists should consider the losses of industrially significant volumes of valuable metals that occur due to the lack of cost-effective technologies for their capture and extraction from naphthides.

***Keywords:** shale plays, trace elements, potentially toxic elements, environment, ecological threats*

INTRODUCTION

With a fairly detailed coverage in the domestic and foreign literature of all the pros and cons of shale horizontal drilling projects, and in particular the negative environmental consequences of hydraulic fracturing, the problem associated with the high content of metals and non-metals in shales and oils is practically not considered. A significant number of them belong to the category of PTE, dangerous to the environment [3], [6].

The development of oil shale deposits, primarily in the United States, has completely refocused the international oil market in recent years. With the start of the shale revolution in 2010, American producers have become one of the key suppliers of raw materials in the world, having increased production by 10% to 9.3 million barrels per day since mid-2016, which is close to the levels of Saudi Arabia and Russia (<http://rusjev.net/2017/05/30/sanktsii-zadushili-slantsevuyu-neft-v-rf/>). Great success was achieved with the use of horizontal and/or cluster drilling. Shale formations are located mainly in the sedimentary basins as platform (Perm, Michigan, Illinois, etc.), and intra-fold (Green River, Winta, Paradox, etc.) types [3], [6].

The negative impact of this technology causes enormous harm to the environment. This facet is well known and frequently noted by many practitioners and scientists. In recent times the controversy over the environmental consequences of shale gas recovery and its role in the future of world energy has not only not abated, but has inflamed with renewed vigor (Fig. 1).

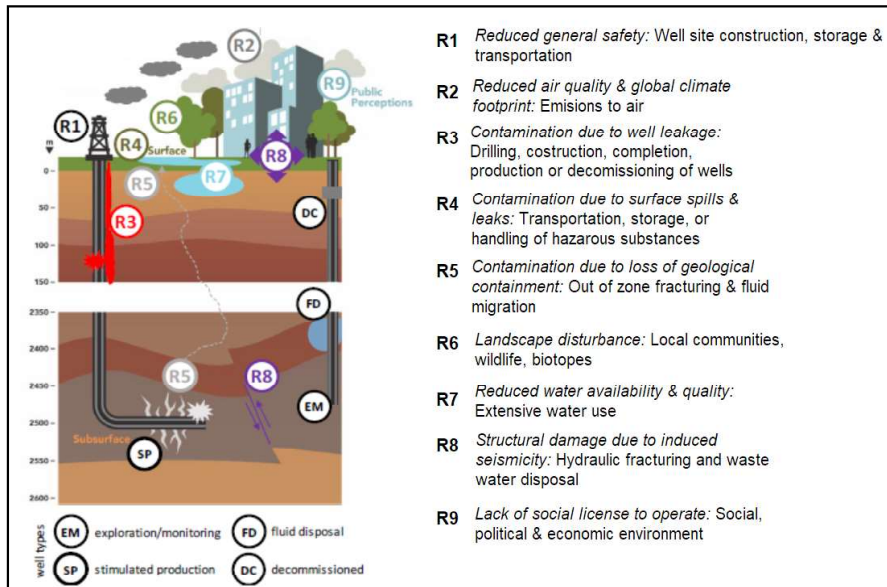


Fig. 1. Shale operation and its environmental impact [11]

In Europe shale gas/oil exploration and development is presently only permitted in 7 countries. This low level of support mostly stems from concerns related to the use of hydro fracturing and its environmental impact. Countries with a possible shale hydrocarbon resource but with no present exploration activities include: Austria, Belgium, Bulgaria, Croatia, Czech Republic, France, Ireland, Italy, Portugal, and Sweden [2].

While the country lacks a shale-specific investment regime, Bulgaria's conventional oil and gas production terms remain attractive. Production licenses extend for 35 years, with royalties ranging from 2.5% to 30% on a sliding scale, with a 10% corporate income tax. The Economy and Energy Minister has suggested that Bulgaria's shale gas resources could be in the range of 0.3 to 1.0 Tm³ but no supporting study has been released. The Shale Gas Research Group, a newly formed consortium of Sofia University and Bulgaria's Institutes of Geology and Organic Chemistry, is conducting long-term studies of organic-rich shale deposits in Bulgaria [2]. In the sedimentary successions of the Moesian Platform in Bulgaria, four intervals dominated by organic-rich dark shale have been identified: Silurian – Lower Devonian (?) shales; Lower Carboniferous shales – Trigorska and Konarska plays; Lower Jurassic shale sediments – Ozirovo Formation (Bucorovo & Dolnilucovit Mbs); Middle Jurassic shales – Etropole Formation (Stefanets Mb). From the estimated 4 targets for shale gas only the Lower Carboniferous shales (in

the western zone) and both Jurassic shale intervals may present a moderate interest [2]. The main target in the Moesian Platform is the Jurassic Etropole Shale, considered the main petroleum source rock in northwest Bulgaria. In particular, its organic-rich lower portion, the Stefanetz Member, contains thick, carbonate-rich (40-50%) black shale with interbeds of marl and limestone. It was deposited in a marine environment and seems similar to the Upper Jurassic Haynesville Shale. TOC ranges from 1.0% to 4.6%, with Type II kerogen predominating. The Etropole Shale generally ranges from 2.5 to >5 km deep and is over-pressured in much of the region, with an elevated pressure gradient of 0.78 psi/ft. Thermal maturity falls in the oil window in the north, increasing to wet and dry gas in the south near the Balkan thrust belt (Ro 1.0% to 1.5%) [3].

With a fairly detailed coverage of all the advantages and disadvantages of horizontal drilling of shale plays, and in particular the negative environmental consequences of hydraulic fracturing, the problem of the TE composition of both shales and shale oil is practically not addressed. However, when developing and extracting oil and gas resources of shale formations, it is necessary to take into account the large concentrations of metals and nonmetals in the formations.

RESULTS AND DISCUSSION

About 15-20% of raw materials produced by HC already contain in their composition toxic TE in quantities exceeding their safe level, and the volumes of its production increase with the years. Hg, Cd, As, etc. are the most migratory-mobile and volatile of them. Among the strongly chemically bound in complex organometallic compounds in HC include V, Ni, Co, Cr, Cu, Zn, and other biologically inert elements in oil and natural bitumen. However, they are actively dangerous in the microdispersed state after anthropogenic impact on raw materials, especially at high-temperature (>450oC). Actinides, regardless of the bond strength with molecular structures of HC, are considered actively dangerous in any state. Therefore, the content of such highly toxic and volatile elements as Cd, Hg, As, Se, Mo, etc. should be assessed at the preliminary stages of the development of any HC deposits, including shale deposits [7], [9].

Thermal effects on the reservoir, increases in pressure, and injections of chemical reagents during hydraulic fracturing with large numbers of perforations over long horizontal sections can lead to the release of organoelemental compounds and possibly volatile metals into the environment. Thus, it is known that thermochemical methods, such as in-situ combustion during the development of vanadienous naphthide reserves, are not acceptable given the significant losses of metals in the reservoir and also because of the possible entry of V and Ni into the overlying aquifers used for water supply of the population. Similar results have already been recorded in sections of in-situ combustion of the Karazhanbas field, from the analysis of reservoir water samples of wells in this section. The possibility of mass transfer of ore and organic material by pore waters, pressed from clay rocks with a high organic matter (OM) content under conditions of geodynamic loads, is confirmed by experimental studies on the compaction of oil shales (kukersites) and the separation of pore waters significantly enriched by TE [1].

Let us consider and estimate in greater detail the content of TE in black and combustible shales. Shales are rocks of mixed lithologic composition, consist of aleuritic and pelitic fractions, and contain schistose and a high content of OM. The permeability of shales, as a rule, is below 1 mD, with the minimum being 0.01-0.001 mD.

The calculated concentration coefficients (for the whole mass of Q_i and for the mineral matter, the ash Q_{iA}), representing the ratio of elemental content in shales to its Clarke (K) in clays, allow us to evaluate the processes of their concentration in shales [9]. Table 1 shows typomorphic elements (according to [4], these are the elements for which $Q_i > K$) in the shales of different regions (according to analytical data [5], etc.).

Table 1. Typomorphic elements of caustobioliths

| Caustobio-lytes | Typomorphic TE* | |
|-------------------|---------------------------------------|---|
| | On a dry weight basis $Q_i > 1.4$ | On a mineral matter basis (on the ashes) $Q_{iA} > 2.0$ |
| Coal | Au, Se, Hg, Re, Ge, As | Au, Se, Hg, Re, Ge , As, W, Mo, Be , (B, Pb), U, Ag, Gd |
| Combustible shale | Se, Hg, (Re, Cs), (Ce, Sc, Nb) | Se, Hg, (Re, Cs), Ce , Sc , Nb , Hf , B, Zn, (W, Ge) |
| Black shale | Re, Se, (Ag, Mo), Hg, (Cs, As, Au, U) | Re, Se, (Ag, Mo), Hg, (Cs, As, Au, U), (Zn, W, V), Ge |
| Oil | – | Hg, Mo, Se, V , Au, Ni , Ag, Cs, Zn, As, Co , U, Cu , Ga , Cr , Rb |

* Highlighted in bold are the TE that are typomorphic only for one type of caustobiolyte. The TE are shown in ascending order of Q_i and Q_{iA} .

Detailed averaged data for 36 TE given in Table 2 confirm the increased concentration of TE in shales (the content of many ore elements is higher than 100 ppm).

Table 2. Distribution of averaged TE content in mineral matter of shale

| An object | Concentration of TE in shales (by decades), ppm | | | | | | |
|-------------------|---|----------|------------|----------------------------------|--|--------------------------|-------|
| | < 0.01 | 0.01–0.1 | 0.1–1.0 | 1.0–10 | 10–100 | 100–1000 | >1000 |
| Black shale | Au | | Hg, Re, Ag | Ge, W, Be, U, Hf, Th, Sn, Cs, Se | Sc, Nb, Co, Ga, Pb, Y, Mo, As, La, Li, Cu, Ce, B, Rb, Ni, Cr | Zr, Sr, Zn, V, Mn, Ba | Ti |
| Combustible shale | Re, Au | Ag | Hg | Ge, Mo, W, Be, U, Hf, Th, Sn, Cs | As, Se, Sc, Nb, Co, Ga, Pb, Y, La, Cu, Li, Ni, Ce, Cr, Zn | Rb, Zr, B, V, Sr, Mn, Ba | Ti |

In Figure 2, using the Periodic Table of D.I. Mendeleev, the author presents a comparative average characteristic of the concentration of TE in on a mineral matter

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shale relative to Clarkes clay rocks. Four gradations of a statistical assessment are allocated. An analysis of these data emphasizes the wide diversity of the composition of TEs in shale plays. The group of elements enriching shale includes rock elements, iron groups, metallic, rare, metalloid, and radioactive.

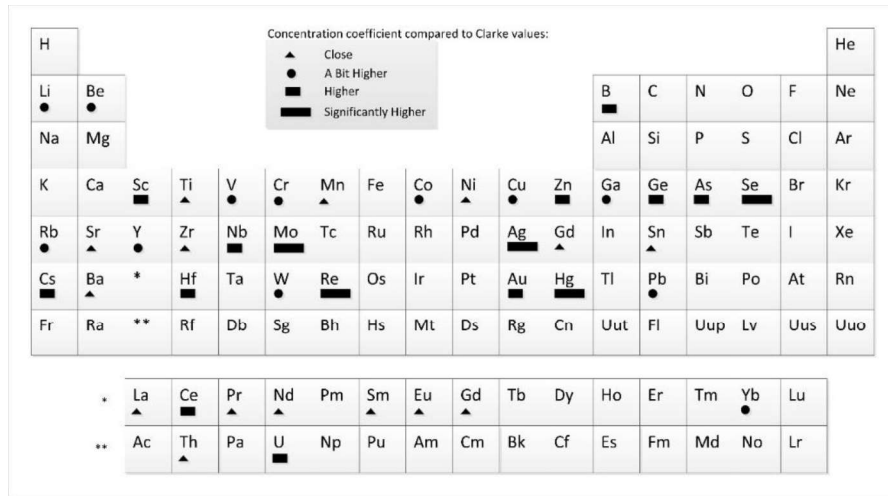


Fig. 2. Concentrations of elements in shales relative to Clarkes

Legend: Close ($Q_{IA}=0.6-1.4$); A Bit Higher ($Q_{IA}=1.4-2$); Higher ($Q_{IA}=2-5$); Significantly Higher ($Q_{IA}>5$)

The maximum enrichment values are characteristic of elements that are highly mobile in the Earth's crust (Hg, Se, Mo, As, Re, Ag, Sc, Ce, etc.). The enrichment values in some cases turn out to be similar to the concentrations of elements in ore deposits, which makes it possible to use shale conjunctly, i.e. as a potential source of a number of ore elements.

Different concentrations of elements in shales of various basins of the world are shown in Figure 3.

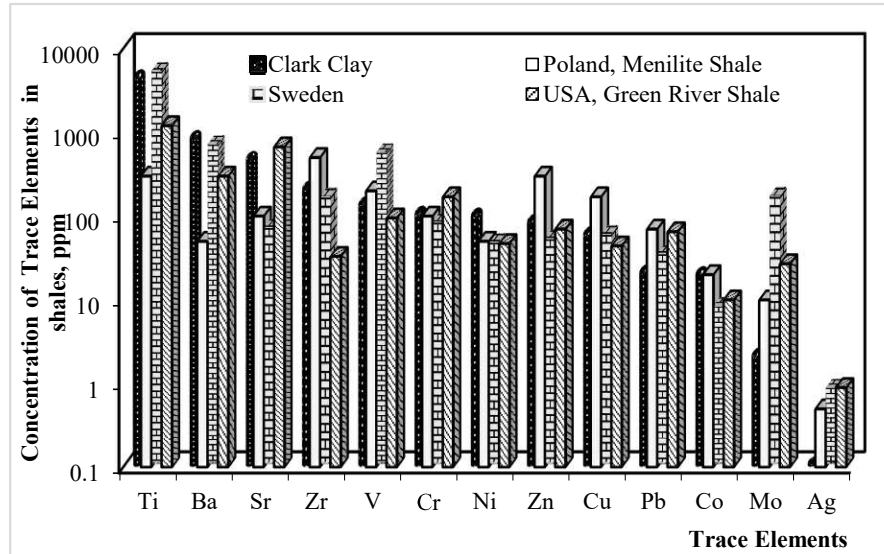


Fig. 3. Distribution of TE in shale of different regions (to analytical data [5], [3], [12]).

The contents of the following ore elements are higher than Clarkes of in shales: in menilite shales of the Polish Carpathians – Zr, Zn, Cu, Ag, Mo, V; in shale formations of Green River (USA) – Sr, Cr, Pb, Mo, Ag; Sweden’s Cambrian dictionemic shales – V, Pb, Mo, Ti, Ag. Analysis of the contents of a large group of TE in shale of the Barnett Formation (USA) also indicates high concentrations of a number of PTE in them: V, Ni, Rb, Fe, Ti. Data on high TE concentrations in the Bazhenov Formation of Western Siberia are also given (in ppm): Au (0.035–0.02), Pt (0.013–0.005), Ni (336.7, which is higher than the values for ordinary clay rocks by a factor of 5.3), Mo (264.5, higher by a factor of 9), Co (30.3, higher by a factor of 2.6), U (66.5), Th (5.0), and K (0.81). It should be kept in mind that the content of elements in the OM shale can be even higher. So, for example, in the Domanic deposits of the Volga-Ural bitumoids, the content of V reaches (ppm) – 1400-1700, and Ni – 1200 [9].

As can be seen from the above material, not all shales are equally rich in PTE. A comparison of TE concentrations in slates of different ages showed that it is impossible to reveal a clear correlation with the age of shale-bearing formations. This is due to the influence of other factors, namely: the facies type of deposits, the geostructural position of the shale basin, and sources of ablation. The maximum TE content of shale is often confined to platform formations (Domenic bituminous rocks of the Russian Platform, Bazhenov Formation of Western Siberia). However, some clay-shale formations of geosynclinal regions can also be enriched in TE (the Baisunsky deposit of Uzbekistan and Suzak shales of Tajikistan). This confinement of increased TE concentrations in caustobioliths is related to the fact that, in these

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basins or their parts, favorable opportunities were created for both syngenetic (with maximum manifestation of transport, resource, barrier, environment-forming, and other functions of living matter and OM) and epigenetic (temperature, hydrothermal, and geodynamic) accumulations of TE in the studied caustobioliths.

Data on the correlation between the TE composition of clays, coals, and oil shales with the chemical composition of the continental crust are presented in Table 3.

Table 3. The relationship of the ME composition of caustobioliths with the chemical composition of a number of geo-reservoirs.

| Clays and caustobioliths | Continental crust | | | Biota | | | |
|--------------------------|-------------------|-----------------|-----------------|-----------------|-------------|---------|-------------|
| | upper | middle | lower | plants | | animals | |
| | | | | marine | terrestrial | marine | terrestrial |
| Clay | *0.90 /41 | 0.85/40 | 0.83/41 | 0.77 /28 | 0.72/29 | 0.53/23 | 0.46/28 |
| Coal | 0.84 /41 | 0.76/40 | 0.78/41 | 0.78 /28 | 0.71/29 | 0.48/23 | 0.50/28 |
| Black shale | 0.82/41 | 0.84 /40 | 0.80/41 | 0.78 /28 | 0.75/29 | 0.57/23 | 0.56/28 |
| Comb. shale | 0.84 /35 | 0.76/34 | 0.79/35 | 0.76 /28 | 0.74/29 | 0.54/23 | 0.55/28 |
| Oil (average) | 0.60/37 | 0.58/36 | 0.63 /37 | 0.61 /26 | 0.58/29 | 0.59/24 | 0.54/28 |

* The value of the correlation coefficient / the number of used values of the logarithms of element concentration; the maximum values in a row are marked in bold

Calculations of the correlation coefficients (r) between the logarithms of the average TE contents [8] show a closer relationship between the TE composition of clays, coals, oil shales (obviously upper crustal formations), and the TE composition of the upper continental crust (r = 0.84-0.90) compared to the TE composition of the lower continental crust (r = 0.79-0.83). The TE composition of black shales has a more notable relationship with the TE composition of the middle crust (r = 0.84). The formation and reformation of black shales takes place at great depths (unlike the formation of oil shales) and over a longer period of geological time. Therefore, the effect of deep penetrations with a set of so-called deep TEs is more likely. In contrast, the TE content in oils is more closely correlated with the TE composition of the lower continental crust (r = 0.63) compared with the upper (r = 0.60) and middle (0.58) ones. Moreover, the correlations obtained for the average TE of the oil composition with the crust composition turn out to be significantly lower than the correlations for clays, coals, and shales, which indicates the greater complexity and possible polygenicity of the formation of its TE composition. High correlation dependencies are revealed between TE compositions of caustobioliths and biota of various origin. The maximum figures (up to 0.78) are characteristic of the relationship between the TE composition of caustobioliths and the TE composition of marine plants. The correlation results indicate that deep components play an important role in the genesis of HC.

CONCLUSION

This research considered the content of TE, including PTE (V, Ni, Mo, Co, Cd, As, Hg, Cr, U, etc.) in shale plays and deposits in various regions of the world (Breznikskoye, Pirinskoye, Borovdolskoye, Radomirskoye in Bulgaria; Barnett Formations, Green River in USA; Meniliths in Ukraine and Poland; Bazhenites in Western Siberia; Domanikits in Volgo-Ural region of Russia; Narke in Sweden). Some of those concentrations significantly exceeded Clarke contents. For example, Bulgaria shales are very rich in Mo and U. Uranium content can reach values from 28.5 to 50 ppm. The correlation of TE content between shales (combustible and black) and the upper continental crust was found to be higher than between shales and the lower continental crust. Hence, the author concludes that the TE composition of shale rocks has received greater contribution from the matrix of the OM of sedimentary rocks than from the deep zones of the earth's crust. About 15–20% of the extracted HC contain PTE in the amounts that exceed their safe levels, and the production volumes continue to increase over the years. The most migratory and volatile of them are Hg, Cd, and As. V, Ni, Co, Cr, Cu, Zn are strongly chemically bonded in complex organometallic compounds in HC but toxic in the micro-dispersed state after technogenic impact on the HC. Actinides, regardless of bond strength with the molecular structures of HC, are actively dangerous in any state.

Thus, the development of shale formations via horizontal drilling, with the use of hydraulic fracturing in order to improve economic indicators, remains a priority worldwide. However, with all the aforementioned advantages in the development of shale deposits by this method, it is necessary to take into account the adverse environmental effects of the high concentrations of PTE (V, Ni, Mo, Zn, U, Hg, As, etc.) in shales and oils due to their possible release into the environment. In the development of an integrated technology for the processing of shale with the recovery of gas, oil, and metals, additional studies are required for evaluating the trace element composition of both shale deposits and their naphthide components in order to avoid negative environmental consequences.

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