IOP Conf. Series: Earth and Environmental Science **272** (2019) 022004 doi:10.1088/1755-1315/272/2/022004

Scanning Electron Microscopy Study of Drilling Cuttings in Tomsk Oblast Sites

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Abstract. The research is focused on determining mineralogical composition of drilling cuttings by scanning electron microscope as well as imaging the sample surface of high resolution that allows studying the structural characteristics of the site. In addition, a number of other techniques permit obtaining information on chemical composition of sample in near-surface layers. The study in drilling cuttings by means of scanning microscopy has revealed the presence of titanium, iron, zirconium oxides, iron sulphide, barium sulphate. The former is a mineral that concentrates rare-earth elements, presumably monocyte, as well as uranium silicate, etc. The results obtained confirm the data of previous X-ray structural analysis, i.e. the study samples consist of alumosilicate matrix. Apart from silicon and aluminium oxides, the matrix includes such elements as Na, K, Mg. Such a composition corresponds to rock-forming minerals: quartz, albite, microcline, clinochlore, muscovite, anorthoclase.

1. Introduction

A large amount of waste is generated because of oil production activities, among them are drill cuttings and used drilling mud. However, the bulk of the waste comprises mostly the drill cuttings that are extracted from the well to the surface. Millions of tons of drill cuttings are annually stored in the territory of Western Siberia [15]. The amount of drilled wells increases every year, more than 70% of which are located in ecologically vulnerable areas with unfavorable climatic and soil-landscape conditions [16]. It is stated that the quality of the environment is degraded in the areas of drilling operations due to drilling waste production [9, 13, 16, 18].

Drilling operations have a significant anthropogenic impact on all components of the environment. Disposal of drilling wastes is the main cause of deterioration of the environment in the areas of drilling operations [13].

When developing oil fields and drilling oil wells a large quantity of cuttings are produced. Due to its diverse composition, a part of its elements has a direct impact on the environment [1, 2, 8-11, 20]. Composition of drilling cuttings is rather various and depends on geological conditions, technical processes of mud cleaning as well as drilling intervals [4, 5]. Drilling cuttings produced in drilling wells can contain up to 7.5 % of oil and up to 15 % of organic chemicals applied in drilling fluids [19]. Drilling cuttings contain a large amount of heavy metals [3, 12, 14, 17].

In the course of oil field exploration and development, rock and waste samples are collected to determine content of valuable substances or study the composition of the samples and their processing

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properties. Having analyzed the production wastes one can develop an optimal technique disposal or recycling of drill cuttings.

In previous studies, there is no detailed description of the mineral and elemental composition of drill cuttings. The present article is aimed at study in the composition of drill cuttings of oil fields in Western Siberia.

2. Methods and materials

The initial materials were samples of drilling cutting from four oil fields of Tomsk Oblast – Pervomayskoye, Katyl'ginskoye, Yuzhno-Cheremshanskoye, Luginetskoye.

X-ray structural analysis of drilling cutting samples was performed in the International Innovative Research Education Center (IIREC) "Uranium Geology", Department of Geoecology and Geochemistry, Tomsk Polytechnic University: diffractometer Bruker D2 Phaser. The samples were studied in IIREC "Uranium Geology", Department of Geoecology and Geochemistry, Tomsk Polytechnic University using scanning electron microscope (SEM) HitachiS-3400N with EDS BrukerXFlash 4010.

3. Results and discussion

The X-ray structural analysis of drilling cutting (DC) samples has revealed quartz, muscovite, and albite in every sample. Quartz and muscovite provide the maximum share in DC composition. The presence of such a mineral association in all drilling cutting samples demonstrates similar composition of initial host rocks. Besides, there are some minerals typical for definite fields, for example, illite was found in Pervomayskoye oil field, kaolinite and anorthoclase were identified when studying Luginetskoye oil field. The results obtained are presented in Fig. 1.

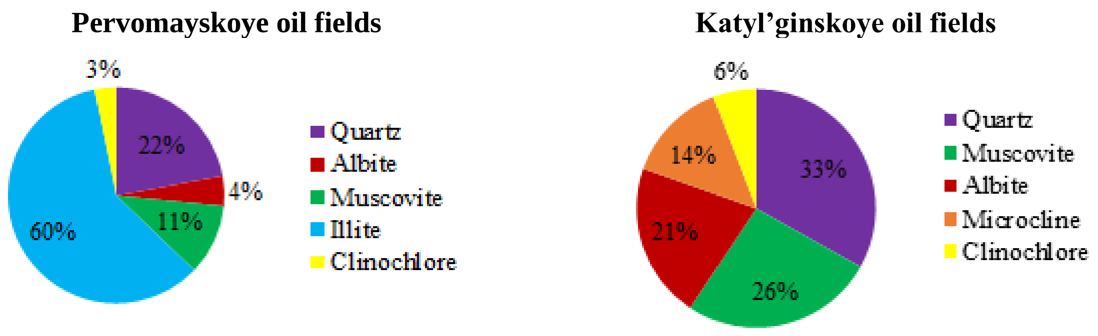

Figure 1. The results of X-ray structural analysis of drilling cutting samples from Pervomayskoye and Katyl'ginskoye oil fields.

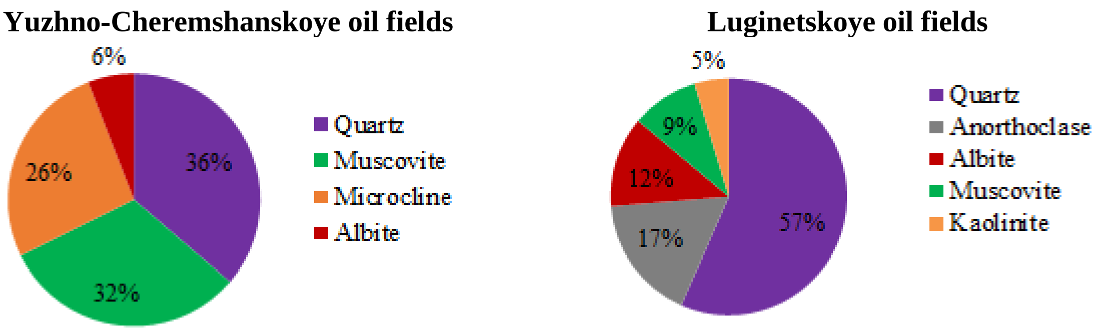

Figure 2. The results of X-ray structural analysis of drilling cutting samples from Yuzhno-Cheremshanskoye and Luginetskoye oil fields

As shown by X-ray structural analysis, the composition of studied drilling cutting includes rock-forming minerals, such as quartz, albite, muscovite, microcline, clinochlore.

The microscopy is of particular interest for studying chemical composition. It allows not only revealing individual substance by registering their size, but also obtaining its image.

Using scanning electron microscope, the drilling cuttings of the Tomsk Oblast oil fields – Pervomayskoye, Katyl'ginskoye and Yuzhno-Cheremshanskoye – has been analysed.

In the course of investigation, the mineral spectral data were collected and the images were made with back-scattered electron, which provided the following results:

The analysis of DC from Pervomayskoye oil field revealed the minerals: among the alumosilicate matrix there are different modifications of pyrite, galena, lead silicates as well as uranium silicate - coffinite.

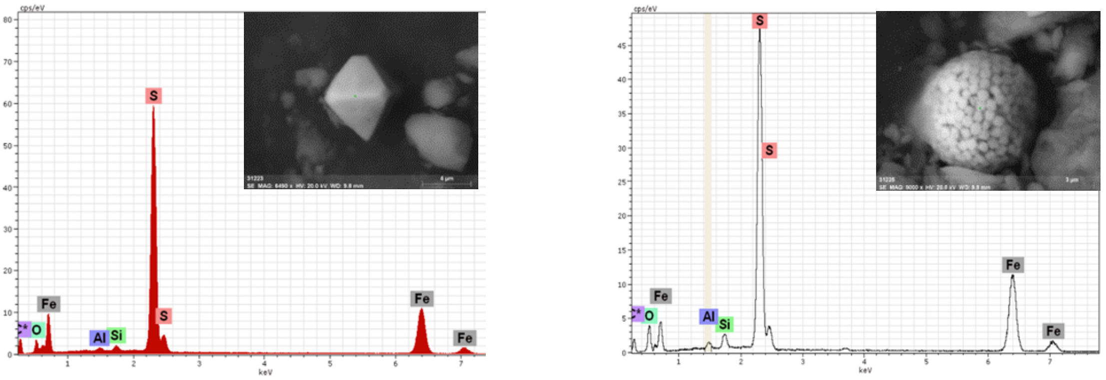

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Figure 3. Back-scattered electron images and spectra of iron-containing particles (pyrite (?)), the size of the first sample is 6.4 μm; that of the second sample is 12μm.

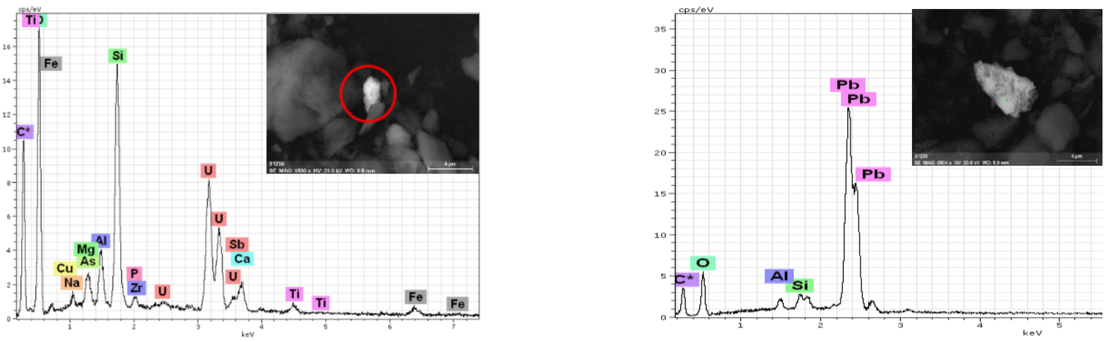

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Figure 4. Back-scattered electron images and spectrum of inclusion – coffinite (?), 4μm in size; 2 - Back-scattered electron images and spectrum of lead-containing particle – lead oxide, 6.7μm in size.

Besides, in the alumosilicate matrix (Fig.4.1) U – containing particle was revealed, its spectrum of chemical elements corresponds to uranium silicate (coffinite (?)), in composition of which there is high content of uranium, oxygen, and silicon. The DC samples from Pervomayskoye oil field often contain inclusions, the spectrum of which matches pyrite mineral of different forms, but with pronounced cubic syngony (Fig. 3). In addition, there are lead-containing particles (Fig. 4.2). The elements in the sample – arsenic and lead found by electron microscope are supported by chemical analysis carried out before.

It should be noted that the matrix includes such elements as Na, Mg, Fe, K excluding silicon and aluminium oxides. Such a composition corresponds to the rock-forming minerals – illite and albite determined by previous X-ray structural diffraction analysis. The size of found mineral phases ranges from 4 to 12 µm.

The studied Katyl’ginskoye oil field is located closer to Pervomayskoye than the other oil fields. Back-scattered electron images showed that DC sample from that oil field contains the following mineral spectra: barite, pyrite, hematite, and almandine. The size of revealed mineral phases ranges from 0.8 to 15 µm.

The DC samples from Yuzhno-Cheremshanskoye oil field are the most remote from the first two oil fields.

The collected spectral data on minerals and images have shown the presence of the following minerals: zircon, baryte, hematite, muscovite, pseudorutile, ilmenite, and monocyte. The size of found mineral phases ranges from 2.5 to 160 µm.

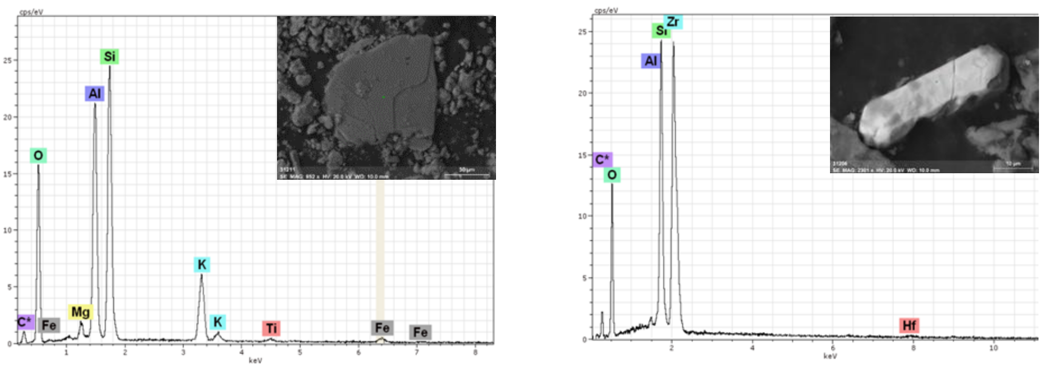

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Figure 5. Back-scattered electron images and spectrum of the particle (muscovite (?)), of 93 µm in size; 2 - Back-scattered electron images and spectrum of Zr-containing particle (zircon (?)), of 160 µm in size.

The sample contains particles (Fig. 5.1), the spectrum and external parameters of which coincide with mica – muscovite, which is conformed by the data of X-ray diffraction analysis, the given mineral belonging to the rock-forming ones. Furthermore, the studies of DC sample revealed the particle corresponding to crystal of zircon (Fig. 5.2).

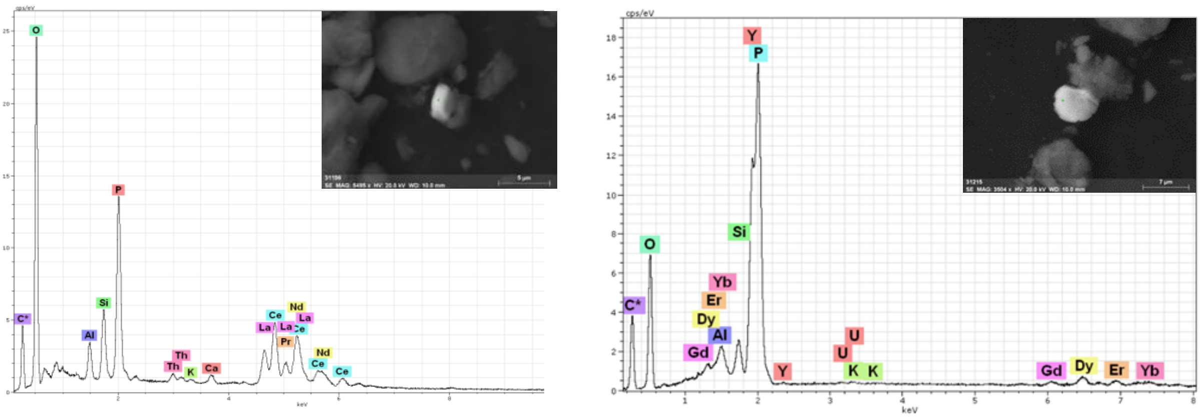

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Figure 6. Back-scattered electron images and spectrum of rare-earth containing particles (monocyte (?)) of 5 µm; 2 - Back-scattered electron images and spectrum of yttrium phosphate inclusions (xenotime (?)) of 7 µm.

The analysis has revealed the particle, the spectra of which coincide with the minerals – ilmenite and pseudorutile. Pseudorutile is distingushed by high content of titanium with respect to iron.

The determined particle (Fig. 6.1) contains rare-earth elements, which is well seen from the spectrum. In the sample (Fig. 6.2) the particle, the spectrum and external parameters of which correspond to yttrium phosphate (xenotime (?)), is found. The inferred mineral often associates with monocyte and zircon and contains rare-earths.

On the whole, one may say that DS sample from Yuzhno-Cheremshanskoye oil field is characterized by high content of Ti, Al, Ba, Zr, which is confirmed by the previous chemical analysis. Apart from SiO_2 and Al, the alumosilicate matrix includes such elements as Na and K. Such a composition corresponds to the rock-forming mineral - albite, microcline, muscovite previously determined by X-ray structural diffraction analysis.

Above all, the DC sample from Luginetskoye oil field was analysed. The oil field is located on the borders of Kargasok and Parabel regions.

The back-scattered electron images and spectra of inclusions found in the sample coincide with such minerals as: pyrite (?), hematite (?), almandine (?), ilmenite (?), chamosite (?), pseudorutile (?), rutile (?), zircon (?), monocyte (?), baryte (?). Moreover, the sample analysis revealed Cu-Zn-containing particle, this is Cu-Zn association, the ratio 2:1 corresponding to brass.

4. Conclusion

Determination of mineral composition using scanning electron microscope and X-ray structural analysis has shown the presence of minerals, in composition of which there are the following elements: As, Pb, Ba, Fe, Ti, Zr, Mn. It was supported by atomic emission analysis of drilling cutting samples.

The results of scanning electron microscopy confirm the data of previous X-ray structural analysis – the studied samples consist of alumosilicate matrix. In addition to silicon and aluminium oxides, the matrix includes such elements as Na, K, Mg. This composition corresponds to rock-forming minerals - quartz, albite, microcline, clinochlore, muscovite, and anorthoclase [6].

Studying drilling cutting samples by scanning electron microscope the accessory minerals were revealed. The presence of titanium oxides, detrital zircon with well-preserved crystal forms was determined. Besides the mineral that accumulates rare-earth elements was found, presumably monocyte (Ce, La, Nd, Th) PO_4.

Mineral iron phases were found everywhere. Iron was observed in association with sulfur forming iron sulphide – presumably, pyrite. The inferred mineral occurs as well-formed crystals. There are different mineral aggregates: cubic, octahedral crystal of pyrite, globular pyrite, framboidal pyrite but with c pronounced cubic syngony.

In addition to iron sulphide there are iron oxides, presumably, hematite. The minerals of the studied drilling cutting samples are composed of barium formations with sulfur suggesting that it is barite.

Studying the drilling cuttings from Pervomayskoye oil field the mineral phases of lead were found. Besides, U – containing particle, presumably, coffinite – uranium silicate was identified.

In DC sample from Yuzhno-Cheremshanskoye oil field the particles were found, spectrum and external parameters of which correspond to yttrium phosphate – xenotime. The given mineral occurs in association with monocyte and zircon which is supported by found mineral phases.

Drilling cuttings from Luginetskoye oil field are distinguished by presence of mineral phases of zinc: Zn is found in reaction with Cu, in ratio 2:1. In view of this, one can suggest that it is brass.

Hence, high concentrations of some elements revealed by atomic emission analysis find their confirmation in study of DC samples from Tomsk Oblast oil fields under electron microscope. A number of chemical elements - Fe, S, Ba, Ti, Zr, U and rare earth elements form their own mineral forms.

As a result of conducted study the data on mineralogical and chemical composition of drilling cutting samples were obtained from Tomsk Oblast oil fields, as well as the results of previous research using atomic emission spectrometry and X-ray structural analysis were confirmed [6, 7].

It should be noted that scanning electron microscopy in combination with X-ray structural analysis and X-ray diffraction analysis is complementary.

5. References

[1] Bobra A M, Shiu W Y, Mackay D 1984 Structure-activity relationships for toxicity of hydrocarbons, chlorinated hydrocarbons and oils to Daphnia magna Ed. Kaiser K.L.E. Dordrecht *Quantitative structure activity relations in environmental toxicology* (Germany: D. Reidel Publishing Co.) pp 3–16
[2] Borovsky N A 1990 Change of hydrochemical indices of water in contact with the drilling components *Gazovaya promyshlennost'* vol 6 pp 30–38
[3] Breuer E, Stevenson A G, Howe J A, Carroll J 2004 Drill cutting accumulations in the Northern and Central North Sea: a review of environmental interactions and chemical fate *Marine Pollution Bulletin* vol 48 pp 12–25
[4] Bulatov A I, Makarenko P P, Proselkov Yu M 1999 Burovye promyvochnye i tamponazhnye rastvory *Moscow: Izdatelstvo nedra* p 424
[5] Khusnutdinov I Sh, Safiulina A G, Zabborov R R 2015 Metody utilizacii neftyanyx shlamov *Izvestiya vysshix uchebnyx zavedenij* vol 58(10) pp 3–10
[6] Klimova (Mekh) A A 2017 Izuchenie burovogo shlama s ispolzovaniem skaniruyushhej elektronnoj mikroskopii na primere obektov tomskoj oblasti *Problemy geologii i osvoeniya nedr: sbornik nauchnyx trudov* (Tomsk: Izdatelstvo TPU) pp 784–785
[7] Klimova (Mekh) A A 2017 Kompleksnaya ekologo-geoximicheskaya ocenka burovyx shlamov neftyanyx mestorozhdenij tomskoj oblasti *Problemy nedropolzovaniya: sbornik nauchnyx trudov* (Russia: Sankt-Peterburg) p 174
[8] Mishunina A S, Klimova A A, Yazikov E G 2017 The effect of drilling waste on Water Resources – the elemental composition of Waste *Key Engineering Materials* vol 743 pp 338–341
[9] Krysa V V, Malyshkin M M 2013 Metodika opredeleniya klassa opasnosti solenyx burovyx shlamov *Zapiski gornogo institute* (Russia: Sankt-Peterburg) pp 50–54
[10] Kryuchkov V N, Kurapov A A 2012 Ocenka vliyaniya otxodov bureniya na gidrobiontov *Vestnik Astraxanskogo gosudarstvennogo texnicheskogo universiteta* vol 1 pp 61–65
[11] Kryuchkov V N, Kurapov A A 2012 Assessing the impact of drilling waste on aquatic organisms *Vestnik Astrakhanskogo gosudarstvennogo tekhnicheskogo universiteta* vol 1 pp 60–65
[12] Minigazimov N S, Minigazimov R Sh 2014 Novaya informaciya o toksichnosti neftesoderzhashhix otxodov *Uralskij ekologicheskij vestnik* vol 2 pp 31–36
[13] Nexorosheva A V, Kirzhakov I F, Avdeeva I I, Axmedzhanov R R 2015 Ocenka citotoksichnosti obrazcov burovogo shlama, sobrannyx na territorii ambara, v prirodnyx usloviyax XMAO-Yugry *Izvestiya Samarskogo nauchnogo centra Rossijskoj akademii nauk* vol 17 N 5 pp 690–694
[14] Okpokwasili G C, Nnubia C 1995 Effects of drilling fluids on marine bacteria from a Nigerian offshore oilfield *Environmental Management* vol 19 **6** pp 923–929
[15] Pashkevich M A, Kulikova M A 2013 Ekologicheskij monitoring: uchebnoe posobie. Sankt-Peterburg. P. 100 (in Russian).
[16] Pashkevich M A, Pashkevich M A, Gvozdeckaya M V 2013 Razrabotka metodologii monitoringa ekologicheskoj opasnosti otxodov bureniya *Gornyj informacionno-analiticheskij byulleten* vol 10 pp. 314–317
[17] Pasko O A, Posternak T S 2015Determination of drill cuttings hazard class and toxicity by means of phytotesting *International Journal of Engineering Science and Innovative Technology (IJESIT)* vol 4 pp 63–66
[18] Pichugin E A, Shenfeld B E 2017 K voprosu razlichiya burovyx i neftyanyx shlamov *Ekologiya i promyshlennost' Rossii* vol 21 (7) pp 14–19

[19] Pikovskij Yu I, Ismailov N M, Doroxova M F, 2015 Osnovy neftegazovoj geoekologii: Uchebnoe posobie (Moscow: INFRA-M) p 400
[20] Volchenko N N, Karaseva E V 2006 Skrining uglevodorodokislyayushhix bakterij – producentov poverxnostno-aktivnyx veshhestv biologicheskoj prirody i ix primenenie v opyte po remediacii neftezagryaznennoj pochvy i nefteshlama *Biotexnologiya* vol 2 p 57– 62