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The Assessment of the Level of Pollution of Slime Pits with **Heavy Metals**

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Abstract. In drilling and running oil and gas wells the great amount of toxic waste is formed and in the surface of the lithosphere and hydrosphere the great amount of different chemical elements and compounds access, they are needed to be isolated from the environment. The most useful way of isolation is their utilization in the slime pits on the wells territory. Heavy metals are dangerous waste in the drilling slime; they accumulate in soil and under some conditions they in form water-soluble parts and migrate in to the soil. The aim of this paper is to organize the chemical and analytical research of the amount of heavy metals in the drilling slime, and research the mechanism of their spreading on different depth and square in the slime pits typical for the oil site placed in KHANTY-Ugra.

Introduction

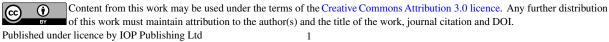
The intensiveness development of the mineral-material complex leads to the annual growth of the drilling volume first of all it is connected with searching and prospecting of the mineral resources in the production of liquid, gaseous and mature mineral resources in the bore hole use.

The borehole drilling influence negatively on the engineering and on all the components of the environment. The most dangerous and negative influence is subjected on the natural eco-system, where is the storage of the drilling waste; the imperfective aspect of the drilling technologies and utilization of the drilling sludge. The placement of the drilling objects (in the environment) containing toxic substances in the environment – is the main reason for the deterioration of the environment on the drilling territories.

On the territories on the West Siberia for a meter of the drilling work form approximately 0.2 -0.6 m³ of the drilling sludge. The less index is marked with the technologies with high recycling degree. For the 2000 meters' wells, the volume of the drilling sludge in the West Siberia is 500 m³ in average [3].

Therefore, on the great volume of the drilling sludge storage on the territory of Russian Federation and their ecological danger to the environment, till now, there are no any effective technological resolutions on their utilization. That's why it is essential to take the complex quantative mark on the negative influence of the drilling sludge on the environment and work new methods of utilization and prevention out and using drilling sludge.

The drilling sludge waste are the most dangerous for the objects of the environment, they keep and store on the territories of the bore-holes, as a rule, in the foundation pits-slime ponds, organized in the mineral or earth banks. As a rule, while designing 5 types of slime pits are foreseen with the general volume of 1000 m³ for the drilling sludge, for collecting the drilling sewage; for collecting the fluide formation; for collecting household sewage; for the water sediment placed near the water scoop; for the horizontal outer flame [6].



The waste consists of the wide range of deposits of mineral and organic origin, presented by the materials and chemical reagents, used for the preparation and working chemical treatment for drilling solutions.

The drilling solutions, in their turn, are of water state and consist of 85 - 89 % bentonite clay -10-11 %. The last 1-5 % may consist of different libricative, antiseptic, foam suppressor, anti-filtrate and hydrophobizing liquids [1].

If the hydro-isolation of the bottom and the walls of the slime pit poor, the pollution of the territories takes place. According to the bio-testing results, the drilling waste belongs to the IV class dangerous compounds [5]. The waste keeping in slime pits depend on the technological drilling features and the compound rock in the bottom in the area of slime pits the high concentration of chloride, oil products and heavy metals: Cd, Pb, Zn, Cr and others are mentioned.

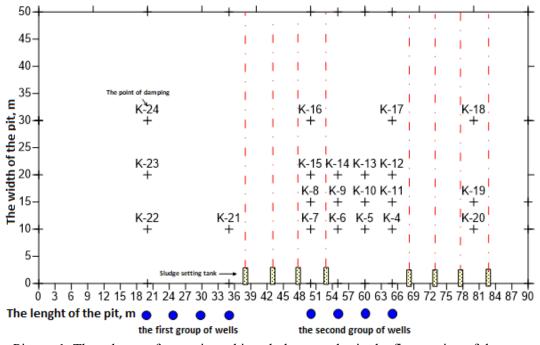
The objects and the research methods

The test specimens of the drilling slime were chosen as the objects for researching from the typical field in KHANTY-Ugra. The test specimens were taken in winter.

The researching pit of the first site section of the following size: 90 m length and 50 m width. The depth of the slime pit was 350 sm. The power of the waste was 280 - 290 sm. The width of the ice in the pit was 70 sm. The depth of the testing level at the time of taking samples was between 80 - 150 sm from the one side and between 80 - 90 sm from the other side.

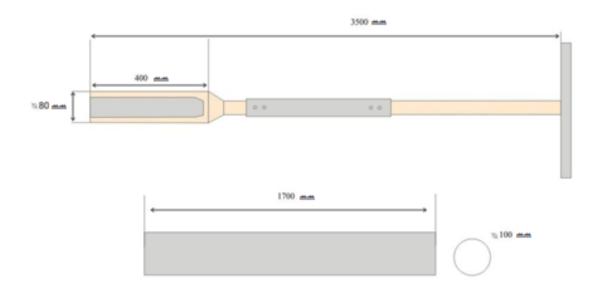
During the drilling the slime disposal to the pit occurred on the sludge setting tank at a distance of 3 - 6 meters of the edge diking of the pit and at 5 - 7 meters height from the bottom.

On the field the cluster's pit consists of 3 sections. Production oil wells are drilled in groups of 4 wells. The distance between the wells in groups -5 m, between wells' groups -15 m. The collection of the drilling sludge occurs on the right part of the pit. The first point of dumping of the 1 group, the first well is at a distance of 38 m from the left edge of the clusters' pit (picture 1).



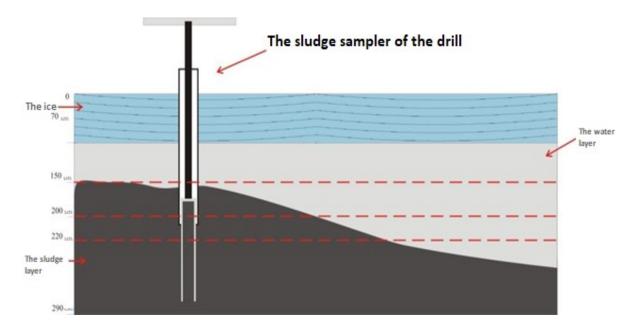
Picture 1. The scheme of screening taking sludge samples in the first section of the cluster`s pit № 12

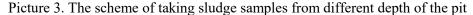
The slime samples were taken by the self-constructed sampler. The construction of the sampler allowed taking samples of different opportunities forming them according to the depth, keeping structural features of the sludge, its different features (picture 2).



Picture 2. The sampler of the sludge

All in all, from the first pit were taken 152 sludge samples out of the 21st point. The general scheme of taking sludge samples at different depth of the pit is given on the picture 3.





The sludge sample was air-dried, freed from different parts, rubbed to power and winnowed it. Then it was weighed and mixed with bi-distilled water for 30 minutes, and then it was filtered.

The extraction of the mobile metal forms was done by the acetate-ammonium buffering solution with pH 4.8. From the extract of the solution the alloy quote was taken. For each part of the experiment the testing probe was prepared, which was lead through for each part of the experiment, the test probe was prepared and it had been done during the procedure of the analysis, it was taken into the account at the final element calculation in the probes. In each probe the scandium solution was added (1 mg/gr) for the calculation of the matrix influence and the drift of the instrument.

The determination of the volume of Ni, Cu, Pb, Zn, Mn was done by the atom-emission method of spectrometry with the inductance connected plasma on the Optima 2000 DV (Perkin Elmer Instruments, USA).

Results and discussion

The results of the quantative chemical analysis of the sludge probes in comparison with the positive concentrations (MPC – maximum-permissible concentration, APC – approximate-permissible concentration) general content of the heavy metals in the soils, given in the table 1. The general characteristics of MPC and APC are given according to the HS 2.1.7.2041-06 and HS 2.1.7.2042-06. In all probes the volume of the heavy metals prevailed the characteristic of MPC.

The code of the point	Ni, mg/kg	Pb, mg/kg	Cu, mg/kg	Mn, g/kg	Zn, mg/kg
К-4	22.9	15.2	22.9	1.1	41.5
К-7	25.0	16.9	65.4	1.2	320.4
К-8	19.2	100.8	85.5	0.7	406.4
К-12	22.1	60.4	61.3	0.8	296.2
К-15	33.0	47.9	40.6	0.9	114.0
К-16	23.3	34.5	35.6	0.7	119.6
К-17	25.0	43.9	50.7	0.8	216.8
К-18	18.8	32.1	68.2	0.8	366.6
К-20	25.1	77.7	51.2	1.1	267.6
К-22	16.0	39.8	18.9	0.4	55.4
К-23	21.5	38.4	28.7	0.7	98.0
К-24	20.1	22.3	23.7	0.9	61.5
Average	22.9	50.5	49.7	0.9	219.9
MPC the mobile form, mg/kg	4.0	6.0	3.0	80 mg/kg	23.0
APC the general content	80.0	130.0	132.0		220.0

Table 1. Contents of heavy metals in sludge probes

The volume of the Cu in the analyzed probes is being changed widely and give rise to oscillations on the pit's square in 3.5 - 8 times. Maximum concentrations are mentioned on the right-side of the pit in the middle and upper layers. It can speak of the fact, that the main source of Cu and other elements are the mountain rock. The main sources of Cu are sulphide ores and cooper sandstones. 200 minerals consist of cooper. In waters the cooper contents consist of approximately from several milligrams or to few tens of milligrams to the litre. Cooper is a strong complex element and can occlude to the weighted substance by the absorption on the hydroxides' metal surface (Fe, Al, Mn), the ionic exchange with the clay minerals and the interaction with other high-molecular connections on the surface of the weighted particles [12].

The high concentration of manganese on the square of the pit is firstly explained by the regional specific feature of KHANTY-Ugra – the high excess abundance of manganese in the rock. But even with the high concentration of manganese, its maximum quantity is marked in the places of sludge dumping to the pit.

The main sources of manganese coming to the surface waters are the iron-manganese ores and some other minerals and many other sources (sewage from the on riched plants, metallurgical factories and other chemical plants). The great amount of manganese is formed as a result of disappearing of living beings the migrations abilities of manganese depends on many factors, such as the reductionoxidation situation, pH, complex substances, the intensity of the absorption processes on the weighted particles.

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The greatest Zn concentrations are mentioned in the middle and in the upper layer in the right side of the pit. Hypothetically, Zn transition is mostly the result of the natural agents – sedimentary rocks and mineral bed waters. Secondly, in some cases, in dominated sources is the managing man's activity. The greatest Zn part is in the water – aqueous solution and its solubility grows with the growth of pH. The main place in its migration takes its complex compounds. The sorption processes are typical for Zn especially on clay particles, Fe, Al hydroxide, silicate minerals.

The greatest Pb concentration is in the upper and middle layer, of dumping sludge in the pit. The difference in the concentration in these layers is in the $14 - 20^{\text{th}}$ times. In nature Pb is met in the endogenic and exogenic minerals. The dissolution of these minerals is one of the Pb sources in the surface waters. Buy now the main source is the anthropogenic sources. The Pb content in clean waters can be from the decimal part to the few milligrams in the litre. The Pb solubility depends on pH and is greatly dropped in the alkaline solutions. It is typical for Pb to have the high ability to form complex connection and the absorption based on the metal hydroxide and clay particles [12].

The Ni content is quiet enough on the square of the pit and on its depth. The difference in concentration is twice. Ni is met in nature mainly in the arsenic connections or sulphur connections. The nickel concentration in surface waters is from the milligram parts to 10 - 20 milligram in the litre. Ni contents are rich in waters with Ni rock. The main Ni source is the people's activity (chemical plants, burning of the fuels). Among heavy metals, Ni is characterized as the metal with the middle complex its greatest part is migrated in the weighted state [12].

Conclusion

The result of the experiment is the following: the drilling sludge in the pit have marked nonheterogeneous allocation of the heavy metals. As a rule, maximum concentrations of the toxic elements in the pit are in the places of the sludge dumping from the deep horizonts with gradual lowering of the concentrations the further one gets from these points. The left part of the pit the drilling consists of much less heavy metals. The deep layer of the drilling sludge in this part is less. Both effects are explained by the fact that the sludge extracted during the drilling the first group wells` conductors, firstly spreading uniformly in the pit and form the outcome layer in the left side of the pit. The conductors` sludge has low concentration of the heavy metals.

Taking account of the non-heterogeneous allocation of the pollution in the pit, it is recommended to use slightly polluted drilling sludge from the left part of the pit (mainly out of conductors' drilling) for the preparation of the disposal mixture with sand and peat. The remained part of the sludge is useful to reduce using the method of forming or mix non- polluted or more polluted layers before preparing the solid mixture. It is necessary to test the out coming content of the heavy metals for the ecological safety of putting sludge waste in the environment, soil.

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