Environmental safety estimation of drill cuttings using a composition mixture based on zeolite

A I Agoshkov, M O Tretyakova, I V Moskovaia and T A Brusentsova

Engineering school, Far Eastern Federal University, 8, Sukhanova Str., Vladivostok, 690091, Russia
E-mail: bgdtsdvfu@mail.ru

Abstract. Drill cuttings is a complex mixture of spent drilling mud with various additives having different chemical properties and drilled solids, and which significantly pollutes the environment when it is buried. This article proposes and studies a zeolite-based composite mixture that converts drill cuttings into environmentally friendly soil. As a result of the experiment, samples of model drill cuttings and soil with different holding times are obtained. A sequential extraction method is used to determine the degree of metal desorption in a laboratory study of samples. The analysis consists of an estimation of metals content (gross form and extracts in 3 extractants), the content of petroleum products and pH value. Concentrations of metals in both gross and mobile form in the processed drill cuttings have significantly decreased in comparison with the original drill cuttings, and do not exceed standard values. Also, oil concentration in the soil is lower than in the drill cuttings. pH reaction has decreased from alkaline to neutral. The proposed zeolite-containing composite mixture allows implementing drill cuttings as a new, sustainable in the environment, useful product.

1. Introduction
Oil production is a complex process consisting of several basic technological operations, such as exploration, well drilling, oil production itself and transportation. Each of these operations is accompanied by a colossal negative impact on the environment.

One of the main problems is the formation of significant amounts of toxic drill cuttings (DC). On average, DC consists of 30–45 % of drilled solids (particles of clay and sand), 30–45 % of drilling mud, and 10–20 % of groundwater and oil [1]. All drilling muds (DM) can be divided into 3 groups: water, hydrocarbon and synthetic. The most dangerous for the environment are hydrocarbon-based DM [2–3], an important component of which is a dispersion medium [4–5] represented by diesel fuel which has a high phytotoxicity [6]. The following are used as additives for DM: corrosion inhibitors, anti-foam additives, emulsifiers, flocculants, lubricating compounds, SAA, dispersing agents, thickeners, weighting agents, etc. [7]. Thus, DM is a multicomponent liquid, and the mutual influence of the components on each other further enhances the toxic effect of each of them.

“Lebedinskoe” oil field in northern Sakhalin, Russia was selected for the study. Drilling invert-emulsion solution based on hydrocarbon with the addition of weighting agent, thickener and stabilizer is used for drilling.

A variety of methods, such as thermal, physical, biological, and physico-chemical methods are used to process DC [8–10]. In world practice, the most commonly used thermal method is incineration, which is inefficient for the removal of heavy metals, as well as when the content of petroleum products in DC
is more than 16% [9, 11]. This process is accompanied by the release of pollutants, and the resulting burned-out soil has not found further application. The physical methods are based on the processes of mixing and physical separation. Physical methods are not applicable to DC, if they contain nonvolatile and dense resins and asphaltenes [11]. The most environmentally friendly physical method is “reinjection” – pumping DC into the inner annulus or into a specially drilled well. The disadvantage is the presence of a receiving layer, waterproof layers above and below the receiving layer, there is a risk of emergency situations. Biological methods involve the addition of microorganisms to waste [10]. Application area is limited to the conditions: range of biological products activity, ambient temperature, acidity, aerobic conditions. Physico-chemical methods are the processing of cuttings with reagents that cause a change in the physico-chemical properties of the waste and allow getting new materials. Adding materials for sorption or coagulation neutralization has become widespread due to the simplicity of the method and relative universality, as well as the possibility of recycling the product [10, 11].

Many previously published works that describe DC processing methods using composite mixtures involve the use of binders such as portland cement, hydrated lime, gypsum, ash, and most are associated with the subsequent disposal of the resulting product or use as a basis for construction [12–15]. For example, a mixture of sand, peat, drywall, and clay-gypsum has been proposed to reduce the toxicity of DC [12]. However, there is no component in this mixture that promotes the transfer of heavy metals into insoluble form and their retention in the sediment, a low level of stability of solidified wastes. There is also a mixture, manure or peat, mineral soil and fertile soil layer, and besides the technology of using this mixture involves drying DC in the sun until the moisture level reaches 8–14% [16], what is applicable not in all climatic conditions. The authors propose a technology with the preparation of 2 mixtures for different purposes - for the lower recultivation layer and for the biological reclamation stage with different percentages of sand or sandy loam, peat, neutralizing additives (aluminosilicate, coal sorbent, “Neftedestruktor”, “Centrin” biological products, mineral, organic, humic fertilizers) of gypsum or phosphogypsum [13]. However, low mechanical qualities, such as strength and elasticity, limit the use of the resulting product in construction, and the use of a large amount of peat is not justified. Also a large selection of additional neutralizing additives with the lack of data on the unique effectiveness of the proposed composite materials is presented.

This paper discusses the use of zeolite as an additive in the composition of mixture. Ion-exchange properties of zeolites are widely used for the treatment of wastewater contaminated with heavy metal salts and petroleum products. The efficiency of zeolite sorption properties with respect to heavy metals and petroleum products has been studied in the works [17–21]. Zeolites were used to treat wastewater from such heavy metals as Fe, Cu, Zn, Al, Mn, Cr, Cd and Pb. The work [22] presents the study results of zeolites sorption capacity with respect to petroleum products, which averaged 2.5 mg/g.

The purpose of this work is to determine the effectiveness of the developed zeolite-based composite mixture for neutralizing DC. For this, immobilization of metals and hydrocarbons in the resulting soil mixture is estimated, as well as the compliance of these indicators with regulatory requirements.

2. Materials and research methods
2.1. Research objects
Drill cuttings. The drilling invert emulsion solution was taken as a prototype for the preparation of a model hydrocarbon drilling mud used for drilling at “Lebedinskoe” oil field, Sakhalin, Russia. The ratio of hydrocarbon phase / aqueous phase was 70:30. The hydrocarbon phase composition included: diesel fuel, Okhinskaya oil, emulsifier, stabilizer, inhibitor / structurant, the aqueous phase composition: fresh water and weighting agent.

The rock that corresponds to the drilled rock of “Lebedinskoe” oil field in the interval from 120 to 2000 m along the wellbore – sandstones, sands, clays in the ratio of 60:20:20 was chosen for the preparation of model DC (Fig. 1 (a)).

Man-made soil. The developed zeolite-based composite mixture was added to DC to obtain samples of man-made soil, and additionally containing peat, sand, gypsum and organic-mineral fertilizer. Zeolite
content in the mixture was 15%. The resulting mixture was kept for 2 months. Sampling from the obtained sample was carried out 2 times - after 1 month and after 2 months, respectively (Fig. 1 (b), (c)).

**Figure 1.** Resulting samples: (a) – DC, (b) – soil after 1 month of ageing treatment, (c) – soil after 2 month of ageing treatment

2.2. **Research methods**

*Extract preparation.* 3 extracts were prepared using extractants to determine the content of various forms of metals: distilled water, ammonium acetate buffer (AAB) with 4.5 pH, 1%-th ethylenediaminetetraacetic acid solution (EDTA) in ammonium acetate buffer with 4.5 pH. Carbon tetrachloride was used as an extractant to determine the total oil content in samples.  

*Sample preparation.* Sample DC and 2 samples of man-made soil were dried on filter paper under an extract for 1 week at room temperature to an air-dry state, and then were sifted on 1 mm filter. Part of the dried samples was used to determine gross content of metals, the other part – for extraction in extracts.

*Sample analysis.* Dried samples were analyzed by X-ray fluorescence method on Innov X-X 50 analyzer to determine gross metal content. The peculiarity of the method is the possibility of simultaneous analysis of qualitative composition and quantitative content of elements in complex multicomponent mixtures.

Extracted samples were analyzed on atomic absorption spectrophotometer AA-6800 “SHIMADZU”. For this, a sample weighing 10 g was selected from each sample, the total number of samples was 9 (3 for each form of extract). Then each sample was diluted with a liquid corresponding to extract shape. The extraction time on a mixing device was 30 minutes, after which the samples were settled for 12 hours. Then the samples were filtered on “blue ribbon” filters. Sample solutions were sprayed into the acetylene-air flame of the high-temperature burner of the atomizer, and then changes in the corresponding absorption signals were recorded.

Samples weighing 0.5 g, which were filled with carbon tetrachloride, then stirred for 1 hour were taken to determine the mass fraction of petroleum products. The extract obtained was filtered through a “blue ribbon” paper filter then extraction followed by filtration was repeated 2 more times with new portions of carbon tetrachloride. All extracts were combined into a measuring cylinder and the total volume was recorded. The mass fraction of petroleum products was determined by the method of IR-spectrometry on the analyzer of AN-2 oil bitumen content.

The pH was determined by a potentiometric method in aqueous extracts using a Multi 340i fluid analyzer.

3. **Results and discussion**

3.1 **Environmental hazard estimation for metals**

Metal concentrations were determined for the obtained DC and soil samples (Table 1).
Table 1. Metal concentrations in samples (gross form)

| Element      | Concentration, mg/kg | MAC/APC, mg/kg |
|--------------|----------------------|----------------|
| Model DC     | Soil after 1 month   | Soil after 2 months |
| Fe^{2+}, Fe^{3+} | 25203 ± 127          | 12265 ± 89     |
| Pb^{2+}     | 43 ± 6               | 18 ± 4         |
| Sr^{2+}     | 132 ± 3              | 65 ± 3         |
| Zr^{4+}     | 183 ± 2              | 92 ± 2         |
| K^{+}       | 25987 ± 322          | 22760 ± 202    |
| Ca^{2+}     | 46668 ± 284          | 29842 ± 197    |
| Cr^{3+}     | 55 ± 3               | 24 ± 3         |
| Mn^{2+}     | 253 ± 5              | 200 ± 4        |
| Cd^{2+}     | 12 ± 1               | 5 ± 1          |
| Cu^{2+}     | 46 ± 28              | 23 ± 6         |
| Zn^{2+}     | 47                   | 25             |

The results showed that due to DC dilution with composite materials, the concentration of metals decreased by almost 2 times. The exceptions are K, Mn and Ca due to the addition of K+ ions in the composition of fertilizer and peat, as well as the processes of substitution of K+, Mn2+, Ca2+ ions in zeolite for metals from DC. MAC and/or APC over lead, copper and cadmium are exceeded in DC. And in the obtained product, only the concentrations of cadmium are exceeded due to the high background content of this metal in the soils of Sakhalin [23].

Since the resulting soil will be placed in the soil, we have analyzed the research results [24–25] and selected those metals that are characterized by the highest degree of danger: Cd, Cr, Pb, Cu, Fe. Metals are contained in several forms in soils, but the most dangerous for the environment are mobile or exchangeable forms of elements, which are extracted from the soil with extractants that mimic to a certain extent the dissolving effect on the soil particles of natural waters and plants. Extracts with the following extractants are used to characterize the group content of metals in soils in addition to the determination of water-soluble element forms [26]:

- ammonium acetate buffer with 4.5 pH – to extract exchangeable and soluble in weak acid forms, which characterizes the current stock of the element in the soil;
- 1%-th EDTA solution in ammonium acetate buffer (pH 4.5), which allows, in addition to the exchangeable and soluble in weak acid forms, extracting elements from organic complexes and determining mobile heavy metal compounds;
- 1N HCl (HNO₃) – to extract the elements making up the amorphous compounds, which characterizes the entire potential stock of the element in the soil.

In order to determine the degree of environmental impact, the first two extracts are of the greatest interest, which allow determining the elements that are prone to ion exchange and are available to plants and living organisms. Thus, we have determined the concentrations of selected most dangerous metals in 3 different exposures to assess the environmental hazards of DC and soil (Table 2).

Having analyzed the study results of aqueous extracts (1), it has been determined that the decrease in water soluble forms due to DC treatment with composite mixture is more pronounced in Fe and Pb. In general, there is a positive trend – the concentration of iron decreased by 105 times, lead – 70 times, cadmium – 1.7 times, copper – 4.5 times, chromium – 1.2 times. The selectivity is explained by the sorption process of ions by zeolite pores. The larger ion radius with the same charge, the better it is sorbed, and the greater ion charge, the stronger ion is attracted to the oppositely charged surface of the zeolite [27]. This is also due to the interaction with humic acids – Fe forms intraspheric complexes, which are more durable [28]. Complex compounds of humic acids with Pb ions are much more stable than complexes with Cd ions [29]. The release of Cd ions can be through the molecular topological
effect [30]. Thus, a decrease in desorption of metals from the obtained soil is observed in the aqueous extract, in comparison with DC.

Comparing the experiment results in all forms of extracts (1)–(3), we see a tendency to increase the degree of metals extraction from aqueous extract (1) to 1 % EDTA extract in AAB with pH of 4.5 (3), which is consistent with study results of other authors. In general, the desorption of metals under the influence of an acidic medium and extractants in DC is significantly higher than in the resulting soil, which indicates the retention of metals strength in the soil due to their sorption by the zeolite and fixation in pores under the influence of gypsum. Over time, the concentration extracts of recoverable metals also decrease, which indicates the rationality of keeping the resulting soil for 2 months.

Thus, a decrease in the ion-exchange capacity of the obtained soil, a decrease in the concentrations of metals in the extracts for 2 months, as well as the absence of MAC exceedances, give grounds for assuming that this material is safe for the environment.

### 3.2 Environmental hazard estimation for petroleum products

We have determined the concentrations of petroleum products (gross form) for the obtained samples. (Table 3).

![Table 3. Concentrations of petroleum products in samples (gross form).](image)

The concentration of petroleum products in the soil after 1 month of exposure decreased by 2.5 times compared with the original DC due to dilution and destruction processes. Concentrations decreased by 2 times in the soil after 2 months of exposure, which is also associated with the processes of petroleum products destruction.

Due to the absence of petroleum products in soils approved by MAC or APC, the obtained data were compared with the project of regulatory and technical document “Standards of permissible residual content of oil and products of its transformation in the soil (SPRCOP) after carrying out recultivation and other restoration work in Sakhalin Region”. The resulting soil can be used for most types of soil, both organic-mineral and mineral, industrial and forestry soils.

### 3.3 PH value

Additionally, pH of aqueous extract of samples has been determined (Figure 2).
It was established that after a month of soil ageing treatment pH value decreased from slightly alkaline to neutral. This may be due to dilution with DC by peat and the addition of humic acids to the mixture, with reactions of dissociation of hydroxyl groups of the zeolite and gypsum mixture.

4. Conclusion
In this paper, we can conclude that a zeolite-based composition mixture can be used to process DC with a view to reduce its environmental hazard. As a result of the experiment, samples of man-made soil with different exposure times were obtained under laboratory conditions.

The concentrations of metals (gross form) in the soil do not exceed standard values, with the exception of cadmium, the background concentrations of which are exceeded throughout Sakhalin. Concentrations of mobile forms of metals that can be available to plants and living organisms after adding a composition mixture based on zeolite, have significantly decreased and do not also exceed standard values. A number of metals according to the degree of their retention in man-made soil are as follows: Fe>Cu>Cd>Pb>Cr.

Also, the concentration of oil products in the resulting soil has decreased, which allows using it in soils of various types. Neutralization of pH also has a positive effect on soil properties.

Thus, the environmental estimation of process using zeolite-containing DC composite mixture allows us to conclude about the possibility of its safe reuse and the application of this technology in general when handling drilling waste.

5. Acknowledgments
The work was supported by British Petroleum Scholarship Program.

References
[1] Batalin B S and Nechaeva A E 2013 Utilization of drill cuttings processing into materials for construction purposes Master's J. 2 148–52
[2] Islamov Kh M 2011 Geoeological safety of chemicals use for the treatment of drilling fluids Geology, Geography and Global Ecology 3 174–9
[3] Iagafarova G G, Mavliutov M R and Barakhmina V B 1998 Biotechnological method of disposal of oil cuttings and drilling waste Mountain Bull. 4 43–6
[4] Petrov V G, Kharkalina E A and Shumilova M A 2011 Integrated disposal and disposal of drilling waste Bull. of Udmurt University 4–2 77–9
[5] Genoveseva M 2008 Bioremediation of benzene, toluene, ethylbenzene, xylenes-contaminated soil: a biopile pilot experiment J. Appl. Microbiol 105(5) 1694–702
[6] Wieczorek D, Marchut-Mikolajczyk O and Bielecki S 2012 Phytotests as tools for monitoring the bioremediation process of soil contaminated with diesel oil Biotechnol. Lett. 93(4) 431–9
[7] Classification of drilling solids 2009 Appendix to J. Oil and Gas Technol. (Moscow: Fuel and Energy)
[8] Mishunina A S 2014 Methods of drilling waste disposal Problems of development of hydrocarbon and ore mineral deposits 1 125–8
[9] Perevalov S N and Ivleva A A 2013 Current technologies and methods of drilling waste disposal *Int. Res. J.* 11–1(18) 63–6

[10] *Information and technical reference book on the best available technologies* 2016 Disposal and disposal of waste (except thermally neutralization (incineration)) (Moscow: BAT Bureau)

[11] Shpinkova M S 2014 *Development of a method for neutralization of oil waste of different composition* Abstr. dis. ... cand. of chemical sci. (Moscow: Russian State University of Oil and Gas named after I M Gubkin)

[12] New technology for reclamation of soil through the processing of drilling waste in the extraction of oil and gas 2015 Explanatory note (sci. background) (Moscow: FSBU UralRI “Ecology”)

[13] Koltsov I N, Mitrofanov N G and Petukhova V S 2013 Sludge-soil soil mixture (versions) for recultivation of disturbed lands and a method of quarrying of quarries and disturbed lands Pat. 2491135 Russian Federation

[14] Tsipper A A et al 2016 *Composite building material “Gumikom”* Pat. 2575950 Russian Federation

[15] Mokrousova M A and Glushankova I S 2015 Remediation of drill cuttings and oil-contaminated soils using humic preparations *Transport. Transport facilities. Ecology* 2 57–72

[16] Burlaka N V, Burlaka I V and Burlaka V A 2010 *Method of disposal of waste drill cuttings* Pat. 2379137 Russian Federation

[17] Valieva I R and Nefedov V A 2012 Sorption of copper and zinc from waste and surface waters by zeolitic and zeolite-montmorillonite rocks of the Urals *Fan-science* 6 57–9

[18] Vatin N I and Chechevichkin V N 2013 Application of clinoptilolite type zeolites for the purification of natural waters *Engineering and Construction J.* 2 81–8

[19] Veisgeim A S, Nazarenko O B and Zarubina R F 2012 Removal of iron from borehole water on the filter with loading from Badinsky zeolite *Siberian J. of Sci.* 4(5) 23–9

[20] Nazarenko O B, Zarubina R F et al 2011 Application of Sahapta zeolite to improve the quality of drinking water *Bull. of Tomsk Polytechnic University* 3 28–32

[21] Chichina S B and Osviannikova O O 2012 Removal of iron from borehole water on the filter with loading from Badinsky zeolite Pat. 2379137 Russian Federation

[22] Obuzdina M V 2010 Natural and modified zeolites as adsorbents of petroleum products from industrial wastewater *Proc. of IrSTU* 4(44) 104–10

[23] Ministry of Natural Resources and Environmental Protection of Sakhalin Region 2016 *Report on the environmental situation and environmental protection of Sakhalin region in 2015* (Yuzhno-Sakhalinsk: LLC Eikon)

[24] Crommentuijn T, Sijm D and Bruijn J 2000 Maximum Permissible Concentrations and Negligible Concentrations for metals, taking background concentrations into account *J. of Environmental Management* 2 121–43

[25] Vodianitskii Iu N 2011 On hazardous heavy metals/metalloids in soils *Bulletin of the Soil Institute named after V V Dokuchaev* 68 56–82

[26] Titova V I, Dabakhova E V and Dabakhov M V 2011 *Agro-and biochemical methods for studying the state of ecosystems: textbook for universities* (N Novgorod: VVASS Publ. House)

[27] Obuzdina M V 2010 Natural and modified zeolites as adsorbents of petroleum products from industrial wastewater *Proc. of IrSTU* 4(44) 104–10

[28] Liu C and Huang P M 1999 Ionic Strength and Cadmium Effects on Surface Features of Humic Acid *Understanding Humic Substances. Advanced Methods, Properties and Applications* 247 87–99
