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THE ASSESSEMENT OF DANGEROUSNESS OF WASTE. CASE STUDY: WASTE ORIGINATING FROM DRILLING MUDS

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Abstract

This paper continues the presentation of the case studies on waste dangerousness assessment. Due to the particularities that shows many of the waste generated in industry, in particular, each analysis represents a special case. The application of the methodology for determining the dangerousness of waste (carried out and used by our institute, still in the absence of rules for the implementation of legislation on waste management), often faces challenges regarding the estimation (with an error as low as possible) of the concentration for the potential components from the waste, necessary to establish the hazardous/non-hazardous character of the waste and, implicitly, for its correct classification in the waste list. In this respect, the case study presented is that of a waste from drilling muds.

Keywords: *hazardous, quality assessment, the waste classification, waste*

Introduction

In order to determine the dangerousness of a waste and to classify it in the European Waste List, first must be sought out a waste stream, in the waste list, which matches it unreservedly. If this cannot be established, an in-depth analysis of the waste should be made. Such a case is that of the waste analysed in the present paper, waste from reconditioning mud and for which there are 6 possible entries in the Waste List. The methodology for determining the dangerousness of waste (carried out and used by our institute) includes nine steps (Guta et al. 2013; Arama et al. 2014; Technical Guidance 2015). First step consists in establishing identification data for the sample waste (waste type, the process from which the waste comes from, the obvious features of the waste such as physical state, appearance etc.). Secondly, it is necessary to obtain as much information as we can about the waste, and the third step is to identify a waste stream, typical for the waste in question, in the list of waste. If you can identify, without reserve, a good flow, it is possible to classify the waste without the need for further analysis. If, however, you cannot do this or if it is not sure that the waste is non-hazardous, analysis of the waste is continued. It follows the fourth step which consists in establishing the potential constituents of waste in order to set the indicators to be determined. Analytical determinations of the quality indicators that have been set and their registration is the next step of the methodology; it is very important to correctly determine the quality indicators, but equally important is to have a good sampling program and chain of custody (storage, transport, pre-treatment) for the waste before the analysis.

The sixth step is to identify the risk statements for the waste components; the waste components are determined analytically or estimated on the basis of all information available, and the risk statements - using reliable sources. The last three steps of the

methodology consist of: assigning of dangerous properties based on identified risk phrases for the waste components, quantifying the level of hazardous properties and the evaluation of the results.

Materials and Methods

At the basis of the analysis were: the waste sample, on which analytical determinations have been made; information on how the waste is generated; the existing regulations on the characterization and classification of waste.

According to the waste legislation in force (L 211/2011), hazardous waste is defined as any waste that presents one or more of the hazardous properties stipulated in the current legal provisions (namely in Regulation (EU) No. 1357/2014) (R 1357/2014). This Regulation indicates in the appendix the 15 properties of the waste that make it hazardous and regulates the limit values for the HP4, HP5, HP6, HP7, HP8, HP10, HP11, HP13 hazardous properties. The quantification of these properties is based on the concentrations of the components presenting a particular hazard statement, responsible for a particular hazardous property. Concentration levels are compared with limits set by law, and the result of comparison indicates whether the sample analyzed waste can be classified as hazardous waste or nonhazardous. For the rest of the properties, the Regulation either does not provide limit values, or specifies the need for specific testing. Also for HP 1 ("Explosive"), HP 2 ("Oxidants"), HP 3 ("Flammable"), there are mentioned: "If the presence of a substance indicates that the waste is explosive (or oxidising or flammable, etc.), it is classified as hazardous waste type HP 1 (or HP 2 or HP 3).

The waste analyzed comes from drilling mud (recovered - by centrifugation and flocculation - from exhausted drilling mud) remaining on the containers walls.

Characterization of the waste was done on the basis of:

1. the results of the analytical determinations (the indicators, representative of the analyzed waste, were established based on the analysis of the waste information); in order to demonstrate the importance of the quality of information to identify representative indicators, it should be noted that there were problems with collecting the relevant information because the waste generator had not communicated at the outset that the drilling mud from which the waste originated was obtained by processing exhausted drilling fluids;
2. information on potential chemical compounds in waste and their related hazard statements provided both by the drilling liquids safety data sheets used for the drilling mud preparation, as well as the literature (Chemical Book) and dedicated legislative documents (R 1272/2008).

These data led to estimateing the waste composition, to identify the potential hazards posed by waste / components of waste and to establish the hazardous / non-hazardous nature of waste.

Results and Discussion

The indicators and the results of the analytical determinations for their quantification are presented in Table 1.

Composition of the waste is further analyzed simultaneously with the dangerousness of waste. For the quantitative estimates of the HP4, HP5, HP6, HP7, HP8, HP10, HP11, HP13 properties, the potential compounds in the waste were taken into account. In the present case, they may be components of the materials used in the preparation

of drilling mud (presented below), as well as compounds that pollute mud derived from previous drilling muds, assuming that their removal from the mud (through centrifugation and flocculation) can not be done complete.

Table 1. Results of analytical determinations carried out on waste

No.	Indicators	M.U.	Values	Methods
1	pH	Unit. pH	7.2	SR EN 10390 :2015
2	Dry matter (d.m.)	%	95.9	SR ISO 11465:1998
3	Loss of calcination	% d.m.	9.31	SR EN 15935:2013
4	Barium	mg/kg d.m.	412852	SR EN ISO 17294-2:2005
5	Calcium	mg/kg d.m.	16305	SR ISO 7980: 2002
6	Iron	mg/kg d.m.	3721	SR 13315 :1996/C91 :2008
7	Sulfates	mg/kg d.m.	263635	SR ISO 11048:1999, 3.6
8	Chlorides	mg/kg d.m.	400	STAS 7184/7-87, 4.2
9	Carbonates	mg/kg d.m.	< 17	STAS 7184/7-87, 4.1
10	Silicon	mg/kg d.m.	38453	SR EN 15309:2008
11	(TOC)	mg/kg d.m.	71000	SR EN 13137:2002 SR EN 15936:2013
12	THP	mg/kg d.m.	92215	ISO 14507:2003
13	THP C10-C40 Fraction	mg/kg d.m.	14072	SR EN 14039:2005

Taking into account the way the waste was generated, its physico-chemical state and the visual examination of the sample, it is appreciated that the waste does not have the properties (defined according to Regulation (EU) No. 1357/2014 (R 1357/2014) that can induce the HP1 ("Explosive"), HP2 ("Oxidants"), HP3 ("Flammable"), HP12 ("Acid Toxic Acid Release") and HP15 («Wastes capable of developing one of the other 14 defined properties which the original waste does not present directly").

The drilling fluid waste analyzed, according to the information provided by the waste holder, contains mainly two products (synthetic drilling fluids). Safety Data Sheets of these products shows the following composition:

- *for Drilling Synthetic Fluid (1)*: anhydrous calcium chloride in a concentration of 4-8%; Quartz (crystalline silica) in a concentration not exceeding 5%; Calcium hydroxide at a concentration of 1 - 2%; Iso-alkanes (42-72%); Barium sulphate (5-25%); Water (7-25%); C10-C18 alkanes (6-24%); Unsaturated fatty acids C14-C18 and C16-C18 (1-2%).
- *for Drilling Synthetic Fluid (2)*: 1-tetradecene ($C_{14}H_{28}$) 14% concentration; Anhydrous calcium chloride 4-8% concentration; 1-octadecene ($C_{18}H_{36}$) 2-3% concentration; Barium sulfate (42%); Water (10-15%); 1-hexadecene ($C_{16}H_{32}$) 5% concentration; 1-dodecene ($C_{12}H_{24}$ 1-2% concentration; Clay (clay) (1-2%); Gilsonite (compound with CAS 12002-43-6, which, according to the literature (Chemical Book) is a resin used as an additive in liquids used in the drilling technique).

In addition to these known compounds, as we have already mentioned, impurities can be found in the waste resulting from the previous uses of the drilling fluids subject to reconditioning. These impurities consist in organic compounds such as petroleum hydrocarbons, as well as other inorganic compounds (other than hydroxide and chloride) based on calcium (silicates, sulfates, carbonates).

Specialty literature indicates for these compounds the hazard statements presented in Table 2. The inorganic compounds possibly present in the waste were quantitatively

evaluated based on the results presented in Table 1. This evaluation is synthetically presented in Table 3 and only takes into account inorganic compounds likely to exist in the analyzed waste and which may influence the dangerousness of the waste, based on the arguments presented above.

Table 2. Potential compounds in waste, hazard phrases and imposed limit concentrations that make the difference between dangerous and non-dangerous wastes

Compounds	Hazard statements	Significance of hazard	Limit value (%)
Calcium chloride	H319	Causes serious eye irritation (Eye Irrit. 2)	20
	H302	Harmful if swallowed (Acute Tox. 4)	25
Crystalline quartz*	H350	May cause cancer (Carc. 1B)*	0.1
	H335	May cause respiratory irritation (STOT SE 3: Specific target organ toxicity/aspiration toxicity)*	20
	H372	Causes organ damage in case of prolonged or repeated exposure (STOT RE 1)*	1
Calcium hydroxide	H314	Causes skin burns and eye damage (Skin Corr.1B)**	1
	H318	Causes serious eye damage (Eye Dam.1)**	10
Iso-alkanes	the literature does not indicate danger phrases		
Barium sulphate	H302	Harmful if swallowed (Acute Tox. 4)	25
	H312	Harmful in contact with skin (Acute Tox.4)	55
	H332	Harmful in case of inhalation (Acute Tox.4)***	22.5
	H315	Causes skin irritation (Skin Irrit. 2)	20
	H335	May cause respiratory irritation (STOT SE 3: Specific target organ toxicity/aspiration toxicity)***	20
1-tetradecene	H304	May be fatal if swallowed and enters airways	10
	H319	Causes serious eye irritation (Eye Irrit. 2)	20
1-octadecene	H304	May be fatal if swallowed and enters airways	10
1-hexadecene	H315	Causes skin irritation (Skin Irrit. 2)	20
1-dodecene	H304	May be fatal if swallowed and enters airways	10
	H317	May cause an allergic skin reaction (Skin Sens.1)	10

*) - in this case, quartz being in a mixture in the form of mud, we consider that these phrases of danger are inapplicable;

**) - Because: 1) The pH determined for waste (7.2 pH units) indicates a practically neutral value, which means that the calcium hydroxide, potentially present in the waste, does not induce corrosion of the waste, so it can be assumed that it is found in waste in a small proportion, possibly under the 1% limit; 2) Can not distinguish between the calcium bound as calcium hydroxide, calcium chloride and other combinations such as calcium sulphate, carbonate or calcium silicate (compounds which may exist, along with the synthetic drilling fluid components, in the analyzed mud obtained from the mud already used) - in these conditions, therefore, we can consider that most of the calcium is in the form of chloride, sulphate, carbonate and silicate; because calcium sulphate, carbonate and calcium silicate can induce danger only if

it is in a dry state (which is not the case of the analyzed waste), only the calcium chloride was considered in the waste hazard assessment analysis;
***) - inapplicable, because barium sulfate is not pulverulent in the analyzed sample.

The results of the waste assessment, presented in Table 3, reveals that both for the property HP4 - "Irritants - skin irritation and eye lesions" and for the property HP6 - "Acute Toxicity" (properties corresponding to compounds in waste that have the potential to induce danger) the limits were exceeded due to the presence of barium sulphate, classified as H315 (Causes skin irritation) and as H302 (Harmful if swallowed) and H312 (Harmful in contact with skin), respectively. Consequently, according to these results and to the definition for the hazardous waste given by Law no. 211/2011 - Annex no. 1, item 11 ("any wastes presenting one or more of the hazardous properties listed in Annex 4 to the Act"), it results that, in relation to inorganic compounds, the analyzed waste constituted from recovered mud is DANGEROUS.

Besides the inorganic compounds, as can be seen from the above description, organic compounds are also found in the waste; their presence in the waste was quantitatively estimated by the TOC (total organic carbon), THP (total petroleum hydrocarbon) and C10-C40 hydrocarbons (without being able to analytically determine the constituent chemical compounds).

Considering:

- the TOC of 7.1% in waste (which translates to a much higher percentage of organic compounds, corresponding to this carbon content);
  the value of the THP concentration of 9.2% and the fact that THP is a complex mixture of petroleum products (according to SR-EN 14039: 2005: n-alkanes, isoalkanes, cycloalkanes, alkylbenzene, naphthalene alkyl, aromatic polycyclic compounds; according to other technical sources, petroleum hydrocarbons may include: hexane, benzene, toluene, xylene, naphthalene and fluorene, other constituents of petrol, mineral oils); some of these compounds (such as benzene, toluene) are characterized by hazard phrases that have very low concentration limits of 0.1% - 0.3%);
- the determined value of 1.4% for the concentration of the C10-C40 hydrocarbon fraction from the waste;
- the impossibility of detecting THP constituents by analytical determinations,

Table 3. Data for waste assessment based on analytical determinations and potential inorganic compounds from waste

No.	Criterion for classification in hazardous waste category, according to Law no. 211/2011 and Regulation (EU) No. 1357/2014	Determined element / associated compound	Determined element, mg/kg d.m.	Associated compound, %	Checking the criterion	The result of evaluation based on the criteria analyzed
1	HP4 Property - «Irritants - skin irritation and eye injuries» Total concentration for materials classified as H315 and H319: ≥ 20%	Chloride / $CaCl_2*6H_2O$	400	0.10	**61.57%>20%**	**The waste is irritant due to the compounds with the H315 and H319 hazard statements**
		Sulfate / $BaSO_4$	263635	61.47		
		TOTAL		**61.57**		
2	HP6 Property «Acute Toxicity» Total concentration for materials classified as: H302≥25% H312≥55% H332: ≥22.5%	Chloride / $CaCl_2*6H_2O$	400	0.10	**61.57%>55%**	**The waste shows acute toxicity due to compounds classified as H302 and H312**
		Sulfate / $BaSO_4$	263635	61.47		
		TOTAL		**61.57**		

it follows that THP and C10-C40 components (characterized by danger phrases corresponding to the very low concentration limits - 0.1%, 0.3%, 0.5%) may be found in the waste in concentrations that exceed the above-mentioned concentration limits. In addition, the possible presence of mineral oils in the analyzed waste, irrespective of their percentage in the waste, causes the waste to be classified as an oil-containing drilling mud, thus as hazardous waste (Guidance 2015).
Therefore, by reference to the organic compounds in the waste, there may be at least one dangerous property for which the concentration limit of the compounds possessing that property is exceeded. As a result, again taking into account the definition of hazardous wastes mentioned above, it results that by reference to organic compounds, the waste analyzed is DANGEROUS.

Conclusions

Considering the above considerations, it results that both organic and inorganic compounds can induce danger to the analyzed waste.
In the European Waste List (EWC 2002; CD 955/2014), the entries for drilling muds are in number of 6, of which two are drilling muds with a dangerous character (*oil-containing drilling muds and wastes* and also *drilling muds and other drilling wastes containing hazardous substances*). As it is obvious that drilling mud analyzed contains barium sulphate in a very high concentration, but in addition the waste contains mineral oil, we believe that the appropriate entry in the list of the waste for the analyzed waste is *oil-containing drilling muds and wastes*.
Of the entire analysis presented it follows that the analized waste is dangerous and can be assigned the code 01 05 05* - *oil-containing drilling muds and wastes*.

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