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Assessment of mechanical parameters and physical and chemical properties of solidified drilling-related waste

Introduction

During the execution of drilling works, the generation of drilling-related waste and used drilling mud as well as the spoil carried away by it are an indispensable element of the entire project. Such type of waste has a varied harmfulness, which depends on the type of agents used for the preparation of the drilling fluid (Steliga and Uliasz 2014; Stryczek et al. 2014, 2015). Legal regulations in terms of environmental protection impose increasing requirements for the drilling industry within the scope of drilling-related waste management. In addition, companies conducting exploration and excavation works are obligated to comply with the rules of waste management. This pertains to the limitation of the harmfulness of the impact of waste on the environment with the use of appropriate methods of its recovery and disposal.

Therefore, research works are conducted at the Oil and Gas Institute – National Research Institute, the purpose of which is the quantitative and qualitative selection of binding agents for the solidification and stabilization of the drilling-related waste i.e. drillings covered by waste drilling mud. The immobilization of the spoil in the form of drilling-related waste depends largely on the selection of the amount and type of the binding additive and the agent

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which activates binding (Brylicki et al. 2009; Uliasz and Kremieniewski 2012). This aims at the transformation of the generated waste into a product demonstrating the properties of a solid with limited leachability of hazardous substances, which are present in the form of soluble compounds. Due to the fact that appropriate parameters of the solidified product depend on the proper binding process, the qualitative and quantitative composition of the binding agents is selected individually depending on the type of layers being drilled and the used drilling fluid.

1. Reasonable management of drilling-related waste

The protection of the environment against the hazards caused by waste starts with actions aiming at prevention from the generation of waste, reduction of its amount and change of more hazardous waste into less hazardous waste. Based on the above aspects, the constant striving to implement an innovative system of managing any waste is observed with the assumption that this management should be performed in specified stages. The transition from stage to another should take place only when the problem can not be solved at the previous stage. The scheme of waste management according to legal requirements (Polish act of parliament Journal of Laws, 2013, item. 21 with further changes) includes:

- prevention of the generation of waste and minimization of its amount,
- processing for reuse,
- utilization of waste in a manner safe for the environment/recycling,
- other recycling processes,
- disposal of waste in compliance with the principles of environmental protection.

Disposal of waste consists of subjecting it to the process of such biological, physical or chemical processing, which will not make it hazardous to the human health or life and to the environment. The alternative method of waste disposal is its storage or thermal or physical and chemical processing, with maintaining the requirements provided for in the appropriate laws (Steliga and Kluk 2010; Steliga 2011; Steliga and Uliasz 2012). Therefore, attempts were undertaken to solidify the drilling-related waste in such a manner that the parameters of the generated product have the properties of waste harmless to the environment and that there is a possibility of its reasonable management. The drilling-related waste generated while drilling a hole consists of drilling fluid and drill cuttings which constitute a part of the rocks present in the geological profile (loams, sands, clays, sandstones, shales, limestones, marls, mudstones, siltstones, dolomites etc.) crushed by an auger with the remains of drilling fluid. Waste muds (according to investigations on the physiochemical properties of waste muds performed in Polish Oil and Gas Institute) contain increased amounts of: insoluble matter, dissolved solid matter (TDS) surface active agents, chloride and sulfate ions, dissolved organic carbon (DOC) as well as trace amounts of heavy metals, i.e. arsenic, barium, cadmium, chromium, copper, mercury, nickel, lead, antimony, selenium, zinc, tin, cobalt (Steliga and Uliasz 2012). This type of waste is stored at landfill sites, and then subjected to subsequent processes of disposal. The storage of waste is classified as methods of disposal which should be performed at installations intended for that purpose. A landfill site is a structure which is considered an installation. Conditions determining the location, construction and operation of landfill sites are specified in the Act on waste dated December 14, 2012 (Journal of Laws of 2013, item 21) and Regulation of the Minister for Environment on waste storages dated April 30, 2013 (Journal of Laws of 2013, item 523). The storage of waste is a method of disposal, which is the manner of handling that has not been economically used or disposed in another manner. Based on D9 code of the appendix No. 2 entitled "Non-exhaustive list of disposal processes", which constitutes an integral part of the Act on waste and lists the actions along with appropriate markings, spoil solidification may be classified as the following item: Physical and chemical processing, not listed in other item hereto as a result of which the final compounds or mixtures are generated which are disposed with the use of any process listed in items D1–D12 (e.g. evaporation, drying, calcination etc.).

2. Waste solidification and stabilization

The processes of waste solidification and stabilization (S/S) are among the methods of waste disposal. In that case inorganic hydraulic binders are most commonly used (Al.-Ansary Marwa and Al.-Tabbaa 2006; Leonadr and Stegemann 2010; Fengler 2012, Jamrozik et al. 2011). Portland cements and binders with pozzolanic properties are most commonly used in solidification and stabilization. Ordinary Portland cement (OPC) is hydraulic inorganic binder composed of Portland clinker and setting time regulator (calcium sulfate of calcium sulfate dehydrate). Portland clinker is material synthesized at high temperature (1450°C) in rotating kiln. It consist of four major phases: alite phase (solid solution of magnesium and aluminium in tricalcium silicate), belite (beta form of dicalcium silicate), tricalcium aluminate and brownmillerite (calcium aluminoferrite) accompanied with some minor phases like alkalis, uncombined lime. When mixed with water, OPC reacts, and the whole process involving dissolution, hydrolysis, precipitation, recrystallization etc. is called cement hydration. As a results of the latter, hydration products are being formed. Among them, the most important are poorly crystalline hydrated calcium silicates (C-S-H phase) and calcium hydroxide. They mostly contribute to strength and durability of resulting material. Additionally, some hydrated aluminates and aluminoferrite products are being formed first of all ettringite and monosulfate. Hydrated cement paste has some unique properties in terms of immobilization of toxic wastes, especially heavy metal ions. Due to its very high specific surface area (about 20 m^2/g), presence of closed gel pores, and high pH, C-S-H phase is very efficient matrix for heavy metal ions immobilization. Immobilization of ions if due to both chemical (chemisorption, formation of hardly soluble compounds at high pH) as well as physical (low permeability of the matrix, high specific surface area) reasons (Kurdowski 2010). Except hydraulic cements, pozzolanic materials are also used for solidification and stabilization of wastes. Pozzolanic materials contain significant amount of reactive silica and alumina, which reacts with calcium hydroxide originating from OPC hydration. It results in formation of additional amount of C-S-H phase what decrease permeability of the matrix (Grabowska and Małolepszy 2017; Juenger and Siddique 2015; Stępień and Małolepszy 2017). New solidifying agent SCQ25 is a type of pozzolanic binder. It is finely grained inorganic material rich in active silica, what results in rapid development of C-S-H phase, responsible for high strength of solidified wastes.

Due to the progressive development of concrete technology, as well as ubiquitous economic reasons, the content of cement is increasingly reduced at the expense of use of other types of additives, for example ground granulated blast furnace slag (Batayneh et al. 2007). Solidification consists mostly in changing the physical properties of waste, thanks to which the obtained monolith will not contain free fluids and will show improved mechanical strength. This process only changes only the physical state of waste through the use of additives, not changing the chemical composition of the given waste. During in storage, solidified waste shows a considerably reduced impact on the natural environment. Waste formed during the solidification process shows considerably reduced permeability values, which decreases the possibilities of filtration of a liquid through the solidified waste and at the same time reduced the release of contaminants (Batchelor 2006; Gonet et al. 2009; Kremieniewski 2014). The basic parameter allowing the assessment of solidification efficiency is the measurement of compressive strength of the monolith obtained from waste. This parameter has been included in some of the specifications on solidification and stabilization. The assessment of the parameters of the solidified waste is usually performed after a short period of time, however this measurement is used for forecasting the behavior of waste in long-lasting deposition (Batchelor 2006). Due to the fact that aqueous cements change their physical properties over time (Kremieniewski et al. 2016), it can be assumed that waste solidified with the use of cement will also demonstrate an analogy to the above. Due to this, the determination of the duration of the given process may constitute some kind of a problem. Reactions which occur during hydration lead to an increase of mechanical strength and reduction of porosity (Gonet et al. 2005). The mixture of Portland cement and pozzolanic binders demonstrates slower kinetics of hydration, and in addition, the wide range of components contained in waste may cause more changes during the long-lasting period of the deposition of the sample. Solidified waste interacts with the environment through leaching the binder as well as solidified substances out of it. The above may result in the reduction of mechanical parameters and an increase of porosity and permeability, therefore the leachability of substances of solidified waste should be determined additionally (Batchelor 2006; Bensted 2002; Gonet 2006).

As a result of the chemical transformations occurring in the waste under the agent used in order to reduce the mobility and toxicity of waste, its stabilization is taking place (Batchelor 2006). The change of mobility consists in the transformation of contaminants from the dissolved phase into the solid phase, which significantly complicates the free migration of contaminants from the inter-pores space to the environment. Immobilization of contaminants in waste transformed into a stable monolith consists in precipitation with the use of binders (among others cements). An alkaline solution resulting from hydration leads to the creation of solid hydroxides of contaminating metals. Waste subject to stabilization with the use of agents on the warp of cements and pozzolanic binders demonstrates the presence of a much tighter porous microstructure (Yu-Chen et al. 2010). Based on the literature data (Batchelor 2006; Glasser 1996) it is believed that the use of significant amounts of cement during the process of stabilization, may result in the achievement of a specific surface of waste on the level of the hydrated cement (200–300 m^2/g). Considering the fact that the previously mentioned adsorption of metals on the surface of hydroxides takes place at a high pH, this mechanism is not without significance. This process may be called an ion exchanger, because as a result of adsorption, equivalent concentrations of ions are released (Batchelor 2006; Koś and Zawisza 2016). Oxidation and reduction reactions occurring during the process of stabilization constitute an important mechanism during the immobilization of contaminants present in waste. This is connected with sometimes different chemical properties dependent on the redox state. An example of this could be chromium, which demonstrates more toxic properties and a higher mobility during oxidation than during reduction, while the antagonist of such a reaction may be arsenic (Ball et al. 2012; Batchelor 2006). Based on such behavior of some metals and correlating them with moderately oxidizing environment created by cements, it is useful to use blast furnace slag as a part of stabilizing and solidifying binder, which will allow for the creation of reducing conditions through the release of sulphides and other reduced sulphur compounds. Stabilization of contaminants may incorporate various mechanisms which are dependent on the qualitative composition of the waste being solidified. However, in most wastes, the most required parameter allowing for the determination of the efficiency of stabilization is the pH factor. It is connected with the reactions of precipitation, adsorption and redox, which prevent the migration of contaminants under the strong impact of pH. Therefore, the success of the solidification and stabilization process is in some way dependent on reactions occurring between the binder used (its pH value) and the reactions dependent on the pH, which determines the degree of stabilization of the contaminants.

To conclude the above considerations, it may be stated that the process of solidification and stabilization of waste is basically mechanical mixing with a specially developed hydraulic and pozzolanic binder, which as a result of the presence of water activates the hydration process, binds and creates the solidified mass. The obtained product has a significant resistance to aggressive fluids and higher mechanical resistance. This enables the safe transport, and then storage of waste in the form of monolith (Tanatwy et. al. 2012; Uliasz et al. 2010; Uliasz and Kremieniewski 2012). The disposal of waste with the use of binding agents consists of:

- chemical binding of contaminants (mainly metal ions) within cement hydration products,
- adsorption of contaminants on the surface of grains of hydrated binder and the encapsulation of these contaminants in the matrix of the stabilization mixture (Stryczek et al. 2011).

It should be noted that, according to the provisions applicable, the efficiency of solidification or stabilization processes is evaluated after 28 days of deposition of the products based on the results of:

- analysis of the concentration of heavy metal ions in water extracts from the test for the leaching of contaminants conducted according to the procedure described in the regulation (Regulation of Minister of Economy dated January 8, 2013 on criteria and procedures of approval of waste for storage at a landfill for a specific type of waste) (Journal of Laws of 2013 item 38);
- compressive strength measurement. According to the Polish legislation the minimum value of the compressive resistance of waste after the process of solidification and stabilization amounts to 50 kN/m2 (0.05 MPa) (Journal of Laws of 2013 item 38).

The processes of solidification and stabilization of drilling-related waste are not commonly conducted. However, the results presented in this paper confirm the high efficiency of solidification of waste and as a result the possibility of its reuse.

3. Research methods

In cooperation with the Laboratory of Sealing Slurries of the Facility of Drilling Technology and the Facility of Formation Fluids Exploitation Technology INiG (Oil and Gas Institute) – PIB (National Research Institute) and the Faculty of Drilling Oil and Gas, AGH University of Science and Technology, a series of tests aiming at the assessment of mechanical parameters and physical and chemical properties of solidified drilling-related waste were performed. Research works were performed in accordance with the applicable standards (EN 10426-2, EN 12457) as well as with a reference to the Regulation of Minister of Economy on deposition of wastes in landfills, dated July 16, 2015 (Journal of Laws of 2015 item 1277).

Tests were performed by INiG-PIB (compressive strength, setting times, leaching tests), as well as in the laboratory of AGH Faculty of Materials Science and Ceramics (observations of microstructure with scanning electron microscopy (SEM), with an analysis of the chemical composition (EDX probe)).

The assessment of mechanical parameters and physical and chemical properties of the solidified waste was performed in order to determine the efficiency of the solidification of liquid and semi-liquid drilling-related waste (drilling-related waste means the drill cuttings covered with drilling fluid). The performed tests sought to achieve a final product with a solid consistency, which should be characterized by proper mechanical parameters (i.e. compressive strength and short time of solidification of waste). In addition, a very important aspect was the achievement of reduced leachability of organic substances, as well as the achievement of a compacted microstructure of the waste, which would prevent the release of substances contained in the waste. Samples of waste were taken from the landfill site, or directly from the opening in the form in which they were deposited there (Phot. 1).

Phot. 1. Drilling-related waste from B-1 opening

Fot. 1. Odpady wiertnicze z otworu B-1

The obtained spoil (Phot. 2) was subject to the process of solidification through dosing the selected hydraulic binders in amounts from 1% to 10% in relation to the waste weight. Disposed waste was characterized by a significant presence of water. The humidity of waste from the B-1 opening amounted to 23.4%, while the humidity of waste from the P-1 opening was equal to 18.3%. Waste and solidifying binder were subject to mechanical mixing in order to homogenize the mixture, and the obtained mass was formed in the form of square blocks (Phot. 3) with an edge of 5 cm (in order to perform the tests of mechanical parameters).

Phot. 2. Spoil sample (drill cuttings + drilling fluid)

Fot. 2. Próbka urobku (zwierciny + płuczka)

Phot. 3. The solidified sample of drilling-related waste

Fot. 3. Zestalona próbka odpadu wiertniczego

The mixture was also placed in the ring of Vicat apparatus (in order to determine the setting time). After 7 days the samples were subject to compressive strength test according to the EN-PN ISO 10426-2 standard with the use of a Chandler Engineering 4207 model testing machine. Based on the analysis of the obtained test results, it was possible to determine the efficiency of binding of the waste sample in quantitative and qualitative terms of the selected hydraulic binders.

The next stage was to perform the test of leaching for solidified drilling-related waste, characterized by optimal times of binding and mechanical parameters. For this purpose, the semi-finished products made of solidified drilling-related waste (presented on Phots. 4–7)

Phot. 4. The solidified sample of drilling-related waste from B-1 opening
(binding additive 2.5% SCQ25 + 0.5% of sodium water glass)

Fot. 4. Zestalona próbka odpadów wiertniczych z otworu B-1
(dodatek zestalający 2,5% SCQ25 + 0,5% szkła wodnego sodowego)

were subject to the test for leaching of the hazardous substances, and then, on the basis of the obtained results, the compliances were determined through checking the actual values of leaching if they fulfill the requirements of the Regulation of Minister of Economy on deposition of wastes in landfills, dated July 16, 2015 (Journal of Laws of 2015 item 1277, appendix 5).

During the leaching test, the water leachate of solidified drilling-related waste with the use of selected binders was analyzed. Leachate was obtained through leaching of solidified drilling waste with water in relation to 1 kg of dry matter of the solidified waste: 10 dm^3 H_2O.

Phot. 5. The solidified sample of drilling-related waste from B-1 opening
(binding additive 10.0% SCQ25 + 0.5% of sodium water glass)

Fot. 5. Zestalona próbka odpadów wiertniczych z otworu B-1
(dodatek zestalający 10,0% SCQ25 + 0,5% szkła wodnego sodowego)

Phot. 6. The solidified sample of drilling-related waste from P-1 opening
(binding additive 2.5% SCQ25 + 0.5% of sodium water glass)

Fot. 6. Zestalona próbka odpadów wiertniczych z otworu P-1
(dodatek zestalający 2,5% SCQ25 + 0,5% szkła wodnego sodowego)

Phot. 7. The solidified sample of drilling-related waste from B-1 opening
(binding additive 10.0% SCQ25 + 0.5% of sodium water glass)

Fot. 7. Zestalona próbka odpadów wiertniczych z otworu B-1
(dodatek zestalający 10,0%% SCQ25 + 0,5% szkła wodnego sodowego)

The tests were conducted with taking the criteria determining the possibility of directing the waste for disposal on a hazardous waste landfill into account, namely, the acceptable limit values of leaching the components such as: total dissolved solids (TDS), dissolved organic carbon (DOC), content of heavy metals (arsenic, barium, cadmium, chromium, copper, mercury, molybdenum, nickel, lead, antimony, selenium, zinc) as well as ions such as: chlorides, sulfates and fluorides were determined. The results of the conducted tests are presented in Tables 1 and 2.

The last stage of the assessment of the efficiency of the solidification of drilling-related waste was to determine the phase composition of the solidified waste as well as to analyze the obtained microstructure of the sample. The test was performed with the use of a scanning microscope.

4. Results and discussions

To solidify the waste, a series of laboratory tests of the solidification of spoil with the use of various binding agents, binding activator in the form of water dispersion of sodium silicate (sodium water glass) or combinations of these agents were conducted. The most effectively acting binders are listed below, which include:

- Ordinary Portland Cement CEM I 32.5R + sodium water glass,
- innovative hydraulic-pozzalonic binder with a large content of active silicate SCQ25 + + sodium water glass,

The effectiveness of the used agent was determined based on the time of binding the spoil as well as the compressive strength after 7 days of hardening. The spoil obtained during drilling the B-1 opening (13 3/8” and 9 5/8” sections) was subjected to the process of solidification, where the drilling was conducted with the use of bentonite drilling fluid and salted polymer-potassium drilling fluid, and from the P-1 opening (16” and 23”sections) obtained from bentonite drilling fluid, as well as (12 1/4” sections), in which the spoil came from polymer-potassium drilling fluid. The results of the tests are presented in Figures 1–4. In the case of drilling-related waste from the B-1 opening, the initial setting time of about 50 minutes, and the final setting time after 50 hours (the amount of 2.5% SCQ25 + 0.5% of sodium water glass) and after 37 hours at the amount of 5% of the SCQ25 + 0.5% of sodium water glass was obtained. When analyzing the setting times for drilling-related waste from the P-1 opening, it was observed that an additive of 2.5% SCQ25 agent + 0.5% of sodium water glass resulted in final setting time of 16 hours and the 5% amount has reduced it to 6 hours. When analyzing the parameters of solidification of the spoil from the B-1 and P-1 openings (Figs. 1–4), a significantly higher efficiency of solidification of the spoil from the B-1 opening was noted. Significantly shorter setting times were achieved (both the initial PW and the final setting times KW – Fig. 1). The obtained monolith of the solidified waste was characterized by higher values of compressive strength (Fig. 3). Based on the obtained

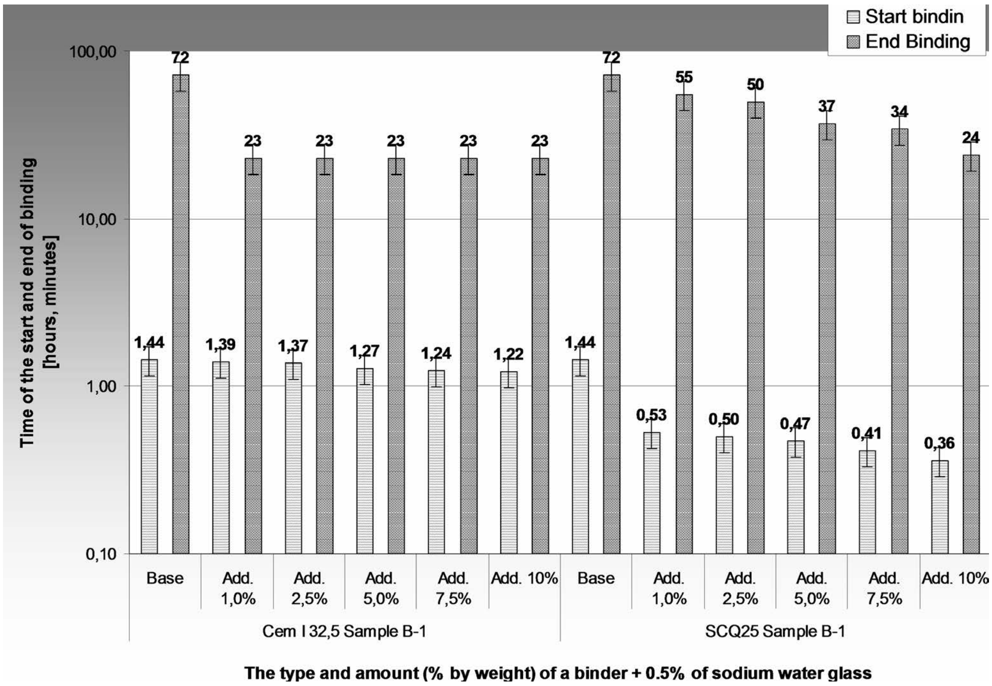


Fig. 1. The summary of the initial (PW) and final (KW) setting times of the drilling-related waste from B-1 opening being solidified

Rys. 1. Zestawienie czasu początku wiązania (PW), oraz końca wiązania (KW) zestalanych odpadów wiertniczych z otworu B-1

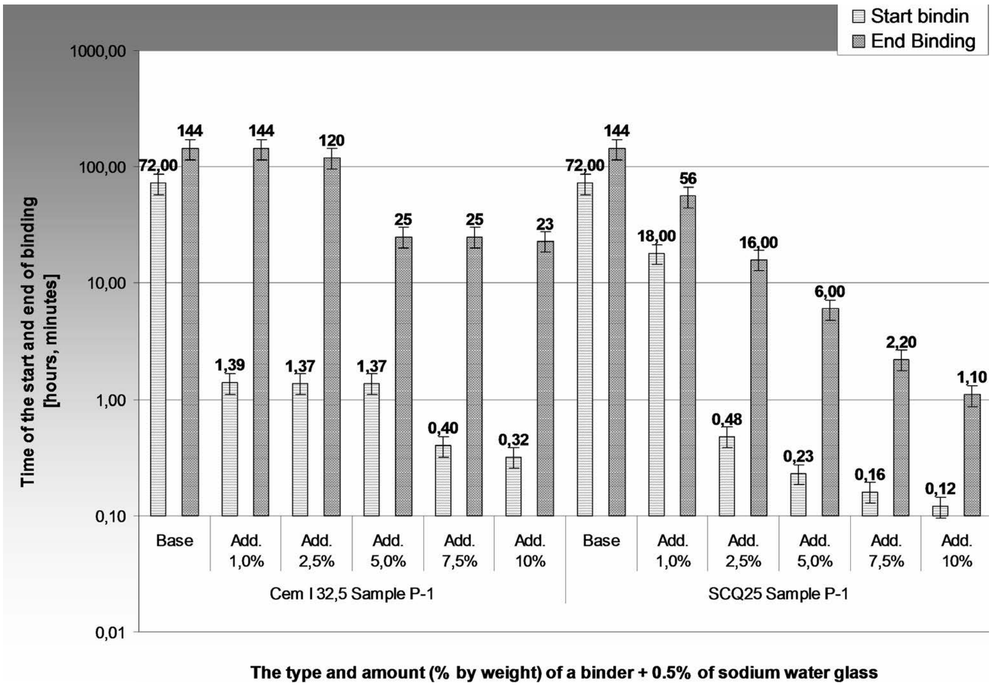


Fig. 2. The summary of the initial (PW) and final (KW) setting time of the drilling-related waste from P-1 opening being solidified

Rys. 2. Zestawienie czasu początku wiązania (PW), oraz końca wiązania (KW) zestalanych odpadów wiertniczych z otworu P-1

test results it was stated that the outcome of the solidification process is influenced by the type of spoil, the properties of which depend on the drilled rock formations and the used drilling fluid. Moreover, the key parameter may also be the humidity of the sample subjected to solidification, because the water content in drilling-related waste from the B-1 opening is at the level of 23.42% while the drilling-waste from P-1 opening has an 18.31% of water concentration, which might have affected the increase of hydration of the solidifying binder. Satisfactory values both in terms of the setting time and mechanical parameters of the solidified spoil were obtained with the use of the SCQ25 binder in the amount from approx. 2% to 5% + 0.5% of sodium water glass.

In order to confirm the efficiency of solidification of drilling-related waste with the use of selected hydraulic binders, tests of leachability were conducted according to the Regulation of Minister of Economy on deposition of wastes in landfil, dated July 16, 2015 (Journal of Laws of 2015 item 1277). For the tests, drilling-related waste with the content of 2.5%; 10% of binding additive + 0.5% of sodium water glass one has selected. The selection of such amounts was determined by an optimal binding activity (2.5% of an additive + water glass), while taking the economic factor into account. Testing the leachability of waste stabilized

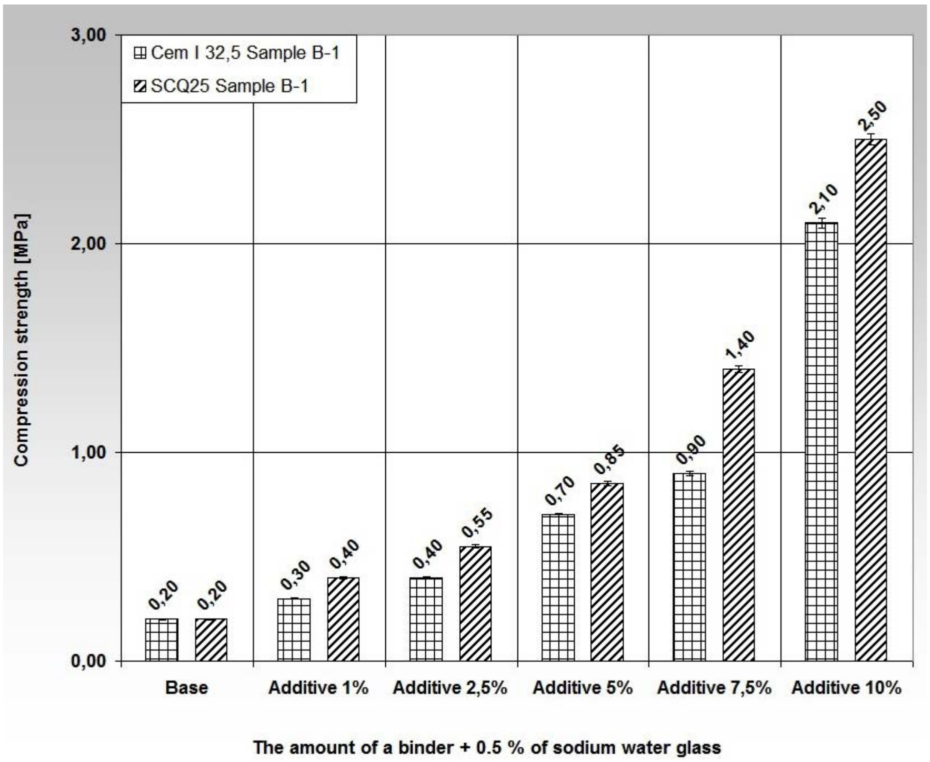


Fig. 3. The summary of the compressive strength of drilling-related waste from B-1 opening being solidified

Rys. 3. Zestawienie wytrzymałości na ściskanie zestalanych odpadów wiertniczych z otworu B-1

with the amount of 10% of the binding agent is a comparative test for the maximum amount. Results of leaching tests performed on solidified drillings obtained from particular bore holes are presented in Tables 1 and 2.

Analysis of results of the leaching tests of drilling-related waste from the B-1 opening, a significantly greater reduction of pH value after the use of SCQ 25 + 0.5% of the sodium water glass additive one has observed than with the same amount of the additive in the form of Portland cement together with the binder activator. The use of 10% of the binder of one and the other type resulted in the achievement of the same value of pH = 9.4. The value of the total dissolved solids was reduced along with the increase of concentration of the additive of the hydraulic binder. The use of 10% of the amount of cement resulted in a greater reduction of the TDS value, up to 3960 mg/kg of dry material, however, the obtained values were higher than with the use of 2.5% of SCQ25 + 0.5% of the sodium water glass additive. In all samples the obtained the results of the TDS tests for 1:10 dilution, which does not exceed acceptable limits (Journal of Laws of 2015 item 1277) (Table 1). The content of ions such as chlorides, sulfates and fluorides in eluate have been reduced along with the increase of the

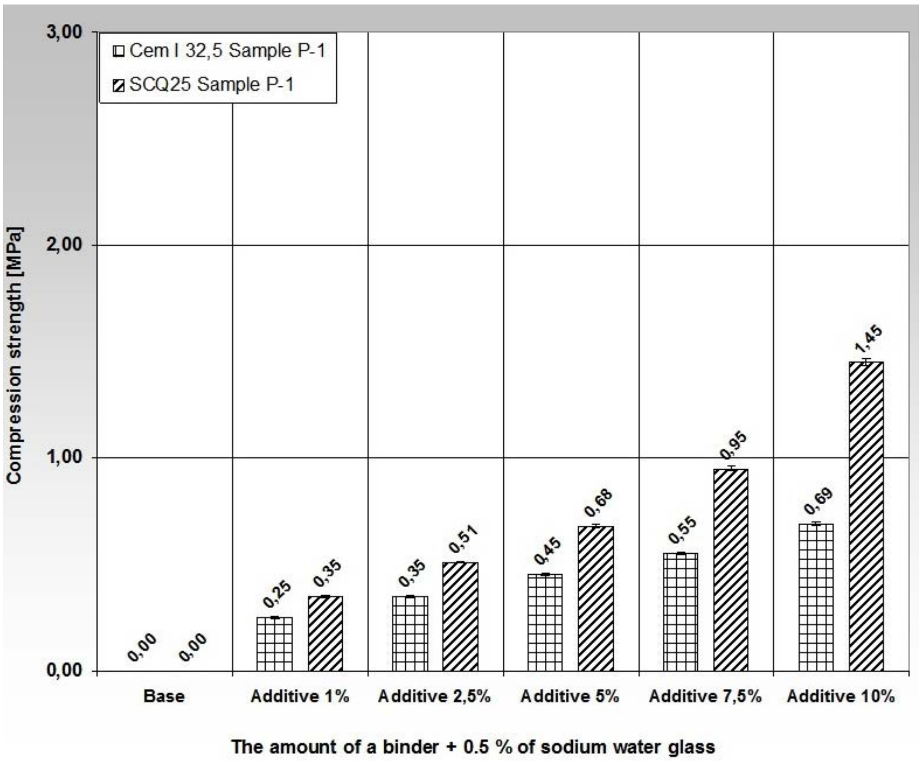


Fig. 4. The summary of the compressive strength of drilling-related waste from P-1 opening being solidified

Rys. 4. Zestawienie wytrzymałości na ściskanie zestalanych odpadów wiertniczych z otworu P-1

amount of the binder, the values of dissolved organic carbon (DOC) have also been reduced after the solidification of drilling-related waste with immobilizing additives. It should be noted that the results of DOC tests exceed the value acceptable in the standard. The obtained values of heavy metals do not exceed the acceptable values (according to Journal of Laws of 2016, item. 1277, appendix no. 5), which is presented in Table 1. Obtained samples fulfill the requirements allowing to deposit obtained material in the landfill for dangerous wastes. Values of dissolved organic carbon (DOC) after solidification of drillings with OPC and setting activator were within the range 1354–2025 mg/kg, while for SCQ25 and water glass used as solidifying agents were lowered to 1580–1710 mg/kg of dry mass. It should be noticed, that in both cases, obtained results are slightly above the limit, which is 1000 mg/kg. Concentrations of heavy metals in eluate do not exceed acceptable values, as can be seen in Table 1.

The solidification of the sample of drilling-related waste from the P-1 opening resulted in the achievement of a slight increase of the pH value of leachate with the increase of the used binder. Such behavior of samples being solidified is favorable from the point of view of the reductive nature of the pH values for the presence of metal ions. In the 1:10 eluate sample

Table 1. The summary of results of water leachate tests (1:10) of the solidified rock spoil from B-1 opening

Tabela 1. Zestawienie wyników badań odcieków wodnych (1:10) zestalonego urobku skalnego z otworu B-1

Designations		Units	Solidified drilling-related waste from B-1 opening				Allowable leaching Values
			0.5% sodium silicate 2.5% Portland cement	0.5% sodium silicate 10% Portland cement	0.5% sodium silicate 2.5% SCQ 25	0.5%.sodium silicate 10% SCQ 25	
pH		–	9.5	9.4	9.1	9.4	
Total dissolved solids (TDS)		mg/kg of dry material	5 680	3 960	4 240	2 760	100 000
Chlorides		mg/kg of dry material	1 241	895	880	275	25 000
Sulphates		mg/kg of dry material	1 033	1 054	936	722	50 000
Fluorides		mg/kg of dry material	5.77	2.16	6.59	3.91	500
Dissolved organic carbon. (DOC)		mg/kg of dry material	2 050	1 354	1 710	1 058	1000
Heavy metals	Arsenic (As)	mg/kg of dry material	0.12	0.11	0.08	0.07	25
	Barium (Ba)	mg/kg of dry material	4.69	3.32	3.74	2.78	300
	Cadmium (Cd)	mg/kg of dry material	<0.0005	<0.0005	<0.0005	<0.0005	5
	Chromium (Cr)	mg/kg of dry material	0.98	0.75	0.84	0.61	70
	Copper (Cu)	mg/kg of dry material	2.87	2.14	1.89	1.56	100
	Mercury (Hg)	mg/kg of dry material	<0.0005	<0.0005	<0.0005	<0.0005	2
	Nickel (Ni)	mg/kg of dry material	1.89	1.58	1.58	1.49	40
	Lead (Pb)	mg/kg of dry material	0,89	0,75	0,71	0,53	50
	Antimony (Sb)	mg/kg of dry material	<0.050	<0.050	<0.050	<0.050	5
	Selenium (Se)	mg/kg of dry material	0.025	0.015	0.020	0.011	7
	Zinc (Zn)	mg/kg of dry material	1.99	1.05	1.59	1.19	200
	Molybdenum (Mo)	mg/kg of dry material	0.74	0.65	0.84	0.56	30

obtained from solidified drilling-related waste from the P-1 opening, one has determined a significantly greater amount of total dissolved solids (TDS), within the range 17920––31480 mg/kg of dry mass as well as chlorides (7099–9926 mg/kg of dry material) than in case of drilling-related waste from B-1 opening. The above may be associated with the use of salted polymer-potassium drilling liquid during drilling (presence of Cl^-). The obtained values of both TDS and ions of Cl^-, SO_4^{2-}, F^-, have been reduced along with the increase of the concentration of Portland cement + 0.5% of sodium water glass additive, while the SCQ 25 + 0.5% of sodium water glass additive caused an increase of the above parameters. However, the obtained results were within the acceptable limits, and fulfilled the demands to be deposited on hazardous wastes landfill (Journal of Laws of 2015 item 1277, appendix 5) as can be seen in Table 2. In the eluate sample (1:10) obtained from the sample of solidified drilling-related waste from P-1 opening, also significantly greater values of dissolved organic carbon (DOC) than the sample of drilling-related waste from the B-1 opening was determined. Obtained results of dissolved organic carbon leaching are within the range 4870–6789 mg/kg of dry material. The obtained values exceed 4 to 6 times the acceptable standard, which should be taken into account during subsequent works aiming at the secondary use of the solidified waste. Heavy metals content in eluate does not exceed limit values.

During tests a more favorable action of SCQ 25 additive as a binder was observed. The results of the tests of the water leachate for the sample of solidified rock spoil from P-1 opening are presented in Table 2.

During the final stage of the works, tests of the microstructure of solidified waste were performed with the use of a scanning microscope. For the analysis of microstructure, the samples with the most favorable parameters obtained during the previously performed tests were selected (additive of 2.5% of SCQ25 + 0.5% of sodium water glass), along with the control sample for comparison. The image of the microstructure and charts of the elemental analysis are presented in Table 3. When analyzing the samples of the solidified drilling-related waste from the B-1 opening, a "loose" structure of the sample not subject to solidification was observed. Single grains are visible. In the sample solidified with the amount of 2.5% of SCQ25 + sodium water glass, the microstructure is much more compacted, and the grains of drilling-related waste are partially covered with an immobilizing agent. An elemental analysis enables the presence of organic carbon to be observed. Single grains are visible in the control sample from P-1 opening. The microstructure of this sample is very poorly-compacted, which confirmed the lower humidity of the spoil noted in the previous tests. After the use of the binder, the microstructure of the sample is more compacted, which favorably affects the reduction of the permeability and leaching of substances from the monolith of the sample. The elemental analysis confirms the presence of syngenit, the grains of fly ash and potassium chloride (probably the components of the binder) are also visible.

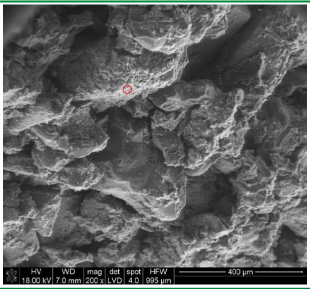
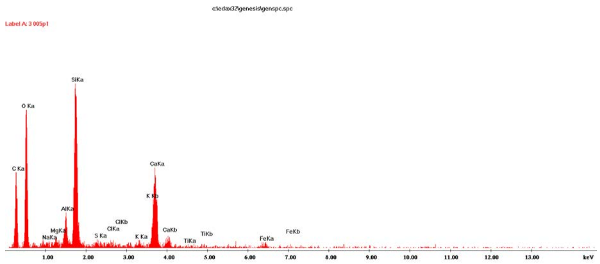
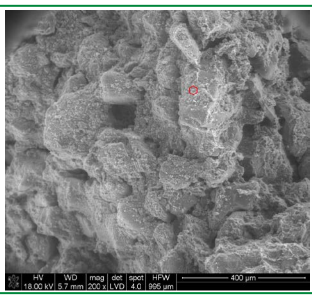
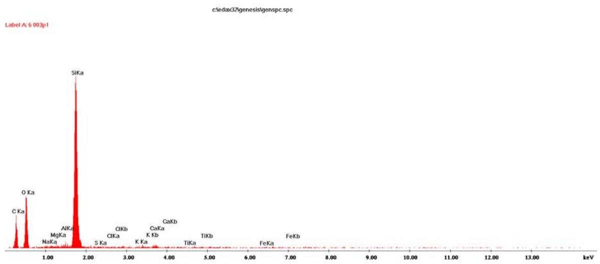
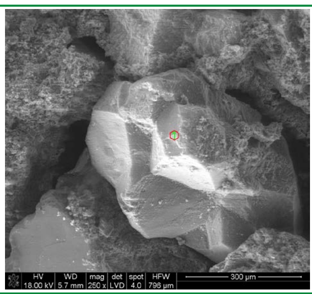
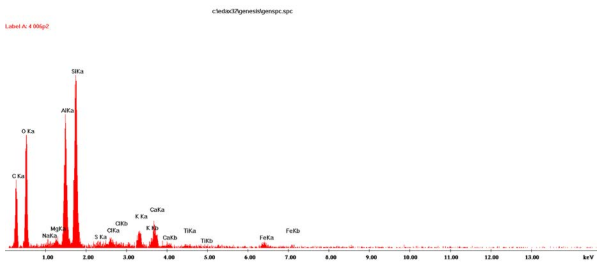
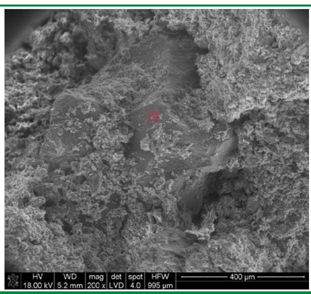
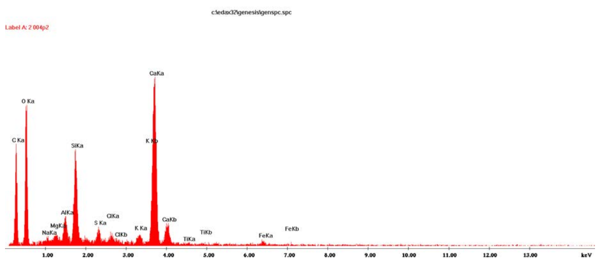
Table 2. The summary of results of water leachate tests (1:10) of the solidified rock spoil from P-1 opening

Tabela 2. Zestawienie wyników badań odcieków wodnych (1:10) zestalonego urobku skalnego z otworu P-1

Designations		Units	Solidified drilling-related waste from P-1 opening				Allowable leaching values
			0.5% sodium silicate 2.5% Portland cement	0.5% sodium silicate 10% Portland cement	0.5% sodium silicate 2.5% SCQ 25	0.5%.sodium silicate 10% SCQ 25	
pH		–	9,1	10,3	8,8	9,8	
Total dissolved solids (TDS)		mg/kg of dry material	27 400	17 920	22 240	31 480	100 000
Chlorides		mg/kg of dry material	9 926	6 735	7 099	9 571	25 000
Sulphates		mg/kg of dry material	1 026	658	895	1 171	50 000
Fluorides		mg/kg of dry material	12.51	8.32	9.67	13.5	500
Dissolved organic carbon. (DOC)		mg/kg of dry material	6 780	5 280	4 780	4 950	1000
Heavy metals	Arsenic (As)	mg/kg of dry material	0.14	0.12	0.12	0.13	25
	Barium (Ba)	mg/kg of dry material	2.53	1.79	1.79	2.04	300
	Cadmium (Cd)	mg/kg of dry material	<0.0005	<0.0005	<0.0005	<0.0005	5
	Chromium (Cr)	mg/kg of dry material	0.56	0.42	0.42	0.75	70
	Copper (Cu)	mg/kg of dry material	1.97	1.06	1.06	1.59	100
	Mercury (Hg)	mg/kg of dry material	<0.0005	<0.0005	<0.0005	<0.0005	2
	Nickel (Ni)	mg/kg of dry material	0.63	0.34	0.34	0.44	40
	Lead (Pb)	mg/kg of dry material	0.59	0.43	0.43	0.61	50
	Antimony (Sb)	mg/kg of dry material	<0.020	<0.050	<0.050	<0.020	5
	Selenium (Se)	mg/kg of dry material	0.015	0.013	0.013	0.018	7
	Zinc (Zn)	mg/kg of dry material	1.59	1.29	1.29	1.49	200
	Molybdenum (Mo)	mg/kg of dry material	0.84	0.57	0.57	0.74	30

Table 3. The analysis of the samples of microstructure and phase composition at point

Tabela 3. Analiza mikrostruktury próbek oraz skład fazowy

Scanning microscopy image	Elemental analysis
Sample B-1 without additives (control)	
	
Sample B-1 2.5% SCQ25	
	
Sample P-1 without additives (control)	
	
Sample P-1 2.5% SCQ25	
	

6. Summary and conclusions

The process of the solidification of drilling-related waste is a very efficient method of the management of spoil. It allows for immobilization through the hydraulic binding of soluble compounds (e.g. chlorides) as well as heavy metals and petroleum-derived substances. The solidification of waste characterized by varied grain size, associated with drilled rock formations, varied hydration and the presence of ions enable the achievement of waste with a solid consistency, demonstrating significant physical and chemical stability as well as mechanical strength. Thanks to this, such a product is easier to transport or/and use as a semi-finished product for construction purposes (ground bases, fillings, supplementary materials). Based on the performed construction works, satisfactory results have obtained, which allow for selecting the favorably acting immobilizing agent, which was SCQ25.

The authors presented the results of the tests for the selection of binding agents and the effectiveness of their action in the process of the solidification of spoil. The selected binding agents limit the harmful impact of waste on the environment as well as may constitute an alternative for immobilizing agents currently used in industrial conditions. The result of the conducted works is the obtainment of solidified samples of spoil, which are characterized by the low leachability of the contaminants and high values of compressive strength as well as compacted structure with the low permeability of the obtained monolith.

When analyzing the obtained test results, significant effectiveness of solidification with the use of the SCQ25 immobilizing agent at the presence of small amount of sodium water glass, used in order to activate the binding process, were observed. An optimal amount may be even 2.5% of the SCQ25 binder in relation to the weight of the solidified waste. However, it should be noted that the time of binding as well as the mechanical parameters of waste are influenced by a number of various factors, from the chemical composition of the waste to the grain size and the water content. Therefore, appropriate tests should be provided for the given type of waste, which will allow for the selection of the amount of the binding agent specified for the given type of waste.

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OCENA PARAMETRÓW MECHANICZNYCH I WŁAŚCIWOŚCI FIZYKOCHEMICZNYCH ZESTALONYCH ODPADÓW WIERTNICZYCH

Słowa kluczowe

zestalanie, zwierciny, odpady wiertnicze, zagospodarowanie, wymywalność szkodliwych zanieczyszczeń

Streszczenie

W Instytucie Nafty i Gazu–Państwowym Instytucie Badawczym podjęto prace badawcze w celu zestalenia odpadów wiertniczych przy użyciu cementu portlandzkiego CEM I 32,5R, spoiwa hydraulicznego SCQ 25 oraz dodatku szkła wodnego sodowego pełniącego funkcję aktywatora wiązania. Celem realizowanych prac była ocena efektywności zestalania odpadów wiertniczych pod kątem możliwości ich dalszego wykorzystania bądź składowania. Zestalone poszczególnymi komponentami odpady wiertnicze poddano badaniom pod kątem możliwości ich składowania na składowisku odpadów niebezpiecznych zgodnie z rozporządzeniem Ministra Gospodarki i Pracy z dnia 8 stycznia 2013 r. w sprawie kryteriów oraz procedur dopuszczania odpadów do składowania na składowisku odpadów danego typu (Dz.U. z 2013 r. poz. 38). W publikacji przedstawiono optymalne metody zagospodarowania odpadów wiertniczych zawierających pozostałości płuczki wiertniczej. Próby zestalania przeprowadzono zgodnie z podstawami funkcjonowania współczesnej gospodarki odpadami biorąc pod uwagę potencjalną szkodliwość dla środowiska wytwarzanych odpadów. Materiałem badawczym były odpady wiertnicze z otworu B-1 oraz P-1 wiercone przy użyciu płuczki bentonitowej i zasolonej płuczki polimerowo-potasowej, natomiast unieszkodliwianie poprzez zestalanie przeprowadzono proponując nową technologię zestalania opracowaną w INiG-PIB przy użyciu środków wiążących wytypowanych na podstawie badań laboratoryjnych (szkło wodne sodowe + dodatki spoiwa hydraulicznego/cement portlandzki CEM I 32,5R oraz spoiwo SCQ 25). Uzyskane wyniki analiz wymywalności substancji szkodliwych po zestaleniu odpadów wiertniczych dowodzą, że zestalone próbki nie spełniają kryteriów dopuszczenia otrzymanych półproduktów do składowania na składowisku. Związane jest to z przekroczeniem dopuszczalnej zawartości rozpuszczonego węgla organicznego (DOC), pomimo iż uzyskane (TDS) oraz pozostałe wskaźniki zawierały się w przedziale dopuszczalnym przez normę. Przedstawiona metoda immobilizacji odpadów wiertniczych umożliwia w przyszłości odpowiednio dobrać skład ilościowy i jakościowy środków immobilizujących. Działanie takie przyczyni się do zagospodarowania odpadów wiertniczych w sposób neutralny dla środowiska naturalnego.

ASSESSMENT OF MECHANICAL PARAMETERS AND PHYSICAL AND CHEMICAL PROPERTIES OF SOLIDIFIED DRILLING-RELATED WASTE

Keywords

solidification, drill cuttings, drilling-related waste, management, leachability of hazardous contaminants

Abstract

Research works were undertaken at the Oil and Gas Institute–National Research Institute, in order to solidify drilling-related waste with the use of Portland cement CEM I 32.5R, hydraulic binder SCQ 25, as well as an additive of sodium water glass fulfilling a function of the binding activator. The aim of the conducted works was to assess the efficiency of the solidification of drilling-related waste in terms of the possibility of its further use or storage. Drilling-related waste solidified with individual components was subjected to tests in terms of the possibility of its deposition on a landfill for hazardous waste according to the Regulation of the Minister of Economy and Labor dated January 8, 2013 on the Criteria and Procedures of Approval of Waste for Storage at a Landfill for a Specific Type of Waste (Journal of Laws of 2013, item 38). The paper presents the optimal methods of the management of drilling-related waste containing the remains of drilling fluid. Attempts of solidification were conducted according to the bases of operation of modern waste management, taking the possible harmfulness of the generated waste on the environment into account. The test material was the drilling-related waste from the B-1 and P-1 opening drilled with the use of bentonite drilling fluid and salted polymer-potassium drilling fluid, while the disposal through solidification was conducted by offering a new technology of solidification developed at INiG-PIB with the use of binding agents selected based on laboratory tests (sodium water glass + additives of hydraulic binder/Portland cement CEM I 32.5R as well as the SCQ 25 binder). The obtained results of the analyses of the leachability of harmful substances after the solidification of drilling waste prove that the solidified samples do not meet the criteria for the acceptance of the obtained semi-finished products to be deposited at a landfill. This is associated with exceeding the acceptable content of dissolved organic carbon (DOC), despite the fact that the obtained (TDS) and remaining indicators were within the range acceptable by the standard. The presented method of immobilization of drilling-related waste allows for the proper selection of the quantitative and qualitative composition of immobilizing agents in the future. Such an activity will contribute to the management of drilling-related waste in a manner neutral to the natural environment.