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UTILISATION OF DRILLING WASTE MUDS FROM DRILLING WASTE DUMP***

1. INTRODUCTION

A dynamically developing drilling industry is connected with some environmental impact. Considerable amounts of contaminated drilling waste is produced, regardless of the applied prevention measures. The generated drilling waste is diversified both chemically and physico-mechanically. These properties make utilization or managing of drilling waste difficult. The waste materials from borehole drilling consist of crushed rock cuttings from the borehole and remnants of drilling mud.

The quantity, composition and properties of typical drilling waste generated in the process of drilling and well testing depend particularly on the type of the drilling muds applied, the lithology of rock layers drilled through, and the drilling technology [3, 4].

The major components of drilling muds are liquid (water, oil, or another organic fluid) and solid (a weighting material, typically barite) components. Various additives are used to improve the technical performance of the mud. Among these are viscosifiers (e.g. polyacrylates and other organic polymers), emulsifiers (e.g. alkylacrylate sulphonate and polyethylene oxide), pH and shale control agents, and deflocculants. The additives applied vary in different drilling operations and in the course of the drilling itself [1].

In Poland the average indices of drilling waste volumes expressed in cubic meters per 1 r.m. of the well have been grouped in the respective end-depth intervals of the well (Fig. 1) [5].

The drilling waste are colloidal suspensions, being most frequently polymer-mineral microcomposites of diversified chemical and mineral phase compositions and also participation of a dispersed solid phase [2].

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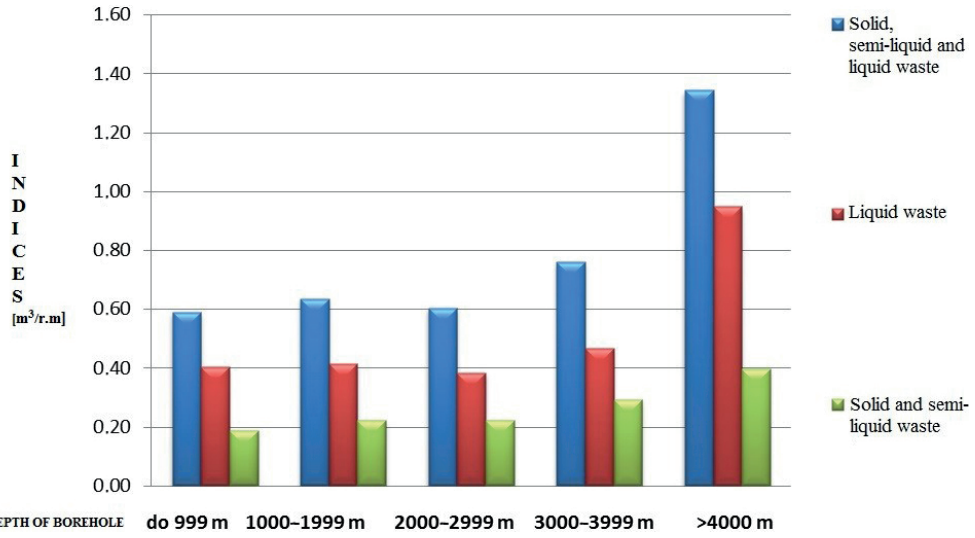

Fig. 1. Indices of drilling waste generated per 1 r.m. of the well for specific borehole intervals [5]

The drilling waste mud in the form of the colloidal system is stable due to such factors as:
- the content of monovalent electrostatic charges of particles making up colloids, which mainly consist of a set of interconnected mineral and organic polymers,
- the size of the hydration covers protecting hydrophilic components of colloidal molecules,
- the share of highly hydrophilic polymers (e.g. derivatives of polyacrylamide, polyglycols and biopolymers).

The electrostatic stabilization of spent drilling muds provides their special properties, e.g. the lack of phase separation or homogeneity. Flocculation of such suspensions is hindered. The phases are kept separated most often with synthetic polymers of a high molecular weight. There are also on-going investigations on new low-molecular cationic copolymers containing amine groups of the first order [6].

The properties of drilling waste have to be accurately specified so that proper decontamination methods are worked out. The produced material composite can have a similar mechanical strength as the ground.

Depending on the obtained results, agricultural or geotechnical utilizations are considered in reference to this type of materials. In Poland the quality of such materials is usually improved either by mixing them with pre-selected soil or with binders. The first method is cheaper, though the environmental assumptions are not always met.

The other method lies in adding a binding material, as a consequence of which:
- heavy metals and salts are bounded,
- chemical stability of the obtained material composite can be improved,
- physico-mechanical properties of the product can be improved.

2. EXPERIMENTAL

Materials

ORDINARY PORTLAND CEMENT

Ordinary Portland cement CEM I 42.5R according to PN-EN 197-1 was used in the experiments. Basic characteristic of cement is presented in Table 1.

Table 1

Basic properties of Portland cement used in experiments

Property		Unit	Value
Specific surface		[cm^2/g]	3,740
Setting time	initial	[min]	205
	final	[min]	250
Mineralogical composition	C_3S	[%]	52
	C_2S	[%]	17
	C_3A	[%]	12
	C_4AF	[%]	11

HYDRATED LIME

Hydrated lime used in the experiment was commercial CL90-S hydrated lime according to PN-EN 459-1:2012

FLY ASH FROM THE FLUIDAL COMBUSTION OF BROWN COAL

Fly ash from the fluidal combustion of brown coal used in experiments originating from the Turów power plant. Loss of ignition of the investigated fly ash was 2.8%. Table 2 presents the chemical composition of used fly ash. A microstructure of grains of fly ash used is presented in Figure 2. It can be noticed, that grains are irregular in their shapes with a rough surface. It results in high water demand of such fly ash what is a desired property in the case of the present investigation, since it will be used as a drying agent for waste mud.

Table 2
Chemical composition of fly ash from the fluidal combustion of brown coal

Compound	Content [%]
LOI	2.8
SiO_2	31.2
Fe_2O_3	5.8
Al_2O_3	20.0
TiO_2	1.3
CaO	26.4
MgO	1.0
SO_3	7.8
Na_2O	1.8
K_2O	1.8
$CaO_{uncombined}$	9.9

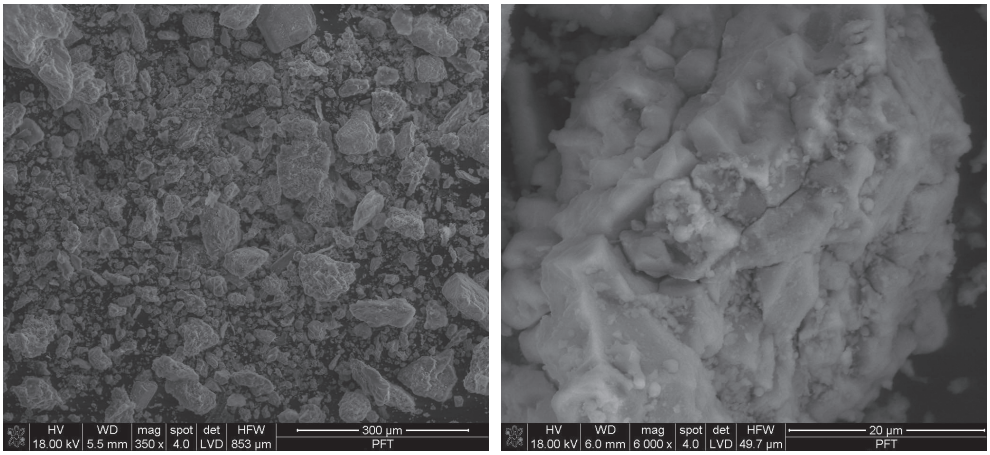

Fig. 2. SEM micrograph of fly ash from fluidal combustion of brown coal from the Turów power plant

Figure 3 presents the grain size distribution of fly ash. In Figure 4 XRD patttern of Turów fly ash was presented. The phase composition of fly ash used is typical for that material: except for the amorphous phase, it is composed of quartz, hematite, anhydride and uncombined lime.

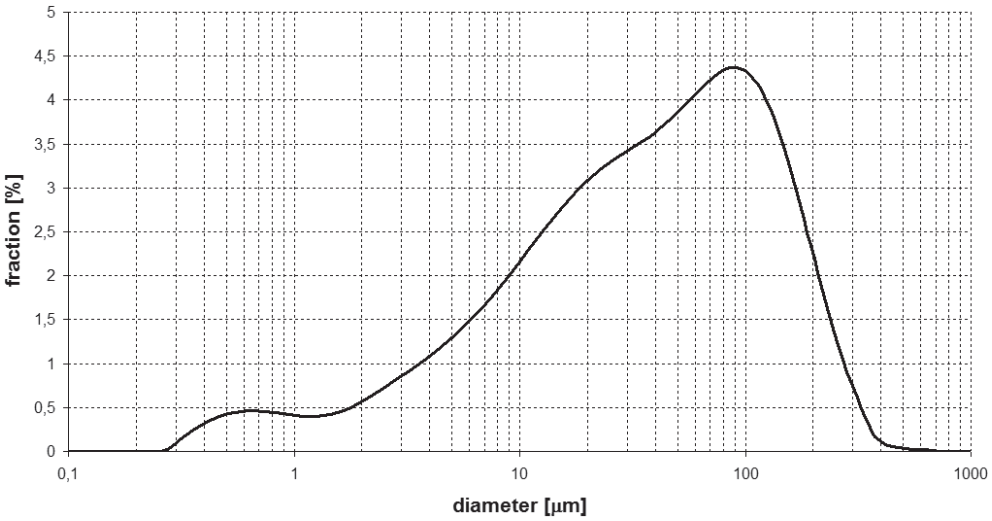

Fig. 3. Grain size distribution of the fly ash from the fluidal combustion of brown coal from the Turów power plant

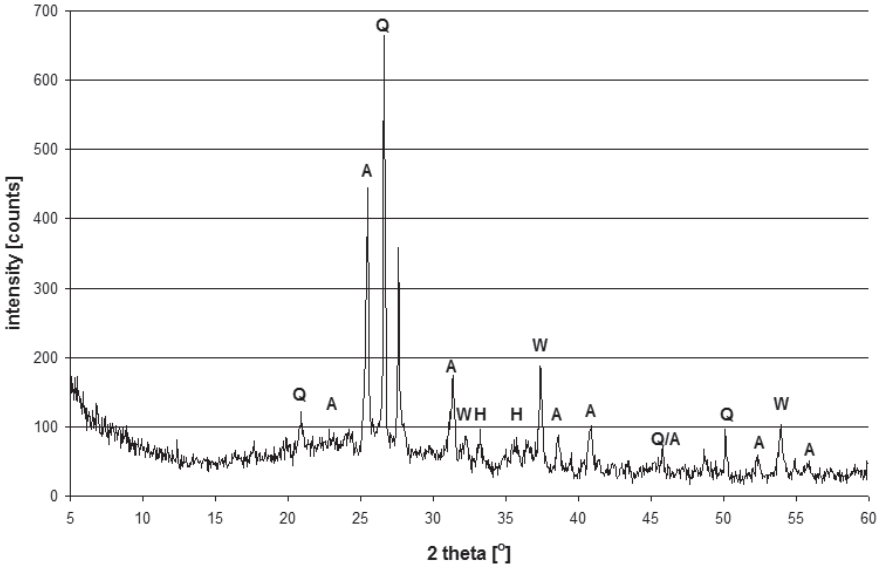

Fig. 4. XRD pattern of fly ash from fluidal combustion of brown coal from Turów power plant Q – quartz, A – anhydride, W – uncombined lime, H – hematite

INERT FILLER

Quartz sand according to PN-EN 196-1 was used as an inert filler. It is sand used for cement strength determination.

3. RESULTS

Examination of waste mud from drilling waste dump

Drilling waste mud from Polish commercial drilling waste dump was used in investigations. Samples were taken from an old lot which is not currently under operation and is provided to be subjected to reclamation. Figure 5 presents the cumulative size distribution curve of drilling waste. Detailed data are presented in Table 3. Figure 6 presents the photographs of solid particles of various fractions of drilling waste investigated. The mud is inhomogenous. Table 4 presents the chemical composition of waste mud determined with XRF. What is most important from the point of view of utilization of waste mud are chlorides and alkali cations, first of all sodium. Since both are easily soluble, it makes this waste difficult to stabilize. In the present case the content of chloride and sodium is high and is supposed to be the most difficult to immobilize. An XRD phase analysis showed a sample of the investigated waste mud to be composed mainly of barite, calcite, quartz, diopside and clay minerals (kaolinite/montmorillonite).

Table 3

Grain size distribution of investigated drilling waste – amount of fractions

Fraction [mm]	Content [% w/w]
0.000–0.063	74.1
0.063–0.125	6.9
0.125–0.250	5.5
0.25–0.50	4.4
0.5–1.0	3.5
1.0–2.0	3.1
2.0–4.0	2.5
Sum	100.0

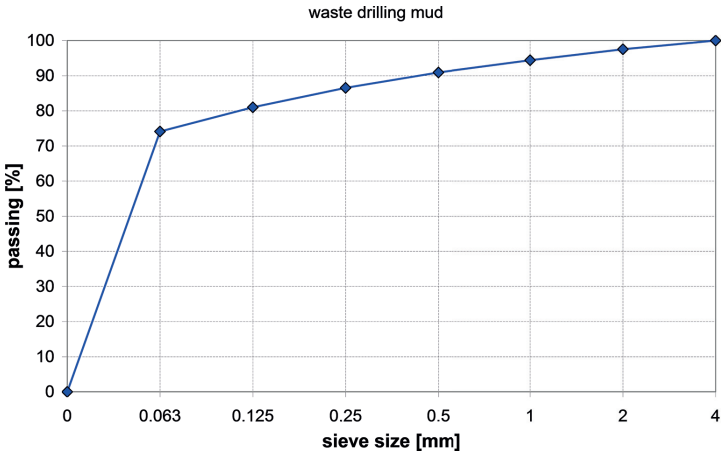

Fig. 5. Cumulative grain size distribution of drilling waste

	
fraction >2 mm inhomogeneous, foil flakes are present	fraction 1–2 mm inhomogeneous, foil flakes are present
	
fraction 0.5–1.0 mm inhomogeneous	fraction 0.25–0.5 mm inhomogeneous
	
fraction 0.125–0.25 mm, relatively homogenous	fraction 0.063–0.125 mm, relatively homogenous

Fig. 6. Photographs of solid particles of various fractions of drilling waste investigated

Table 4

Chemical composition of waste mud investigated

Compound	Content [%]
SiO_2	21.1
CaO	5.3
Al_2O_3	6.6
Na_2O	12.1
K_2O	0.8
SO_3	11.3
Fe_2O_3	3.3
MgO	1.4
Cl	6.2
BaO	19.9
Cr_2O_3	11.2

In order to determine the amount of ions which are not bounded within the material, dried sample of drilling waste was subjected to a leaching test. Results are shown in Table 5.

Table 5

Results of leaching tests for waste drilling mud

Ion	Concentration [mg/dm^3]
Na^+	3,225
K^+	298
Cl^-	5,315
SO_4^{2-}	2,643
Ca^{2+}	261
Mg^{2+}	1.4
Sr^{2+}	4.6

Investigation on the influence of additives on the leaching of ions from the mud

Samples were prepared by mixing proper amounts of materials in a mixer (according to PN-EN 196-1). The mix proportions were first designed. The goal was first to reduce the leaching of ions. Additionally rheological properties were found to be crucial for the practical use of the final material. The idea of a mix design was to add the proper amount of additive, considered as a drying agent (fluidal fly ash possesses high water demand) in the

amount allowing us to obtain material of optimal moisture content resulting in maximum reference density. Mix design tests were made using waste drilling mud and Turów fly ash. Figure 7 presents the plot showing the relationship between moisture content and Proctor density. The calculated moisture content for maximal Proctor density was found as basis for fly ash content calculations. Optimal moisture content was 31.7%. Reference density for the test mixture was 1,316 kg/m^3. on the basis of those calculations five mixtures were designed. The mix proportions are presented in Table 6. After mixing, samples were compacted using the Proctor apparatus. Next they were cured in sealed containers over the water surface in order to ensure the atmosphere saturated with water vapor. After 21 days samples were analyzed for leaching.

Table 6

Proportions of mixes used in leaching experiments

Component	Content [wt.%]				
	1	2	3	4	5
Drilling waste	55	55	55	55	55
Fly ash Turów	40	35	35	35	45
Hydrated lime	5	10	5	–	–
CEM I 42,5 R	–	–	5	10	–

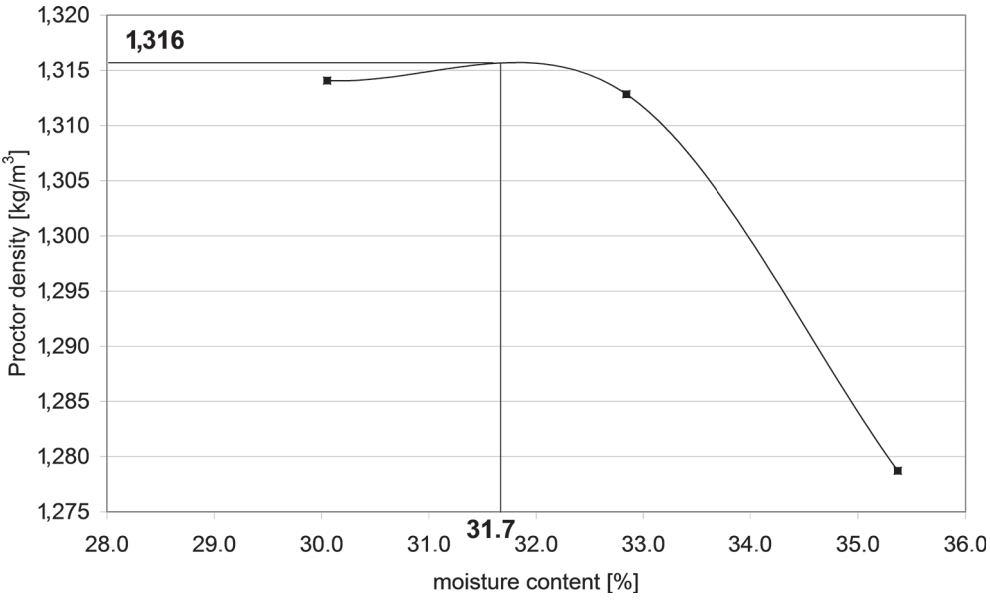

Fig. 7. Relationship between moisture content and Proctor density for fly ash – drilling waste mixture

Table 7

Leaching results for mixes containing waste mud and various additives compared to raw waste mud

Ion	Concentration [mg/dm^3]					
	WM	1	2	3	4	5
Na^+	3,225	1,561	1,066	1,711	1,671	1,530
K^+	298	168	141	208	223	160
Cl^-	5,315	3,088	1,997	3,315	3,166	2,753
HCO_3^-	–	217	241	230	253	92
SO_4^{2-}	2,643	1,401	777	879	1,305	4,212
Ca^{2+}	261	140	23	72	134	502
Mg^{2+}	1.4	0.0	0.0	0.0	0.0	0.3
Sr^{2+}	4.6	1.1	0.2	0.6	1.2	2.9
Al^{3+}	0.9	10.5	9.9	6.4	3.6	7.5

Results of tests showed that investigated waste drilling mud contains a large amount of soluble ions, mainly: chloride, sulfate, sodium, potassium and calcium. The elution of mentioned ions using investigated additives can be lowered to some degree. The best results were noticed in the case of the sample with hydrated lime. Mix no. 2 exhibits the lowest elution of ions. Mix no. 2 contains 10% of hydrated lime. However, the amount of eluted ions is still high. On the basis of the obtained results some conclusions were drawn. It seems to be impossible to decrease the amount of eluted ions below legal demands using relatively small amounts of stabilizing agents. Due to that, it was decided to go further towards the solidification of the drilling waste. The option chosen was to produce aggregates by the solidification of drilling waste in a cementitious matrix with the incorporation of an additional inert filler.

Ordinary Portland cement based aggregates manufacturing

The First step was to determine the best drying agent for moisture reduction in the drilling mud bearing mixes. Hydrated lime, and fluidal fly ash were taken into account. The compressive strength was assumed to be the most important parameter. Table 8 presents the composition of mixes used in the experiment.

Mixtures for aggregate manufacturing were prepared in a planetary mixer. Waste mud was poured to the bowl first, than binders in the order: burnt lime/ fly ash and cement. The next mix was cast in 10 cm cube moulds and covered with plastic foil and wet towels. After 2 days samples were unmolded and transferred to plastic bags with wet towels inside in order to ensure proper humidity. After 7 and 28 days samples were crushed in a jaw crusher and dried. The obtained aggregates were subjected to tests.

Table 8

Mix proportions of mixtures used for aggregate manufacturing

Compound	Content [%]		
	C1	C2	C3
Drilling mud (dry mass)	100	100	100
CEM I 42.5R	30	30	30
Burnt lime	–	10	–
Fly ash Turów	–	–	32

Table 9 shows the results of compressive strength determination. It can be noticed, that mixes prepared with cement and fly ash possess the best mechanical strength. On the basis of the obtained results, mix no. 3 was found to be the best for aggregate manufacturing.

Table 9

Compressive strength of mixtures used for preliminary aggregate test

Curing time	Compressive strength [MPa]		
	C1	C2	C3
7 days	7.0	7.4	17.3
28 days	8.9	9.3	25.8

Figure 8 presents size distribution curve of obtained aggregates. Basic physical properties of obtained aggregates presented Table 10.

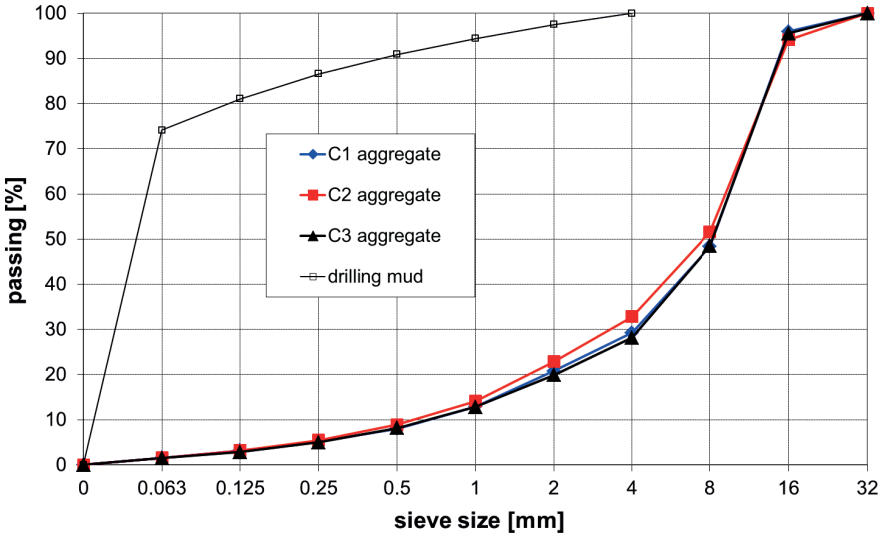

Fig. 8. Grain size distribution of aggregates obtained by the solidification of waste drilling mud

Table 10

Basic properties of cement solidified aggregates

Parameters	Fraction [mm]	Aggregate C1	Aggregate C2	Aggregate C3
Water absorption [%]	4–8	32.8	27.5	30.1
	8–16	29.0	25.8	28.7
Density [kg/m^3]	4–8	2,940	2,780	2,810
	8–16	2,900	2,730	2,770

Fig. 9. C3 aggregate, fraction 8–16 mm

Obtained mixtures were crushed and tested for grain size distribution, water absorbability and density. Figure 9 presents the grains of the C3 aggregate.

In the next step an inert filler was incorporated into mix C3. Table 11 presents the proportions of mixes used for the aggregate preparation.

Table 11

Mix proportions of the mixtures used for the solidification of waste mud with quartz sand. C3 is the control sample for quartz sand samples

Compound	Content [% of waste mud]		
	C3	S1	S2
Drilling waste (dry mass)	100	100	100
CEM I	30.0	30.0	30.0
Fluidal fly ash	32.0	32.0	32.0
Quartz sand	–	100	200

Table 12 presents the compressive strength of the mixes used for the preparation of aggregates with an inert filler. It can be noticed, that the introduction of quartz sand caused a significant increase of compressive strength. Aggregates were crushed and subjected to leaching tests in order to determine the immobilization of harmful ions within the cementitious matrix. Grain size distributions were very similar for those obtained for aggregates without an inert filler. Table 13 presents the results of leaching tests. One can notice, that the introduction of a quartz sand allowed to obtained material with improved mechanical properties comparing to non-filled material. This is probably due to the fact, that the introduction of a relatively coarse filler (0–2 mm) allowed for a decrease in the shrinkage of the hardening material. What is especially important, the leaching ability of the ions decreased significantly due to the dilution effect.

Table 12

Compressive strength of matrices obtained by the solidification of waste drilling mud with quartz sand

Sample	Compressive strength 28 days [MPa]
C3	25.4
S1	38.3
S2	35.8

Table 13

Results of leaching tests for matrices obtained by the solidification of Wronów SK II waste with Quartz sand. Test performed on 2–4 mm fraction after 28 days of curing. Sample C3 is the control sample for the S samples

Ion	Concentration [mg/dm^3]		
	C3	S1	S2
Li^+	0.58	0.48	0.25
Na^+	1,608	898	633
K^+	239	187	126
Cl^-	2,769	1,534	1,139
Mg^{2+}	0.00	0.20	0.20
Ca^{2+}	1.0	7.2	8.2
Ba^{2+}	<0.001	<0.001	<0.001
Cu^{2+}	0.028	0.025	0.019
Sr^{2+}	0.00	0.10	0.10
SO_4^{2-}	375	110	84
Al^{3+}	3.5	7.9	12.8
Cr^{3+}	0.082	0.047	0.410
Fe^{3+}	0.13	0.14	0.06
V^{5+}	0.00	0.01	0.01
Mo^{6+}	0.38	0.05	0.03

4. CONCLUSIONS

On the basis of the results obtained in the investigations some conclusions may be drawn. The first is that investigated waste drilling mud stored in the waste dump contains high amounts of unbound ions, which can be leached out of the sample. It causes the method of utilization to fulfill two goals: the first it should allow to solidify the material in order to obtain material easy to transport and process and second the method should allow us to decrease the amount of ions which can be leached out of the final material. This paper presents a method which allowed for the achievement of the goal. Results obtained in first stage of investigations showed, that the best immobilizing properties can be obtained with the use of hydrated lime as a drying and immobilizing agent. However, lime turned out to result in low compressive strength of the resulting hardened material. Fly ash from the fluidal combustion of brown coal was used as a drying agent and it allowed for the production of materials with high compressive strength which can be used as an aggregate. The resulting materials due to the chemical bonding of the ions, and on the other hand the dilution effect caused by the presence of an inert filler exhibit markedly lower leaching abilities compared to the raw waste drilling mud. The presence of an inert filler not only results in a decrease in the leaching of the ions, but also causes an increase in the strength of the hardened material, probably due to a reduction in shrinkage.

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