Curing Experiments Researching on Waste Oil-base Shale Gas Drilling Mud

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Abstract. Curing research on waste oil-base shale gas drilling mud was performed for optimal additions matching. Destabilizing experiments on waste drilling mud demonstrated that Aluminum potassium sulfate ($KAl(SO_4)_2$) played a best role of destabilizing effects when compared with $FeCl_3$ and $AlCl_3$ based on demulsification mechanism about oil-in-water type. Aluminum potassium sulfate emerged an impact influence on curing effects simultaneously when compared to sodium silicate, alumina, lime and complex Portland cement. Orthogonal test on curing waste drilling mud revealed that the optimal operation conditions of handling waste drilling mud was 4% aluminum potassium sulfate, 4% sodium silicate, 4% alumina, 4% lime and 16% complex Portland cement. Under this condition, unconfined compressive strength of the curing product was 1.80MPa, and lead leaching concentration cannot be detected after 7d maintenance. The curing mechanism was mainly the encapsulation of C_3S and solid waste contaminated by mineral oil can be efficiency treated after breaking the interface of oil-in-water type.

1 Introduction

There are 100×10^{12} m^3 shale gas in Central Asia, which is second to North America possessing the biggest shale gas reserves [1]. With exploiting shale gas increasing, waste oil-base shale gas drilling mud (WOSM) was discharged in corresponding increase. Oil-base mud, a mixed waste, contains two main components. One is the rock cuttings from drilling, and the another is the waste drilling fluid. It discharged without control will bring a series of environment problems, such as ecology system crash and soil deterioration [2]. Therefore, it must be preprocessed before disposal [3].

Currently, methods to dispose waste drilling mud includes devastating approaches (microwave digestion, oxidation) [4,5,6], contaminants extraction [7], resource recycling [8] and stabilization/solidification (S/S) [9,10]. Devastating and contaminants extraction approaches consumes considerable energy, and resource recycling method is limited by the natural characteristics of waste drilling mud. By contrast, solidification/stabilization (S/S) of waste drilling mud is practical and economic.

Al-Ansary and Al-Tabbaa applied the Portland cement and blast-furnace slag to solidify waste drilling cuttings successfully and found that 30 % of their mixture performed better [9]. Leonard and Stegemann acted a systematic treatability study to treat waste drilling mud by stabilization with Portland cement (CEM I) and high carbon power plant fly ash (HCFA) [11]. It revealed itself effective on inhibiting contaminants leached out [11]. However, these findings were almost about the petroleum drilling mud rather than shale gas drilling mud. Besides, mineral oil of waste drilling mud has a harmful influence on stabilization [12]. Therefore, waste shale gas oil-base drilling cuttings must be destabilized before curing, different from petroleum drilling muds.

This paper uses a destabilizer to disperse mineral oil and drilling cuttings and further stabilize the drilling muds by applying multifold binders, which is an innovative way to treat the waste oil-base shale gas drilling mud.

2 Materials and methods

2.1 Materials

Waste shale gas oil-base drilling mud was collected from de-oiling station in the Sinopec shale gas exploration and development projects in Chongqing, China. Waste oil-base mud was dried by natural drying and seized to obtain 100 mesh powder, then it was stored in desiccators throughout the duration of the study. According to demulsification mechanism about oil-in-water type, ferric chloride ($FeCl_3$), aluminum chloride ($AlCl_3$) and aluminum

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potassium sulfate ($AlK(SO_4)_2$) were selected to be destabilizing agents; Complex Portland cement (CPC) , calcia (CaO), sodium silicate (Na_2SiO_3) and alumina (Al_2O_3) were selected to be curing agents.

2.2 Destabilizing experiment

Weighting quantities of waste oil-based drilling mud (10 g), destabilizing agents and water (15 ml) were mixed and stirred for 10 min by using paste mixer. Then, mixture was laid for 20 min without any activities, and the morphology of the waste oil-base drilling mud broke with destabilizing agents was observed. Finally, mixture was moved to centrifuge tube, turning 20 min (3000 r/min). Destabilizing effect of waste drilling mud was characterized with morphology of mixture, moisture content of centrifugal mud cake and pH values of the centrifugal liquid.

2.3 Curing experiment

Homogeneous drilling mud particles were weighted for 50 g, mixed with destabilizing agents, curing agents and water (20 ml), then mixture was stirred for 10 min by use of paste mixer. The mixture was poured into steel molds (20·20·20 mm) to fill them with three times and entrapped air bubbles were removed through vibration (5min). The molds were sealed in plastic bags to prevent possible carbonation due to exposure to air and cured for 24 h in a humidity chamber with a relative humidity of 98 ± 2% and a temperature of 21 ± 3°C before demolding. In the end, demolding products were transferred back into the humidity chamber for further curing prior to testing. Stabilizing effects were characterized with unconfined compressive strength of curing product and lead leaching concentrations.

2.4 Characterizing effect

Chinese Standard GB/T 17671-1999 [13] was used as a guideline to determine the compressive strengths of the samples and testing machine (Shimadzu, Japan) was used for this purpose with three replicates. Lead leaching concentration were tested according to <Solid waste leaching toxicity leaching methods H_2SO_4/HNO_3> [14]. Lead leaching concentration was determined by flame atomic absorption spectrophotometer (Shimadzu AA-6300C, Japan). Mineral phases of raw materials and curing products were assessed by use of XRD (PANalytical, Holland) with CuK_α radiation in the 2θ range from 20° to 80° at a scanningrate of 0.2°/s for 2θ.

3 Results and discussion

3.1 Oil-base drilling mud

Heavy metals and fundamental composition analysis of the original WOSM are summarized in Table 1. Analysis for drilling mud reveals that the main contaminant is total petroleum hydrocarbon (TPH) and heavy metals (Pb and Zn). Therefore, according to National Catalogue of Hazardous Wastes [15], waste oil-base drilling mud belongs to hazardous waste. However, the bad consistency between oil and cement inhibit the process of cement hydration [16], which means that waste oil-based drilling mud should be pretreated by adding destabilizing agents before S/S. From Table 1, the leaching concentration of lead is remarkable and the lead content of drilling cuttings is larger than other reports [17], which indicates that it can character the curing effects of waste drilling mud. Besides, considering the further using of curing products compressive strength must be too.

Table 1 Composition of waste oil-base drilling mud:

Fundamental composition analysis					
Material phase	Moisture content	Volatiles	Ash	TPH [a]	
content (%)	7.93	11.0	81.1	1.23	
Heavy metal analysis					
elements	Cd	Cr	Cu	Pb	Zn
Content (mg/kg)	24.0	92.6	54.3	598	1401
Leaching concentration (mg/L)	0.01	0.13	n.d.	1.02	0.02

[a] Total petroleum hydrocarbon
n.d. represents Not detected.

3.2 Screening destabilizing agent

Destabilizing effects of waste drilling mud responding to various destabilizing agents are summarized in Fig.1. Compared with other destabilizing agents, aluminum potassium sulfate ($AlK(SO_4)_2$) has the highest moisture content of mud cake and morphology of destabilized mud looks like fine particles with dissociation (Fig.1a), which indicates that aluminum potassium sulfate ($AlK(SO_4)_2$) performs the best destabilizing effects. It is because the Al^{3+} can neutralize the negative charge of surface for oil-based drilling cuttings. Besides, turbidity of centrifugal liquid is pellucid and pH value of centrifugal liquid is the most and closer to 7, in which the further curing by binders can be in favor. By contrast, aluminum chloride ($AlCl_3$) and ferric chloride ($FeCl_3$) has a lesser influence on waste drilling mud in destabilizing effects. Thus, aluminum potassium sulfate ($AlK(SO_4)_2$) was selected to be destabilizing agent for further researching. Correlation to moisture content with aluminum potassium sulfate content is showed in Fig.1b. Moisture content of centrifugal mud cake increases with aluminum potassium sulfate adding in initial. When aluminum potassium sulfate content is up to 4g/100g mud, the moisture content reaches the peak (moisture content, 18.34%), and then moisture content decreases. This phenomenon can be explained by considerable interspaces emerged by separation of mineral oil and drilling cuttings in initial. However, the complete separation of mineral oil and drilling cuttings derived from the excess of aluminum potassium sulfate can reduce the moisture content of mud cake due to itself densification during centrifugation. The pH of centrifugal liquid reduces with $AlK(SO_4)_2$ increasing and levels off with destabilizer continuing to increase, which is owing to the hydrolysis of Al^{3+}. Based on above analysis, optimal addition of

aluminum potassium sulfate is 4 g/100g waste drilling mud for further researching.

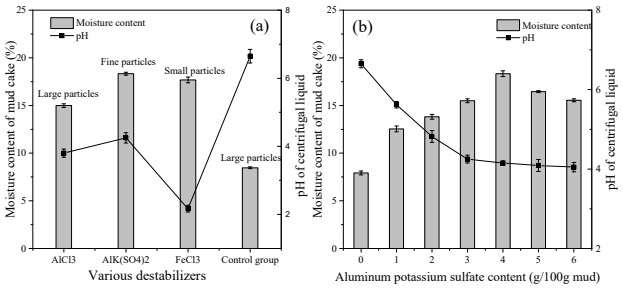

Fig.1. Response of destabilizing effects: (a) Destabilizing effects of various destabilizers with 3g/100g mud; (b) Destabilizing effects of different aluminum potassium sulfate contents

3.3 Curing experiment

3.3.1 Cement curing experiment

Fig.2 shows that curing effects change with cement adding. The unconfined compressive strength of curing products increases with cement addition, but the increase degree of USC gets slow down after the cement addition at 20 g/100g mud. The increase of USC is because C-S-H, hydration products of cement, provides the compressive structures [18]. With cement addition increasing, the drilling mud get a little influence on curing products, which can explain the slowing trends. In addition, the value of unconfined compressive strength was low, which indicates that mineral oil of oil-based drilling cuttings inhabits the formation of C-S-H and results in the small USC [3]. The leaching concentration of lead is cut down with cement addition to 20g/100g waste drilling mud and then is opposite. The decrease in lead leaching concentration was due to the encapsulation of hardened lattice with CPC hydration, but when the cement addition reached above 20g/100g mud, the alkalinity of curing products boost so that the lead leaching concentration increases due to itself amphoteric. Therefore, according to above analysis, optimal addition of complex Portland cement is 20g/100g mud.

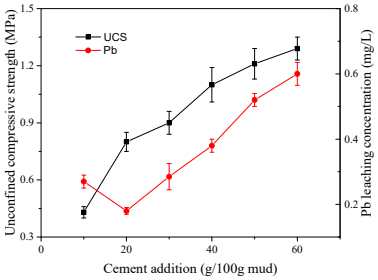

Fig.2. Curing effects of various cement content addition on waste drilling mud.

3.3.2 Co-curing experiment

Fig.3 shows the comparison of alumina, lime and sodium silicate based on the curing effects including unconfined compressive strength and lead leaching concentration. The unconfined compressive strength of curing products with alumina and lime addition are in the same growing trend, but that of sodium silicate increases all the time (Fig.3a). Alumina can fill in the gaps left by cement hydration initially, and the decrease in USC with alumina continuing to increase can be explained by the excess alumina, inert particles, existing in the curing products. Besides, the increase in USC with lime addition was due to the hydration of lime and cement, similarly the excess lime can be become calcium hydroxide or itself filling in the curing products to cut down their USC. Sodium silicate can significantly increase the UCS of curing products with itself boosting due to itself resin properties. In contrast, the Pb leaching concentration of three co-curing agents demonstrates three different trends (Fig.3b). Compared with USC, the lead leaching concentration of sodium silicate decrease with itself adding but slowing down in the latter, which means that sodium silicate can be selected to be the main co-curing agents and the optimal of it was determined for 6 g/100g mud. Lead leaching concentration of curing products decreases with alumina adding in initial, and then increase with alumina adding, which is due to the same reason for UCS. The optimal of alumina was determined for 4 g/100g mud. However, lead leaching concentration of curing products increase with lime adding all the time because of the alkalinity ascending of curing products and the native amphoteric metal of lead. As a sequence of UCS needing to satisfy the landfill of curing products and curing products emerging low lead leaching concentration, lime can become one of the co-curing agents. Therefore, the optimal of lime was determined for 4 g/100g mud.

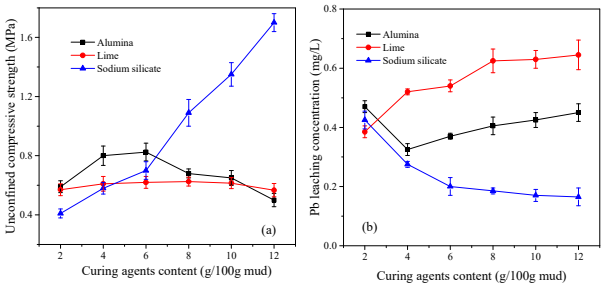

Fig.3. Curing effects with co-curing agents adding

3.4 Characterization of cured waste drilling mud

According to previous researching on curing drilling mud, orthogonal $L_9(4^5)$ options and experiment results are shown in Table 2. The UCS of sample S5 is the maximum and reaches 1.65 MPa, with a 0.05 mg/L of lead leaching concentration. Besides, the Pb leaching concentration of S2 is the least and cannot be detected, with a 0.97 MPa of UCS. Range analysis of UCS and lead leaching concentration is showed in Table 2. All factors have a significantly influence on UCS of curing products, the most remarkable of these factors is aluminum potassium sulfate ($AlK(SO_4)_2$), and the sequence of curing effects as follows: $AlK(SO_4)_2$ > Na_2SiO_3 > Portland cement > Al_2O_3 > CaO. Based on UCS of curing products, optimal

matching of curing agents is A2B3C1D2E2. However, the range analysis of lead leaching concentration indicates that aluminum potassium sulfate ($AlK(SO_4)_2$) has an obvious influence on curing effect of Pb leaching concentration with other factors having a little influence, and exhibits the following order: $AlK(SO_4)_2$ > Al_2O_3 > Portland cement > Na_2SiO_3 > CaO. Based on lead leaching concentration of curing products, optimal matching of curing agents is A3B2C2D1E4. Considering the UCS and lead leaching concentrations, the best match is the A2B2C1D2E2. Under this condition, unconfined compressive strength of the curing product was 1.80MPa, and lead leaching concentration cannot be detected after 7d maintenance.

Table 2 Orthogonal experiment option and results.

Samples	$AlK(SO_4)_2$ (A,g)	Al_2O_3 (B,g)	Na_2SiO_3 (C,g)	CaO (D,g)	Cement (E,g)	UCS (MPa)	Pb leaching concentration (mg/L)
S1	3.00	2.00	4.00	2.00	12.00	0.68	0.10
S2	3.00	3.00	6.00	4.00	16.00	0.97	n.d.
S3	3.00	4.00	8.00	6.00	20.00	0.7	0.2
S4	3.00	5.00	10.00	8.00	24.00	n.d.	0.09
S5	4.00	2.00	6.00	6.00	24.00	1.65	0.05
S6	4.00	3.00	4.00	8.00	20.00	1.42	0.11
S7	4.00	4.00	10.00	2.00	16.00	1.41	0.17
S8	4.00	5.00	8.00	4.00	12.00	0.71	0.17
S9	5.00	2.00	8.00	8.00	16.00	0.5	0.04
S10	5.00	3.00	10.00	6.00	12.00	0.42	0.12
S11	5.00	4.00	4.00	4.00	24.00	1.52	0.12
S12	5.00	5.00	6.00	2.00	20.00	0.96	0.04
S13	6.00	2.00	10.00	4.00	20.00	0.97	0.41
S14	6.00	3.00	8.00	2.00	24.00	1.03	0.36
S15	6.00	4.00	6.00	8.00	12.00	0.85	0.49
S16	6.00	5.00	4.00	6.00	16.00	1.35	0.49
Range analysis of UCS							
k1	0.59	0.95	1.24	1.02	0.67		
k2	1.3	0.96	1.11	1.04	1.06		
k3	0.85	1.12	0.74	1.03	1.01		
k4	1.05	0.76	0.7	0.69	1.05		
range	0.71	0.37	0.54	0.35	0.39		
Range analysis of Pb leaching concentration							
k1	0.10	0.15	0.20	0.17	0.22		
k2	0.12	0.15	0.15	0.18	0.18		
k3	0.08	0.25	0.19	0.22	0.19		
k4	0.44	0.20	0.20	0.18	0.16		
range	0.36	0.10	0.05	0.05	0.06		

n.d. represents Not detected.

3.5 Characterization of cured waste drilling mud

Fig .4 shows XRD graphics of the initial and cured WOSM at the curing age of 7d. The crystalline phases of the original waste drilling mud mainly consist of quartz (SiO_2, PDF #46-1045), vaterite ($CaCO_3$, PDF #33-0268), xonotlite [$Ca_6Si_6O_{17}(OH)_{12}$, PDF #23-0125], magadiite ($Na_2Si_{14}O_{29}\cdot 10H_2O$, PDF #42-1350) and calcium sulfate hydrate ($CaSO_4\cdot 0.62H_2O$, PDF #41-0225). When compared to the original WOSM, the mineral composition of cured WOSM almost have no obvious changes except the XRD peaks of Calcium silicate (Ca_3SiO_5, PDF #42-0551) and calcium silicate hydrate ($Ca_2SiO_4\cdot H_2O$ PDF #29-0373) [19]. In addition, the intensity of crystalline phases in cured WOSM were lower than that of the original due to the dilution of minerals. Therefore, the curing mechanism of waste drilling mud was mainly the encapsulation of C_3S, resulting from the obvious strengthen of the characteristic peak of C_3S (29.35° and 51.7°).

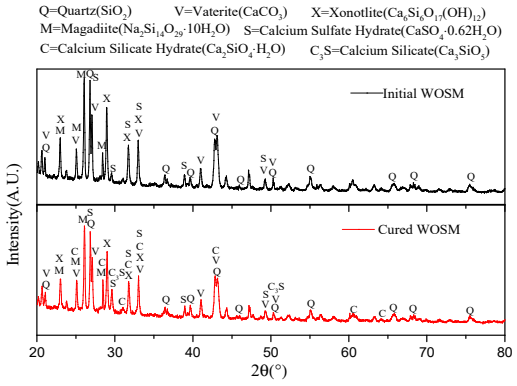

Fig.4. The XRD graphics of the initial WOSM (waste oil-base shale gas drilling mud) and cured WOSM.

4 Conclusion

In this work, waste oil-base shale gas drilling mud was successfully stabilized by cement after destabilizing. The aluminum potassium sulfate is the best destabilizing agent, followed by ferric chloride, aluminum chloride in the end. Through designing curing orthogonal test of waste drilling mud, it shows that destabilizing agent has a significant influence on curing effects, and the formula of dealing with drilling mud is put forward. Dealing with 1t drilling mud needs 4% aluminum potassium sulfate, 4% sodium silicate, 4% alumina, 4% lime, and 16% Portland cement. The curing mechanism of waste drilling mud was mainly the encapsulation of C_3S. Mineral oil inhibits curing effects of curing products, therefore, solid waste contaminated by mineral oil can be effeiciently treated after breaking the interface of oil-in-water type. This method can be applied in other similar fields.

Acknowledgments

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