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Characterisation of oil based mud waste to explore the possibility in transforming waste into a value added product

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Abstract

Waste characterisation is an essential factor in designing sustainable waste management plan. However, waste composition profile is underestimated in oil and gas exploration and production (E&P) industries in the United Kingdom. A three years long investigations on the valuable and environmentally significant chemical constituents present in oil based mud (OBM) waste stream has been conducted at Robert Gordon University, Aberdeen to fill the information gap in literature and to provide opportunities to recover resources in this waste stream. Initially twenty elements including alkali earth metals (Mg, Ca, Ba), alkali metals (Na, K), Transition metals (V, Cr, Mn, Fe, Ni, Cu, Zn, Cd), post transition metals (Al, Pb), metalloids (Si, As), polyatomic non-metals (P, S), and actinide (U) have been determined in spent drilling fluids using Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES). Further analysis such as Fourier Transform Infrared (FTIR) Spectroscopy, Scanning electron microscope (SEM), and Energy Dispersive X-Ray Analysis (EDXA) have been carried out to highlight the chemical characteristics of this OBM waste. Findings from this study draws the attention from the OBM waste management authority to step up to consider extended resource recovery plan which helps to protect the valuable resources discarded in landfill site.

Keywords: oil based mud waste, resource recovery from waste, oil based mud waste characterisation, environmental protection, sustainable waste management.

1. Introduction

A drilling fluid is an essential part of drilling operation in oil and gas industry to perform certain functions such as removing and cleaning drill cuttings from the downhole, cooling and lubricating the drill bit, controlling the hydraulic pressure to protect well blowouts (Caenn *et al*., 2011) (Fink, 2015) (Khodja *et al*., 2010). Among different drilling fluids, Oil Based Mud (OBM) is preferable especially where reliable shale inhibition and excellent lubricity is needed (Patel *et al*., 2007). This drilling fluid predominantly OBM which is used in deep drilling operation ended up with a large amount of pollutants introducing in drilling fluids addressing a big concern for the oil and gas industry and government regulators (Veil, 2002) (Force, 2009). Different mechanisms have been developed and applied for treating drilling fluid waste including solidification technology (Tuncan *et al*., 2000), the solid-liquid separation technology (Zou *et al*., 2011), MTC (mud transform to cement) technology (Nahm, 1993), incineration technology (Onwukwe *et al*., 2012) and some other thermo-mechanical treatments (Mokhalalti *et al*., 2000). These processes have certain benefits and limitations, but the detrimental effects on environment is common (Ball *et al*., 2012).

In 2011 Colborn *et al*., published an article on hazard assessment of natural gas operations from a public health perspective which reflects how different chemicals from different sources may harm the environment predominantly human health. This report provides very useful information regarding the hazardous effects of different chemicals/pollutants accumulated during natural gas operations. According to their findings, the potential health effects of 353 chemicals are available in Chemical Abstract Service (CAS) numbers, although 632 chemicals are used in natural gas processing operations. Among different contamination media, soil is prone to high risk associated with the OBM waste (Carls *et al*., 1995) (Rojas *et al*., 2007). Soil contamination is hazardous to health and environment through its action on surface waters, ground waters and vegetation (phytotoxicity, bioaccumulation). Oil and gas industries, like other process industries, have a detrimental effect on environment (Khodja M. *et al*., 2010). The hazardous effect of the environmentally significant constituents in the produced drilling wastes is predominantly dependent on each constituent, its concentration at exposure, biotic environment at point of discharge and the duration of exposure.

The typical type of drilling wastes and their potential constituents are (Onwukwe S, Nwakaudu M., 2012):

- WBM cuttings: Heavy metals, inorganic salts, biocides, hydrocarbons

- OBM cuttings: Heavy metals, inorganic salts, hydrocarbons, solid/cuttings
- Spent OBM: Heavy metals, inorganic salts, hydrocarbons, solid/cuttings, BOD, surfactants
- Spent WBM: Metals including heavy metals, inorganic salts, hydrocarbons, biocides, hydrocarbons, solid/cuttings, BOD,
- Waste lubricants: Heavy metals, organic compounds.

The potential effects of these elements on human health is briefly described in Table 1.

Table 1: Environmentally significant pollutants in drilling fluid wastes and their effects on human health.

Chemicals	**Hazardous effects**	**Reference**
Acetaldehyde	-severe eye irritation -harmful if swallowed or inhaled -affects central nervous system, liver and kidneys -carcinigenic	Hammer *et al.*, 2012 Jackson *et al.,* 2013
Acetic acid	-may cause severe burn to body tissues -may cause lung and tooth damage	Clark *et al.*, 2002 Ferrer, I. Thurman, E.M., 2015
Ammonium bisulfite	-source of releasing poisonous and flammable hydrogen sulphide (H_2S)gas -maximum 8 hours exposure to H_2S (>100 ppm) will cause haemorrhage and death. Concentrations above 600 ppm can be fatal in 3 to 5 minutes	Amosa *et al.,* 2010 Waxman *et al*., 2011
Aldehydes	-some aldehydes are carcinogenic -respiratory, eye, and skin irritant	O'Brien *et al*., 2005 Clark *et al.*, 2002 Wang RS *et al*., 2002
Dodecylbenzene sulfonic acid	- may cause eye, skin, nose throat irritation - can damage human skin	Cserháti T *et al*., 2002
Heavy metals	- nose and throat irritation, bronchoconstriction and dyspnoea are usually experienced after exposure to certain heavy metals such as arsenic, nickel and vanadium - Arsenic predominantly affects different organs in human body mainly kidneys. It also affects vascular system, causes hyper tension, cardiovascular diseases. It is also evident that arsenic can cause cardiomyopathy, peripheral neuropathy and the gastrointestinal effects in human body - Cadmium exposure may cause kidney damage, also may cause bone effects and fractures - Mercury is considered as a responsible element which causes different kinds of disorders including neurological, nephrological, immunological, cardiac and even genetic -Lead is a ubiquitous toxic heavy metal with possible carcinogenic, clastogenic, and mutagenic effects on human	Kampa M, and Castanas E., 2008 Jomova K. *et al*., 2011 Järup L., 2003 Zahir F, *et al*., 2005 García-Lestón J., *et al.*, 2010; Tong S. *et al*., 2000
Polycyclic aromatic hydrocarbons (PAHs)	- Some PAHs are increasing concern because of their carcinogenic, mutagenic, and teratogenic effects on human being.	Hammer *et al*., 2012 Jackson *et al*., 2013 Grieve, A., 1988

1.1. Research objectives

Although the negative effects of OBM waste has been presented in different study, but the potential resource recovery of critical elements which are considered as hazardous materials such as heavy metals in the waste stream and their separation process and the fate of the residues is unknown. Centre for Advanced Engineering Materials at Robert Gordon University has investigated the potential sources of drilling wastes and compositional characterisation in last few years (Adegbotolu, 2014) (Siddique, 2017). As part of the next phase of this work, this study aims answer the first part of the question to determine the possible natural resources associated with this OBM waste by performing different analysis. This paper provides the valuable information by performing different characterisation and analysis which would help understanding the necessity of resource recovery from this OBM waste stream and thus ensure the environmental pollution prevention is in practised by the oil and gas industry.

1.2. Paper structure

Research methodology including sample collection and preparation and different analysis processes are introduced in Section 2. The elemental analysis results are mentioned in Section 3.1 followed by the FTIR spectroscopy analysis in Section 3.2 and at the end the morphology study is mentioned in Section 3.3. Finally conclusions are presented in Section 4.

2. Experimental method

2.1. Sample collection and preparation

The OBM waste was donated by a local oil and gas service company in Aberdeen, UK. To characterise the solid content in this OBM slurry the petroleum hydrocarbon has been eliminated by using thermal treatment process. Since the aim of this study is to identify the possibility of resource recovery from the OBM slurry, the hydrocarbon content is ignored in this study. To obtain the solid residue, the OBM slurry is heated sporadically by following the stages: 50°C for 12 hours (1st heating) followed by 80°C for a further 12 hours (2nd heating); finally the residue is heated at 700°C for 12 hours (3rd heating). To facilitate to carry out different analysis, this solid residue is now crushed into smaller pieces using a grinder followed by a further size reduction to produce powder by using IKA UltraTurrax ball mill. Montmorillonite (MMT), K10 is supplied by Sigma-Aldrich, UK is used as a reference material to compare different characteristics between MMT and OBM powder.

2.2. Elemental analysis

2.2.1. Elemental analysis of raw OBM waste

Elemental compositional analysis were carried over using a spent drilling fluid supplied by a local company in Aberdeen, UK. The samples were replicated three times to make the results more analytically acceptable and reproducible. This analysis can be divided in two sections; a) sample digestion procedure and b) sample analysis using ICP-OES instrument.

Sample digestion procedure is a step by step process where the drilling fluid sample (0.5 g) was transferred to Teflon beakers, followed by adding 8 mL of HNO_3 in the beakers. Digestion was performed in triplicate for drilling fluid sample. They were kept in a closed system in a microwave oven (ETOH) for 15 min on the temperature ramp (13.33ºC/min) until to reach at 200ºC. The samples were kept in the same temperature environment in the digester for an additional 15 minutes for completing the samples digestion process.

After digestion, all extracts were filtered through Whatman 1, 542 (Hardened Ashless) filter paper and transferred to 50 mL volumetric flasks (Fisher Scientific), filling with deionised water. Glassware was cleaned and decontaminated in a 5% nitric acid solution for 24 h and then rinsed with deionised water.

2.2.2. Elemental analysis of OBM powder waste

To determine the elemental composition of dry OBM waste, energy dispersive x-ray analysis (EDXA) (Oxford Instruments INCA Energy) was carried out.

2.3. FT-IR spectrum analysis

Attenuated Total Reflectance- Fourier Transform Infrared (FTIR) Spectroscopy was carried out for 32 scans between 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. A blank measurement was taken to minimise the influence of water vapour and carbon dioxide from the atmosphere.

2.4. Morphology study

Scanning electron microscope (SEM) was performed using a Zeiss EVO LS10 instrument with a magnification of 10000 times, 8.0 mm working distance (WD) and accelerating potential of 5.0 kV.

The samples were coated with gold and palladium using sputter deposition for 2 minutes prior to the analysis.

3. Result and discussion

3.1. Elemental analysis

Calibration was performed for metal analysis using standard 10,000 mg L^{-1} solution supplied by Fisher Scientific, UK.

Table 1: Elemental analysis of raw OBM waste using ICP-OES

	Concentration (µg/g)			
Elements	**Sample 1-1**	**Sample 1-2**	**Mean**	**±SD**
Ba	174	108	141	46
Ca	82241	89799	86020	3779
Na	77	79	78	2
Fe	337	356	346	13
Al	174	177	176	2
Mg	46	48	47	1
K	55	49	52	4
Mn	365	379	372	10
V	26	27	27	0
Ni	19	20	19	1
As	0	0	0	0
Cr	39	44	42	3
Cd	0	0	0	0
Zn	256	278	267	15
Cu	47	46	47	0
Pb	138	146	142	6
Si	51	59	53	4
P	108	114	111	4
S	4694	4931	4813	168
U	199	217	208	12

Table 1 highlighted the recovered elements present in OBM waste. Sample analysis were performed only when the r^2 of the calibration curve was higher than 0.999. The concentrations of alkaline earth metals (Mg, Ca, Ba), alkali metals (Na, K), transition metals (V, Cr, Mn, Fe, Ni, Cu, Zn, Cd), post-transition metals (Al, Pb), metalloids (Si, As), polyatomic non-metals (P, S), and actinide (U) in the extracts were determined by using PerkinElmer Optima 8000 ICP-OES instrument.

EDXA was carried out to determine the elemental composition of dry OBM waste which is presented below in Table 2.

Table 2: EDXA analysis of OBM waste powder

Element	**Weight%**
O	29.12
Na	0.59
Al	1.4
Si	4.49
S	9.95
Cl	2.49
K	0.31

Ca	6.32
Fe	0.86
Ba	44.47
Totals	100

3.2. FT-IR spectrum analysis

The resulting spectra from ATR-FTIR analysis of OBM waste slurry and its solid contents is presented in Fig. 1.

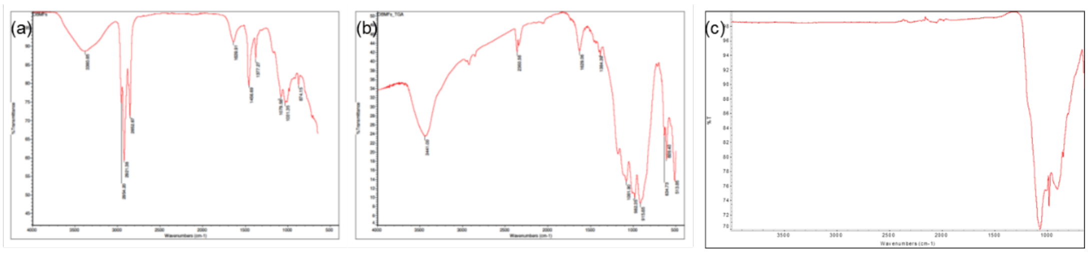

Fig. 1: ATR-FTIR full scale spectra of (a) OBM waste slurry; (b) OBM waste residue after TGA analysis and (c) OBM waste dry powder.

Fig. 1(a) shows different OH bending presence in OBM slurry which correspond to the hydrocarbon presence in the substance. Fig. 1(b) and 1(c) represents different peaks corresponding to different chemical bonds in OBM waste after TGA and in OBM waste powder. A broad band near 3380 cm^{-1} corresponds to the H-O-H vibrations of adsorbed water. The clay minerals in OBM waste show Si-O stretching and bending as well as OH bending absorptions in the range of 1300-400 cm^{-1}. Variations in the layers arrangements are reflected in the shape and positions of the bands. Strong band peaks at 1120-1000 cm^{-1} corresponds to the Si-O stretching vibrations of kaolinite and dickite. The main Si-O band peak corresponds to chrysotile is observed at a lower frequency of 980 cm^{-1}. The band peak at 1080 cm^{-1} represents the montmorillonite whereas the band peak at 980 cm^{-1} corresponds to the saponite minerals in OBM waste. The band peaks in the region of 980-900 cm^{-1} represents the dioctahedral minerals while the band in the region of 700-600 cm^{-1} range corresponds to the trioctahedral minerals. The band peak at 600 cm^{-1} represents the presence of Mg_3OH. The peak at 916 cm^{-1} reflect the partial substitution of octahedral Al by Mg in montmorillonite. Band spectra profile published in the literature is very helpful to identify different clay minerals present in OBM waste (Madejová *et al*., 2003).

3.3. Morphology study

In Fig. 2, the micrograph shows the tightly stacked platelets of montmorillonite and OBM waste powder with size ranges up to 1000nm.

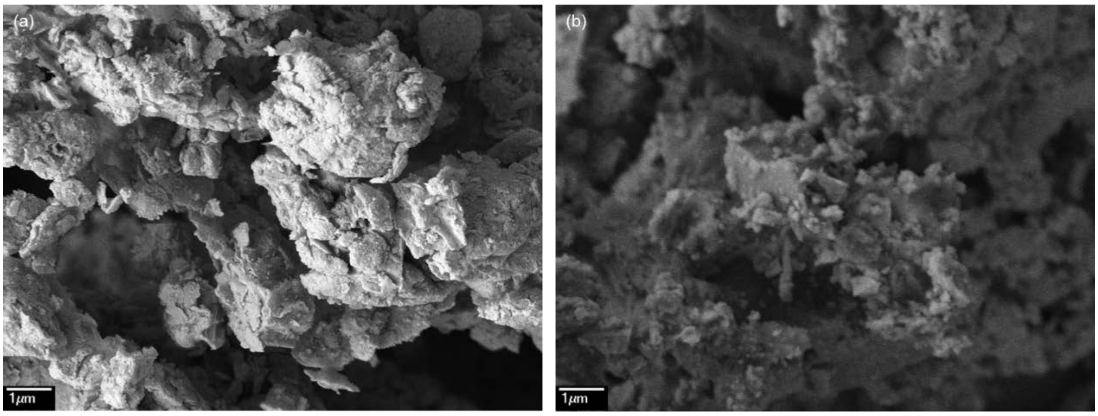

Fig. 2: SEM images of (a) Montmorillonite as a reference material and (b) OBM waste dry powder.

The SEM micrographs were used to investigate the morphological representation of different clay minerals present in OBM waste which is compared with that of standard montmorillonite sample supplied by Sigma-Aldrich. Both micrographs represent the platelet structure, however OBM shows tightly stacked the platelets with variant sizes of platelets with different shapes whereas montmorillonite shows regular platelet shapes with uniform structure. It can articulate here that different clay minerals may influence the structure and shape of the platelets present in OBM waste. A detail morphology will be discussed in the next study where different clay minerals can be identified by observing the structure and shape of different platelets present in OBM waste.

4. Conclusions

This experimental investigation is an attempt to characterise OBM waste to explore the opportunity to recover useful compounds associated with this waste which is disposed off in landfill site now and causes risks of serious environmental pollution. Elemental analysis of OBM waste slurry and OBM waste powder have been analysed by using ICP-OES and EDXA respectively which clearly showed the presence of precious metals in both waste stream significantly. The ATR-FTIR spectra of both OBM waste slurry and OBM powder waste confirms the existing different clay minerals molecular structure in the waste. Furthermore, SEM also illustrates the morphological structure of clay-platelets in the OBM powder waste. To determine the different phases of compounds exist in OBM waste, X-ray powder diffraction (XRD) has been carried out (not reported) to fully understand the physio-chemical nature of this waste. Since thermal treatment is the predominant process in the oil and gas industry to manage this OBM waste before disposing in landfill site, the thermal behaviour of this waste is also important to understand which has been completed in this study and will be published comprehensively in the next report.

Having identified the presence of different clay minerals associated with various metal compounds which is considered as hazardous materials in the environment, the next stage of the current research will be to propose different resource recovery plans or utilising them by introducing new recycling process. Finally, zero waste approach will be established by adopting circular economy strategy which will help to design a sustainable waste management process for oil and gas industry.

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