AADE-05-NTCE-64

Onsite Treatment of Oily Drilling Waste in Remote Areas

Gary R. Barnes, Darryl Hartley - MUD-loc USA Inc



This paper was prepared for presentation at the AADE 2005 National Technical Conference and Exhibition, held at the Wyndam Greenspoint in Houston, Texas, April 5-7, 2005. This conference was sponsored by the Houston Chapter of the American Association of Drilling Engineers. The information presented in this paper does not reflect any position, claim or endorsement made or implied by the American Association of Drilling Engineers, their officers or members. Questions concerning the content of this paper should be directed to the individuals listed as author/s of this work.

Abstract

Use of the S-E-S (Stabilization – Encapsulation - Solidification) Process For Treatment Of Oil-based Drilling Fluid Waste using pozzolans as preliminary stabilizers.

Introduction

There are many examples of remote areas where oilfield drilling is undertaken the authors have had experience in many areas world wide, however our main scope of treatment has taken place in the Northern Alberta and the North West territories regions of the Alberta Petroleum basin.

The Alberta petroleum basin is mature and any new prospects explored by Western Canadian companies tend to be located in areas and formations that represent difficult drilling conditions. An example of this situation is the active Belly River play, with its sensitive shales. Advanced recovery methods in mature fields often involve horizontal or inclined holes, particularly in the heavy oil regions.

To overcome excessively tight holes, avoid stuck pipe, avoid excessive hole caving and drill string drag problems, the use of oil-based mud has become more widespread than at any time in the past.

Handling oil-based mud requires care and training for rig crews and for the operator of the lease, as some of the mud constituents are toxic. To avoid health problems for the rig crews and environmental contamination of the site, both leftover and spent mud must be rendered harmless before disposal.

Oil-based mud is a mixture of barite, bentonite clay, mineral oils (usually diesel fuel) and chemical additives (Gray, 1980; Chilingarian and Vorabutr, 1983; Devereux, 1998; American Association of Drilling Engineers, 1999). It differs from water and synthetic-based mud only in the ratio between water and oil present. The current oilfield practice is to drill with water-based mud until a significant bend is planned or until a particular depth has been reached. The reason for this is the superior lubricity of oil-based mud; the well bore stabilization properties of invert and its insensitivity to high temperatures (up to 270C). While formation damage due to oil-based mud invasion is severe, the depth of invasion is much less than for either water or synthetic-based muds.

Diesel-fuel-based mud remains the formulation of choice because of its low cost relative to lower toxicity oils and its greater availability. As a result, it will likely remain popular for the foreseeable future.

Chilingarian and Vorabutr (1983) define invert-emulsion mud is simply oil-based mud in which the internal phase is freshwater or HCl brine ("water-in-oil"). While there is a technical distinction between oil-based and invert mud, the terms are often used interchangeably. Since water is always present in spent oil-based mud, the balance of this report will use the term "invert mud" to include both variants. Technically, if water is present at less than 5% by volume, the fluid is not an invert emulsion.

Oil and water are normally immiscible. When preparing an inert emulsion mud, the fluids are emulsified with a surfactant to produce a homogeneous fluid phase to which the barite, clays and other solids are added and blended before being introduced into the drilling rig mud system. Diesel/brine ratios range from 50/50 to 95/5 in fresh, unused mud. The ratios are varied during drilling operations, particularly for underbalanced drilling, to ensure a gauge hole and to keep the borehole fluid in laminar flow (Hanna, 2000).

State-of-the-Art, high penetration rate drilling rigs are entering Alberta in larger numbers at the time of writing that include a totally enclosed mud system to ensure oil-based muds are handled safely (Teichrob and Baillargeon, 2000). The new generation of drilling rigs should be discharge-free.

When introduced into the borehole, invert mud forms a semi-permeable membrane with respect to the chloride ion. When the salinity of the formation fluid exceeds mud salinity, water will pass from the borehole into the formation, and vice versa. Control of salinity, in part, determines how tough the mud cake is and how much formation damage occurs in each formation penetrated. If salinity is too high, formation fluids will dilute the borehole fluid and expand the volume of mud in the system. A slight excess salinity in borehole fluid is desirable to inhibit shale formations and keep the volume of borehole fluids within safe limits for the rig.

Spent invert mud contains the original drilling fluid constituents, formation fluid, drill cuttings, cavings and metal fragments. Depending upon the formations penetrated by the well, high chloride concentrations can be expected in the water phase. To be effective, the disposal technology of choice must be able to cope with all components of the waste efficiently and economically. Nothing should be left to contaminate the environment or reduce the aesthetics of the drill site.

Use of Portland cement to stabilize inorganic wastes has been a standard industrial procedure for over a decade (Stegemann, 1991; Young, 1992; Newman, 1992; Fogg and Berzins, 1993). The high pH environment is extremely effective in containing metals (Ivey et al, 1992) and containing other solids. It has not been used extensively in the upstream

oil and gas industry for drilling waste stabilization because the relatively high permeability of ordinary concrete has made it suspect for containing hydrocarbons.

The authors introduced a pozzolanite product based on naturally occurring, hydrothermally altered volcanic ash. When combined with Portland cement and water, the product stabilizes and encapsulates hydrocarbons at the molecular level, immobilizes metal ions and solidifies the spent drilling fluid.

Molecular sieve technology as described by Gottardi and Galli, 1985; and Dyer, 1988 is the enabling body of knowledge for encapsulation of hydrocarbons. Molecular sieves have been used in the petroleum refining industry for over fifty years.

Use of Portland cement for stabilization of heavy and trace metals has been practiced in Europe and North America for over 15 years (Clark and Perry, 1985; Poon et al, 1985; Adaska et al, 1991; Young, 1992; Newman, 1992; Ivey et al, 1992); Beckefeld, 1992; Conner et al, 1992; Collins and Luckevich, 1992; Fogg and Berzins, 1993; Haggerty and Bowman, 1994; Porter et al, 1995; Li and Bowman, 1997; li et al, 1998; Apak, 2000; Boyce and Almskog, undated). The end product is concrete that has very low permeability with respect to both water and oil and petroleum hydrocarbons, particularly diesel fuel, to be incorporated into a phillipsite lattice (Zhao et al, 1999). This means that even when pulverized, the concrete will not bleed oil, allowing secondary use of the material for road construction or to be disposed of on site. Since aggregate is not used in the process, volume expansion is minimized.

Process Information

Stability Monitoring Assay

The objective of the assay step is to obtain an estimate of known accuracy of the composition and properties of the drilling waste to be treated.

Before acceptance for treatment, a characterization assay should be conducted by a third-party laboratory, which should include the following:

- 1. Oil content
- 2. Water content
- 3. pH, Eh and specific conductance
- 4. ICP metals scan for the elements shown in Table 1
- 5. Salinity
- 6. Calcium, magnesium, sodium
- 7. Chloride, sulphate, carbonate, bicarbonate

To ensure the laboratory testing samples are representative of the entire body of material to be treated, 250g sub-samples should be obtained from random locations within the body of drilling waste and combined in a 25-litre pail to produce a uniform sample. The mixing and combining should be performed in such a way that volatile materials are preserved.

Treatment

The objective of this step is to establish the optimum ratio of stabilizer, Portland cement and water that must be added to

achieve certification criteria with a minimum of volume expansion of the body of waste. To be effective, a pH of at least 8.5 must be attained. At that hydroxide concentration, hydrated volcanic glass is changed to phillipsite (Goodman et al, 1974) and metals are immobilized in the cementicious matrix (Adaska et al, 1991).

A 25-litre sample of drilling waste must be collected in the same manner, and preferably at the same time, as the assay sample. The sample is sub-sampled into four equal parts, one each for:

- 1. Incremental addition of stabilizer
- 2. Incremental addition of Portland cement
- 3. Incremental addition of water
- 4. Control sample

Each sub-sample is further sub-sampled into five equal quantities. Treatment is then applied to each in 5 wt. % increments between 5 and 25 wt. %, at ambient temperature and pressure with the other two variables held constant at 10 wt. %. Nothing is added to the control.

Samples are left to solidify for at least 72 hours and then submitted for leaching (USEPA Toxicity Characteristic Leaching Procedure, TCLP) and unconfined compressive strength (UCS) testing as specified in Environment Canada (1991) and described in detail in Stegemann and Coté (1991). The optimum combination of constituents is selected from this data for application to the main body of the waste.

Homogenization

Oil-based and invert drilling waste tends to be well mixed and thixotropic as received. There will be cases where the waste has been stored long enough for separation to occur, particularly if the oil/water ratio is low (<0.10). In these cases, stirring will be necessary. A hoe can perform this task if the waste is stored in a pit or by a mud or slurry pump if tank storage is used.

Reagent Addition and Mixing

Both pozzolan and Portland cement are delivered in sacks of known weight. Using characterization assay and treatment testing data, the drilling waste and reagents are combined with sufficient make-up water to produce the selected constituent ratios. The mixture is then stirred to produce a reasonably uniform composition and placed on a lined, bermed pad for curing. A pad thickness of 1.0 m has been used successfully to support the product and contain any possible leachate.

Following ambient temperature curing for 56 days as suggested by Stegemann and Coté (1991) and TCLP/UCS testing as described below, the slab can be disposed of as per the certificate for the site.

Handling and Storage of Materials during the Treatment Process

The drilling waste should be held in a mud tank or sump before and during processing. Transfer to the process vessel will be via mud pump and tubing. In the case of drilling waste held in a sump, track-hoe mixing will be employed.

Experience suggests that cold weather operations are

possible in Temperatures as low as -20C.

Characterization of the Waste Material

Spent invert mud contains the original drilling fluid constituents, formation fluids, drill cuttings, cavings and metal fragments. An effective disposal technology must be able to render all components of the waste environmentally safe both efficiently and economically. Nothing should be left to contaminate the environment or reduce the aesthetics of the drill site.

The best available chemical characterization of spent invert mud was reported by Macyk et al., 1992. Table 1 is an

extract of their report, together with the appropriate limit for each constituent derived from the current Guidelines for Canadian Drinking Water Quality (Health Canada, 2001). This table is in publication through the Core and CuttingsDivision of the Canadian Society of Petroleum Geologists.

A standard characterization for spent oil-based or oilcontaminated drilling fluid is described in the section on methods, below.

Table 1: Chemistry of Invert Drilling Fluids After Macyk et al (1992)							
Parameter	Solid Phase (ppm)		Liquid Phase (ppm)		Solid Phase Saturated Paste Extract		Canadian Drinking Water Guideline
	Mean	Std. Dev.	Mean "	Std. Dev.	Mean	Std. Dev.	(ppm)
pН	8.93	1.29	8.21	1.78	8.44	1.16	6.5 - 8.5
CI	-	-	777.26	829.75	11,599.88	10,551.44	250.000
NH4	-	-	0.88	2.30	2.17	3.39	0.000
Al	-	-	1.47	1.13	388.95	530.98	0.000
Cr	-	-	0.02	0.01	0.01	0.01	0.050
Fe	-	-	0.20	0.68	0.04	0.12	0.300
V	-	-	0.03	0.06	0.03	0.05	0.000
Cd	-	-	0.01	0.06	0.01	-	0.005
Cu	-	-	0.05	0.03	0.42	0.07	1.000
Pb	_	_	0.12	0.06	0.07	0.08	0.050
Zn	-	_	0.14	0.17	0.29	0.19	5.000
Mn	_	_	0.15	0.20	0.14	0.69	0.050
Li	_	-	0.06	0.03	0.14	0.20	0.000
Sr	_	-	2.59	4.12	77.42	91.21	Note 1
В	-	_	0.20	0.24	0.97	1.48	5.000
Ва	_	-	0.32	0.71	1.04	1.95	1.000
Mo	_	-	0.05	0.05	0.32	0.19	0.000
Se	_	-	0.18	0.07	0.17	0.09	0.010
Co	-	_	0.02	0.01	0.05	0.01	0.000
SO4	_	-	383.88	589.95	610.24	534.97	500.000
As	-	_	0.06	0.05	0.16	0.16	0.050
Oil	6.22	3.47	10,742.03	25,920.95	-	-	Note 2
Benzene	-	-	1.71	2.63	-	-	Note 3
Toluene	_	-	0.03	-	-	-	
Ethyl Benzene	_	-	0.03	_	-	-	
P-Xylene	_	-	0.03	_	-	-	
O-Xylene	_	-	0.03	-	-	-	
Trout LC50 (%)	_	-	18.69	31.68	-	-	
EC50 (%)				220			Note 4
5 Min.	10.20	17.21	10.41	22.73			•
15 Min.	9.32	15.59	11.03	22.88			
SAR	5.5 2				25.60	47.29	

End Product Characterization

Level 0 and level 1 testing as prescribed in Environment Canada (1991) is recommended as the least-biased approach to:

- 1. Establishing a reasonable end-use for the stabilized material.
- Determination of long-term disposal options for the stabilized material if no local use can be found.

Level 0 is the collection of basic information about the waste material and the containment matrix. The procedure is described above.

Level 1 is the determination of leaching potential and characterization of the leachate and also the chemical durability of the end-product concrete.

The goal of drilling waste treatment is to allow unmonitored disposal of the material after it has been demonstrated as being stable. We believe a two-year monitoring period is sufficient to prove the stability of the end product. Over that period of time, the treated waste should have been exposed to two complete annual march of seasons, direct contact between the concrete and both rain and groundwater, been frozen and thawed completely (in cold locations)twice and have been subjected to summer heat with high enough intensity to establish its weathering characteristics.

A suitable monitoring procedure will be:

- 1. Reading of area below the end product slab or aggregate placement: before placement to establish baseline conditions
- 2. At the initiation of the verification period
- 3. After one year of weathering
- 4. After two years of weathering

The specifications for the monitoring are established to reflect the actual site conditions.

Recovery of a suitable sized core from the product slab or a representative sample from product aggregate for leaching:

- 1. At the initiation of the verification period
- 2. After one year of weathering
- 3. After two years of weathering.

Certification

Certification of the site is granted after two years of monitoring showing satisfactory performance.

Quality Assurance/Quality Control for Field and Laboratory Operations

Stegemann and Coté (1991) is the definitive work on assessment of stabilized/solidified waste treated with Portland cement. Verification of encapsulation of both metals and hydrocarbons can be easily performed qualitatively by scanning electron microscopy (SEM) analysis (Stegemann and

Coté, 1991; Ivey et al, 1992). Since the sample to be mounted and scanned is very small (<<1 mm in diameter), the technique can be applied equally to granular and monolithic products. Interpretation is straightforward. If waste particles or liquid phase globules are completely separated from one another and enclosed by the matrix materials, encapsulation has been successful. An extension of the method involves using an electron microprobe or Energy Dispersive x-ray (EDX) analyzer to determine the extent of diffusion of toxic substances through the cementicious matrix over time. This method is also valuable for determining the depth of leaching associated with the TCLP test conducted on pulverized product.

The SEM approach is rapid and lends itself to semiquantitative analysis. The main drawback is the amount of variability present at the sub-microscopic level. Encapsulation variability is less of an issue for EDX analysis, however data from more than one sample should be obtained to ensure encapsulation is not confined to a small area.

A QA/QC protocol is presented in Appendix 1.

Disposal/Closure

Once the product has cleared TCLP and UCS testing, it can be used for road topping, non-residential structural purposes or simply buried at the well site. Waste tracking/manifesting documentation will be created and controlled as per local regulations.

During the wellsite study period, soils impact and vegetative success will be monitored. A full report is be made to local regulators on soil/vegetation impacts at the end of the pilot project.

References / Bibliography

- Adaska, Wayne S.; Stewart W. Tresouthick and Presbury B. West (1991) "Solidification and Stabilization of Wastes Using Portland Cement", Portland Cement Association, Skokie, IL, 16pp.
- Akinlade, M.O.; A. Adenipekun and J.A. Wind (1997)
 "Drilling Residue Disposal, Nigeria", Shell Petroleum
 Development Company of Nigeria Limited, posted on the
 Australian EIA Network website,
 http://www.environment.gov.au/epg/eianet/case_studies/cs_8
 7.html
- American Association of Drilling Engineers. (1999) Shale Shakers and Drilling Fluid Systems. Gulf Publishing Company, Houston, Texas.
- 4. Apak, Resat (2000) "Sorption Solidification of Selected Heavy Metals and Radionuclides from Water Interim Status Report (Extract)", posted on the NATO/CCMS website http://www.int/ccms/s13/report/interim18.html. 2 pp.
- Beckefeld, Petra (1992) "Qualification Test and Quality Control for Solidified Wastes", in Proceedings of the First

- International Symposium, Cement Industry Solutions to Waste Management, Canadian Portland Cement Association, Toronto, Ontario, October 7-9, 1992 pp. 677-692
- Boyce, Paul K. and Kris E. Almskog (undated) "Much ado about mercury: evaluation of treatment options for mercury contaminated soil at BNL",
- Caldwell, Robert J., Julia A. Stegemann, Pierre Coté and Chih C. Chao (1992) "Treatability of Organic Residues by Sorbent-Assisted Solidification", in Proceedings of the First International Symposium, Cement Industry Solutions to Waste Management, Canadian Portland Cement Association, Toronto, Ontario, October 7-9, 1992 pp. 333-342
- 8. Cetin, U. and R.K. Mehta (1999) "Sorption of uranium, strontium and cesium on pozzolan", Mining Engineering, Vol. 51, No. 11 pg. 51-58
- Chilingarian, G.V. and P. Vorabutr (1983) Drilling and Drilling Fluids (Developments in petroleum science; 11) Elsevier Science Publishers BV, Amsterdam, The Netherlands, 801 pp.
- Clark, A.I. and R. Perry (1985) "Cement-based stabilization/solidfication Processes for the disposal of toxic wastes", Proceedings from a Workship on Environmental Technology Assessment, P.W.R. Beaumont, R.K. Jain and R.S. Engelbrecht, editors, pp. 1-44
- Collins, Robert E. and Lydia Luckevich (1992) "Portland Cement in Resource Recovery and Waste Treatment", in Proceedings of the First International Symposium, Cement Industry Solutions to Waste Management, Canadian Portland Cement Association, Toronto, Ontario, October 7-9, 1992 pp. 325-331
- 12. Conner, Jesse R., Sherwood Cotton and Paul R. Lear (1992) "Chemical Stabilization of Contaminated Soils and sludges Using Cement and Cement By-products", in Proceedings of the First International Symposium, Cement Industry Solutions to Waste Management, Canadian Portland Cement Association, Toronto, Ontario, October 7-9, 1992 pp. 73-97
- 13. Danielson, R.M., N. Okazawa and W.J. Ceroici (1989) "Disposal of Oilfield Wastes by Landtreatment: Effects on the Environment and Implications for Future Land Use, 1988 Research Report", University of Calgary and Alberta Environment, prepared for The Canadian Petroleum Association and Environment Canada. 64pp. plus Data Appendix.
- Devereux, Steve (1998) "Practical Well Planning and Drilling Manual" PennWell Publishing Company, Tulsa, Oklahoma, 522 pp.
- Dyer, A. (1988) "An Introduction to Zeolite Molecular Sieves", John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore, 149pp
- Environment Canada (1991) "Proposed evaluation protocol for cement-based solidified wastes", Minister of Supply and Services Canada, Report EPS 3/HA/9, 45 pp.

- Fogg, Graham and Bill Berzins (1993) "Stabilization and Solidification: Principles", Bovar Environmental Services, Calgary, Alberta. 12pp.
- 18. Gottardi, G. and E. Galli (1985) "Natural Zeolites", Springer-Verlag Berlin, Heidelberg, New York, Tokyo 409pp.
- Gray, George R. and H.C.H. Darley (1980) "Composition and Properties of Oil Well Drilling Fluids", Fourth ed., Gulf Publishing Company, Houston, London, Paris, Tokyo, 630pp.
- Haggerty, Grace M. and Robert S. Bowman (1994) "Sorption of Chromate and Other Inorganic Anions by Organo-Zeolite", Environmental Science and Technology, Vol. 28, No. 3 pp. 452-458
- Hanna, Iskandar S. (2000) "Methods for Handling Offshore Oil-Based Mud Waste", Saudi Aramco Journal of Technology, Fall 2000, pp. 50-60
- Ivey, D.G., W.W. Lam, M. Neuwirth, D.J. Conrad and R.B. Heimann (1992) "Heavy Metal Containment in Alite", in Proceedings of the First International Symposium, Cement Industry Solutions to Waste Management, Canadian Portland Cement Association, Toronto, Ontario, October 7-9, 1992 pp. 271-288
- Li, Zhaouhui, and Robert S. Bowman (1997) "Counterion Effects on the Sorption of Cationic Surfactant and Chromate on Natural Clinoptilite", Environmental Science and Technology, Vol. 31, No. 8 pp. 2407-2412
- Li, Zhaouhui, Stephen J. Roy, Yiqiao Zou and Robert S. Bowman (1998) "Long-term Chemical and Biological Stability of Surfactant-modified Zeolite", Environmental Science and Technology, Vol. 32, No. 17, pp. 2628-2632
- 25. MacKay, Michael and John Emery (1992) "Stabilization/solidification of Contaminated Soils and Sludges Using Cementitious Systems", in Proceedings of the First International Symposium, Cement Industry Solutions to Waste Management, Canadian Portland Cement Association, Toronto, Ontario, October 7-9, 1992 pp. 135-151
- 26. Macyk, T.M., S.A. Abboud and F.I. Nikiforuk (1992) "Alberta Drilling Waste Sump Chemistry Study, Volume 1: Report", Alberta Research Council, Edmonton Alberta, Report # ARTAC 92-6, 60pp. plus 28 Data Appendices
- Nelson, Darrell W., Shyilon Liu and Lee E. Sommers (1980)
 "Plant Uptake and Accumulation of Metals Derived from Drilling Fluids", Agricultural Experiment Station and the Agronomy Department, Purdue University, West Lafayette In 47907. 97pp.
- Newman, Alan (1992) "Is Cement all it's Cracked Up to be?";
 Environmental Science and Technology, Vol. 26, No. 1, 1992
 pp. 42-43
- 29. P.W. Grosser Consulting Engineer & Hydrogeologist, posted on the State University of New York at Sunnybrook website http://pbisotopes.ess.synysb.edu/lig/Conferences/Abstracts99/boyce.htm

- Poon, C.S.; C.J. Peters and R. Perry (1985) "Mechanisms of metal stabilization by cement based fixation processes", the Science of the Total Environment 41(1985) 55-71, Elsevier, Holland
- 31. Porter, Craig L., Susan D. Carson and Wu-Ching Cheng (1995) "Exiting RCRA Subtitle C Regulation Data Supporting a New Regulatory Path for Immobilized Mixed Debris", Jetseal Inc. and Sandia National Laboratory, posted on http://inel.gov/resources/rese.../1995Conference/track2/pmt-17.htm
- Samsonek, J., M. Vondruska and O. Stranel (1998)
 "Influence of Specimen Size on Leachability Test Results of Waste ST/SO", Practice Periodical of Hazardous, Toxic and Radioactive Waste Management, October 1998 pp. 154-157
- Stegemann, J.A. and P.L. Coté (1991) "Investigation of Test Methods for Solidified Waste Evaluation - A Cooperative Program", Report EPS 3/HA/8, Environment Canada Wastewater Research Centre, Ottawa, 116 pp.
- Stegemann, Julia (1991) "Proposed Evaluation Protocol for Cement-based Solidified Wastes", Report EPS 3/HA/9, Wastewater Technology Centre, Environment Canada, Ottawa 45pp.
- 35. Sullivan, Enid J.; Douglas B. Hunter and Robert S. Bowman "Fourier Transform Raman Spectroscopy of Sorbed HDTMA and the Mechanism of Chromate Sorption to Surfactant-Modified Clinoptilite", Environmental Science and Technology, Vol. 32, No. 13, pp. 1948-1955
- Young, J. Francis (1992) "Dense High Strength, Low Permeability Cement-Based Materials for Containment" in Proceedings of the First International Symposium, Cement Industry Solutions to Waste Management, Canadian Portland Cement Association, Toronto, Ontario, October 7-9, 1992 pp. 13-22
- Young, J. Francis (1992) "Dense High Strength, Low Permeability Cement-Based Materials for Containment" in Proceedings of the First International Symposium, Cement Industry Solutions to Waste Management, Canadian Portland Cement Association, Toronto, Ontario, October 7-9, 1992 pp. 13-22
- 38. Zhao, Tie-Jun; Zhu, Jin-Quan and Chi, Pei-Yun (1999)
 "Modification of pore chemicals in evaluation of highperformance concrete permeability", ACI Materials
 Journal, Vol. 96, No. 1 pp. 84-9