EXTRACTION OF DISTILLATE 822 FROM DRILL CUTTING-WATER SLURRIES USING SUPERCRITICAL CARBON DIOXIDE

Christopher R. Jones[1], Christianne G. Street[1], Selma E. Guigard*[1], Amber Smith[2], Richard Bingham[2], Karen McCosh[2] and Warren H. Stiver[3]

[1] Department of Civil and Environmental Engineering, University of Alberta
[2] M-I SWACO
[3] School of Engineering, University of Guelph

* 3-089 Markin/CNRL NREF Building, University of Alberta, Edmonton AB, Canada, T6G 2W2
Email: selma.guigard@ualberta.ca, Phone: (780) 492-8585, Fax: (780) 492-8198

Supercritical fluid extraction (SFE) using carbon dioxide is a promising new technique for the removal of hydrocarbons from drill cuttings, which enables the reuse of the drilling fluid hydrocarbons and safe disposal of the clean solids. SFE is a proven method for treating drill cuttings on a lab-scale, semi-batch process. However, for the process to be economically feasible on a commercial scale, it must be continuous. A continuous system for treating naphthalene-contaminated soils has previously been developed and will be adapted to treat hydrocarbon-contaminated drill cuttings. The continuous process will require drill cutting-water slurries for extraction. The purpose of this research is to investigate the treatment of these slurries using supercritical carbon dioxide (SC CO_2). The objectives are to determine the effect of water content on the extraction efficiency and the suitability of the recovered hydrocarbons for reuse. In addition, qualitative observations will be made regarding the "flowability" of the slurries.

The highest hydrocarbon extraction efficiency obtained in the study was 98.1% on a slurry prepared at a 1:1 ratio of drill cuttings to water when the SC CO_2 was introduced at the bottom of the lab-scale, flow-through extraction vessel. This vessel arrangement with the SC CO_2 introduced at the bottom of the reactor is thought to better represent the countercurrent flow of a continuous extraction system. However, this arrangement led to issues with system plugging and, after treatment, the slurry was no longer free flowing. These results suggest that higher water contents may be required for the continuous system.

The hydrocarbons extracted by the SC CO_2 were collected and analyzed using gas chromatography (GC). Visual comparison of the hydrocarbon GC chromatograms before and after extraction from the drill cuttings with SC CO_2 suggests that the quality of the hydrocarbon mixture is not changed by the treatment process. This result indicates that the extracted hydrocarbons may potentially be reused in future drilling operations. However, some water is collected with the hydrocarbons as a result of solubilization and entrainment. Consideration will have to be given to separating the hydrocarbon and water phases prior to reuse of the hydrocarbon phase as a base for new drilling fluids.

The results of this research will contribute significantly to the development of the continuous SFE treatment system, which can be commercialized for use in the oil and gas industry.

INTRODUCTION

Drill cuttings are produced during rotary drilling for petroleum resources, when rock fragments, or cuttings, are generated from boring with the drill bit and coated in the drilling fluid being used [1]. Drilling mud is composed of a continuous fluid base, either water or hydrocarbons, and additives such as bentonite or barite to control the density and other physical properties such as rheology and filtration characteristics [2]. Drilling muds cool and lubricate the drill bit, stabilize the borehole wall, and carry the cuttings to the surface of the well [3-5]. Hydrocarbon-based drilling muds are considered superior to their water-based counterparts, particularly for use in challenging drilling operations such as deep or deviated wells, or when drilling in contact with highly reactive formations such as shale [2,4]. However, the hydrocarbon-based drilling muds are much more expensive and, because of their hydrocarbon content, the cuttings they generate must be handled and disposed of carefully [6, 7]. Numerous technologies have been developed to treat drill cuttings generated from the use of hydrocarbon-based drilling muds including bioremediation technologies (such as composting and landfarming) and cleaning technologies (such as incineration and solvent washing) [8].

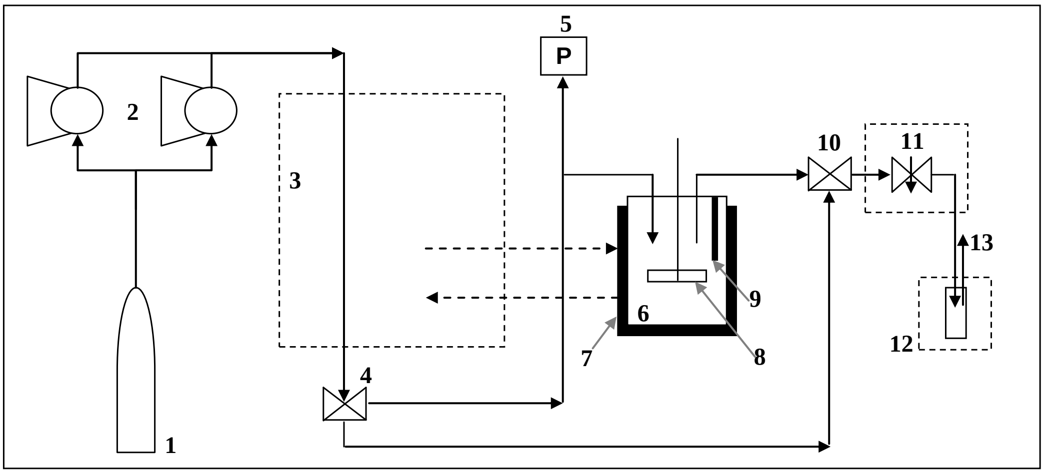
SFE is a promising new technique and an attractive option for the treatment of hydrocarbon-contaminated drill cuttings. Since SFE was first commercialized for the decaffeination of coffee and tea, researchers have successfully applied the technology as a treatment for hydrocarbon-contaminated drill cuttings on a lab-scale, using various supercritical fluids [8-14]. The main benefit of using SFE for the treatment of drill cuttings is the recovery and potential reuse of the expensive hydrocarbon base fluid and the subsequent release of the cleaned solids to the environment [8, 13-16]. A recent study employing the use of SC CO_2 in a flow-through, lab-scale reaction vessel achieved 98% extraction efficiency at 14.5 MPa and 40°C [16]. SC CO_2 is often selected for SFE as it has a readily attainable critical point (7.4 MPa and 31°C) and it is non-flammable, non-toxic, chemically inert, and inexpensive [17].

To date, SFE studies for the treatment of hydrocarbon-contaminated drill cuttings have used semi-batch processes. In order for SFE to become a commercially viable treatment option, a continuous process needs to be developed [18]. A pilot-scale, continuous SFE system for the treatment of hydrocarbon-contaminated cuttings is currently being developed at the University of Alberta. This system will use a countercurrent flow scheme, thereby requiring the drill cuttings to be continuously pumped into the pressurized vessel against the flow of SC CO_2. The design is based upon a lab-scale, continuous SFE system developed at the University of Guelph for the treatment of naphthalene-contaminated soils [19, 20]. To facilitate pumping in the proposed continuous system, a slurry of cuttings and water will be used. Therefore, the current lab-scale study was undertaken to investigate the effect of water content on the extraction efficiency of hydrocarbons from drill cuttings. In addition, qualitative observations were made to determine “flowability” and “pumpability” of the slurries, before and after treatment with SC CO_2. In order to determine the suitability of the recovered hydrocarbons for reuse, the gas chromatograms of the hydrocarbon before and after treatment were compared.

MATERIALS AND METHODS

Drill cuttings samples for this study were provided from an active drill rig site in Alberta, Canada by M-I SWACO (Houston, Texas, USA). The cuttings were coated with an invert-emulsion drilling fluid containing the base hydrocarbon mixture Distillate 822.

Figure 1 is a simplified schematic diagram of the lab-scale system used for the current study. The complete details of the system and the procedures used for the current study are presented in Street et al. [16] and Jones and Guigard [21].



Legend:

1. Carbon dioxide feed cylinder
2. Syringe pumps
3. Hot water bath
4. 3-way valve
5. Pressure transducer
6. Extraction vessel
7. Heating jacket
8. Mixer
9. Thermistor probe
10. 3-way valve
11. Metering valve, hot water bath
12. Sample vial, ice water bath
13. Vent

Figure 1 – Schematic diagram of the lab-scale SFE system used in this study, adapted from Street et al. [16]

The system consists of a 300- mL stainless steel extraction vessel, equipped with a heating jacket for maintenance of a constant temperature and a MagneDrive® mixer (Snap-tite, Inc., Erie, Pennsylvania, USA) with a helical-type impeller for even distribution of the drill cuttings and SC CO_2 during the extraction.

Uniform slurries were produced by introducing the cuttings sample and water into a jar, followed by vigorous wrist-action shaking for one minute. In some instances, an additive was incorporated into the cuttings at a mass ratio of 0.2:1 prior to adding the water to aid suspension.

The slurry to be treated was placed into the vessel, which was then pressurized to 14.5 MPa with SC CO_2 from two syringe pumps (Teledyne Isco, Inc., Lincoln, Nebraska, USA). For the current study, most of the tests were conducted by introducing the SC CO_2 at the top of the vessel, thereby relying on the mixer to ensure adequate contact between the slurry and the SC CO_2. Modifications to the vessel were made later in the extraction runs that allowed the SC CO_2 to be introduced to the bottom of the vessel. The extractions were completed at a temperature of 40°C.

The extraction was conducted using a 30-minute static period, followed by a 90-minute dynamic period. Mixing was maintained at 100 rpm for both the static and dynamic periods. SC CO_2 flow through the system was maintained at approximately 38 g/min during the dynamic period using a metering valve. The metering valve was placed in a water bath at 70°C to prevent freezing due to SC CO_2 depressurization at the valve. The hydrocarbons were collected in 40-mL glass sample vials that were changed every 15 minutes during the dynamic period. The sample vials were maintained in an ice-water bath to minimize losses of lighter hydrocarbons.

The concentration of hydrocarbons in the SFE-treated slurries and the untreated cuttings was determined using a Dean-Stark solvent extraction followed by GC analysis. The Dean-Stark procedure involves the reflux of the sample with toluene for 5 hours, after which the toluene is injected into a GC equipped with a flame ionization detector (FID) [21]. The GC/FID was calibrated and operated according to standards outlined by the Canadian Council of Ministers of the Environment [22]. The Dean-Stark extraction also determines the quantity of water in the sample, which is collected in a separate trap during the reflux period. The extraction efficiency was determined by comparing the hydrocarbon concentration of the treated cuttings slurry to the hydrocarbon concentration in the cuttings prior to slurrying (both on a dry mass basis) [21]. The mass of water collected in the hydrocarbon sample vials was determined by subtracting the mass of water remaining in the treated slurry, as determined through the Dean-Stark test, from the initial water content of the slurry.

RESULTS AND DISCUSSION

Table 1 summarizes the results from the extractions completed on the drill cuttings slurries. Each test numbered in the table presents the average results of triplicate extraction runs. The hydrocarbon extraction efficiency results from Table 1 are also presented in Figure 2. The variance shown as error bars in Figure 2 are the 95% confidence intervals calculated for each test in Table 1.

Table 1 - Summary of results for SC CO_2 extractions of Distillate 822 from drill cuttings slurries at 14.5 MPa and 40°C

Test No.	Water to cuttings ratio, by mass	Mass of cuttings, g	Total slurry volume, mL	Hydrocarbon extraction efficiency		Residual hydrocarbon content		Water extracted, $\times 10^{-4}$ g water per g of CO_2
				% by mass, dry	st. dev.	% by mass, dry	st. dev.	
No additive, CO_2 inlet at top of vessel								
1	0:1	25	15	91.5	4.4	1.5	0.8	2.0
2	0.5:1	25	27	62.5	11.9	6.7	2.1	19.4
3	1:1	25	40	64.1	12.2	6.9	2.2	17.3
4	2:1	25	65	35.4	3.1	11.4	0.6	4.0
5	5:1	25	140	54.8	6.7	8.0	1.2	33.2
6	1:1	38	60	45.1	4.6	12.7	1.5	6.3
7	2:1	23	60	36.4	4.3	13.7	0.9	7.3
8	5:1	11	60	44.3	1.5	12.0	0.3	7.7
Additive, CO_2 inlet at top of vessel								
9	1:1	25	40	59.2	9.1	7.2	1.6	32.1
No additive, CO_2 inlet at bottom of vessel								
10	1:1	25	40	98.1	0.5	0.3	0.1	20.1

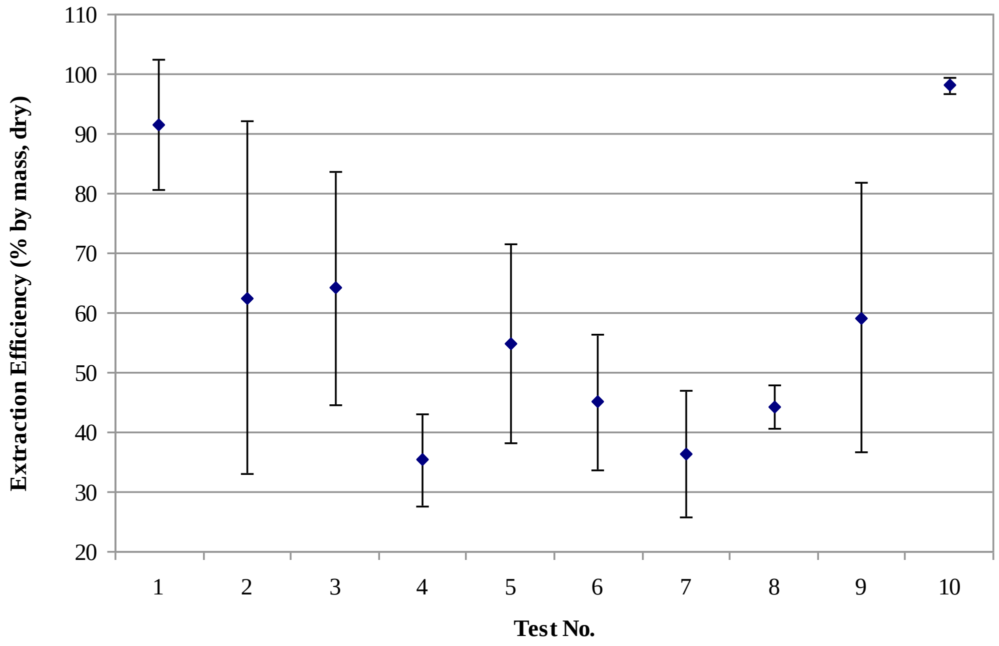


Figure 2 – Extraction efficiency results for SC CO_2 extractions of Distillate 822 from drill cuttings slurries at 14.5 MPa and 40°C.

For Tests 1 to 5, 9, and 10, the untreated drill cuttings contained 17.7% hydrocarbon on a dry mass basis. For Tests 6 to 8, the untreated cuttings contained 21.6% hydrocarbon on a dry mass basis. The untreated cuttings used in all tests contained 3.1% water on a mass basis.

In Tests 1 to 5 in Table 1 and Figure 2, slurries with water to cuttings ratios of 0:1, 0.5:1, 1:1, 2:1, and 5:1 were produced using a set mass of drill cuttings (25 g). All slurries were observed to be free flowing and “pumpable” prior to extraction. The extraction efficiency dropped from 91.5% in the 0:1 slurry (cuttings only), to a minimum of 35.4% in the 2:1 slurry, then increased to 54.8% in the 5:1 slurry. The best extraction efficiency obtained in these tests was in the 1:1 slurry at 64.1%. The 0.5:1 slurry had a similar extraction efficiency as the 1:1 slurry, but after treatment the cuttings remaining in the vessel was not free flowing and, therefore, would not be suitable for pumping in a continuous SFE system. This initial drop in efficiency with the addition of water, followed by an increase in efficiency at higher slurry water contents is consistent with results presented in the literature for supercritical fluid extraction of selected contaminants from soil and drill cutting slurries [8, 17, 23, 24]. It is hypothesized that, at low water contents, the water acts as a barrier to SC CO_2-hydrocarbon contact during the extraction [8, 23]. At water contents higher than 2:1, it is hypothesized that the hydrocarbon-coated solid particles become dispersed in the slurry, creating a larger surface area for contact with the SC CO_2 thereby leading to increased extraction efficiencies [21].

Tests 6 to 8 in Table 1 and Figure 2 were conducted to determine if the total volume of the slurry in the vessel had an effect on extraction efficiency. The slurries for tests 6 to 8 were created with water to cuttings ratios of 1:1, 2:1, and 5:1 in order to facilitate comparison with Test 3 to 5. However, in the case of Tests 6 to 8, the total slurry volume was held constant at 60 mL while varying the mass of drill cuttings. The efficiency of the 1:1 slurry in Test 6, containing 38 g of cuttings, dropped to 42% in comparison to 64.1% in Test 3. The efficiency of the 2:1 slurry, containing 23 g of cuttings, remained approximately the same as Test 4 at 36.4%. Finally, the efficiency of the 5:1 slurry, containing 11 g of cuttings, dropped from 54.8% observed in Test 5 to 44.3% in Test 8. It is concluded that both the mass of the cuttings and the volume of the slurry affect the extraction efficiency. However, these factors are related to the extraction equipment design, the optimization of which was not one of the study objectives. Therefore, no further investigation was undertaken in this study to fully delineate these effects.

For all the tests in Table 1 and Figure 2, a measureable mass of water was collected in the sample vials along with the hydrocarbons during the extraction. The presence of water in the sample vials is due to either solubilization or entrainment of the water in the flowing SC CO_2. It is impossible to quantify these effects separately within the current extraction set up and sample analysis. The mass of water collected (Table 1) ranges from 0.2 to 3.3 $x10^{-3}$ g water/g CO_2 while the estimated water solubility is 2×10^{-3} g water/g CO_2 (at 14.5 MPa and 40°C). The solubility has been estimated using the solubility calculator provided in Stiver and Rampley [25], the Chrastil model [26] and the water solubility data provided in King et al. [27]. The results are also consistent with the water solubility data presented by Sabirzyanov et al. [28]. Therefore, solubilization explains some, if not most, of the water collected in the hydrocarbon sample vials. Whether the consequence of solubilization or entrainment, these results indicate that oil-water separation will likely be an integral part of any continuous extraction system for treating slurries.

Throughout this study, it was observed that generating a stable slurry with drill cuttings and water is difficult. In this study, a stable slurry was defined as an evenly dispersed drill cuttings-water suspension that did not readily separate by visual observation when left undisturbed for a period of two hours. Drill cuttings by nature are heterogeneous, containing coarse material in addition to clay-size particles. Also, because of its hydrocarbon content, drill cuttings display oil-water immiscibility. The formation of a stable slurry with wrist action shaking was not achieved in Tests 1 – 8 and 10. The slurries for these experiments required intense and continued agitation to remain dispersed. Without continued agitation, the drill cuttings immediately began to settle out of the suspension. In an attempt to produce a more stable slurry, Test 9 incorporated an additive into the drill cuttings at a ratio of 0.2:1 (additive:cuttings) prior to adding the water. The resulting slurry was stable and required much less agitation to achieve. Note, however, that the extraction efficiency for Test 9 did not demonstrate significant improvement in comparison with Tests 3 and 6 that were completed under similar extraction conditions.

Later in the course of the study, modifications were made to the extraction system that allowed the SC CO_2 to be introduced at the bottom of the vessel. It was believed that such an arrangement for the SC CO_2 inlet would better represent the flow conditions that would be expected in the proposed continuous system. Test 10 was completed under the same conditions as Test 3 with the SC CO_2 inlet at the bottom of the vessel. The new vessel arrangement produced excellent results in terms of hydrocarbon extraction with an average extraction efficiency of 98.1%. This extraction efficiency is a significant improvement over the 64.1% extraction efficiency observed in Test 3. The new vessel arrangement did, however, lead to some operational challenges during the extractions because of the upward flow of SC CO_2 and the resulting increase in cuttings solids entrainment. In all the extractions completed with the new inlet arrangement, complete system plugging was observed during vessel depressurization.

It is believed that the system plugging is a result of the configuration and size of the lab-scale system and such plugging issues should not occur in the continuous system. Additionally, with the new vessel inlet arrangement, visual observation of the slurry after treatment revealed that it was no longer free flowing, perhaps a result of increased water solubilization and/or entrainment. In a continuous treatment system, the extraction of water from the slurry to the point that it is no longer free flowing would undoubtedly cause a plug at the vessel outlet, leading to system failure. To avoid such a failure, a slightly higher initial slurry water content may be required. However, a higher water content may decrease the extraction efficiency, as previously discussed. Thus, the challenge in developing a successful continuous treatment system will be to determine a window of operational conditions, including slurry water content, which will produce acceptable extraction efficiencies while allowing for the cuttings to flow into and out of the vessel without becoming plugged.

Figure 3 compares the GC/FID response for the Distillate 822 hydrocarbons in the drill cuttings prior to formation of the slurry and after the slurry is extracted with SC CO_2. The "Before extraction" chromatogram is from a sample of drill cuttings following Dean-Stark extraction. The "After extraction" chromatogram is from a sample of SC CO_2 treated cuttings from one extraction run of Test 6. Visual comparison of the two chromatograms shows peaks representing the various hydrocarbons in the Distillate 822 mixture in similar locations. For reference, the elution times of decane (C_{10}), hexadecane (C_{16}), and tetratriacontane (C_{34}) are marked on Figure 3 with dashed grey lines. The similarity between the two chromatograms suggests that the overall hydrocarbon quality is unchanged by the SFE process and that it may be suitable for reuse in new drilling fluids. This result is supported by other super- and near-critical cuttings hydrocarbon extraction studies in the literature [8, 13-16]. However, it is reported in by Tunnicliffe and Joy [11] that the hydrocarbons recovered from the SC CO_2 cuttings treatment process have a lower flash point, lower kinematic viscosity and a higher API gravity. These results indicate that, for the extraction equipment and conditions tested by Tunnicliffe and Joy [11], the collected hydrocarbons shifted in composition towards lower carbon numbers (lighter hydrocarbons). In view of the results from Tunnicliffe and Joy [11], further quantitative investigation will have to be undertaken to fully understand the reuse potential of the extracted hydrocarbons in the current study.

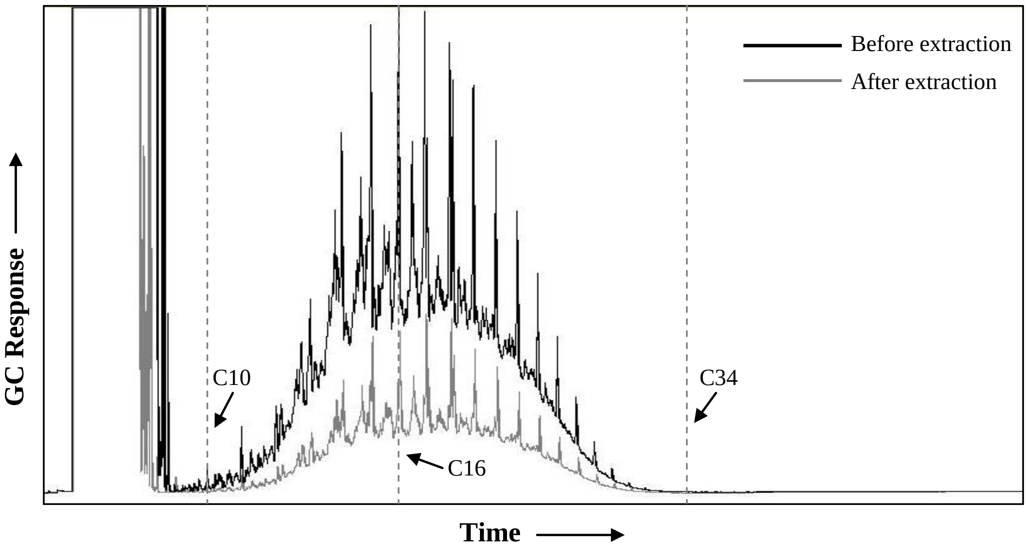


Figure 3 – Comparison of chromatograms for Distillate 822 hydrocarbons in drill cuttings prior to and after extraction with SC CO_2.

CONCLUSION

The purpose of this study was to investigate the effect of water content on the extraction efficiency of hydrocarbons from drill cuttings slurries in preparation for the development of a pilot-scale continuous flow extraction system. At the same time, observations were made as to the “pumpability” and “flowability” of the slurries before and after treatment with supercritical carbon dioxide. In the initial extractions of this study, the carbon dioxide inlet was located at the top of the vessel. In these extractions, it was found that increasing the slurry water content from 0:1 by mass to 2:1 by mass resulted in a decrease in extraction efficiency. Further increasing the slurry water content to 5:1 by mass showed a minor recovery of the extraction efficiency.

In addition to extracting the hydrocarbons, an appreciable amount of water was also collected in the outlet sample vials. The presence of water in the sample vials is the result of either solubilization and/or entrainment of water from the cuttings slurry in the supercritical carbon dioxide. Based upon results for water solubility in supercritical carbon dioxide from others, solubilization may account for most of the extracted water, but it is not possible to distinguish between the two effects in the current extraction system. Regardless, in the design of the proposed continuous flow system, oil-water separation will have to be taken into consideration.

The maximum extraction efficiency for the conditions tested in this study was 98.1%, which was achieved using a 1:1 slurry of drill cuttings and water, with the carbon dioxide inlet positioned at the bottom of the vessel. The positioning of the inlet at the bottom of the vessel more closely approximates the countercurrent flow regime of the proposed continuous extraction system. While the extraction was highly successful in regard to extraction efficiency, the new inlet arrangement caused system plugging on the lab-scale equipment due to increase entrainment of the cuttings solids. The observed system plugging is believed to be a result of the lab-scale system size and configuration and is not expected to be an issue in the continuous extraction system. In addition to the operational difficulties, the resulting treated slurry was no longer free flowing, most likely owing to the increased solubilization and entrainment of water. Such an outcome on a continuous system would cause a plug at the vessel outlet and is not desirable. A higher slurry water content would prevent plugging of the system, but might reduce the extraction efficiency as well. Therefore, the operation of the continuous system will have to balance the slurry flow requirements against contact time to achieve a desired extraction efficiency.

Finally, visual comparison of the gas chromatograms of the Distillate 822 hydrocarbons from the drill cuttings before and the cuttings slurries after treatment with supercritical carbon dioxide has shown that the quality of the hydrocarbons is unchanged by the treatment process. This implies that the collected hydrocarbon, once separated from any collected water, could potentially be reused by the drilling industry. Further quantitative tests will be required to confirm the possibility for reuse.

ACKNOWLEDGEMENTS

Funding for this research is provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada and M-I SWACO. Scholarship support for C. R. Jones and C. G. Street is provided by NSERC and Alberta Ingenuity.

REFERENCES

[1] VEIL, J. A. *Journal of Energy Resources Technology*, vol.125, **2003**, p. 238.
[2] MELTON, H. R., SMITH, J. P., MAIRS, H. L., BERNIER, R. F., GARLAND, E., GLICKMAN, A. H., JONES, F. V., RAY, J. P., THOMAS, D., CAMPBELL, J. A. *Proc. 7th SPE International Conf. on Health, Safety and Environment in Oil and Gas Exploration and Production*, Calgary, Alberta, **2004**, SPE 86696.
[3] ARGONNE NATIONAL LABORATORY, CHEVRONTEXACO, MARATHON, & U.S. DEPARTMENT OF ENERGY, Drilling Waste Management Information System, available online at http://web.ead.anl.gov/dwm/index.cfm, accessed Jan. 18, 2010.
[4] CANADIAN ASSOCIATION OF PETROLEUM PRODUCERS (CAPP), Offshore Drilling Waste Management Review, **2001**, available online at http://membernet.capp.ca/raw.asp?x=1&dt=PDF&dn=25022, accessed Jan. 18, 2010.
[5] BURKE, C. J., VEIL, J. A. *Oil and Gas Journal*, vol. 93(48), **1995**, p. 59.
[6] GUO, Q., ABOU-SAYED, A. S. *Proc. SPE/EPA/DOE Exploration and Production Environmental Conference.*, San Antonio, Texas, **2003**, SPE 80587.

[7] MINTON, R., MCGLAUGHLIN, J. *Oil and Gas Journal*, vol. 101(38), **2003**, p. 51.
[8] SAINTPERE, S., MORILLON-JEANMAIRE, A. *Proc. 2000 SPE Annual Technical Conference and Exhibition*, Dallas, Texas, **2000**, SPE 63126.
[9] EPPIG, C. P., PUTNAM, B. M., DE FILIPPI, R. P. United States Patent #4,434,028, **1984**.
[10] ELDRIDGE, R. B. *Industrial and Engineering Chemistry Research*, vol. 35, **1996**, p. 1901.
[11] TUNNICLIFFE, I., JOY, R. United States Patent #7,201,804, **2002**.
[12] GOODARZNIA, I., ESMAEILZADEH, F. *Iranian Journal of Science and Technology*, vol. 20, **2006**, p. 607.
[13] ODUSANYA, O. O. M.Sc. Thesis, Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta, **2003**.
[14] LOPEZ-GOMEZ, J. J. M.Sc. Thesis, Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta, **2004**.
[15] SEATON, S., HALL, J. *Proc. 2005 SPE International Symposium on Oilfield Chemistry*, Houston, Texas, **2005,** SPE 92963.
[16] STREET, C. G., TESCHE, C., GUIGARD, S. E. *SPE Drilling & Completion*, vol. 24, **2009,** p. 413.
[17] SALDANA, M. D. A., VAGPAL, V., GUIGARD, S. E. *Environmental Technology*, vol. 26, **2005**, p. 1013.
[18] LAITINEN, A., MICHAUX, A., AALTONEN, O. *Environmental Technology*, vol. 15, **1994**, p. 715.
[19] RYAN, M., STIVER, W. H. *The Canadian Journal of Chemical Engineering*, vol. 85, **2007**, p. 233.
[20] FORTIN, M., STIVER, W. *Proc. 6th International Symposium on Supercritical Fluids*, Versailles, France, **2003**, p. 481.
[21] JONES, C. J., GUIGARD, S. E. *Proc. IASTED International Conference of Environmental Management and Engineering*, Banff, Alberta, **2009**, p. 86.
[22] CANADIAN COUNCIL OF MINISTERS OF THE ENVIRONMENT. Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method, **2001**, available online at http://www.ccme.ca/assets/pdf/final_phc_method_rvsd_e.pdf, accessed Jan. 18, 2010.
[23] CAMEL, V., TAMBUTE, A., CAUDE, M. *Journal of Chromatography*, vol. 642, **1993**, p. 263.
[24] LOW, G. K. C., DUFFY, C. J. *Trends in Analytical Chemistry*, vol. 14, **1995**, p. 218.
[25] STIVER, W., RAMPLEY, G. Supercritical Fluid Solubility Calculator v2.03, **2001**, available online at: http://www.soe.uoguelph.ca/webfiles/wstiver/Research/download-v203.html, accessed Jan. 26, 2010.
[26] CHRASTIL, J. *Journal of Physical Chemistry*, vol. 86, **1982**, p. 3016.
[27] KING, M. B., MUBARAK, A., KIM, J. D., BOTT, T. R. *Journal of Supercritical Fluids*, vol. 5, **1992**, p. 296.
[28] SABIRZYANOV, A. N., IL'IN, A. P., AKHUNOV, A. R., GUMEROV, F. M. *High Temperature*, vol. 40, **2002**, p. 203.