CONTAINMENT OF SPILLED PETROLEUM IN SOIL USING ACTIVATED COAL[1]

Terril E. Wilson, Debasmita Misra, Wei Zhou, Abhijit Dandekar, and Neil D'Cunha[2]

Abstract. Investigation to determine the feasibility of containment of spilled petroleum in soil or near surface mineral matter, using finely-divided, heat-activated sub-bituminous coal as a sorbent and binder, has begun. Cylindrical samples (75mm diameter x 150 mm height) prepared separately from organic-rich soil and an underlying silt-clay horizon, both typical of substrates in the central Alaskan zone of the Trans-Alaska petroleum pipeline, were studied, along with a well-sorted sand (used in concrete-making) as a reference material. Downward permeation of run-of-pipeline crude petroleum through the organic soil, clay-rich subsoil, and sand, at one hour, eight hour, and 24 hour intervals, with and without a 30-minute delayed topical application of fine coal, is determined. Direct adsorption of the crude petroleum and formation of coal-oil agglomerates occurs when supernatant oil remains on the sample surface (as in the case of the clay-rich substrate). Wicking and partial adsorption occurs if the crude petroleum has migrated below the sample surface. Separation of the coal-oil agglomerate may be possible by simple mechanical means – or if necessary, by froth flotation – to yield a value-added fuel which can be briquetted for ease of handling. Phase One of this study, reported here, addresses phenomena at ambient indoor temperature. Phase Two will address similar phenomena under frozen conditions, typical of Alaskan continuous and discontinuous permafrost zones. Phase Three will address the absorption of oil remaining in the substrate long after an oil spill or leak has occurred.

Additional Key Words: petroleum-contaminated soil, coal-oil agglomeration, adsorption

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Introduction

As a consequence of transportation of crude petroleum via pipeline, rail, or highway, leakage or accidental spills are of concern not only because of loss of the petroleum but because of environmental contamination – especially of surface and ground waters. Two purposes of this investigation are:

1. to discover transport phenomena relating to the movement of crude petroleum through a typical organic-rich surface soil horizon in central Alaska, and the immediately-underlying horizon consisting of clay and organic matter.
2. to determine the effectiveness of reducing the migration of spilled crude petroleum through soil horizons by applying finely-divided activated sub-bituminous coal as a sorbent / agglomerating agent. Although other sorbents are commonly in use, the oleophilic nature of coal and experience to date with coal-oil agglomeration (Capes, 1991; Arnold, 1993; Hower et. al., 1997) suggest that finely divided coal might be an effective binder for crude oil. Moreover, the recovery and separation of agglomerated coal / oil from a soil substrate (by ordinary excavation if possible, or by froth flotation if necessary) potentially can yield a value-added fuel.

The investigation is being conducted in three phases:

Phase One – under indoor ambient temperature conditions (T = 20 +/- 2 degrees C)

Phase Two – under subarctic winter conditions (air temperature range minus 10 to minus 30 degrees C; soil temperature range 0 to minus 15 degrees C)

Phase Three – under outdoor ambient conditions, to determine the uptake and holding properties of finely-divided, activated coal for oil that has been in the soil for a length of time (cf. freshly-spilled oil).

Preliminary results of Phase I are reported here. It is anticipated that freezing conditions in the substrate will inhibit the movement of crude petroleum due to increased viscosity of the crude and the coalescence of wax fractions. Inhibited movement is favored from the pollution control standpoint.

Experimental

Materials

Soils typical of Central Alaska, sampled within 25 km of Fairbanks, AK – namely a surface layer containing dark organic vegetative matter, and an immediately-underlying organic clay-rich horizon – were obtained for the tests (see Figure 1). Details are:

Surface Layer: approx. 200 mm thickness, dark brown, abundance of leaves, twigs & roots, spongy texture (vegetative mat); moisture content 50.3%

Lower Horizon: depth 200 mm & downward (total depth not established), light brown, abundance of twigs and roots, clayey texture with a few 6 to 30 mm pebbles, adheres to digging tool (sticky); moisture content 26.3%

Soil particle size distributions are shown in Appendix A-1.

Sub-bituminous coal was obtained through the courtesy of the Usibelli Mine, Inc., Healy, AK, provider of fuel for electric power generation in Central Alaska. Rank of the coal is sub-bituminous "B" to "C". The sample used for this experiment consisted of blended run-of-mine coals from Seams 2, 4 and 6 of the Hoseanna Creek mine area, after crushing to 2-inch topsize and separation of plus 12 mm particles. The minus 12 mm coal was pulverized to nominally minus 75 micrometers (200 mesh) and activated by drying at 105 degrees C for 48 hours, to remove inherent moisture. The as-received coal contained 3 % surface moisture and 18.3 % inherent moisture. Ash content of this coal was approximately 18 % and Sulfur content 0.4% (dry basis). Particle size distributions of the coal are shown in Appendix A-2.

Concrete sand for use as a reference material in determining the gravity-induced migration of crude oil in a granular substrate was obtained from a concrete, sand, and gravel supplier in Fairbanks, AK. The sand was nominally 3mm x 0.15 mm (8 mesh x 100 mesh; see Appendix A-3), having been washed to remove very fine particles, and air-dried to 2% moisture prior to oil permeation tests.

Crude oil from the North Slope production region of Alaska was obtained through the courtesy of the Williams Company North Pole, AK, Refinery, as run-of pipeline (Trans-Alaska Pipeline System). Specific Gravity of the particular crude sample was measured as 0.83. Other properties of the crude oil are listed in the Appendix B.

Procedure

For uniformity throughout tests and ease of observation of oil permeation within each soil type, cardboard cylinders, having uniform dimensions of 75 mm inside diameter x 150 mm height, were cut from standard map-mailing tubes. Paraffin wax was applied to inside surface of each cylinder to prevent absorption of oil. Soil of each type, or sand, was formed in a tare-weighed cylinder by adding successive one-inch unconsolidated lifts of soil (sand), and tamping each lift uniformly with the hard rubber handle-end of a 0.84 kg geology hammer. Each lift was tamped for fifty (50) 25 mm blows (akin to the standard Proctor compaction test for soils, but with less impact per blow to avoid over-consolidating the soil). Each cylinder was filled with successive lifts to a measured depth of approximately 115 mm of the soil, then weighed to determine compacted density. Individual samples of upper horizon soil, lower horizon soil, and sand were then inoculated with 22 ml of crude oil (22 ml = 0.5 cm depth for a 75 mm I.D. cylinder) in a series of timed tests of the following durations:

- one hour
- eight hour
- twenty-four hour

At the end of each test period, each cylindrical sample was sliced in half longitudinally, the sample halves laid side-by-side for inspection, and the depth and pattern of oil penetration measured and photographed (see Figures 2, 3, and 4).

This series of tests was repeated a second time, with the application of 11.8 grams of activated fine coal to the top surface of the sample at a time interval 30 minutes after initial oil inoculation. Thirty minutes was deemed the mean minimum response time for application of the powdered coal sorbent after the occurrence of a spill. 11.8 grams corresponds to equal-volume application of powdered coal to spilled crude oil, i.e. 0.5 cm depth.

The depth and pattern of penetration of crude oil in each test constitute a data set in which the independent variables were:

- soil type
- time of penetration
- fine coal sorbent addition (yes / no)
- and the dependent variable was penetration (and pattern) of oil permeation.

Observations

Permeation of the crude oil into the sand and upper (dark organic) soil samples occurred rapidly in all cases. Permeation into the lower (clay plus organic) soil samples was markedly less (see Figure 5); in most cases, supernatant remained even after 24 hours, and was removed by a paper-towel absorbent (weight difference being noted before and after absorbtion for quantity estimate).

When finely divided coal was applied (in all cases, 30 minutes after crude oil inoculation), a wicking phenomenon in which the coal acquired a damp appearance occurred within one minute for the sand samples, and within two to three minutes for the upper (organic) soil samples. For the lower (clay-organic) soil samples, the supernatant oil formed a slurry or paste with the coal. The slurry either congealed to a semi-solid top layer, or was absorbed as a viscous liquid prior to slicing the sample for inspection.

In the case of the relatively-impermeable lower, clay-rich soil, channeling of the supernatant oil to the bottom of the sample along fissures in the soil at the cylinder wall occurred in approximately 30% of the lower soil tests. This phenomenon is estimated to reflect what will occur under natural conditions; i.e. fissures will probably occur in the lower soil horizon, and the oil will find downward migration pathways. The agglomeration of oil by finely divided coal will reduce the net downward migration. Consolidated results of the tests are listed in Table 1. Figure 6 illustrates the comparative penetrations of crude oil in the various substrates with and without the addition of activated coal.

Recovery of the discrete coal oil paste or slurry at the top of each sample, for quantitative determination of crude oil retained, remains a challenge. However, the capture of oil by the coal was distinct. This important item will be addressed prior to the Phase Two test series, in which frozen conditions are an added parameter.

Table 1. Consolidated test results – crude oil permeation in test cylinders

Test No.	Material	Net Wt. of Contents, gm	Vol. of Contents, cc	Compacted Density, gm/cc	Coal Applied y / n	Time of oil permeation, hrs	Depth of oil penetra., cm
1	sand	858.92	451.6	1.90	n	1	4.5
2	sand	866.66	472.7	1.83	n	8	7.5
3	sand	790.75	417.2	1.90	n	24	6.7
4	sand	850.37	447.3	1.90	y	1	4.3
5	sand	829.76	455.0	1.82	y	8	8.0
6	sand	820.48	430.1	1.91	y	24	4.4
7	sand	864.02	472.7	1.83	y	24	4.7
				mean =1.87			
8	soil, upper	547.19	469.5	1.17	n	1	4.4
9	soil, upper	544.05	449.0	1.21	n	8	5.0
10	soil, upper	525.80	412.9	1.27	n	24	7.7
11	soil, upper	574.51	463.9	1.24	y	1	4.0
12	soil, upper	553.01	474.6	1.17	y	8	4.5
13	soil, upper	554.71	443.0	1.25	y	24	nil[a]
				mean = 1.22			
14	soil, lower	722.89	455.0	1.59	n	1	0.6
15	soil, lower	717.77	438.1	1.64	n	8	2.1[b]
16	soil, lower	790.12	438.7	1.80	n	24	nil[c]
17	soil, lower	769.41	455.0	1.69	y	1	nil[d]
18	soil, lower	739.04	443.0	1.67	y	8	4.9[e]
19	soil, lower	726.24	430.1	1.69	y	24	9.2[f]
				mean = 1.70			

Notes: a. not clearly discernable; most of oil had agglomerated in coal

b. approx. 16 ml. oil (73% of total) removed as supernatant after 8 hr.

c. an estimated 15 ml. (68% of total) oil had channeled down side of cylinder to bottom

d. approx. 11 ml. (50% of total) coal/oil mixture removed as supernatant after 1 hr.

e. 4.9 cm. penetration through channel on one side of cylinder; most of oil absorbed by coal

f. 9.2 cm. penetration through channel; most of oil had agglomerated in coal

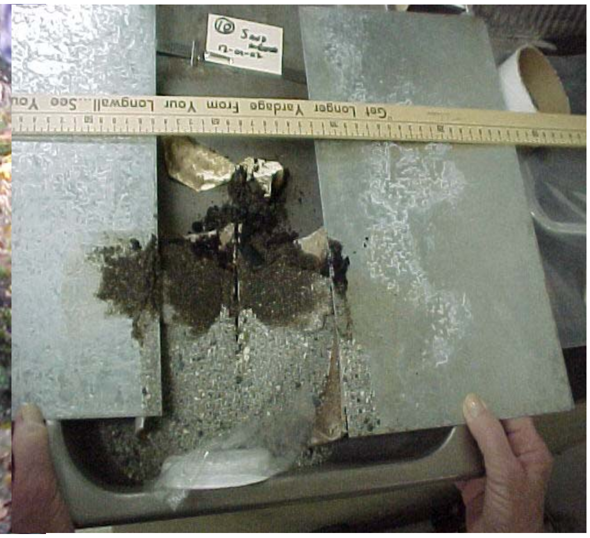

Figure 1. Sampling site of soil, 25 km north of Fairbanks, Alaska. Note upper layer of dark, organic soil (approx. 200 mm thick) and lower layer of lighter clay-rich soil (below 200 mm)

Figure 2. Sand sample, showing method of splitting for inspection. Note oil permeation pattern, and agglomerated coal layer at top of sample

Figure 3. Oil permeation in upper (organic-rich) soil after 24 hours, with coal added tosurface 30 minutes following oil addition. Note pattern of oil migration, detected with absorbent paper

Figure 4. Oil permeation in lower (clay rich) soil after eight hours, with coal added to surface 30 minutes following oil addition. Note pattern of oil migra- tion, detected with absorbent paper

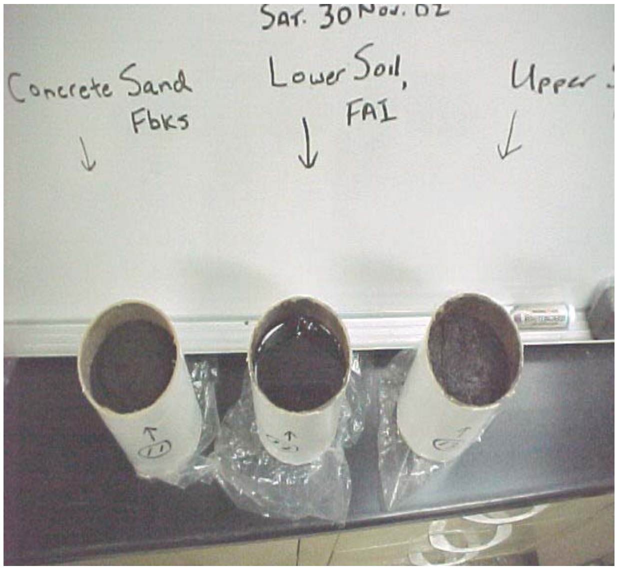

Figure 5. Cylindrical samples of sand, lower (clay-rich) soil and upper (organic-rich) soil approximately 20 minutes after crude oil inoculation. Note supernatant oil on clay-rich soil.

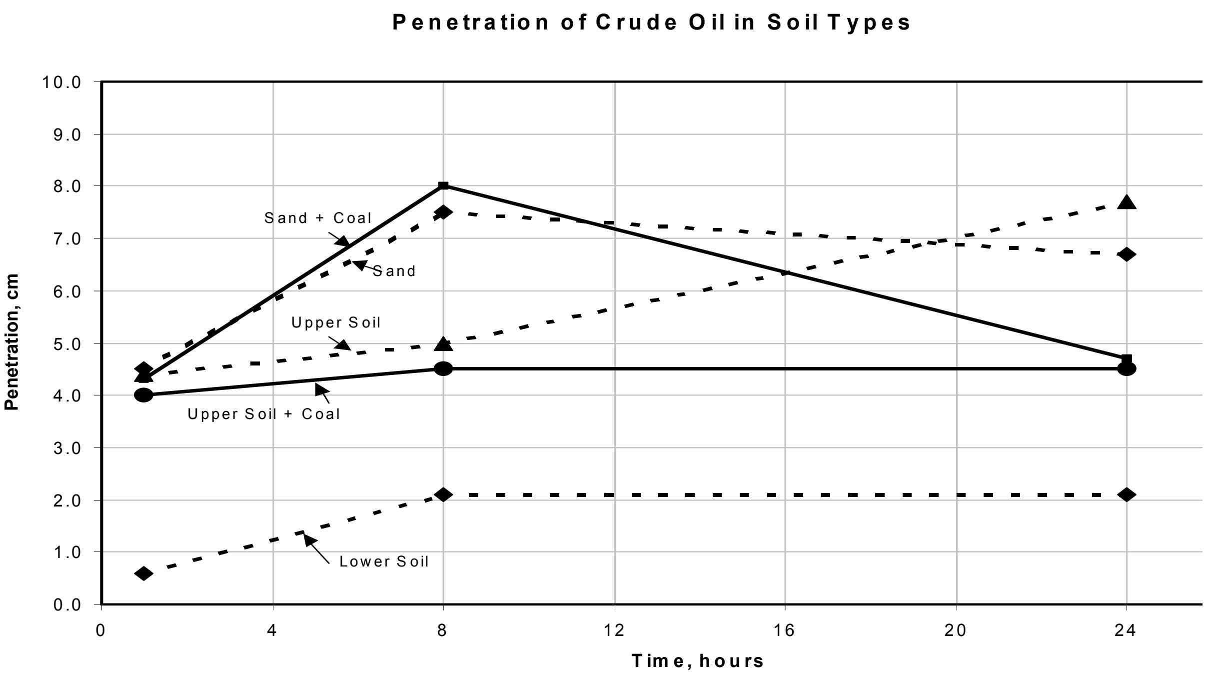

Figure 6. Comparative penetration of crude oil in sand, upper (organic) soil, and lower (clay-rich) soil, with and without the addition of activated coal.

Discussion

As a method for amelioration of oil spills, it is envisioned that a supply of nominally minus 10 mm coal would be kept available in the vicinity (say, within 10 km) of potential spill locations, and that devices for transporting the coal to the site, heat-activating the coal (probably by microwave energy), pulverizing, and pneumatically distributing the coal at the spill site (all of which are technically-feasible) could be assembled. Explosion potential for such a system could be averted by inert gas generation, e.g., carbon dioxide from an accompanying combustion source. The use of finely-divided coal as a sorbent and binder will depend on:

- time required to apply the sorbent after the spill has occurred
- permeability and surface chemistry of the substrate
- temperature and heat transfer conditions of the oil and substrate
- amount and phase of moisture in the substrate

Each of these items is an objective of current investigation.

The merits of coal, versus other sorbents (example: bentonite or cellulose products) are that finely-divided coal appears to have superior wicking power, coal is oleophilic, and the resulting coal-oil agglomerates can potentially be separated and briquetted as a value-added fuel rather than another waste product requiring disposal.

Conclusions

- Initial tests on permeation of crude petroleum through typical interior Alaskan soil types plus a reference sand, at indoor ambient temperatures, indicate uniform permeation patterns for the surface layer (a dark vegetative mat) and sand, and low transmission or channeling for the secondary layer (clay plus organic matter). The addition of finely-divided heat-activated sub-bituminous coal at a 30 minute time interval after oil addition (as a simulated oil spill) results in formation of coal-oil agglomerates in a paste or slurry form if standing oil remains present, or a wicking-up of oil from the sand or soil substrate into which the oil has permeated. Work is continuing to:
- determine the effects of freezing conditions on crude oil migration patterns in near-surface soil horizons

- evaluate the capture of residual crude oil by finely-divided coal after time has elapsed since the spill.

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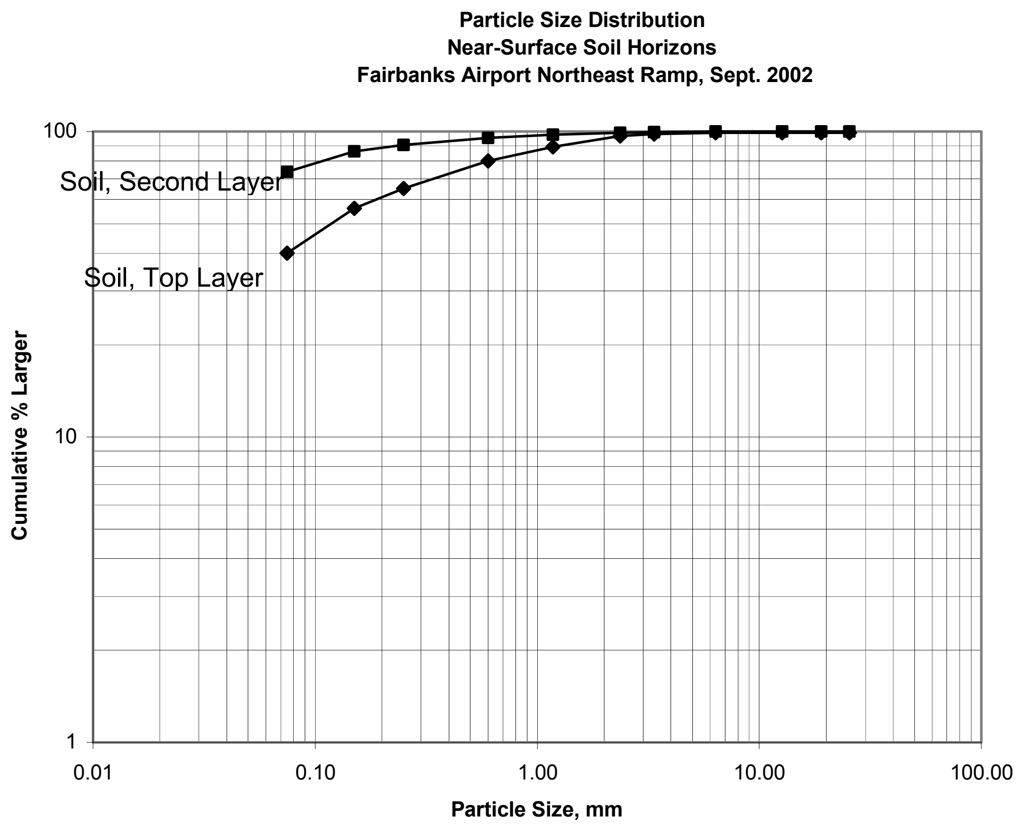
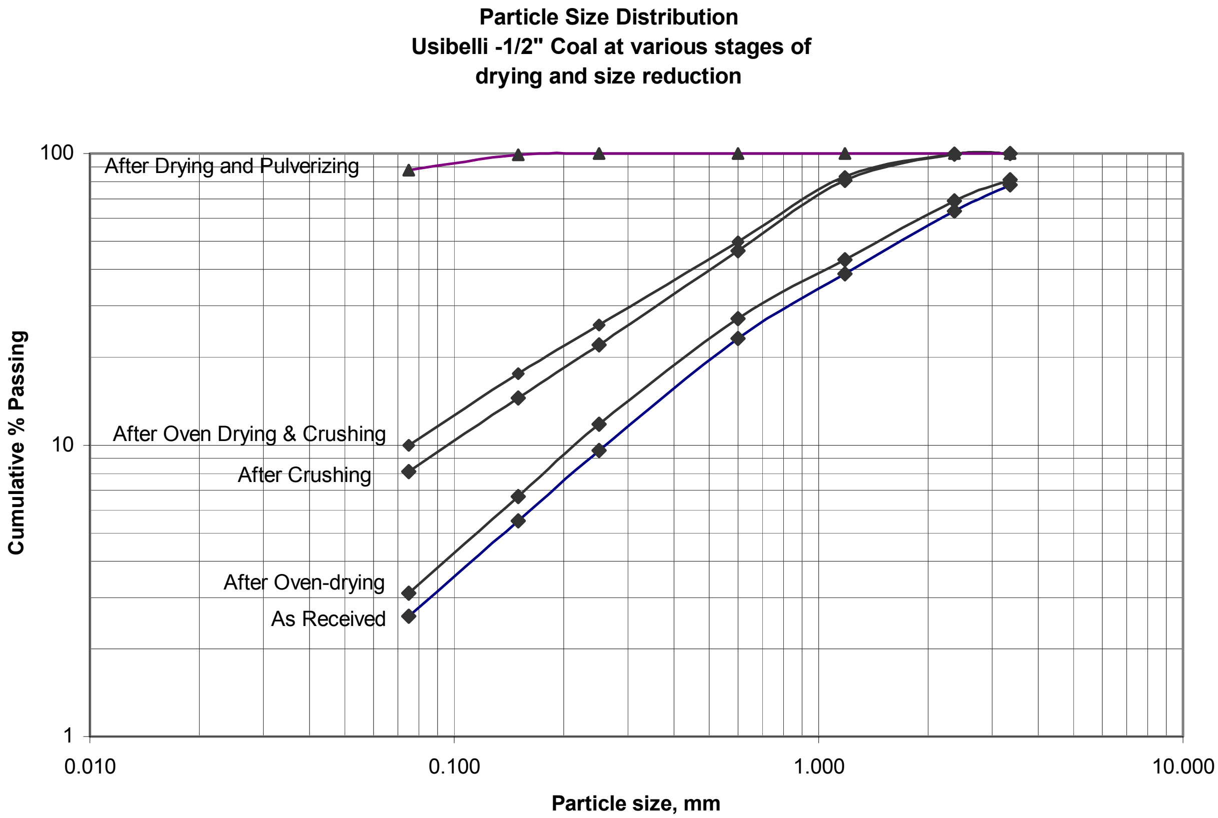
Appendix A-1

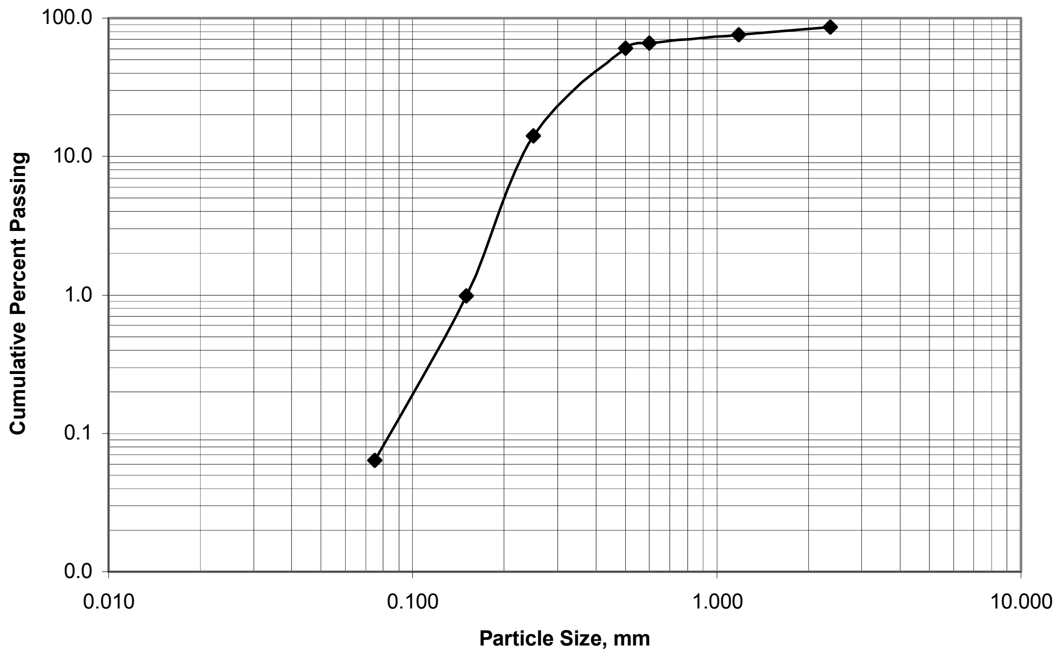


Appendix A-2


Particle Size Distribution
Usibelli -1/2" Coal at various stages of
drying and size reduction
100
10
1
Cumulative % Passing
After Drying and Pulverizing
After Oven Drying & Crushing
After Crushing
After Oven-drying
As Received
0.010
0.100
1.000
10.000
Particle size, mm

Appendix A-3

Particle Size Distribution
Concrete Sand, Fairbanks West Pit
Sept. 2002



Appendix B

Typical Crude Properties 28 Aug. 2002
Williams North Pole Refinery
basis: Crude Unit 3 Fractionation Design Package

Gravity	API	32.0
Water	wt%	0.2
Asphaltene Content, IP-143	ppmw	1.4
Total Chloride, microcoulometry	ppmw	<1.0
Organic Chloride, microcoulometry	wt%	<1.0
Ramsbottom Carbon Residue, D-524	mgKOH/g	4.57
Neutralization Number, D-664	ppmw	0.05
Arsenic, ICP	ppmw	<1.0
Copper, ICP	ppmw	<0.05
Iron, ICP	ppmw	<0.08
Sodium, ICP	ppmw	5.6
Nickel, ICP	ppmw	31
Selenium, ICP	ppmw	<2.4
Vanadium, ICP	ppmw	28
Pour Point, D-97	deg F	-5
Reid Vapor Pressure, D-323	psia	3.2
H2S, UOP 163	ppmw	<1.0
High Temperature Sulfur, S-1552	wt%	1.1
Mercaptan Sulfur, UOP 163	ppmw	13.4
Viscosity @ 100 F	cSt	6.78
Viscosity @ 60 F	cSt	14.99