

Soil remediation by agglomeration with Blue Creek coal

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Abstract

Fine sized Blue Creek coal can be used to remove high molecular weight hydrocarbons from coarse size soils. Heavy crude oil contamination of sand can easily be reduced to a tenth of a weight percent. An added benefit is that lower grade coal can be used and is simultaneously upgraded by this process. Fine sized soils are more difficult to clean, but gross contamination can be reduced to around a half a weight percent while converting the lower grade coal to a high quality fuel.

1. Introduction

Contamination of soils with crude or refined oil products is a problem often associated with production, refining, and distribution of petroleum hydrocarbons. Excavation and incineration of the soil is an effective, but expensive, technology to remediate the contaminated soil [1]. An alternative is bioremediation, however, after reviewing the "Exxon Valdez" experience, the Alaska Department of Environmental Conservation concluded that bioremediation is useful as a polishing step, but conventional manual and mechanical techniques must be used on heavy concentrations of oil [2].

A significant part of Alabama coal is very fine. While this creates handling and environmental problems for coal producers and users, it also provides a material that can be used for remediation of coarse soils heavily contaminated with high molecular weight hydrocarbons. Oil agglomeration is a well known process to clean and recover coal. This work describes using

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Alabama Blue Creek seam coal fines in an agglomeration process to remove heavy hydrocarbons from coarse soil.

2. Coal cleaning and soil remediation by oil agglomeration

The technology of oil agglomeration for treating fine coal was first developed in the 1920's but due to the cost of oil has never been deployed on a large scale for the processing of run-of-mine coal. In state-of-the-art oil agglomeration, diesel fuel added to a slurry of fine coal causes the organic coal particles to adhere to one another forming coal agglomerates while leaving the inorganic mineral particles dispersed. The coal agglomerates formed are readily separated from the ash-forming mineral constituents by screening, skimming or flotation. Relative to other fine coal-cleaning technologies, oil agglomeration results in a product with lower effective surface area and moisture content [3–5]. Several commercial waste recovery projects have been implemented in the last decade using lower oil levels than previously required, and interest continues in the process for economical and environmental reasons [6–8]. Figure 1 is a simplified schematic of a process for cleaning coal by oil agglomeration. At The University of Alabama this approach has been studied for cleaning and recovering fine Blue Creek coal [9].

Recently investigators at Alberta Research Center (Canada) have investigated modifying the conventional oil agglomeration process to remediate soil [10, 11]. They were quite successful at removing high molecular weight hydrocarbons from coarse soils. Traditional oil agglomeration works by having the oil bind or stick the coal particles together. In remediation of oil contaminated soil with fine coal, the contaminate oil serves as the binder to stick the coal particles together. Figure 2 is a simplified schematic of the agglomeration procedure adapted to be used to clean soil.

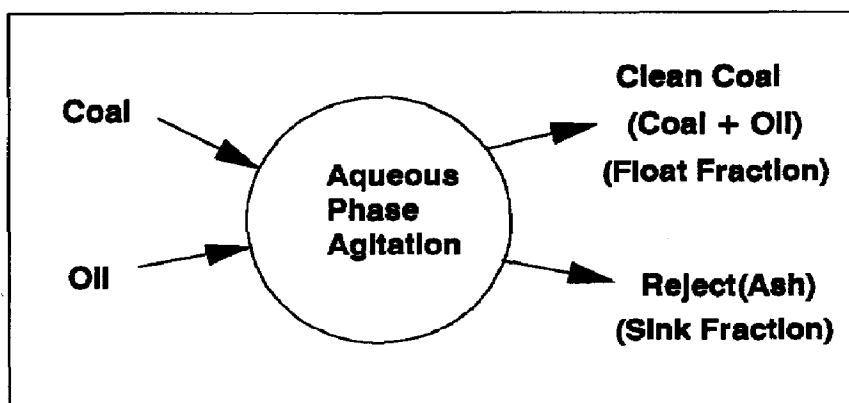


Fig. 1. Simplified schematic of coal cleaning by oil agglomeration.

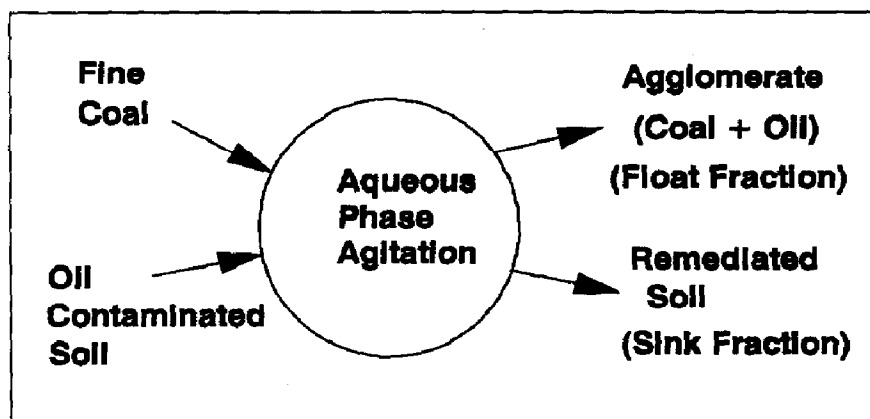


Fig. 2. Simplified schematic of soil remediation by agglomeration.

3. Materials

3.1 Soil

The sand and silty loam soils used in this study were local soils. A soil sample from Kuwait contaminated with crude oil was received early in the fall of 1991 for use in this study. Table 1 gives characteristics of the three soils used in this study. Soil particle size distributions were determined with a Microtrac® II (model 7997) on the standard range bench (700–0.9 μm). The non-combustible content (ash) of all three soils was determined by ASTM D 3174-89 after they had been air dried overnight at 75 °C following ASTM D 2216-80 procedures. Soxhlet extractions were done on the three soils using reagent grade toluene as the solvent. The contaminated soil material from Kuwait was well mixed and samples were extracted with toluene. The material was determined to be 46 weight percent toluene extractables. These extractables were considered to be crude oil. After extraction the Kuwaiti soil was also ashed and the weight percentage is given in Table 1. In this work all compositions are given as weight percentages.

A sample of uncontaminated silty loam was separated into three fractions by sedimentation. The volatiles in the fraction with particles larger than 75 μm are about 0.5 wt% (percent volatiles given by $100 - \% \text{ash}$). The volatiles in the fraction comprised of particles smaller than 75 μm but larger than 2 μm are around 1.5 wt%. The majority of the volatiles are in the < 2 μm fraction which is 93.72 wt% ash or 6.28 wt% volatiles.

3.2 Blue Creek coal

Coals used in this work were obtained from the Jim Walter Resources, Inc. (JWRI) No. 4 and No. 7 mine preparation plants located in Brookwood, Alabama. Several samples of filter cake were obtained over the course of this study and their typical characteristics are given in Table 2. The proximate analyses

TABLE 1

Characteristics of the three soils used in this work

Particle size (μm)	Weight percent in each fraction		
	Sand	Kuwaiti	Silty loam
> 600 (30 mesh)	61.5	23.4	0.0
> 300 (50 mesh)	35.0	27.9	9.1
> 150 (100 mesh)	3.3	18.2	18.8
> 75 (200 mesh)	0.2	10.9	19.1
> 45 (325 mesh)	0.0	2.5	6.4
> 38 (400 mesh)	0.0	3.9	9.4
< 38 (400 mesh)	0.0	13.2	37.2
Total	100.0	100.0	100.0

Weight percent ash of original soils and Kuwaiti soil before and after extraction with toluene

Soil material	Ash (wt%)
Sand	99.89
Silty loam	97.29
Kuwaiti soil (before extraction)	54.00
Kuwaiti soil (after extraction)	95.21
Original silty loam fractions separated by sedimentation	
> 75 μm	99.49
> 2 μm	98.40
< 2 μm	93.72

(D 3172-89) were performed by the analytical section of the Mineral Resources Institute of The University of Alabama. Coal particle size distributions were obtained on grab samples of No. 4 and No. 7 filter cake. Coal particle size analysis was carried out on the Microtrac® in the same manner as described for the soil samples.

3.3 Oil

Three oils were used to contaminate the soil samples. Maya crude oil was obtained in November of 1989 and No. 5 fuel oil in July of 1991 from the Hunt Oil Company Refinery in Tuscaloosa, Alabama. A heavy coal-derived oil, V1074, was received in March of 1990 from the Wilsonville, Alabama coal liquefaction pilot plant. Table 3 gives the specific gravities and flash points from the specifications sheets received with the oils. Viscosities were determined at room temperature on a Haake® RV-12 viscometer. The Kuwaiti soil was received as is, contaminated with crude oil from the area of the Gulf War.

TABLE 2

Typical characteristics of the No. 4 and No. 7 filter cake used in this work

Proximate analysis (wt%)	Filter cake	
	No. 4	No. 7
Moisture	0.87	0.79
Volatile	24.24	20.10
Ash	8.65	8.49
Fixed carbon	66.24	70.62
Total	100.00	100.00
Particle size (μm)		
> 600 (30 mesh)	1.9	7.6
> 300 (50 mesh)	17.2	25.5
> 150 (100 mesh)	22.8	23.4
> 75 (200 mesh)	22.5	16.7
> 45 (325 mesh)	10.5	7.6
> 38 (400 mesh)	3.2	2.4
< 38 (400 mesh)	22.0	16.8
Total	100.0	100.0

TABLE 3

Characteristics of oils used in this work

Oil	Specific gravity	Viscosity (cP @ 78 °F)	Flash point
Maya crude oil	0.918 @ 60 °F	97	< 60 °F Tag closed cup
V1074	1.027	2700	250 °F (Closed cup)
No. 5 Fuel oil	0.89–0.92	100	130 °F (COC)

4. Experimental section

Figure 3 is a schematic of the soil remediation procedure used in this study. First soil contaminated with crude oil was placed in a Waring® blender (Model 34 BL97) with stepwise adjustable speeds. A known weight of coal that had been wet screened and dried under a flowing stream of argon was also placed in the blender. Water that had been heated to a temperature of 74 °C was then added to the blender to bring the solids content to approximately 10 to 20 wt%. This gave a coal–oil–water slurry temperature in the blender of 62 °C. For coarse soils, the slurry was mixed at 16,000 rpm (unloaded, speed number 7) for 3 min and at 8,000 rpm (unloaded, speed number 3) for 7 min. This blender was

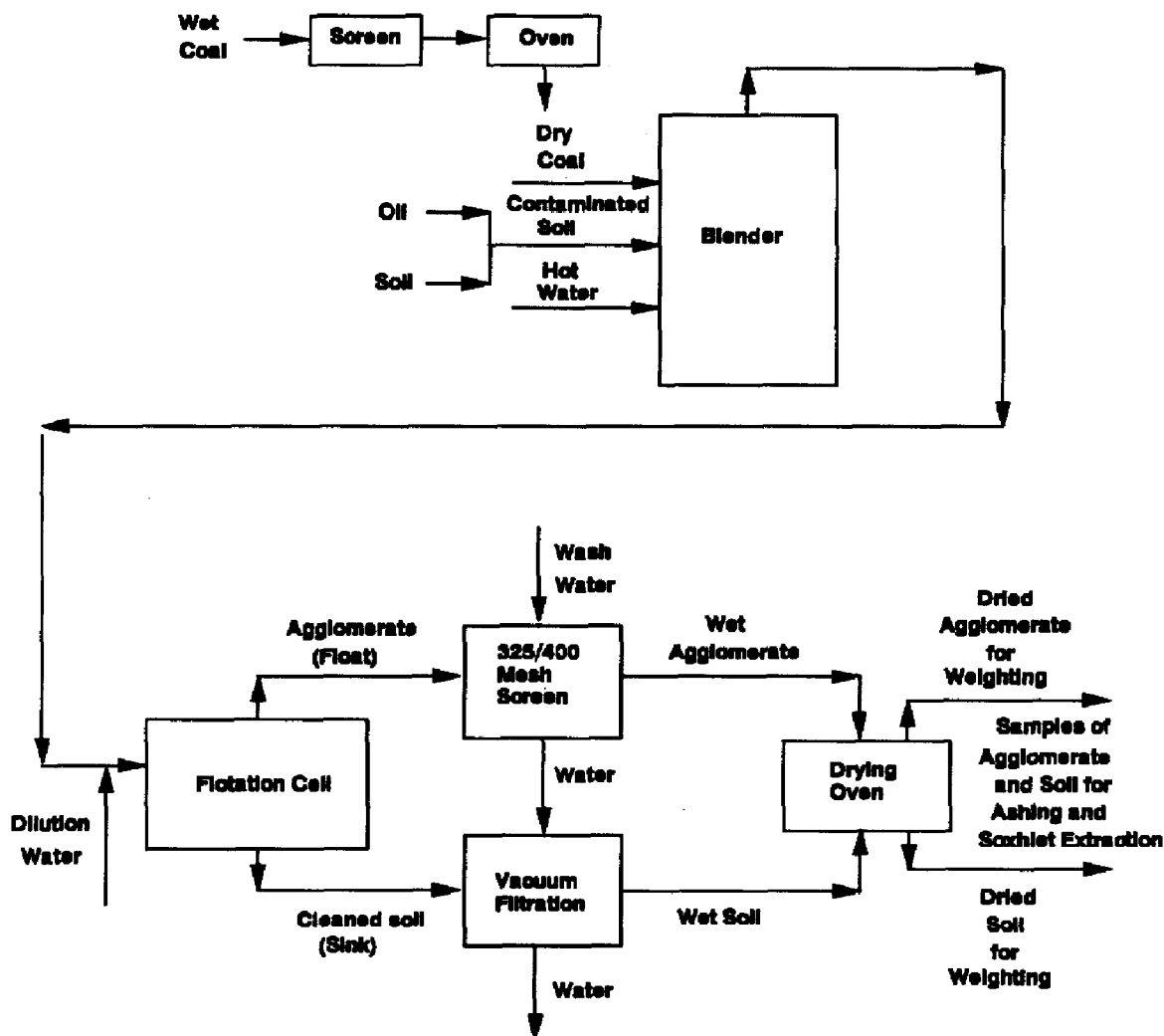


Fig. 3. Schematic of soil remediation process.

not equipped with a tachometer, but a similar blender showed an rpm-drop from 16,000 rpm to 12,750 rpm and from 8,000 rpm to 6,750 rpm when loaded with the coal–oil–water slurry. For fine soils, the slurry was mixed at speed number 7 for 7 min and at speed number 3 for 3 min. The entire batch was transferred to a Wemco® flotation unit with a 2.8 liter tank, approximately 1.5 liters of dilution water was added, and floated without chemical additives. The agglomerates that floated were skimmed off and washed on either a 325 or a 400 mesh screen and the soil (sink) that remained in the tank was filtered using aspirator vacuum. Both the total wet agglomerate and the total wet sink (cleaned soil) were air-dried overnight. Samples were dried at 75 °C instead of at 105 °C as in the standard ASTM D 3173-89 moisture test to reduce evaporation of oil. After overnight drying the total weight of both the agglomerate and cleaned soil was determined. Weighing to constant weight of argon-dried coal, uncontaminated

soil, agglomerates, and cleaned soil were all done after the samples had equilibrated at room temperature. Samples were redried to verify their constant weight. Samples of original uncontaminated soil, coal, agglomerates, and cleaned soil were taken for soxhlet extraction and ash (ASTM D 3174-89) determination.

Eight agglomerations were performed on sand, 12 on Kuwaiti soil, and 73 on silty loam. Results from fourteen representative runs are presented in Table 4. The run number is the chronological order in which the experiments were performed. Sand and silty loam were saturated with Maya crude oil; the Kuwaiti soil was used as received. Also shown in the table is the amount of 74°C tap water added to the blender which gave a coal–oil–water slurry temperature of 62°C in the blender. The weight and the percent ash of the agglomerates and cleaned soil recovered from the Wemco® flotation cell is also presented. Weight percent volatiles on the cleaned soil was calculated by the formula:

$$\text{Volatiles on cleaned soil (wt\%)} = \text{Ash of blank (wt\%)} \\ - \text{Ash of cleaned soil (wt\%)}$$

The cleaned soil and the blank were ashed by the same process with the ash of the original soil given in Table 1 serving as the blank.

5. Analysis of soil remediation results

5.1 Contaminated sand

Volatiles left on the sand can be lowered below 0.1%, as shown in Table 4, without significantly degrading the fuel (agglomerate) quality by raising its ash level above that of the starting coal. The coal used for runs 65 and 66 was a +50 mesh fraction of No. 7 filter cake that was ground to pass a 400 mesh sieve. This fraction had an ash content of 6.80% and the ash content of the agglomerate was slightly higher than this. Run number 67 was with a No. 7 filter cake fraction passing 100 mesh but retained on a 200 mesh screen. The ash of this fraction was not checked, but previous work indicates that it would be expected to have slightly higher ash content than the +50 mesh fraction. This larger size coal fraction yielded a slightly higher volatiles remaining on the sand. The coarse nature of the sand, 61.50% of the particles greater than 600 µm, make it an easy soil to clean.

5.2 Kuwaiti contaminated soil

Finer than the sand, cleanup is somewhat more difficult with the Kuwaiti soil. In general, volatiles and toluene extractables can be reduced to the level of around one percent. Except for one remediation trial, the level of ash in the agglomerate did not greatly exceed that of the ash in the feed coal. The 6.80% ash coal was the +50 mesh material ground to minus –400 mesh and the 8.49% ash coal was the original No. 7 filter cake.

TABLE 4

Volatiles and toluene extractables on three soils treated with No. 7 Blue Creek coal at a coal-oil-water slurry temperature of 62 °C

Run number	Contaminated soil (g)	Crude oil on soil (%)	Weight of coal (g)	Ash of coal (%)	Weight of water (g)	Weight of agglomerate (g)	Ash of agglomerate (%)	Weight of cleaned soil (g)	Ash of soil (%)	Volatiles on soil (%)	Toluene extractables (%)
<i>Sand</i>											
65	50.0	5.0	29.4	6.80	350.0	31.5	7.70	46.6	99.80	0.09	
66	50.0	5.0	30.0	6.80	350.0	32.8	9.40	47.2	99.80	0.09	
67	50.0	5.0	30.0		350.0	32.6	11.40	47.1	99.60	0.29	
<i>Kuwaiti soil</i>											
74	60.0	46.0	60.0	6.80	400.0	79.4	8.60	36.1	93.80	1.41	0.39
75	60.0	46.0	60.0	6.80	400.0	81.6	6.90	32.2	93.00	2.21	0.64
76	61.1	46.0	56.1	8.49	450.0	75.5	9.00	35.6	93.70	1.51	
77	77.2	46.0	84.5	8.49	450.0	118.6	14.80	40.1	95.10	0.11	0.64
79	76.0	46.0	127.0	8.49	450.0	149.4	8.20	42.8	94.40	0.81	1.05
<i>Silty loam soil</i>											
63	50.0	15.0	21.0	6.80	350.0	27.5	9.07	41.8	94.40	2.82	
107	50.0	15.0	21.5	19.90	500.0	45.1	22.20	30.9	97.00	0.22	0.14
110	50.0	15.0	21.5	19.90	500.0	38.8	20.10	31.3	96.99	0.23	0.44
111	50.0	15.0	21.5	19.90	500.0	29.9	15.98	36.5	95.90	1.32	0.90
112	50.0	15.0	21.5	19.90	500.0	35.9	21.40	37.6	96.20	1.02	0.50
114	40.0	15.0	22.8	19.90	500.0	25.3	13.60	733.3	95.97	1.25	0.32

5.3 Contaminated silty loam

The silty loam (37.2% less than 400 mesh) used was a fine soil that proved more difficult to clean than the coarser textured materials. Volatiles could usually be reduced to 1% and toluene extractables to 0.5% without significant fuel degradation. Runs 107, 110, 111, 112, and 114 were made with the natural –400 mesh fraction of the No. 7 filter cake which is 19.90% ash. The cleaned soil from run number 107 was sized on 200 and 325 mesh screens. Weight percent of the soil retained on each screen and the ash of each fraction is given in Table 5. The +200 and +325 mesh fractions had ash levels above 99 wt% (<1% volatiles) while the –325 mesh fraction had an ash level of 94.33 wt% (5.67% volatiles) indicating that this fine fraction contained the bulk of the volatiles (oil) and is hence considered to be the most difficult soil fraction to clean. Ash of the total soil aggregate was 97.00% (3% volatiles).

To verify that toluene extraction removed most of the Maya crude oil, an extraction test was performed. Two samples of dry silty loam were fortified with 15 wt% Maya crude oil. After Soxhlet extraction with toluene, the 15 wt% oil added to the two soils had been reduced to 14.82% and 14.87%, respectively. This indicates that 99 wt% of the Maya crude was extractable by toluene. Based on these blank runs and the soil blanks, toluene extraction was concluded to be a good method to determine the quantity of oil left on the soil.

5.4 Material balances

Soil, oil, coal, and water were added by weight to the blender for runs with sand and silty loam. All solids were accounted for as either agglomerate or tailings. A total material balance was then computed for each run with the average being 2.94 g lost for the 71 runs where quantitative transfers were made. This is about 96% closure on the total material balance. For runs with sand the total material balance tended to check because smaller amounts of oil were used. Drying tests indicated that up to 30% of the Maya crude was lost to evaporation by drying overnight at 75 °C. For a typical silty loam run this amounted to 2.25 g, which accounts for most of the 2.94 g material balance discrepancy. Component material balances were not performed.

TABLE 5

Ash content of three soil fractions from run No. 107

	Mesh		
	+200	+325	–325
Weight percent in size fraction	41.9	10.4	47.7
Weight percent ash of soil	99.49	99.20	94.33

5.5 Effect of selected variables on process performance

Table 6 shows ash and volatiles on soil cleaned with various particle size fractions of coal. The runs were all made with silty loam contaminated with 15 wt% Maya crude at a coal-oil-water slurry temperature of 62 °C. Particle size distributions for the three coal fractions are given in Table 7. No. 4 and No. 7 filter cake was separated on 50, 100, 200, 325, and 400 mesh screens. The

TABLE 6

Ash and volatiles content (wt%) of silty loam treated with coal fractions of different particle sizes

Filter cake No	Mesh						Coal type
	+50	+100	+200	+325	+400	-400	
<i>Ash</i>							
4	91.30	90.20	90.80	91.60	90.30	95.00	Natural
7	92.50	91.80	91.00	92.00	92.60	94.80	Natural
4	90.90	91.20	91.60	92.50	94.20	95.50	Ground
<i>Volatiles</i>							
4	5.99	7.09	6.49	5.69	6.99	2.29	Natural
7	4.79	5.49	6.29	5.29	4.69	2.49	Natural
7	6.39	6.09	5.69	4.79	3.09	1.79	Ground

TABLE 7

Particle size distribution (wt%) of three coal fractions

Particle size (µm)	-400 Mesh natural fines		Ground +50 mesh
	No.4 Filter cake	No.7 Filter cake	No.7 Filter cake
> 60	6.6	7.3	0.0
> 40	13.5	13.1	0.0
> 30	15.1	12.0	0.2
> 20	15.8	12.8	4.7
> 10	13.1	12.4	10.4
> 15	11.8	11.6	16.4
> 5	15.4	18.1	34.4
> 3	5.8	5.1	21.2
> 2	1.7	5.6	6.4
< 1	1.2	2.0	6.3
Total	100.0	100.0	100.0

fractions retained on each screen and the fraction passing 400 mesh and caught in the pan were used to clean the soil. The naturally occurring –400 mesh fines from the No. 7 filter cake has an ash of 19.90%. In addition to the natural filter cake fractions, the third coal type is a +50 mesh fraction of No. 7 filter cake that was wet ball milled to produce low ash fines. The +50 mesh coal has an ash level of 5.81 weight percent which is lower than the natural –400 mesh ash level. Volatiles on the soil from Table 6 are plotted in Fig. 4. The finer the coal the better the cleaning that occurred, the greatest effect being obtained with the ultrafines from the ground +50 mesh fraction of which 85% was smaller than 10 μm .

The optimum amount of coal necessary to achieve the minimum content of volatiles remaining in the soil is illustrated in Fig. 5. It was concluded that increasing ratio of coal to oil beyond a 4-to-1 ratio does little to increase cleaning. The coal used for these tests was natural –400 mesh No. 7 filter cake with silty loam containing 15 wt% Maya crude at a coal–oil–water slurry temperature of 62 °C.

The effects of oxidation on the cleaning performance of coal were simulated using samples of coal that were “aged” by heating at 105 °C in air for varying time intervals. These samples were used to clean soil to determine the effect of aging and the results are illustrated in Fig. 6. These tests did not indicate that a significant aging, or oxidation, effect existed for coal heated less than 25 hours.

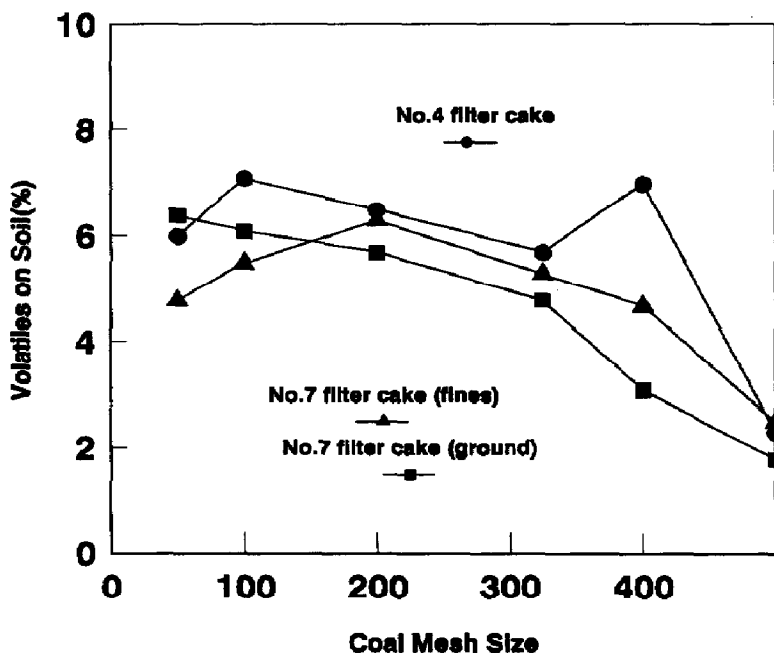


Fig. 4. Volatiles on soil versus coal mesh size for silty loam contaminated at a level of 15% crude oil.

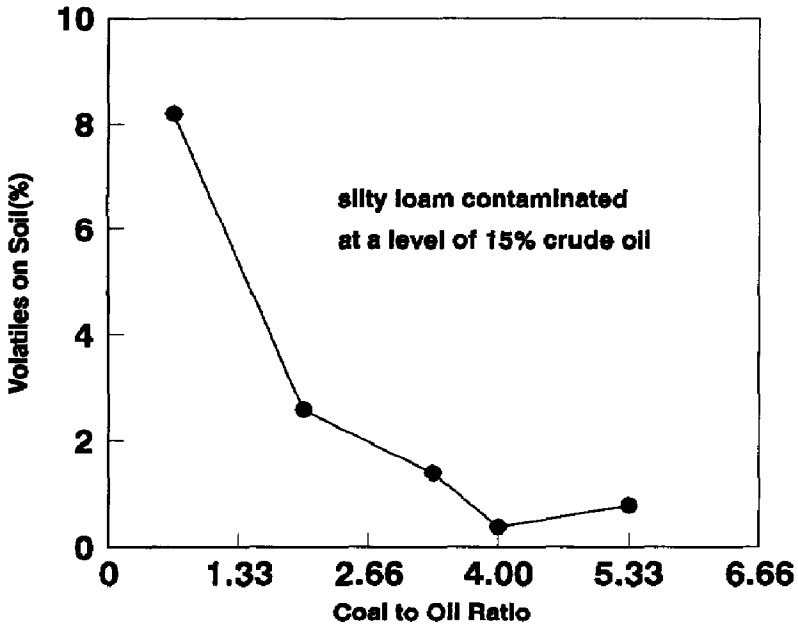


Fig. 5. Volatiles on soil versus coal to oil ratio for silty loam contaminated at a level of 15% crude oil.

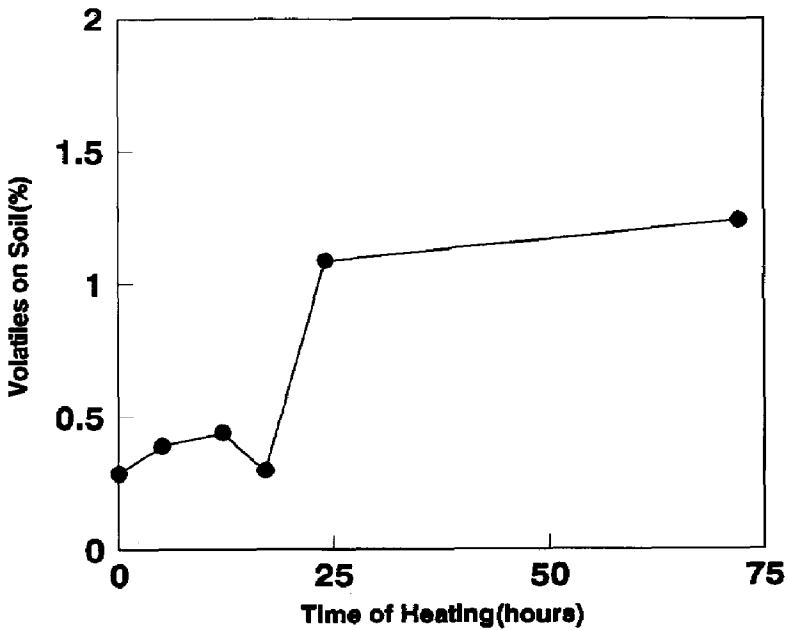


Fig. 6. Volatiles on soil versus time of heating (age of coal) for silty loam contaminated at a level of 15% crude oil.

6. Conclusions

Coarse soils heavily contaminated with high molecular weight hydrocarbons such as crude oil can be cleaned to a level of about 0.1% residual hydrocarbon by mixing with coal using a coal agglomeration process. For all soils, high levels of contamination can easily be handled by increasing the amount of coal. The treat rate of coal is in the range of 3 to 4 grams of coal per gram of oil. The optimum treat rate is easily determined for individual soils and coals. The final level of cleaning is not affected by the initial oil contamination level. This was concluded to be one of the advantages of this method. For finer textured soils, such as the silty loam, the amount of oil remaining after treatment with the fine coal was greater than coarse textured soils and the residual was demonstrated to concentrate in the smaller particle size fractions of the soil. One point to note is that the –400 mesh natural fines clean the soil better than the larger size coal fractions. This fraction of natural coal fines is the most troublesome for the coal industry. This material is the dustiest and has the highest ash content of any of the fractions that can be separated by screens. Thus, using this material to remediate soil both removes oil contaminants from the soil and lowers the ash of the coal while improving its calorific content and handling characteristics due to the agglomeration by the oil removed from the soil. This troublesome material can be simultaneously upgraded while the soil is cleaned.

The major factor affecting clean-up was the particle size of the soil. Gross contamination was easily removed with fine coal treatment but cleaning to less than 1% volatiles was difficult with the fine-textured soils. Washing with hot water is not expected to produce nearly as good a result. The next factor of importance is the particle size of the coal. Coal below 30 to 90 μm in particle size is needed for maximum cleaning effectiveness.

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