Coal agloflotation and supercritical wet oxidation: Novel remediation techniques for ultra-cleaning of contaminated soils

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Abstract

Soil contaminated with toxic organic compounds is a serious environmental problem facing the global community. Over time, organic pollutants which are trapped in the soil matrix leach through inadequate holding facilities and migrate deep into the earth, finally making their way to ground water aquifers. Once contaminated, these aquifers carry the toxins through the ecological system, bringing them into the food chain. Current technologies aimed at remediation of contaminated sites are inadequate in that they are site specific and often require secondary remediation. Coal agloflotation and supercritical wet oxidation (SWO) are two methods of soil remediation which can be utilized successfully to decontaminate polycyclic aromatic hydrocarbon (PAH) contaminated soil. Soil samples obtained from industrial town gas sites, with a total PAH contamination ranging from 2 to 17 mass percent, were remediated to environmentally acceptable standards with an end result of clean soil and usable byproducts from the processes. Hydrocarbon removal efficiencies were better than 95 percent for agloflotation and 99 percent for wet oxidation. A description of the individual processes is given as well as pertinent data to show the success of these two processes as primary and/or secondary treatment for soil remediation. A comparison between both processes is also given.

Introduction

Contamination of soil by toxic and/or hazardous organic pollutants is of serious environmental concern [1]. Coal gasification for household and industrial use became widespread during the second half of the 19th century and reached its peak around 1930 [2]. Coal tar, a liquid by-product of coal gasification rich in polycyclic aromatic hydrocarbons (PAHs) was commonly disposed of in unlined pits on the grounds of the gas works [3]. PAHs include a group of organic priority pollutants of critical environmental and public health concern

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due to the following characteristics: (a) chronic health effects (carcinogenic-ity), (b) microbial recalcitrance, (c) high bioaccumulation potential, and (d) low removal efficiencies in traditional waste water treatment processes. These compounds are produced by high-temperature industrial processes (e.g., petroleum refining, coke production, wood preservation, and synthetic oil and gas production) and are associated with a wide range of hazardous-waste-soil sites [4].

The impetus to clean these contaminated sites thus has been not only the inability to use these sites but also a very serious other environmental concern: deteriorating ground water quality around these sites [5].

Various remedial techniques such as absorption, extraction, and inciner-ation have been proposed and explored. However, application of any of these techniques has to be evaluated on an individual basis which is largely dependent on the type of matrix and contamination, accessibility and most importantly, cost effectiveness [6, 7].

Typical, primary cleanup methods of contaminated soil include conventional techniques such as immobilization, dechlorination, thermal desorption, froth flotation, and solvent extraction. However, most of these methods do not reduce the extent of contamination to acceptable levels. At these levels, primary cleanup methods are neither effective (except incineration) nor eco-nomically advantageous in reducing the tar contamination further down to more acceptable levels [8]. In other words, soil samples with low levels of contaminants have to be treated by methods which target very low and safe levels of contaminants.

Two novel methods for cleanup of contaminated soils are currently under study. Coal agloflotation can be used as primary cleanup method to treat soils with relatively higher hydrocarbon concentration, whereas wet oxidation could be used to treat soils even with low contaminant concentration. Both of these processes can be installed on mobile units, thus providing more flexibility in the treatment strategy.

Process description

Coal agloflotation

Coal agloflotation is a double beneficiation process in which coal acts as a cleaning agent to strip off the contaminants from the soil, and in turn liberating its heavy mineral matter thereby becoming a better product itself. This is possible because of the dramatic differences in the adsorptive affinities between coal and mineral matter towards tarry/oily material [9]. In principle, the process is based on oil agglomeration, with organic contaminants acting as the bridging liquid [6].

The process is primarily based on abrasion mass transfer and it can be divided into four stages (Fig. 1) [10]. The first stage is the *layering*. In this stage the coal and soil particles are gently tumbled in a tumbler where the coal
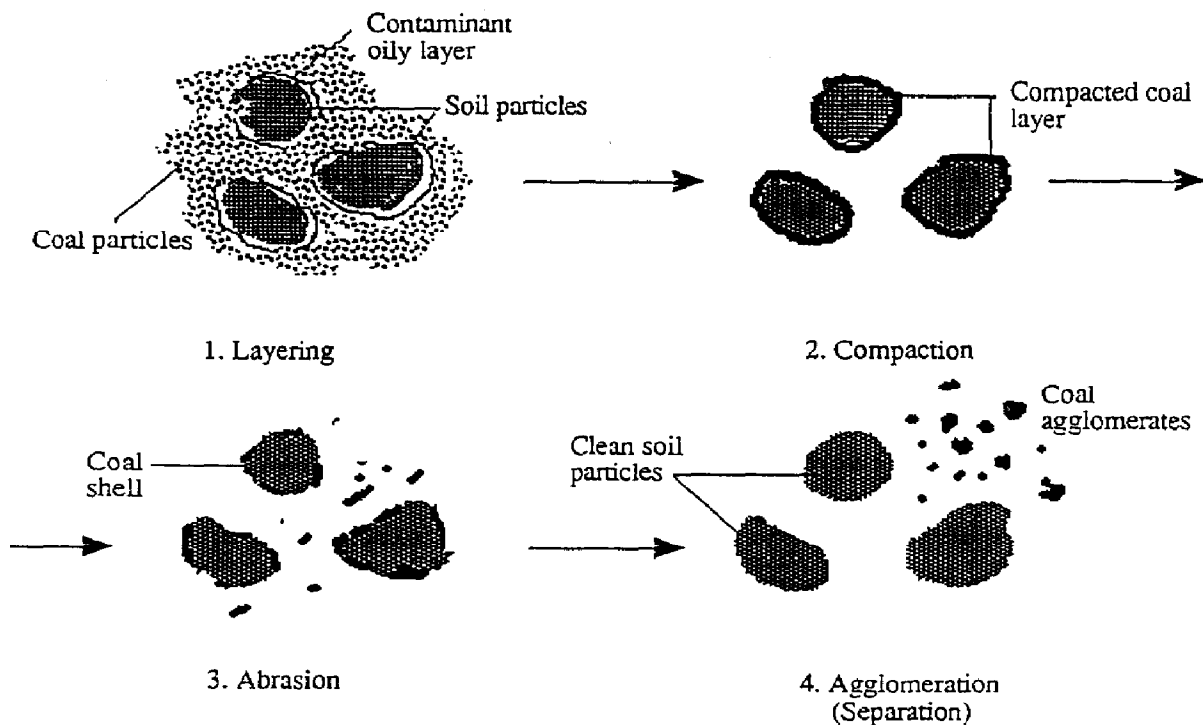
Fig. 1. Process mechanism of coal agloflotation.

particles stick around the contaminated soil particles. This stage is completed when all oil containing surfaces are covered with coal particles. Then it is the *compaction*, as the name indicates, the slurry mixture (coal–soil–water) undergoes compaction or reduction in void volume, changing the oil saturation in the coal layer. During this stage the strength of the coal particles adhering to each other increases so that a strong and hard coal layer is formed around the soil particles. It is during these two stages the contaminants get adsorbed on to the coal particles and the soil is cleaned up. The next stage is the *abrasion* where coal and the soil particles are physically separated by high shear stripping. The slurry mixture is transferred from the tumbler to the flotation cell. The mixture is then subjected to high shear mixing where the bonded coal particles (which are now oil rich) are liberated. Finally it is the *agglomeration*. This is an important stage which would help to separate the coal particles easily. This is done by high shear mixing as well as addition of oil to increase the agglomeration of the coal particles. This is done to improve the handlability of the final product.

Supercritical wet oxidation

SWO is a chemical process in which oxidation reactions occur in a supercritical water phase [11]. This process utilizes oxygen, air, or hydrogen peroxide as the oxidant, and supercritical water as the reaction medium. In SWO,

there is a significant level of oxygen solubility in supercritical water. Compared to the room temperature solubility, this level is practically infinite [12, 13]. Supercritical water also exhibits a very strong solvent power towards most organic chemical species. This dramatically increased solvating power is attributed to the sharp decrease in fluid density as well as the decreasing inherent polarity of the solvent [14, 15]. Since many organics are completely miscible in supercritical water, the problem of mass transfer resistances can be alleviated, thereby achieving a complete and unhindered oxidation reaction.

In SWO process, materials partially or completely dissolve into a homogeneous, condensed phase mixture of oxygen and water, and chemical reactions between the material and oxygen take place in the bulk water phase. This condensed phase makes wet oxidation an ideal process to transform materials which would otherwise be insoluble in water to a harmless mixture of carbon dioxide and water. Since oxidation reactions are exothermic in nature, the high thermal mass of supercritical water makes this reaction medium better suited for thermal control, reactor stability, and heat dissipation.

Experimental

Soil samples

The samples used for all experimental runs were from actual industrial sites and were contaminated with PAHs. Analysis of the original coal–tar liquid by GC/MS was carried out. A standard BNA + 25 analysis was performed to provide quantified data on the base/neutral and acid extractable compounds. In addition to the BNA analysis, 25 largest unknown peaks in the GC/MS total ion chromatogram were matched with the NBS library. These tentatively identified compounds were reported on a semiquantitative basis. The aim of this study was to identify and determine the PAH content in the coal–tar contaminated soil. The compounds detected in the original coal–tar are listed in Table 1.

The concentration of the contaminant in all the samples was determined on a mass basis by soxhlet extraction using methylene chloride as the solvent for 15 hours. For soxhlet extraction, 10 g of original sample was extracted with 300 ml of methylene chloride. The extracted soil sample was dried overnight at 65 °C in a vacuum oven (NAPCO Model 5831-120). The methylene chloride extract containing soluble oil from the soil was evaporated using a Rotovapor (Model RE-111). The residual oil content was determined using a Mettler analytical balance. A list of soil samples and their respective contamination concentrations is presented in Table 2.

Coal samples

The coal used in agloflotation was a Midwestern bituminous coal from Indiana. This coal was Indiana #5 obtained from the St. Petersburg seam. The

TABLE 1

PAHs detected in original coal tar of site 1-1

Compound	Concentration (μg/l)
d_4-1,4-Dichlorobenzene	40
2-Fluorophenol	125
Phenol-d_5	114
d_8-Naphthalene	64
2-Methylnaphthalene	144
d_{10}-Acenaphthene	40
2-Fluorobiphenyl	113
Acenaphthylene	147
Acenaphthene	32
Fluorene	114
2,4,6-Tribromophenol	47
d_{10}-Phenanthrene	378
Anthracene	104
Fluoranthene	106
d_{12}-Chrysene	40
Pyrene	1018
Terphenyl-d_{14}	269
Benzo [a] anthracene	126
Chrysene	101
d_{12}-Perylene	40
Benzo [b] fluoranthene	106
Benzo [a] pyrene	95
Dibenzo [a, h] anthracene	24
Benzo [g, h, i] perylene	120

TABLE 2

Hydrocarbon concentration in soil samples

Soil source[a]	Mass concentration (%)
Site 1-1	16.05
FC 1-1	2.73
Prepared	16.52
Site 1	3.37
Site 2	14.78

[a] Source sites specification:
Site 1-1, Northeast Utilities, New Jersey;
FC 1-1, Soil from first flotation train, Alberta Research Council, Devon, Canada;
Site 1, Northeast Utilities, Berlin, Connecticut; and
Site 2, Public Service Electric & Gas Co., Lyndon, New Jersey.

coal sample was prepared by ball mill size reduction to obtain a particle size of less than 65 Tyler mesh. The proximate analysis of the coal is given in Table 3.

Agloflotation procedure

A typical run was initiated by mixing 500 g of contaminated soil with 250 g of −65 mesh Indiana 5 coal in a 5 liter tumbler. One liter of hot water (73 °C) was added to the coal – soil mixture. The resulting coal–soil–water suspension was subjected to tumbling at 60 rpm for 12 minutes. The slurry containing coal–oil agglomerates and mineral matter was then separated in a standard Wemco flotation cell.

Approximately 2 ml of frother (Aerofroth) was added to aid the froth production. The resulting slurry was then charged to a 5.5 liter mixer (Wemco Model 71260-01) run at 2400 rpm to induce abrasion between the coal and soil particles. The slurry was then held at 1500 rpm for 30 minutes. Air was introduced into the slurry mixture at the end of the 30 minute period to produce froth. This permitted oil rich coal to separate out, as it is lighter and sticks to the bubble surface. The froth was then skimmed off. The process ensured that inherent mineral matter present in the coal was removed as it settled at the bottom of the flotation cell with the now clean soil. The process flow sheet is shown in Fig. 2.

Supercritical wet oxidation procedure

Supercritical wet oxidation of PAH contaminated soil was performed semi-batch in a 1-liter micro-pilot plant. Figure 3 shows a schematic representation of the micro-pilot plant. The heart of the system is a stirred bolt-closure wet oxidation vessel made of Hastelloy C-276. This unit is equipped with 0.32 cm and 0.64 cm Hastelloy C-276 feed delivery and product outlet lines respectively. The pilot plant is also equipped with a micro-metering solvent delivery pump capable of delivering the solvent against a 35 MPa back pressure. Oxygen is delivered to the oxidation vessel via a high pressure oxygen compressor. A more detailed description of this unit may be found elsewhere [16, 17].

Experiments were initiated by charging the primary oxidation vessel with 15 grams of soil. Once charged, the oxidation vessel was brought up to the

TABLE 3

Proximate analysis of −65 mesh Indiana #5 bituminous coal from St. Petersburg seam (supplied by Midwest Ore Processing Co.)

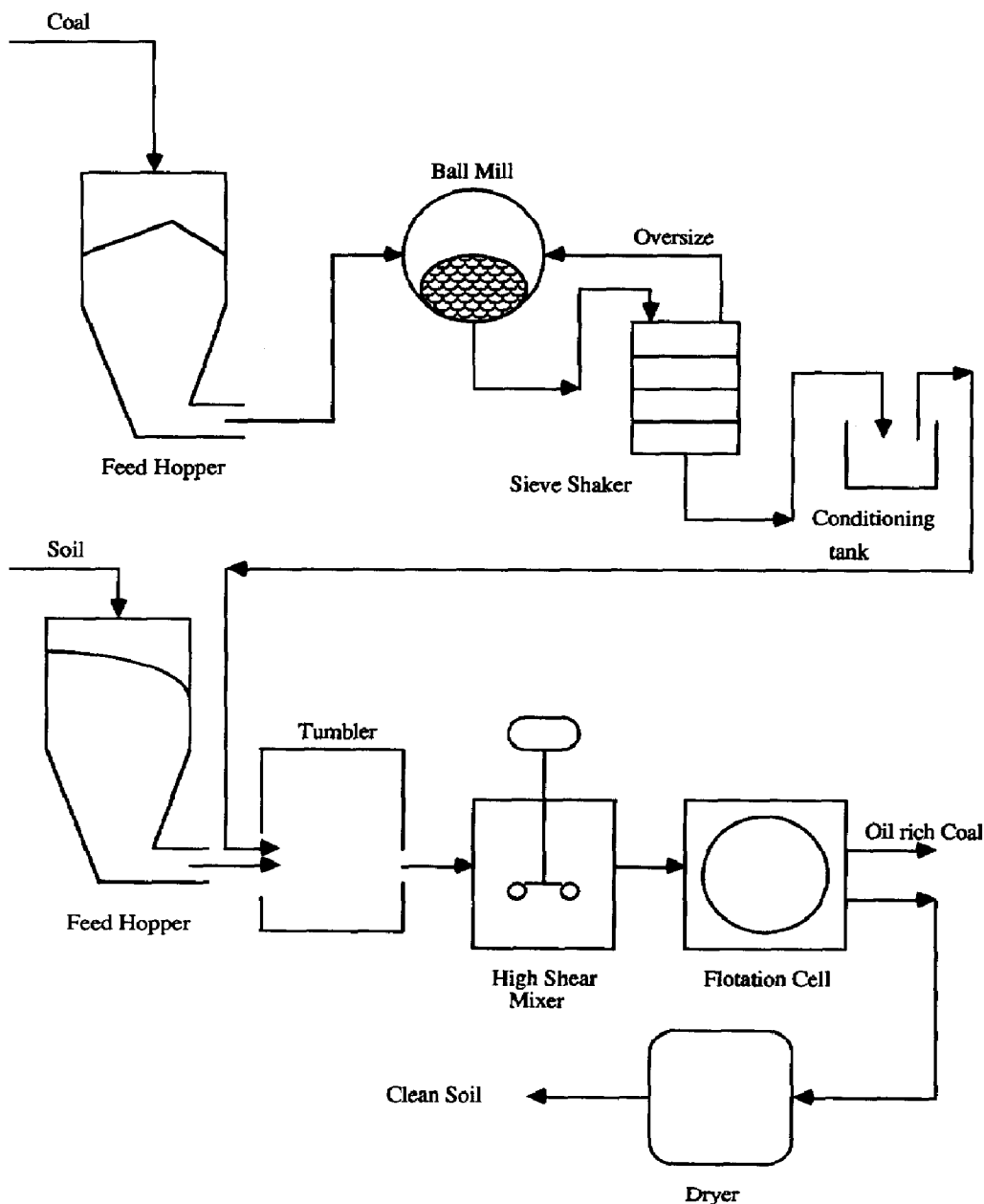| Proximate analysis of coal	(wt%)
Moisture	1.55
Volatile matter	33.31
Ash	19.99
Fixed carbon	45.15

Fig. 2. Process flow sheet of coal agloflotation.

desired reaction temperature and pressure by heating and constant addition of supercritical water. The oxidation temperature was maintained at 388 °C with a constant pressure of 23.4 MPa for this investigation. Once reactor stability was attained, oxygen was permitted to flow into vessel to oxidize the contaminated soil. Oxygen space velocities ranged between 0.09 and 1 cm^3 O_2/min per cm^3 reactor volume. At the end of the experiment, the reactor was
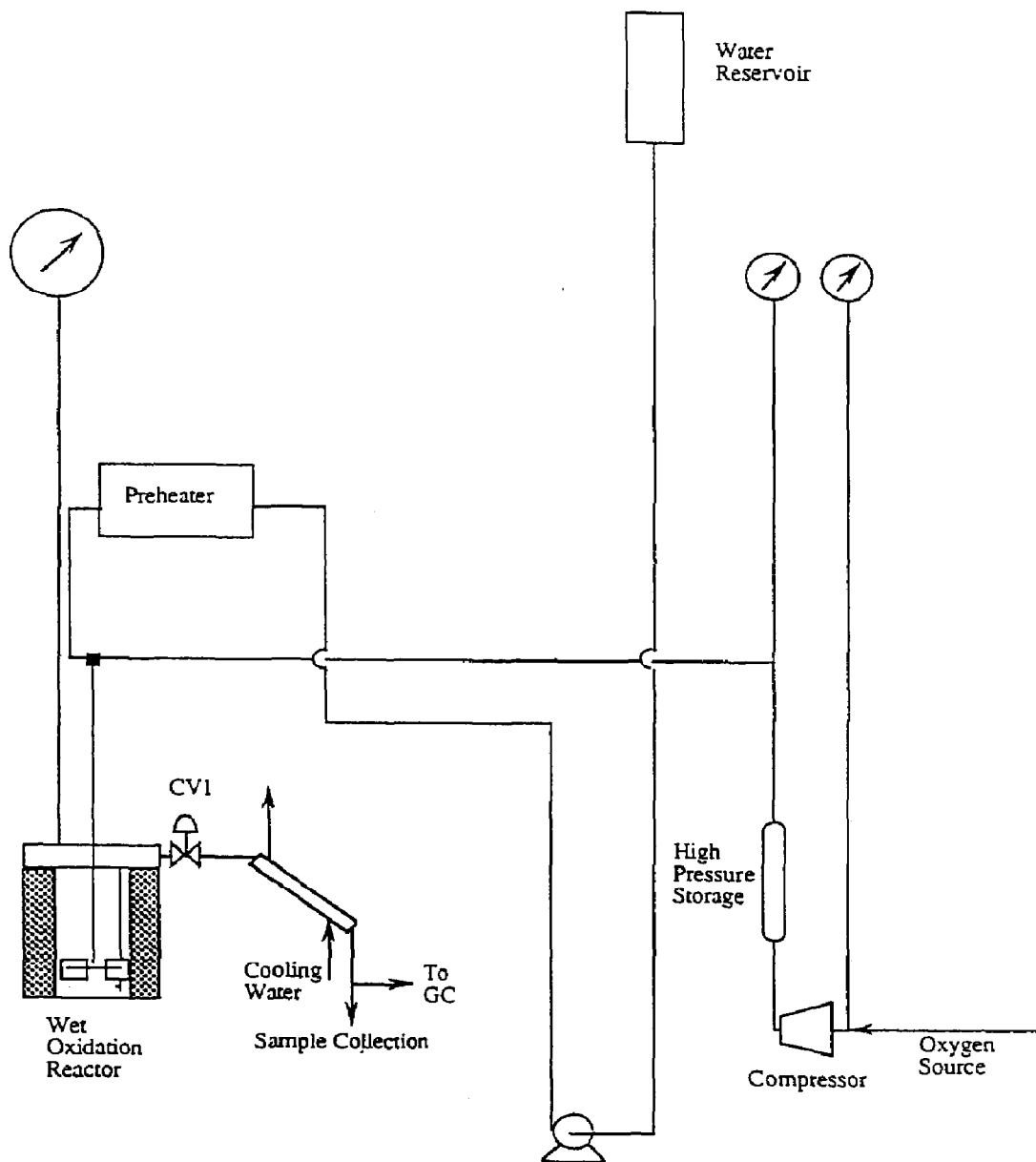
Fig. 3. General schematic of the wet oxidation pilot plant.

depressurized and cooled, after which the soil sample was collected and sent for analysis.

Results and discussion

Agloflotation

The soil samples were analyzed by soxhlet extraction to determine the extent of concentration as discussed earlier. Three different samples were used. The

analysis results are presented in Table 4. The process effectiveness is largely dependent on the nature of the contaminants. The contaminants were highly viscous and hydrophobic, which leads us to the fact that these soils cannot be cleaned up simply by washing with water. These contaminants act as the binding agents for the coal particles and it was seen that when samples with higher contaminant concentrations were treated, bigger coal agglomerates formed and the separation was much easier. The residence time in this case was considerably shorter; about one-third the usual time of 30 minutes. It was observed that the soil samples with excessive char and coke material had a slightly higher end concentration after treatment than the ones with less chars and coke. This was substantiated by the agloflotation on sample FC 1-1. These chars and coke have a good affinity for the hydrocarbons and hence the samples rich in chars and coke showed a higher contaminant concentration after being treated. These were also difficult to separate from the soil samples as they had a higher density than the coal particles and settled at the bottom of the flotation cell along with the clean soil. These char and coke particles could be removed either by size reduction of soil samples or a high shear grinding in flotation cell which would increase the residence time. Depending on the desired end concentration the samples could be treated accordingly and the process could be optimized for those conditions. The treated coal with a hydrocarbon coating is a better fuel than coal alone, and is shown to pass the EPA TCLP test [4]. Elemental CHN analysis indicates that the heating value of the treated coal is approximately 12,000–15,000 Btu/lb. In conclusion, coal agloflotation would be a very effective process for treatment of hydrocarbon contaminated soils.

Supercritical wet oxidation

Decontamination of PAH contaminated soil from site 1 was successfully demonstrated with wet oxidation. A decontamination efficiency of 99.5 percent was achieved with an oxygen space velocity of 0.5 cm^3 O$_2$/min per cm^3 reactor volume (cc/min/cc) and a soil residence time of 5 min (Table 5). This efficiency

TABLE 4

Agloflotation process results

Sample	Contaminant concentration (wt%)		Removal (%)
	Original soil	Treated soil	
Site 1-1	16.05	0.558	96.5
Prepared sample	16.52	0.454	97.3
Site 2	14.79	0.780	94.7
FC 1-1	2.73	1.010[a,b]	63.0

[a] Excessive chars and coke in the sample.
[b] Slightly lesser residence time.

TABLE 5

Residual PAH concentration in treated soil. (Numbers are reported on a dry ppm basis)

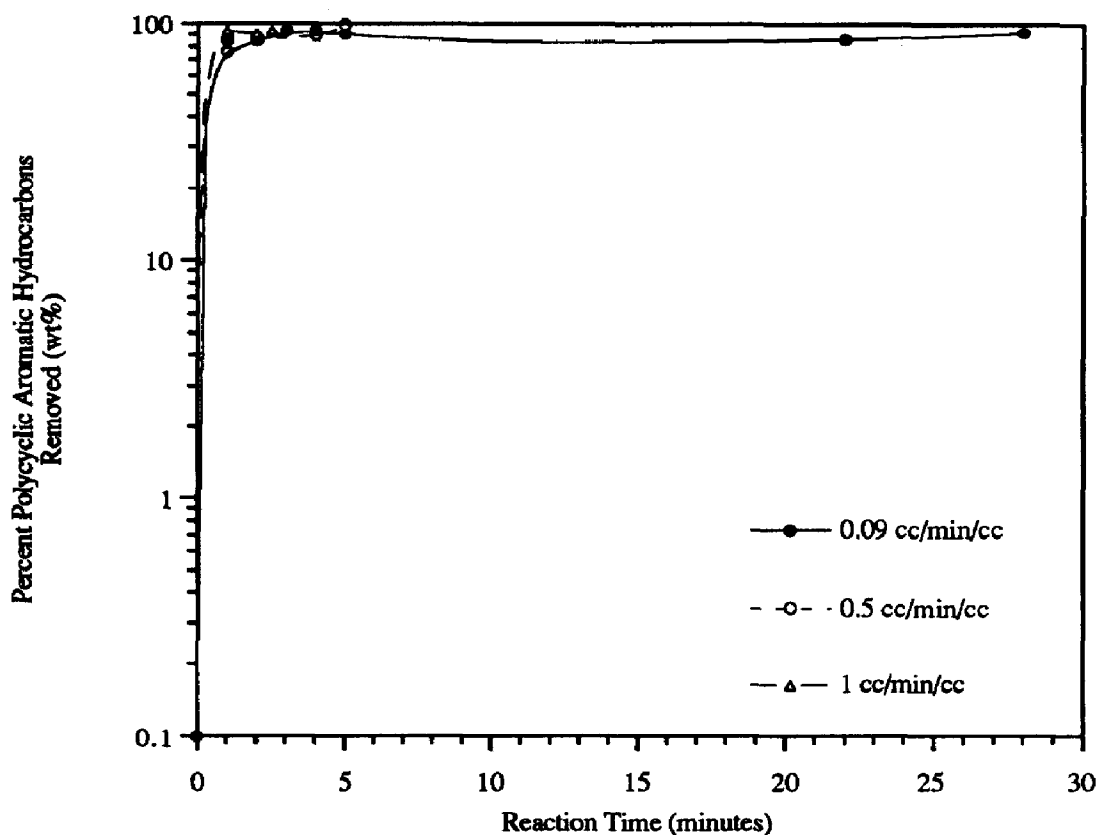| Time (min)	Space velocity (0.09 cc/min/cc)	Space velocity (0.05 cc/min/cc)	Space velocity (1 cc/min/cc)
0	33,700	33,700	33,700
1	4970	8300	2170
2	4300	5040	3100
2.5	–	–	223
3	2086	–	–
4	2040	3680	–
5	3300	170	–
22	4642	–	–
28	263	–	–

Fig. 4. PAH removal vs. oxygen to contaminant ratio for supercritical wet oxidation at different oxygen space velocities.

resulted in PAH contamination level of less than 175 ppm. Several experiments were performed at different reactor residence times and various oxygen space velocities (Figs. 4 and 5). It is interesting to note that increasing the space velocity from 0.09 to 0.5 cc/min/cc for the same residence time actually decreases the decontamination efficiency. On the other hand, increasing the oxygen space velocity from 0.5 to 1 cc/min/cc results in an increase in the decontamination efficiency for the same residence time. It is also of further significance to note the behavior of the extraction percentage curve at the different space velocities. In comparing the 0.5 and 1 cc/min/cc space velocities, it is clearly visible that an intersection of these two curves occurs at 1.6 g O_2/g PAH. At this point, 1 cc/min/cc space velocity curve surpasses the 0.5 cc/min/cc space velocity. The same is true when comparing the 0.5 and 0.09 cc/min/cc space velocities, except this intersection occurs at approximately 2.2 g O_2/g PAH. This may be attributed to the fluid dynamic conditions within the reactor. As the oxidation vessel is flooded with oxygen, an entrainment occurs thereby causing an over-abundance of available oxygen which allows the reaction to proceed at a faster rate in a shorter amount of time.
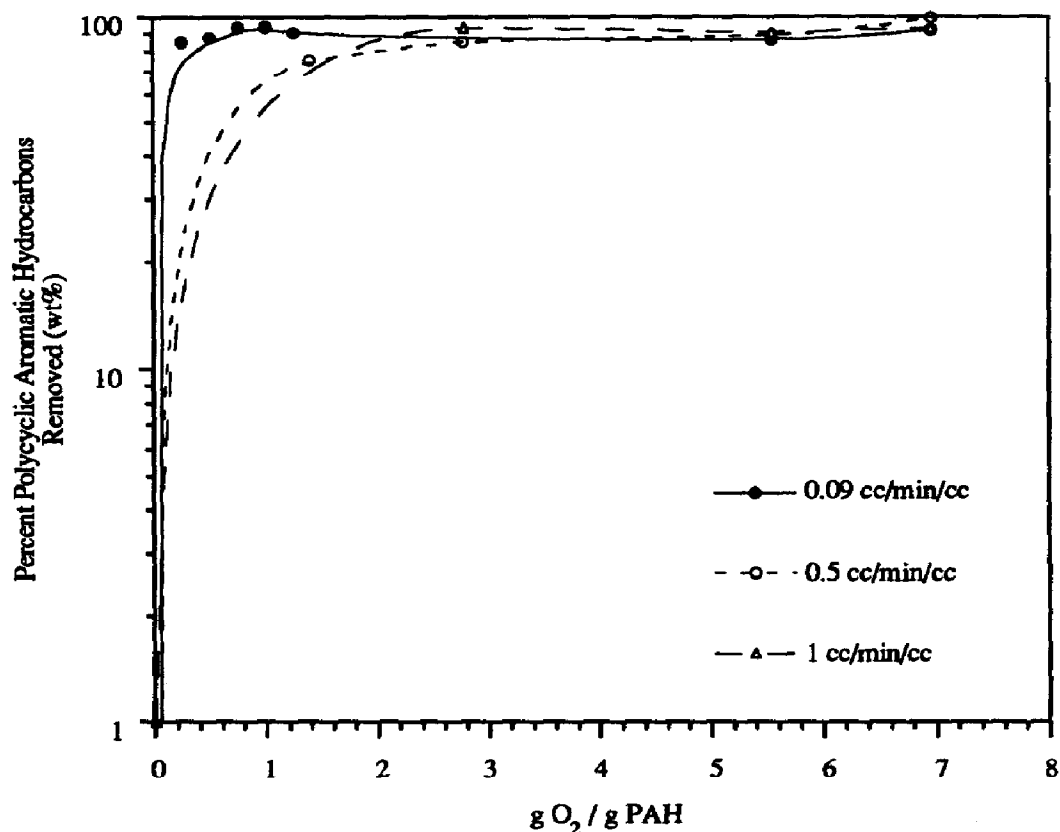

Fig. 5. PAH removal vs. reaction time for supercritical wet oxidation at different oxygen space velocities.

Figure 5 illustrates the percent PAHs removed as a function of residence time. As expected, to achieve below a 200 ppm residual PAH concentration, as the space velocity is reduced, the residence time must be increased. This is expected since the complete oxidation of hydrocarbons depends on the availability of oxygen to sustain the reaction. It should be noted that wet oxidation processes are independent of the level of contaminant in the soil. By controlling the operating parameters, a full cleaning of the soil can be achieved. This makes wet oxidation attractive as a primary cleanup method for ultra-cleaning of contaminated soil.

TABLE 6

Coal agloflotation appraisal

Advantages	Disadvantages
1. Makes use of less expensive and readily available coal to clean (economical).	1. Difficult to process soil rich in clay.
2. Low pressure and low temperature system.	2. Low boiling point hydrocarbons are difficult to handle.
3. Simple and easy handling of the equipment	3. Soils with excessive chars and coke need additional treatment.
4. Low power requirements.	4. Bigger particles (>3.3 mm) are to be treated separately.
5. Portable to any site.	
6. Reuse of the cleaned soil.	
7. Coal beneficiation (removal of mineral matter from coal).	
8. Increase in the Btu value of coal (better combustible product).	
9. Recycle of process water.	
10. High capacity treatments could be done effectively (time saving).	

TABLE 7

Supercritical wet oxidation appraisal

Advantages	Disadvantages
1. Short reactor residence time.	1. High temperature operation.
2. Better destruction efficiency.	2. High pressure operation.
3. Near-zero discharge.	3. High initial capital cost.
4. Recycle of solvent.	
5. High throughput per reactor volume.	
6. Possible to implement on a mobile unit.	

Conclusions

Soil samples from different industrial sites were treated to remove the polycyclic aromatic hydrocarbons (contaminants), as these would represent the removal efficiencies of the processes under actual conditions. It is seen that both agloflotation and supercritical wet oxidation are capable of removing these contaminants to an extent of 95% or greater which could be further enhanced to undetectable levels with process optimization. It was also interesting to note that both the treatments have very high throughputs which would favor the implementation of these processes on mobile units as well as on large industrial contaminated sites. The process economics also look very encouraging for both the processes since in case of agloflotation, coal could be reused and process water could be recycled whereas in wet oxidation initial capital investment costs are somewhat expensive but on the long run works out to be economical. The advantages and disadvantages of both processes are summarized in Tables 6 and 7. Finally, coal agloflotation and supercritical wet oxidation (SWO) are attractive and promising methods of soil remediation.

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