

A MULTIPLE-PRODUCT APPROACH TO THE PROCESSING OF USED TIRES

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ABSTRACT

The disposal of used tires by landfilling is becoming an increasingly serious problem in the U.S. From an environmental and economic standpoint, a better solution is to reprocess tires into valuable products such as activated carbon, other solid carbon forms (e.g., carbon black), and liquid and gaseous fuels. A process design is proposed which involves pyrolysis of tires, activation of the solid residue, partial combustion of liquids to produce carbon black, and the use of the high-BTU gas for process heat. The activation of the solid residue is done using CO₂, which produces CO and activated carbon. The CO₂ is regenerated and the lost carbon is recovered using the Boudouard reaction to produce CO₂ and finely divided carbon. The latter material may be used as a substitute for carbon black. A preliminary assessment of the process is presented.

INTRODUCTION

Scrap tires present formidable disposal problems. The very same properties that make them desirable as tires, notably their durability, also make their disposal and reprocessing difficult. Tires are well known to be virtually immune to biological degradation. The disposal of 280 million tires generated each year in the U.S. by landfill is increasingly becoming an unacceptable solution [1]. The tires take up large amounts of valuable landfill space and also present fire and health hazards. Recently, a large mountain of tires caught on fire in Canada with widespread environmental consequences due to the oils and gases generated from the decomposing tires. A better solution from an environmental and economic standpoint is to thermally reprocess the tires into valuable products [2]. Large-scale efforts employ tires either as a fuel (Oxford Energy Corporation, Modesto, CA) or as a filler for asphalt (Rubber Asphalt producers, Phoenix, AZ). These two technologies annually consume about 5-6 million tires. However, tire burning has had repeated problems with feeding the tires and slagging, while the rubber asphalt costs 40% more than conventional material. RW Technology, Cheshire, CT, has also tried to convert tires into other plastic products, but the market niche is small and the process is unreliable.

Three features underlie the problem of converting used tires and other waste polymers into useful, marketable products. The first problem is the low level of understanding of the chemistry and physics of tires during thermal degradation. Secondly, even if the thermal degradation processes were well understood, they would have to be monitored carefully to maintain product quality. The tire feedstock varies with time, and the process engineer must be able to monitor reactions and respond to changing conditions as necessary. Finally, the technology must produce a high yield of a product with a viable market. The best solution to disposing of waste tires is to develop a chemical process to convert the tires into another commodity material.

The proposed solution is to thermally reprocess the used tires into activated carbon, other solid carbon forms (e.g., carbon black, graphite, or carbon fibers) and/or liquid and gaseous fuels. The process is based on pyrolysis of tires and the key to its successful development is understanding and controlling the chemistry of low temperature carbonization so that the yield and physical properties of the products can be optimized.

Pyrolysis has been widely used for converting solid fossil fuels, e.g., coal, into liquid and gaseous hydrocarbons, a process which results in a solid char residue. Used automotive tires contain polymeric aromatic structures which are similar to those of coal in some respects. Not surprisingly, typical elemental compositions of both materials are also similar (rubber -- 88% C, 8% H, 2% O, 0.5% N, 1.5% S; and coal -- 82% C, 5.5% H, 8% O, 1.7% N, 2.4% S). Coal pyrolysis has been extensively studied [3-5] but investigations of tire pyrolysis are rarely reported in the open literature.

The most commonly used vulcanized tire rubber is a styrene-butadiene-copolymer (SBR) containing about 25 wt.% styrene [6]. A typical composition of tire rubber is: 60-65% SBR, 29-31% carbon black, 1.9-3.3% zinc oxide, 1.1-2.1 sulfur, ~ 2% extender oil, and ~ 0.7% additives (wt.%, as received) [6, 7]. In most cases, tire pyrolysis studies were performed under inert conditions [6, 8, 9]. Pyrolysis may also be carried out in mildly oxidizing atmospheres, such as steam and carbon dioxide, to improve the quality of pyrolytic products [9-11].

Tire pyrolysis experiments have usually been conducted in the 773-1173 K temperature range [6-8]. Similar to coal pyrolysis, the principal products from thermal degradation of tires are gases, liquid oils and solid carbon residues. The following yields of tire pyrolysis are typical (on an as-received basis): 33-38 wt.% char, 38-55 wt.% oil, and 10-30 wt.% gas. The product yields are affected by the pyrolysis conditions, such as pyrolysis temperature and heating rate. The literature on the analysis of products from tire pyrolysis is summarized below.

Gas Analysis -- Gases produced from tire pyrolysis are mainly hydrogen, carbon dioxide, carbon monoxide, methane, ethane and butadiene, with lower concentrations of propane, propene, butane and other hydrocarbon gases [6].

Oil Analysis -- The yield of oil from tire pyrolysis is high (~50 wt % of initial tire rubber), reflecting the potential of tire rubber to act as a substitute for fossil fuel and chemical feedstocks. The oils have high aromaticity, low sulfur content, and are considered relatively good fuels [11]. The molecular weight range for the oils is up to 1600, with an average molecular weight between 300 and 400 [6]. Infrared analysis of the oils indicates the presence of alkanes, alkenes, ketones or aldehydes, aromatic, polyaromatic and substituted aromatic groups [6]. The derived oils may also be an important source of refined chemicals, because it has been reported that they contain high concentrations of valuable chemical feedstocks, such as benzene, toluene and xylene [6].

Carbon Residue Analysis -- The carbon residue could become a marketable product if its properties were similar to those of manufactured carbons. The simultaneous production of valuable solid products and gaseous and/or liquid fuels from what is currently a waste material would make tire pyrolysis economical if a large supply is readily available. This situation exists in many regions of the U.S.

As mentioned before, tire pyrolysis performed in an inert environment can produce 33-38 wt. % of carbon residue. It has been reported that the char yield increases with decreasing pyrolysis temperature and decreasing heating rate [6]. The surface area of the tire char also depends on pyrolysis temperature and heating rate. The surface area of a tire char produced by pyrolysis in an inert gas usually ranges from 30 to 90 m²/g [6-8].

Basically, there are two uses of tire chars: as a reinforcing filler and as an adsorbent. Commercial carbon black is usually used for filling polymers and vulcanizates. Use of tire char as an end product for the tire and printing ink industries has been reported to be unsatisfactory [6, 8]. This is due to the high ash content of tire char. Chars from tire pyrolysis contain as much as 15 wt. % of ash, with the majority of this ash being zinc oxide [8]. A means of removing the ash from tire char is an important issue in the process of producing useful carbon black from the solid residue from waste tires. An alternative approach, which is advocated in the current study, is to use the solid residue to produce activated carbon for which the ash content is less critical. High-quality carbon black can be made from the liquid products, which are absolutely ash-free, and finely divided carbon can additionally be obtained from the CO produced during char activation.

Carbon as an adsorbent is usually evaluated by its surface area, and this is why an activation process is necessary to produce salable activated carbons from tire char. To develop a high internal surface area, char can be activated by mild oxidation with steam or carbon dioxide at high temperatures. The slow kinetics of carbon gasification in steam and CO₂ allow gas molecules to diffuse into the micropores and enlarge the existing surface area. The activation process usually follows hydrocarbon pyrolysis performed in an inert environment, but it is possible to accomplish pyrolysis and activation in one stage by pyrolyzing under mildly oxidizing conditions [7].

Ogasawara et al. [7] carried out the pyrolysis and activation of tires in one stage. The carbon residue from 1 hour of steam activation at 1173 K was found to have a surface area of 1260 m²/g,

while pyrolysis in helium yielded char with a surface area of 87 m²/g. The carbon residue produced from this "wet method" is as good as the commercial activated carbon in terms of surface area, but the carbon yield was only 9 wt. % of the starting tire material. Therefore, a method to increase char yield from tire pyrolysis is one of the most important issues in making activated carbon from waste tires. In a recent study [12], a high surface area activated carbon (> 800 m²/g) was produced in relatively high yields from pyrolysis of tires at temperatures up to 1173 K, followed by CO₂ activation at the same temperature. The surface area of this carbon is comparable with that of commercially available activated carbons.

The objective of the present study is to propose and carry out preliminary assessment of a process leading to the conversion of waste tires into marketable products such as activated carbon or carbon black. Some quantities of gaseous and liquid fuels can also be produced. Process flexibility, in terms of the type and amounts of particular products, is a desirable feature in view of high variability of markets. This work is based on the results of a recent laboratory study of scrap-tire reprocessing [12].

PROCESS DESCRIPTION AND DISCUSSION

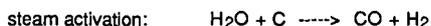
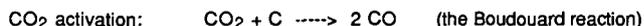
A schematic of the proposed process is shown in Figure 1. A stream of scrap tires enters the pyrolyzer where it is contacted with a recycle stream of pyrolysis gas. Mixing used tires with other waste material and solid-waste pretreatment are optional features of the process and they are discussed below. The pyrolyzer operates at approximately 1173 K, and the product streams are fuel gas, which also contains pyrolysis liquids, and char. The pyrolysis liquids are separated from the gas in a condenser, and they are subjected to partial combustion in an oil furnace to produce carbon black. The high-BTU gas is combusted to supply the process heat requirements. The solid product does not have sufficient surface area to make it commercially attractive and thus needs an activation step. Char activation is carried out using CO₂ at approximately 1173 K, which results in CO₂ reduction to form carbon monoxide. The consumed CO₂ is regenerated in a Boudouard reactor with simultaneous formation of finely dispersed carbon (Boudouard carbon). The net result of the process is the conversion of used tires into three marketable products: activated carbon, carbon black, and Boudouard carbon. The particular elements of the process scheme are described in more detail below. Pyrolysis and char-activation units constitute the heart of the process and their integration is very much a novelty in the proposed scheme. Carbon-black and Boudouard-carbon production will be integrated into the process by adapting existing technologies.

Feed-Stream Preparation -- The tires are first shredded and then possibly combined with another waste stream. The use of mixed wastes would improve the appeal and the number of sites where a plant could be installed. This feature, however, increases the complexity of the design as well as the operating costs. The amount of size reduction required for scrap tires does not appear to be excessive. In fact, higher char activation efficiencies were reported when coarser waste material was used (~170 mg pieces versus -50 mesh particles) [12]. The size of scrap tire material that would be optimal for the process is still to be determined. Since shredding costs are high (at least \$0.20/kg), there is an economic incentive to make the tire pieces as large as possible. For smaller particle sizes, pretreatment with O₂ was found to increase char yields and surface areas [12]. Pretreatment with chlorine would probably have a similar effect but would also likely have negative consequences from the associated HCl formation.

Pyrolysis and Char-Activation Units -- While a rotary kiln reactor has been successfully used for pyrolysis of tires, this is not likely to be the optimal solution for a high throughput system [8]. A kinetic analysis of tire pyrolysis indicates that the process is relatively fast and can be completed in under a second at 873 K. This fact would allow the use of an entrained-flow reactor, which is quite appropriate for high-throughput applications. Unfortunately, only relatively small particles can be fed into such a reactor, mainly due to heat-transfer limitations. For larger pieces of tire material, a fluidized-bed reactor operating at a lower temperature can be used. In either case, a hot cyclone is desirable to separate char particles from the oils. According to scheme presented in Figure 1, char activation by CO₂ takes place in a separate reactor. This has the advantage of allowing the oxides of carbon to be cycled between the activation step (producing CO) and a disproportionation step (producing CO₂ and carbon). In this way, CO₂ is periodically consumed (activation) and regenerated (disproportionation); both CO and CO₂ stay relatively pure in this scheme.

Another possibility is to use a moving-bed countercurrent system. While solids throughput would necessarily be lower, this disadvantage would be offset by combining the pyrolysis and char-activation stages in a single reactor. In this scheme, tire pieces would be fed into the reactor at the top and CO₂ at the bottom (Figure 2). A temperature of about 1173 K would prevail at the bottom of the reactor so that the char would be progressively pyrolyzed and then activated as it moves through the reactor. Such a design, shown schematically in Figure 3, simplifies the process of feeding the tire pieces and eliminates the requirement for a hot cyclone since the oil and char come out of opposite ends of the reactor. The moving-bed concept has been employed in the large-scale gasification of coal at a plant in North Dakota which is producing synthetic pipeline gas [13]. There are some differences between the two schemes, however. The tire-processing unit would operate under atmospheric pressure since there is little or no advantage in producing activated carbon at an elevated pressure. Secondly, the coal gasification system is internally heated by introducing oxygen at the bottom and partially combusting a portion of the coal. In the tire-processing reactor, the pyrolysis gases which come off the top of the unit would be combusted externally and the hot exhaust gases (mostly CO₂ and H₂O) would be introduced into the bottom of the reactor for char activation. The reactor would be insulated to prevent heat losses. The disadvantages of a single-reactor scheme of Figure 3 are: (1) the pyrolysis gas has a lower heating value due to dilution with the flue gas; and (2) if Boudouard carbon is to be produced, a fairly complex separation step is required to recover pure CO from the pyrolysis gas (Figure 4). Previous work has demonstrated that the final product is not very sensitive to the conditions under which pyrolysis is carried out [12]. This allows for greater design flexibility and for the possibility to consider several feasible schemes.

It was demonstrated that activation using an 8% CO₂/He mixture at 1173 K for 3-10 hours was sufficient to obtain high surface area chars [12]. This residence time could be reduced by raising the temperature, increasing the CO₂ partial pressure, or by using steam rather than CO₂. The char activation chemistry can be represented by the following two reactions:



Both reactions are endothermic and the equilibrium becomes more favorable as the temperature increases. The use of steam would offer advantages in terms of a higher reaction rate and a higher surface area product. The use of CO₂ would increase the production of CO from the activation step. The CO could then be subjected to the reverse Boudouard reaction for the production of finely divided carbon [14-17].

Carbon-Black Production -- The oils resulting from tire pyrolysis can be used to produce carbon black since their properties are known to be similar to those of the petroleum fraction used in carbon-black production [11]. In the oil-furnace process, a highly aromatic feedstock is converted to carbon black by partial combustion and pyrolysis at 1673-1923 K in a refractory-lined steel reactor. The carbon-black properties which are important in reinforcement-material applications (e.g., in tires) are the particle size and structure (degree of agglomeration into three-dimensional networks). These properties are controlled by the nozzle design, reaction-chamber geometry, temperature, residence time, and turbulence intensity [18]. An example of a carbon-black furnace is shown in Figure 5. As an alternative to carbon-black production, tire pyrolysis oil can be used for its fuel value, although further processing to remove aromatic components would be required. The conversion of the oil stream to carbon black is a more attractive option for a number of reasons: (1) a solid product is easier to store and handle; (2) the value of the solid product is higher than any possible fuel uses; (3) little or no upgrading of the material is required; (4) possible transportation fuel uses would require upgrading because of the relatively high aromatic content of oil; and (5) since carbon black is required to make tires, the production of carbon black from the oil is a form of tire recycling and is more practical than trying to recover the original carbon black.

Boudouard-Carbon Production from CO -- This process step was recently discussed by Walker [14] as a part of his coal-processing scheme. The temperature of the Boudouard reactor is maintained at 773-800 K and the carbon product is ash-free and of a particle size much smaller than can be obtained by grinding [19]. In fact, the particle size of the Boudouard carbon is small enough to burn completely in a Diesel engine [20]. The Boudouard carbon is similar to carbon black (except for

having a zero hydrogen content) and in some cases can probably be substituted for carbon black. The envisaged applications of this product include its use as a colorant or lubricant.

The Energy Balance -- The fuel gases produced during pyrolysis can be used to provide process heat for the pyrolysis and activation stages. Some heat can also be recovered from the manufacturing of carbon black by partial combustion of the oil; an additional amount of heat will be generated by the production of Boudouard carbon from CO. Preliminary estimates show that the process outlined in Figure 1 will be self-sufficient from an energy standpoint. The net yields of the products depend on the degree of activation required in the production of activated carbon. A high degree of activation would correspond to a larger amount of Boudouard carbon produced from the CO stream.

Process Economics -- A preliminary cost analysis for the process indicates that the proposed tire-reprocessing scheme could be profitable. The following estimates have been used: the cost of scrap tires -- about \$0.20/kg (tire-disposal charge: \$0.01-0.35/kg; transportation: ~ \$0.04/kg; size reduction: \$0.20-0.60/kg); the typical pyrolysis yields -- 35% char, 20% gas, and 45% oils; 50% carbon loss during char activation; selling prices for the activated and Boudouard carbons of \$2.22/kg and \$0.67/kg, respectively; zero profit from the high-BTU gas and oils which would be used mainly to provide the process heat requirements. These figures lead to a net income of ~ \$0.30 per kilogram of the original tire material. Of course, more detailed economic analysis needs to be performed, but even the above simplified and fairly conservative treatment demonstrates the high commercial potential of the proposed approach. It should be pointed out that, in most cases, the raw material costs for the project will be negative due to increasingly high tire-disposal charges.

For the sake of comparison, the cost of scrap-tire incineration without heat recovery is about \$0.04-0.07/kg [21]. The cost of burning used tires for energy generation is 1.5-5.1 times higher than the corresponding cost for coal, depending on whether whole or ground tires are used [21]. Depolymerized scrap rubber (DSR) can also be used as liquid fuel but, in general, depolymerization is difficult and involves extensive high-pressure treatment. Clearly, reprocessing of waste tires into fuels does not seem to be an economically attractive option.

Pyrolysis processes can be made somewhat more profitable. Nippon Zeon estimated that the break-even cost of its tire-pyrolysis pilot plant was \$0.25 per tire [22]. According to a different estimate [23], a plant processing 81,000 tons of scrap tires per year could be made profitable, based on sales of reclaimed products. As mentioned before, pyrolysis processes involving direct carbon-black recovery suffer from difficulties related to ash removal and, generally, low final-product quality. Asphalt rubber is probably the most competitive tire-derived product currently available on the market. Although nearly twice as expensive as regular asphalt pavement, asphalt rubber has already demonstrated superior performance and durability. According to legislation passed in 1991, the use of asphalt rubber may be required in 5% of new pavement as early as in 1994, with a projected increase to 20% by 1997 [24]. Unfortunately, the estimated total demand for this product is still at about 2% of the amount of scrap tires available [21]. It can be concluded, therefore, that a large market exists for other technologies targeted at scrap-tire reprocessing into useful products.

CONCLUSIONS

A preliminary process design was developed in which scrap tires are used as the input and in which activated carbon, carbon black (or fuel oil), Boudouard carbon and fuel gas are produced as the output. The proposed technology has the potential to convert an unmitigated waste stream of tires into marketable products (activated carbon, Boudouard carbon and carbon black). Tire-derived activated carbons could be used, for example, in waste-water treatment, stabilization of landfills and in the recovery of organic solvents and vapors. The Boudouard carbon may have a variety of uses which are yet to be explored; they include the manufacture of colorants and lubricants. The liquid stream can be utilized in the production of carbon black and/or fuel oil. The oil-derived carbon black can be reused in tire manufacturing, which forms a recycle loop for this material. Since the typical feedstocks for activated carbon and carbon black are either coal or petroleum, the proposed technology would obviate the need to deplete these resources. The process allows a high degree of flexibility in the relative amounts of each product to reflect changes in the feed stream and market conditions. Another advantage of the system is the production of both activated carbon and carbon black from used tires, with inorganic material ending up in the product with a high tolerance for this

component. Finally, following additional research, the proposed technology should be able to find applications in reprocessing other polymer wastes found in American industry (e.g., end cuttings from automobile hoses or products which do not pass quality control).

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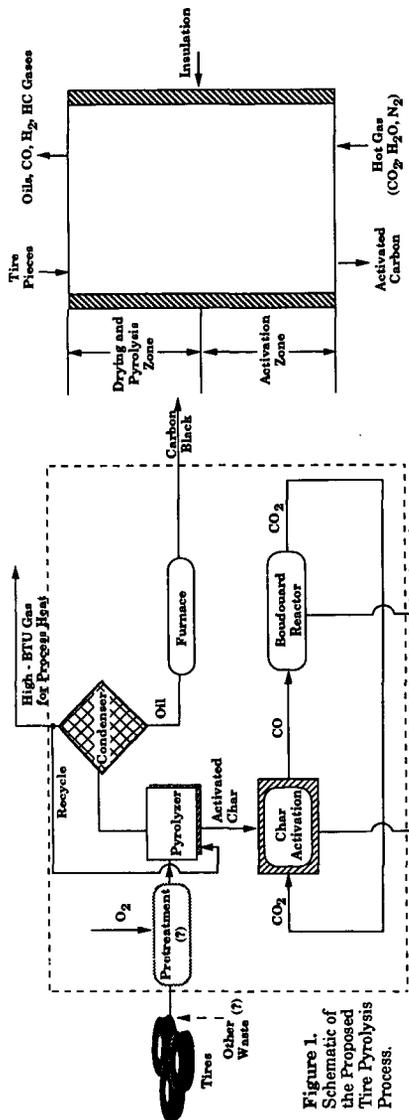


Figure 1. Schematic of the Proposed Tire Pyrolysis Process.

Figure 2. Schematic of the Countercurrent Moving-Bed Reactor Concept which Combines Tire Pyrolysis and Activation into a Single Unit.

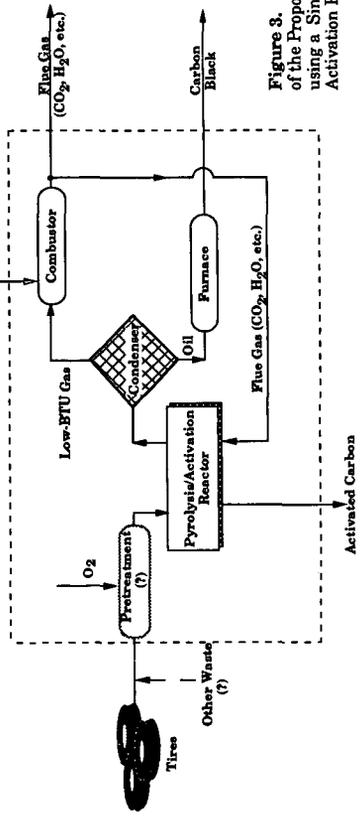
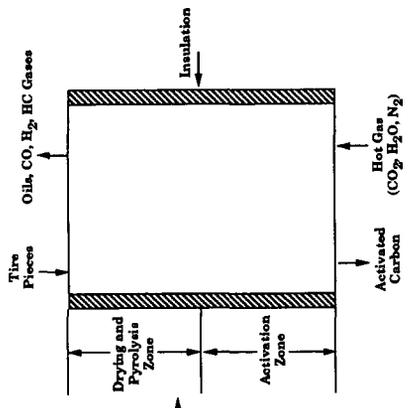


Figure 3. A Schematic Representation of the Proposed Tire-Pyrolysis Process using a Single Pyrolysis/Char-Activation Reactor.

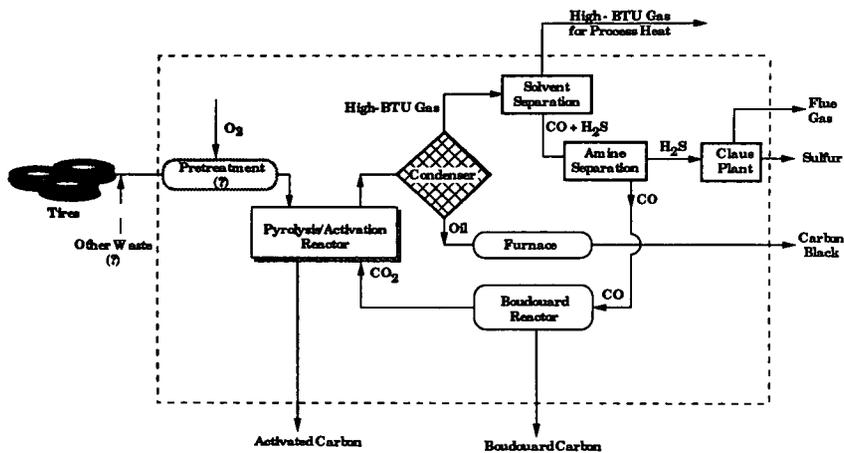


Figure 4. A Schematic Representation of the Proposed Tire-Pyrolysis Process using a Single Pyrolysis/Char-Activation Reactor and CO Separation from the Pyrolysis Gas.

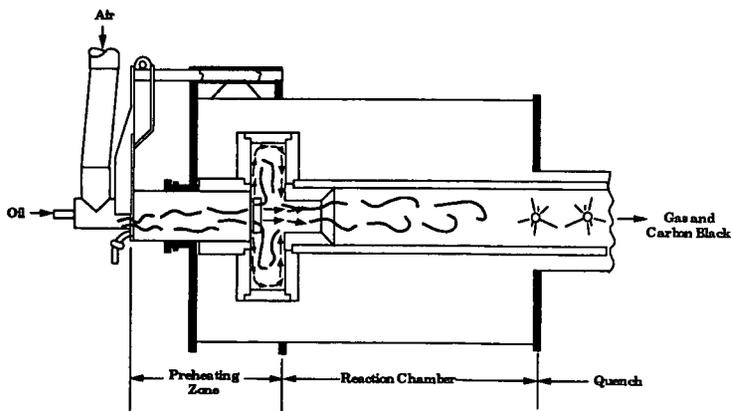


Figure 5. Flow Chart, Carbon Black Furnace Process. [Chem. Week 88 (24) 79 (1962)].

DERIVATION OF ADSORBENT CARBONS FROM OIL SHALE RESIDUES

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Introduction

Active adsorbent carbons can be derived from the pyrolysis residues of low-ash oil shales. Besides producing liquid fuels, oil shales, like coal, may be utilized as a source material to produce high-value added products. This utilization also leads to the reduction of waste material.

Oil shale is a sedimentary rock which contains sufficient organic matter (Kerogen) which produces oil and gas when pyrolyzed. In the past, oil shale research has predominantly focussed on maximizing the liquid hydrocarbon yield [1-3]. The primary goal was to produce a substitute for naturally occurring petroleum. These efforts have proven the commercialization of oil shale to be very difficult. Shale oil is simply not, economically, a reasonable substitute for crude oil. Based on current market forces, which suggest the continuation of low crude oil prices and high supply, oil shale commercialization does not appear to be a near-term prospect. To make oil shale more competitive, the development of new high value products needs to be examined.

After pyrolysis, as much as half of the carbon remains in the retorted (spent) shale. This carbon-rich product is generally considered a waste material. Its disposal represents an economic and environmental problem. It is, therefore, important that the pyrolyzed shale be utilized, either in the retorting process as a source of energy, or as a source of new products. The former strategy is the basis for the development of the KENTORT II technology for Eastern US oil shales [4,5]. This technology completely utilizes the carbon on the pyrolyzed shale by incorporating integrated gasification and combustion steps. The latter strategy, the utilization of the spent shale carbon for new products, is the focus of this study.

In previous work it was shown that a range of materials can be manufactured from oil shale residues, including cement and asphalt additives [6,7]. However, the utilization of carbon-rich residues of oil shales as precursor materials for the production of adsorbent carbons has not been examined. The objective of this project is to fabricate adsorbent carbons from low-ash oil shale residues. The production of high-value solids such as adsorbent carbons, in addition to oil, would make the economics of oil shale development more attractive.

Experimental Procedures

Two oil shales from the Turkish Goynuk [8] and the Australian Alpha [9] deposits were selected for this study based on the following criteria: (1) low ash contents and; (2) high oil yields upon retorting. The oil shales were pyrolyzed at 550 °C under a continuous flow of nitrogen. Proximate

and ultimate analyses of the raw and spent shale materials are illustrated in Table 1. The N₂-swept fixed bed pyrolysis experiments were performed in a 1.5 inch stainless steel reactor. The reactor conditions are discussed in detail elsewhere [10]. During pyrolysis, the alginite-rich, low-ash oil shales were observed to form a macroporous network of charred carbonaceous material. Heating stage microscopic (HSM) examination allowed the observation of the spatial relationships between macropores generated by the volatilization of alginite macerals and the char and minerals that stabilize the macrostructure. The HSM apparatus utilized in this study consists of a Zeiss Universal polarized light microscope, a heating stage, and temperature and gas flow controllers.

After pyrolysis, the spent shale was activated in a steam reactor (gasifier) at 880 °C. Water was pumped through a 1/16 inch capillary and entered the reactor below the shale distributor plate, where it is released into the hot zone as superheated steam. The steam passed through the shale zone and exits the reactor, where it is condensed.

Surface area measurements were performed on the samples to investigate porosity development resulting from both the pyrolysis and steam retorting processes. Standard nitrogen adsorption using a static volumetric flow process was used, employing an Autosorb-6 sorption system at a temperature of 77 °Kelvin. All surface area measurements were calculated using the standard BET equation [11] between relative pressures of 0.05-0.25. Micropore volume approximations were calculated using the Dubinin-Radushkavich equation [12] over a linear region of the D-R plot. Samples were outgassed under vacuum at a temperature of 200 °C prior to analysis.

Scanning electron microscopic (SEM) examination of the pyrolyzed and steam activated samples, using a Hitachi S-2700 (magnification up to $\times 10^4$), allowed a comparison of the morphological features.

Samples of the shale carbons were monitored for their gas adsorption characteristics using thermogravimetry/mass spectroscopy (TG-MS). A temperature programmed adsorption/desorption (TPA/D) analysis was performed using H₂S, NH₃ and NO gases as adsorbates.

Results and Discussion

Pyrolysis Induced Porosity

The pyrolysis induced porosity (PIP) in the retorted shale corresponds to a BET surface area of only 8 - 10 m²/g for both shales (Table 2). However, this framework provides excellent accessibility for steam to infiltrate the chars at 880 °C during activation. The HSM experiments showed that the bulk of the macropores formed when alginite macerals volatilized. These large elongated macropores are inherited from the structure of alginite and vitrinite (desmocollonite) macerals (Figure 1). The temperature at which constituents boiled in these macerals occurred in the HSM experiments at 467 °C. The extensive macroporosity of the carbon-rich pyrolysis residues (from Goyruk and Alpha) indicates these shales to be promising precursors for adsorbent carbons. This is based on the abundant macropores in the chars contributing to an intricate infrastructure that readily allows steam and/or catalyst metals to infiltrate. The action of steam is expected to cause extensive micropore development in the chars. The validity of this working hypothesis was examined by enhancing the inherent porosity (PIP) by catalyzed and uncatalyzed steam treatments at 880 °C.

Steam Induced Porosity

The purpose of the pyrolysis experiments was to provide spent (pyrolyzed) shale for steam activation experiments. The steam induced porosity (SIP) was generated using run times from one to ten hours. The SEM study of the steam treated chars revealed a much rougher surface compared to the pyrolyzed char (Figure 2). The increase in microporosity was documented by the substantial increase in BET surface area of the steam treated samples (Table 2). The SIP was more pronounced after mineral matter removal by acid treatment. This was probably due to the removal of minerals blocking pore entrances. Studies of the effects of steam retorting the spent shale showed that the overall surface area could be increased up to 110 fold by retorting under extremely slow steam flow conditions for prolonged periods of time (up to 10 hours). However this resulted in an extensive loss of carbon. Steam activation at 880 °C for four hours, using steam flow rates of 2 grams/minute, developed a BET surface area of around 400 m²/g with a 43% loss of carbon (Table 2). An inverse relationship was observed between overall surface area and carbon yield from the retort. The percent carbon loss and the relatively high mesopore volumes of the carbons may be dependent on the high reactivity of the shale precursors, or the presence of finely dispersed mineral matter, both of which has yet to be determined. Preliminary studies on the effects of catalytic metals (ZnCl₂; CaCl₂) finely dispersed on the shale surface during activation indicated some improvement over simple steam activation (Table 2).

Adsorbent Carbons from Oil Shale Precursors

Samples of the carbons from shale precursors were monitored for their gas adsorption characteristics using TG-MS. Both the Goynuk and Alpha derived carbons showed higher adsorptive capacities for H₂S and SO₂ than a commercially available carbon. The TPA/D profile for the steam activated Goynuk sample using H₂S as adsorbate indicated the adsorption capacity of the Goynuk carbon material at 70 °C was 0.06 g/g of carbon. The adsorption capacity was based on the weight gain during adsorption, weight loss during desorption, and the identification of H₂S as the only desorbed gas (Figure 3). Samples of shale-derived carbon also demonstrated significant adsorptive capacity for NO and NH₃ (Figure 4), indicating potential uses of shale derived adsorbents as industrial gas scrubber carbons.

Synopsis

Adsorbent carbons can be produced from the pyrolysis residues of the Turkish Goynuk and Australian Alpha oil shale samples. Both materials have low ash contents and produce high oil yields upon retorting at 550 °C. During pyrolysis, a macroporous network of charred carbonaceous material forms. The development of the pyrolysis induced pores (PIP), and that of the macrostructure stabilizing char and mineral matter, were observed using a heating stage microscope. The PIP in the retorted shale corresponds to a BET surface area of only about 10 m²/g, but provides sufficient access for steam to infiltrate the char during activation at 880 °C. The steam induced porosity (SIP) corresponds to a BET surface area of 300-400 m²/g at 43 % burn off. The steam activation treatment results in increased gas adsorption capacities: the Goynuk and Alpha derived carbons showed promising adsorptive capacities for NO, NH₃ and H₂S compared to a commercial carbon. The carbon-rich pyrolysis residues of the two shales under investigation have shown excellent potential as feedstocks for the production of adsorbent carbons. Utilization of the retorted or spent shale can not

only result in new high-value added products, but can also lead to the reduction, and hence regulation, of a waste material.

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Table 1 Ultimate and Proximate Analyses for Goynuk and Alpha

	Goynuk Raw Shale	Goynuk Spent Shale	Alpha Raw Shale	Alpha Spent Shale
C wt%	54.7	49.9	76.6	73.1
H wt%	8.3	1.8	9.9	3.2
N wt%	1.4	1.7	1.1	1.7
S wt%	2.8	2.2	1.3	2.9
Moisture wt%	12.1	3.2	0.9	1.2
Ash wt%	17.2	41.6	4.4	15.6
Volatiles wt%	60.1	16.7	87.7	33.4
Fixed C wt%	10.9	38.2	10.1	49.4
BTU/lb		9150		13400

Table 2 BET - Surface Area Development for Goynuk and Alpha Shales

Sample	BET	BET	BET
		1 h *	4 h **
Goynuk: Pyrolysed	8.8		
Goynuk: Steam Activated		180	350
Goynuk: Steam Activated/ZnCl ₂ -Catalyst		190	400
Goynuk: Steam Activated/ Acid Washed		210	370
Alpha: Pyrolysed	10		
Alpha: Steam Activated		170	280
Alpha: Steam Activated/ ZnCl ₂ -Catalyst		170	310
Alpha: Steam Activated/ Acid Washed		200	350

* 1 hour steam treatment using steam flow rates of 2 grams/minute

** 4 hour steam treatment using steam flow rates of 2 grams/minute

BET-surface area (calculated using standard BET equation [9])

Steam Activation at 880 C

Acid Washing with 0.5 molar HCl for 1 hour.



Figure 1 SEM micro-photograph showing PIP after steam pyrolysis of the Goynuk oil shale. The elongated cavities formed after volatilization of the alginite macerals. Char and mineral matter stabilize the macro-structure.



Figure 2 SEM micro-photograph showing SIP after steam activation of Goynuk shale char. Flaky surface with abundant macropores is depicted.

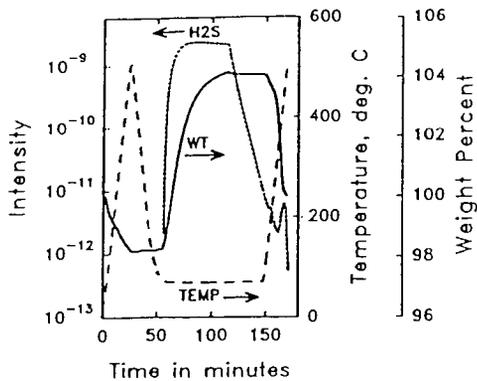


Figure 3 Temperature programmed adsorption/desorption analysis of the Goynuk adsorbent carbon. The carbon was activated at 880 °C using steam using ZnCl₂ catalyst. Mineral Matter was reduced after steam activation using 0.5 molar HCl.

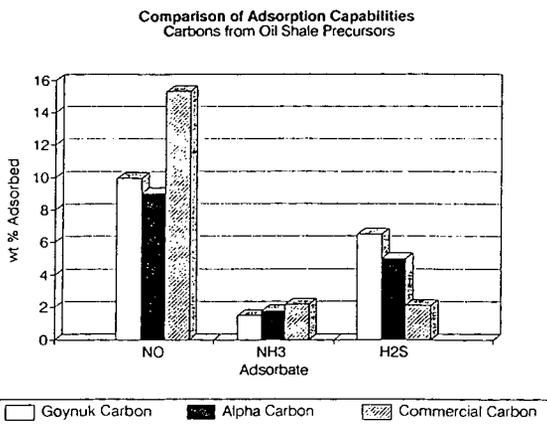


Figure 4 Comparison of the adsorption capabilities of Goynuk and Alpha derived adsorbent carbons with a commercial carbon. Goynuk and Alpha carbons have a BET surface area of about 350 m²/g. BET surface area of the commercial carbon corresponds to 450 m²/g.

CHARACTERIZATION OF CONCRETES FORMULATED WITH BLENDS OF PORTLAND CEMENT AND OIL SHALE COMBUSTION ASH

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ABSTRACT

Previous experimental studies of the use of oil shale combustion fly ash in Portland cements have been reported by Germany, Israel, China, Jordan and the United States. In the current study seventeen samples of a standard concrete mix (49% coarse aggregate, 30% fine aggregate, 13% cement and 8% water) were prepared, containing various percent substitutions of Portland cement with oil shale fly ash from the pilot combustor of Occidental Oil Shale Company and commercial additives, and tested for unconfined compressive strengths. An increase in strength, consistent with observations in Israel and China, was found with substitution at 15%. Four standard mechanical tests were carried out preliminarily with the formulation with 45% substitution and a commercial additive, which gave a 90-day compressive strength of 5310 PSI. The freeze-thaw tests were confounded by poor coarse aggregate performance. The samples containing oil shale ash had less resistance to scaling than those containing no ash. Three zero-slump materials containing oil shale ash were investigated, again preliminarily. Three samples of compressed/autoclaved ash/lime paste ranged up to 2870 PSI. One of two samples of concrete masonry unit reached 1590 PSI. A sample of light-weight concrete, containing 40% fly ash, set up quickly, was hard and strippable in one day and had a density of 40 lb/ft³.

INTRODUCTION

As a portion of a broader study of the beneficial use of ash from the combustion of oil shale from deposits owned by the Occidental Oil Shale Company in the western United States, the replacement of portions of Portland cement in standard concrete and of fine aggregate in zero-slump formulations by fly ash from a pilot plant combustor were evaluated at the University of Pittsburgh. Elements of this portion of the study include:

- a literature survey, identifying similar studies that have been carried out in several other countries, particularly in Israel and China;
- production of seventeen batches of concrete, containing oil shale combustion fly ash, and the measurement of the compressive strength of each over time;
- determination of two mechanical properties of a particular concrete, produced by one of the better formulations;

- a preliminary evaluation of zero-slump products containing oil shale combustion fly ash, specifically the preparation and examination of three samples formulated as brick, two samples as concrete masonry units and one sample as light-weight concrete.

LITERATURE

Previous experimental studies of the use of oil shale ash in cements have been carried out in the Federal Republic of Germany, the United States, Israel, China, the (former) USSR and Jordan. The work in the FRG and in the USSR has been reported only in German [1-6] and Russian [7-9], respectively. A review article by the Israelis [10] provides an excellent and comprehensive description of work in that country, as well as of the work in the Federal Republic of Germany and the United States. Four papers describing the Chinese work in English [11-14] are rather extensive, but they can be found only in a publication with, unfortunately, very limited circulation. The Jordanian paper is easily available and very informative [15].

ASH PROPERTIES

Three samples of fly ash from the Occidental Oil Shale pilot combustor were used in this study. The combustion temperature and percentages of shale and coal being fed to the pilot unit during the period of collection of each sample were:

Sample Period	Temperature (°F)	% Shale	% Coal
3	1550	54	46
4	1594	54	46
6	1500	65	35

Samples of the fly ash from Sample Periods 3 and 4 were analyzed by the Coal By-Products Utilization Laboratory (CBUL) of the ND Mining and Mineral Resources Research Institute at the University of North Dakota. Elemental compositions and LOI (Loss on Ignition) of these two samples, which relate to those found for other ashes were:

Comp.	SOURCE OF OIL SHALE ASH					
	FRG[10]	Israel[10]	China[12]*	Jordan[15]	Samp. 3	Samp. 4
CaO	16-60%	44.5	1.29	39.7	18.4	17.4
SiO ₂	12.25	19.0	60.64	35.4	50.4	45.2
Al ₂ O ₃	9-12	8.3	20.09	3.8	12.6	10.9
Fe ₂ O ₃	6-7	4.3	11.89	2.0	4.6	4.5
MgO	1.4-2.0	0.7	0.83	4.0	6.6	6.6
SO ₃	9-10	8.5	0.61	4.0	7.47	6.59
L.O.I.		11.3	0.55	7.3	0.38	0.24

* 860°C ash

The relatively high magnesia content of the fly ash from Sample Periods 3 and 4 does not appear to be a cause for concern. It is likely present in a bound form inside the ash particles. This is strongly suggested by CBUL's results, which determined that the expansiveness of the fly ash was almost an order of magnitude lower than the ASTM C618 Specification for both Class C and Class F fly ash.

CBUL also reported particle size distributions for which between 78 and 87 percent passed a #325 sieve. The fly ash thus meets the ASTM C618 Specification that at least 66 percent must pass this sieve to be a Class C or Class F fly ash.

CONCRETE FORMULATION AND COMPRESSIVE STRENGTHS

The basic concrete formulation used for seventeen test batches of ash-containing concrete, made during this study, was a standard mix of:

- 49 percent coarse aggregate;
- 30 percent fine aggregate;
- 13 percent Type 1 Portland cement;
- approximately 8 percent water.

[All formulation percentages throughout this paper are on a weight basis.] The water content was adjusted to provide a slump of two inches. Six batches also contained a workability (water-reduction) additive. Two of these six batches also used Type 3 Portland cement in place of Type 1 Portland cement.

Several trends were noted from a comparison of the 3-day, 7-day, 14-day and 28-day compressive strengths of cylinders (6 inches in length and 3 inches in diameter) formed from these seventeen batches. At low levels of Portland cement replacement (15 percent), oil shale fly ash behaves as a workability (or water reduction) agent and leads to a 9 percent higher compressive strength than that of standard concrete. This enhancement is lost by 30 percent replacement, which leads to a 9 percent lower compressive strength than that of standard concrete. The addition of the workability agent restores the high strengths, even at 45 percent replacement where it leads to a 9 percent higher compressive strength than that of standard concrete. Type 3 Portland cement does not appear to be effective in building compressive strength.

It is difficult to make direct comparisons to the work of other investigators because of differences in methodologies. The Germans, for example, make a special "oil shale cement" containing 27 percent oil shale ash and 73 percent Portland cement. It has compressive strengths up to 8800 PSI (60.8 MPa) at 28 days [10]. The Israelis make and compare pastes of Portland cement and oil shale. Portland cement pastes (water to cement ratios of 0.3 to 0.6) at 20 days reach 10,660 PSI (73.5 MPa), while oil shale ash pastes reach only 2830 PSI (19.5 MPa), when it has a water to cement ratio of 0.8 to 1.0 (which gives it the same consistency as the Portland cement paste). However, in making cement blends (Portland and oil shale ash together), the Israelis found that Portland cement replacement by 15 to 25

percent oil shale ash yielded concrete with slightly increased strength [10]. The Chinese report 28-day strengths as high as 11,200 PSI (77 MPa) with ash/Portland cement blends. They also found an increase in strength at replacements up to 25 percent [14]. The Jordanians, on the other hand, saw a drop in compressive strength when ash was added to Portland cement. Their paste strengths were much lower, peaking at 6530 PSI (45 MPa) for pure Portland cement paste at 28 days at a water/cement ratio of 0.4 [15].

MECHANICAL PROPERTIES OF CONCRETE

Two sets of concrete forms were prepared for physical testing. The first set, a control sample, was prepared with the basic concrete recipe without fly-ash replacement, while the second set with 45% fly-ash replacement (fly ash from Sample Period 3), was prepared with the workability agent (12 oz per 100 lb cement + ash) mixed with the cement separately.

The 17-day compressive strength of the standard formulation was 4010 PSI, while that for the ash-containing formulation was 5050 PSI. The length change test (ASTM C157-86) showed that from Day One to Day Seven the average shrinkage was 0.0023 inches for ash-containing specimens, compared to 0.0133 inches for specimens of standard concrete.

The abrasion test (ASTM C944-80) was performed on six two-inch-high cylinders, cut from two six-inch-in-diameter cylinders. One cylinder was standard concrete and the other was fly ash-containing concrete. The cut surfaces were abraded. The results are:

<u>Specimen</u>	<u>Loss by Abrasion (Gram)</u>			<u>Average Loss</u>
X-1-1	0.7	0.5	0.6	0.60
X-1-2	0.5	0.5	0.6	0.53
X-1-3	0.8	0.9	1.0	0.90
X-15-1	0.7	0.8	0.8	0.77
X-15-2	1.0	1.1	1.3	1.13
X-15-3	0.9	0.8	0.8	0.83

The freeze/thaw (ASTM C666-84) and deicing tests (ASTM C672-84) were performed by CBUL, using test specimens prepared at the University of Pittsburgh. The freeze-thaw tests were confounded by poor coarse aggregate performance. The samples containing oil shale ash had less resistance to scaling than those containing no ash.

The Chinese report that, for pastes in which 35 to 40 percent of the Portland cement has been replaced by shale ashes, sulfate resistance increases by 166 percent and the bleeding ratio drops nearly to zero. Other physical properties of the oil shale-containing cements appear to the Chinese to be comparable to cements containing coal fly ash [12].

ZERO-SLUMP MATERIALS

Compressed/Autoclaved Ash/Lime Pastes

Three two-sample sets of short, compressed cylinders (2.5 inches in diameter and 2 inches high), using fly ash from Sample Period 7, were prepared by R. I. Lampus Company, a member of the National Precast Concrete Association (NPCA) from Springdale, Pennsylvania (a suburb of Pittsburgh). The specimens had the following formulations:

<u>Specimen ID Number</u>	<u>Percentage</u>		
	<u>Lime</u>	<u>Ash</u>	<u>Ash + Sand</u>
1	8	--	92
2	10	90	--
3	15	85	--

An optimum amount of water (10 percent based upon dry weight) was added for maximum compaction. The cylinders were autoclaved at the University of Pittsburgh for eight hours at 170 psi (350°F) to obtain calcium silicate bonding. The compressive strengths achieved were 1500, 2130 and 2870 PSI respectively.

Concrete Masonry Units

Eight sets of zero-slump concretes, similar in formulation to concrete masonry units, were prepared at the University of Pittsburgh, two of them containing oil shale combustion fly ash. In all cases, cylinders four inches high and two inches in diameter were fabricated and then allowed to set at room temperature in a humid environment for five hours. Next, they were heated to 150°F at one atmosphere with steam over a two-hour period and then cured at 150°F and one atmosphere for twelve hours within a steamed environment before being cooled to room temperature.

The first set of four cylinders was prepared with fly ash partially substituting for Portland cement. The following formulation was used:

- 1119.8 grams sand;
- 136.9 grams Portland cement (Type 1);
- 63.0 grams oil shale fly ash;
- 49.3 grams water.

The particle size distribution of the sand was adjusted to an optimal one by screening and blending. The final sand blend was 14 percent greater than 4 mesh, 20 percent in the range of 4 to 8 mesh, and 66 percent less than 8 mesh. The cylinders were formed by pressing the concrete into the molds, followed by ten seconds of vibration at 900 CPM with a handheld unit. Release from the molds was difficult and the average compressive strength of the final product was very poor. The molds were oiled for future tests to make release more easily accomplished.

The second, third, fourth, fifth and sixth sets of four cylinders each (twenty in all) were made without fly ash substitution. Their purpose was to test various formulations and preparation techniques. An air entrainer was added for the fourth and fifth tests. For the sixth set the sand particle size distribution was set by screening and blending, according to the method suggested in the Technical Bulletin No. 5 of the National Concrete Masonry Association. All twenty cylinders were rodded, rather than vibrated. The oversized, handheld vibrator, used for the first set, tended to eject portions of the mix from the cylinders. The maximum compressive strengths of these cylinders after curing was 2000 PSI. It should be noted that the three-day strength of commercial concrete block is between 2000 and 2400 PSI.

The seventh and eighth sets of four cylinders each were prepared with 1344 grams sand, 150 grams water and either 240 grams Type 1 Portland cement (seventh set) or 168 grams Type 1 Portland cement and 72 grams oil shale fly ash (eighth set). The average compressive strength of the vibrated, cured cylinders was 1590 PSI for both sets.

Light-Weight Concrete

The third, and final, zero-slump product line that was examined was light-weight concrete. This material generally has a very low density (down to 25 lb/cubic foot) and a correspondingly low compressive strength (down to 60 PSI). It is used for fireproofing and insulation in structures. The "foaming approach" to produce this material, applied in this project, uses a foaming agent in the concrete mix. The agent introduces and stabilizes air bubbles during mixing at high speed. A sample of oil shale ash was provided to Elastizell Corporation of America in Ann Arbor, Michigan. A test using 60 percent Type 1 Portland cement and 40 percent oil shale ash yielded a well-mixing, quick-setting formulation, which resulted in a hard, strippable product in one day. The cast density of the sample was 40.3 lb/ft³. Elastizell concluded that, based upon this limited investigation, oil shale combustion fly ash is a viable addition to light-weight concrete mixes.

CONCLUSIONS

The literature survey, conducted within the framework of this project, identified fifteen articles on the use of oil shale combustion ash in cement. These come from Israel, China, Jordan and the (former) USSR.

The ash from the combustor tests with 54 percent shale/46 percent coal is moderate in both CaO and MgO. The MgO is bound inside the particles and does not negatively impact the soundness of the ash.

Standard concrete with 15 percent substitution of Portland cement with ash shows an improvement in compressive strength at the same consistency (slump) of the wet mix, as standard Portland cement concrete. The addition of a wettability agent allows an additional 30 percent replacement without a drop in compressive strength below that of standard Portland cement concrete.

A first exploratory set of four physical tests were applied to the concrete which had 45 percent of the Portland cement replaced by ash, along with the addition of a wettability agent.

Preliminary specimens of three zero-slump products were prepared -- compressed/autoclaved ash/lime paste, concrete masonry units and light-weight concrete. The properties of the first product were sufficiently interesting that one manufacturer entered into direct negotiations with Occidental Oil Shale Company to test this product further. The second and third products met or exceeded one or more basic minimum standards, the third sufficiently so that one manufacturer desired to continue further testing. It is regrettable that Occidental Oil Shale Company has ceased operation, thus halting work in this promising area.

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Utilization of Coal-Tar Pitch in Insulating-Seal Materials

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Substances obtained from coal, in light of their physicochemical properties, can find a number of interesting applications. Among these substances are tars and coal-tar pitch. Collin (1) has described a variety of applications using coal-tar pitch (see Fig. 1). The majority of these applications, however, are realized only in a narrow scope. At the industrial level, pitch is most often treated as a by-product of the process of continual distillation of coal-based tar. One path that leads to the improvement of thermal and rheological properties of bitumens derived from coal is their modification by means of the addition of polymers. This creates the possibility of attaining greater utility from coal-tar pitch. One example is the improvement of binder quality in insulating-seal materials. This capability permits, in a relatively straightforward manner, the application of coal-tar pitch on a large scale. We feel that, in addition to the applications of pitch described by Collin, it is important to understand that pitch can be used as a binder or as a base substance in insulating-seal materials for the building, road construction and machinery industries.

Compositions based on petroleum asphalts are examples confirming the usefulness of this approach. The literature pertaining to the modification of petroleum bitumens by polymers is very extensive, the majority of which has been published in patents. For the most part, these works deal with the physical modification of asphalts by means of plastics, with the intention of obtaining homogeneous mixtures (2-6). Polymers produce diverse changes in the properties of petroleum bitumen. This is related mostly to an increase in stability and durability of the bitumen's physico-colloidal structure (7).

On the other hand, combining coal-tar pitch with polymers has generated a significantly smaller level of interest. Nevertheless, various types of polymers have been utilized to modify the properties of tars and coal-tar pitch. These polymers provided the means of attaining homogeneous and stable compositions. In particular, the goal of these works was to obtain binders used in the building of roads (8) and in tar-based lacquers (9). At present, the mechanisms for the composition of coal-tar pitch/polymer mixtures has not been elucidated. Neither has the interaction between these two types of constituents been distinctly explained. In both petroleum-asphalt/polymer compositions and pitch-polymer arrangements, it is accepted that homogeneity is the uniform dispersion of (a) polymer particles and (b) elements of resinous asphaltene pitch in its oil phase. Mutual interactions between the continuous phase of the bitumen (low molecular weight oils and resins) and the polymer as well as between the polymer and the dispersed phase of the pitch (resinous and asphaltenic substances, beta- and gamma- forms) determine the final physico-colloidal structure of the composition (7). Compared to petroleum asphalts, coal-tar pitch comprises relatively small amounts of the continuous phase. It is therefore appropriate to enrich coal-tar pitch with additional plasticizing substances.

The goal of the investigations was to determine the pitch-polymer composition which would fill the role of the matrix, having as a basis high-molecular weight insulating-seal materials. The investigations were carried out in two stages.

In the first stage, problems relating to the attainment of homogeneous and stable compositions made from the chosen types of polymers, plasticizers and coal-tar pitch were investigated. The first stage is outlined in Fig. 2. In the second stage, the formulations of the compositions were established. These mixtures were able to define beneficial characteristics for bituminous insulating-seal materials.

The following materials were studied:

1. Normal coal-tar pitch at its softening point of 87°C as well as the contents of components insoluble in toluene (21.45%).
2. Polymers. Atactic polypropylene (aPP, molecular weight: 32,600); isotactic polypropylene (iPP, MW: 220,000) with an isotactic index above 95%; polyvinyl chloride (PVC, MW: 139,000); polystyrene (PS, MW: 304,000); styrene-butadiene rubber latex containing 24.5% combined styrene and 59% rubber substances.
3. Plasticizers. Dibutyl phthalate; anthracene oil; furfuroil extract.
4. Fillers. Milled chalk; talc; colloidal silica.

The following determinations were performed on the obtained compositions:

1. Fragility point (Fraass).
2. Softening point (Pierscien and Kula).
3. Penetration and stability at elevated temperatures according to the Tube Test (10). The stability index was determined from the mutually relative densities of upper and lower layers of samples heated to 150°C for 4 days.
4. Adhesion. Concrete, glass, wood and aluminum were used as substrates.
5. Flow along vertical surfaces.
6. Resistance to freezing.
7. Elasticity at negative temperatures, as low as -20°C.
8. Aging tests. Twenty cycles, where one cycle lasted 48 hr and involved exposure to UV radiation, artificial rain and heating to 70°C and freezing to -25°C.

In the case of compositions made up of coal-tar pitch and polymers, certain intrinsic factors play a particular role with regard to obtaining mixtures which are homogeneous and which will not delaminate. These factors include: temperature, the time needed to reach homogeneity and the order of addition of components. Another important factor is the elimination of circumstances which may destroy the polymers.

The polymers that were examined differed in structure and characteristics. Beneficial properties were attained only in the case where pitch was combined with polar PVC. Mixtures containing 10% w/w PVC in pitch were homogeneous and stable. The addition of PVC increased the softening point to 114°C, with a concurrent lack of improvement in elasticity.

In the cases involving other polymers, the results were not as fruitful. Differences in the chemical make-up and the colloidal structure of pitch and PP prevented the attainment of mixtures that did not delaminate. In order to obtain homogeneous mixtures of pitch and PS, a temperature range of 260-310°C was required. This led to the destruction of the polymer and provided no changes in the properties of the pitch.

Plastification of pitch by means of oil fractions that are coal-based (anthracene oil) and petroleum-based (fuel oil, furfuroil extract), as well as artificially-produced dibutyl phthalate obtained from industry was studied. It was demonstrated that the most beneficial changes in properties were obtained using dibutyl phthalate at 25-30% w/w. The dibutyl-phthalate-modified pitch provided new qualities in pitch-plasticizer binders. For example, the fragility point

(according to Fraass) of pitch-phthalate mixtures is -24°C . Mixtures of pitch and furfuroil extract or anthracene oil at 20-25% w/w provided similar improvements.

In order to be eventually applied as base substances for insulating-seal materials, two-component mixtures of pitch-polymer and pitch-plasticizer required further modification. This was made possible by improving their mechanico-rheological properties. The three-component systems were comprised of coal-tar pitch, polymers and plasticizers. The best properties were obtained by compositions having 25% w/w dibutyl phthalate relative to pitch and 5-8% w/w PVC relative to pitch-plasticizer binder. Phthalate was used as plasticizer because it efficiently enabled the elimination of the elastomeric properties of PVC in a pitch environment.

The compositions were also modified with styrene-butadiene rubber in order to impart resistance to elevated temperatures and to provide high elasticity at negative temperatures. The following composition provides advantageous properties: coal-tar pitch (58.6% w/w), phthalate (22%), PVC (7.4%), styrene-butadiene rubber latex (7.4%). The fragility point of this mixture was -36°C and the softening point was 58°C . The penetration at 25°C was about 100×10^{-4} m and the stability index was 0.4%. These properties permitted the mixture to behave like an insulating-seal material.

The second part of the investigation involved determining the formulation of the final mixture, which had coal-tar pitch as a fundamental component. The composition was defined by standard specifications used for dilatant putties and hydroinsulation linings used in the building industry. As a rule, fillers and adhesion agents comprise materials of this type. The influence of the types and amounts of fillers (milled chalk, talc, colloidal silica) as well as that of adhesive media (balmi rosin, coumarone-indene resin) on the properties of butadiene-styrene pitch-phthalate-PVC-latex mixtures was studied. It was found that, regardless of the choice of filler, the most beneficial changes in applied properties were attained with filler mixtures containing chalk or talc with colloidal silica in a mass ratio of 4:1. Testing was performed by examining levelling at higher temperature, vertical flow at 60°C , resistance to freezing at -10°C and -20°C . At the same time, the amount of filler in the entire substance, depending on the application, should be 15-30% w/w. On the other hand, balmi rosin, in quantities of 2-3% w/w, was used as the adhesive agent. The rosin increases cohesion between the binder and the fillers. This provides an increase in the breaking strength (>0.1 MPa).

The results of the investigation provided the optimal formulations, which are listed in Table I. These compositions have many practical applications, such as the filling of horizontal slits in concrete as well as strengthening the bonds between metal-glass and wood-glass interfaces. Other applications include bituminous dilatant putties, sealing vertical surfaces in building elements, and hydroinsulating linings (1-3 mm thickness) formed by the hot rolling method, for use in the building industry.

The thermomechanical, rheological and practical properties of these compositions are comparable to the properties of analogous mixtures based on petroleum asphalts. In some instances, the properties of the pitch-based mixtures exceed those of the petroleum-based ones (e.g., adhesion to concrete, metallic or glass substrates). Modified pitch-polymer compositions can be used in general and specialized building applications. Examples include the construction of roads, airports, underground objects. Other examples can be found in the machine industry, where these mixtures are used as materials to prevent water penetration and to deaden vibrations.

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TABLE I - OPTIMAL QUANTITIES of COMPONENTS

Component	Sealing Compound (% w/w)	Sealing putty (% w/w)	Pitch-polymer lining (% w/w)
Coal-tar pitch	56.10	48.90	48.30
Dibutyl phthalate	18.70	16.30	16.10
PVC	6.50	5.70	7.10
Styrene-butadiene rubber latex	6.50	5.70	7.10
Talc	9.76	--	17.10
Milling chalk	--	17.00	--
Colloidal silica	2.44	4.30	4.30
Balmy rosin	--	2.10	--

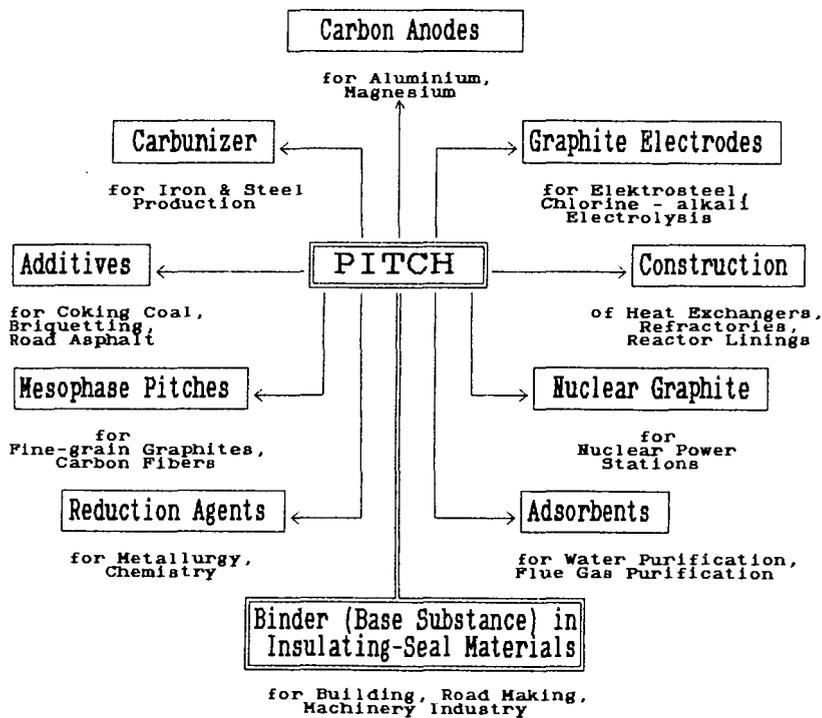


Fig.1. Application of Coal-Tar Pitch [G.Collin]

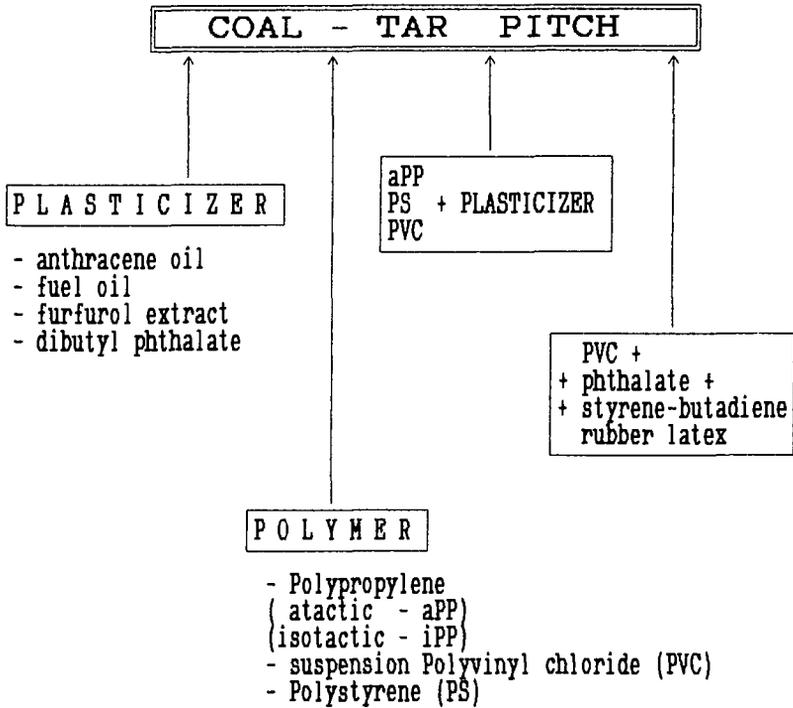


Fig. 2. Essential directions of investigation concerning modification of properties of coal-tar pitch

BRIQUETTING ANTHRACITE FINES FOR RECYCLE

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Keywords: Anthracite fines, Briquetting, Recycle

ABSTRACT

Pennsylvania anthracite is employed at QIT as reductant in electric arc furnaces, for the production of metal iron and Titanium dioxide rich slag from ilmenite. Fines are generated at the drying stage of anthracite, prior feeding to the electric arc furnaces, and represent approximately 3.4 % of the annual amount of anthracite used at QIT.

The size of these anthracite fines make them unsuitable for their direct use at the electric arc furnaces, because during feeding, they would be lost to the wet gas scrubbers. Briquetting of anthracite fines allows recycle of these materials for smelting ilmenite at QIT.

The paper presents results of a laboratory study for briquetting anthracite fines with a pitch binder, on the physical properties and chemical composition of the briquettes and, also discusses the proposed plant flowsheet for briquetting.

QIT's metallurgical operations in Quebec consist of an open pit mine located in the Allard Lake region, 500 miles north of Montreal, where an ilmenite ore is extracted and, the operations in Sorel where, the ore is beneficiated before smelting in electric arc furnaces. Smelting produces a titanium dioxide rich slag which is used as feed stock by pigment producing companies, and liquid iron metal which is processed further for production of different grades of pig iron, production of steel billets at QIT's steel plant and, production of iron and steel powder products at QIT's metal powders plant QMP.

Smelting at QIT in electric arc furnaces, consists of a carbothermic reduction of iron oxides present in the ilmenite in a molten bath. The reducing agent employed for smelting is Pennsylvania anthracite which is delivered to Sorel by boat.

The anthracite reductant prior to feeding to the electric arc furnaces is dried in three rotary louver type driers, which use the arc furnace fuel gas (85 % CO and 15 % H₂) produced from the iron oxide reduction. The drying operation removes 8 to 8.5 % moisture from anthracite as received at Sorel.

Fines are generated in the drying stage and are entrained in the gas exiting the driers. Fines represent approximately 3.4 % weight of the total annual amount of anthracite used at QIT, which is separated from the gas by cyclones and wet gas scrubbers.

Typically anthracite fines contain 75.38 % fixed carbon, 5.7 % volatile matter, 0.68 % sulfur 18.92 % ash, and 79 % of the particles are bigger than 38 microns. The relative high ash content in the fines relative to the 9.6 - 10 % ash content in dry anthracite, is consistent with the fact that, coal fines in general are associated with higher ash content.

The laboratory experimental work was carried out at the Energy Research Laboratories of CANMET in Ottawa. A batch laboratory size twin roll briquetting machine manufactured by K. R. Komarek, model B-100 was employed for the tests, this machine is equipped with, 130 mm diameter and 50 mm width rolls, and produces pillow shape briquettes with 12 x 12 x 40 mm dimensions.

The only binder tested was type II roofing asphalt, because this carbonaceous binder is compatible with the nature of anthracite reductant.

The experimental range of conditions for briquetting were: 5 - 14 % wt binder, and 6880 - 13760 pounds briquetting pressure, as summarized in Table 1.

Good quality green briquettes were produced for 10 and 12 % binder additions at 6800, 10320 and 13760 pounds of pressure, with more than 90 % of the initial mixture weight briquetted with the 12 x 12 x 40 mm target size.

Green briquettes with the best drop and abrasion resistance properties, were produced for 12 % binder addition and 10320 pounds pressure, these briquettes, withstood 9 ft drop tests without breakage while, the rest of the briquettes withstood only 6 ft or less high drop test.

The green briquettes containing 10, 12 and 14 % binder additions were crushed, for producing briquetted anthracite material smaller than the original 12 x 12 x 40 mm briquette size produced. A roll crusher was employed for crushing the briquettes, and the particle size distribution ranges from 1.13 cm (3/8") to 130 microns (100 mesh), as shown in Figure 1.

The + 10 mesh fraction of crushed green briquettes were subject to abrasion tests, employing an ASTM tumbler for coal, which procedure was modified to accommodate to the coarse granulometry and smaller weight of the crushed samples. Once again, the crushed green briquettes containing 12 % binder addition and briquetted with 10320 pounds of pressure, exhibited the highest abrasion resistance, with only 16.6 % decrease in the average particle size from 6420 microns before to 5355 microns after tumbling while, larger average particle size reductions ranging from 29.4 to 37.2 % are experienced after tumbling the + 10 mesh fraction of crushed briquettes containing 10 % binder additions.

In summary, use of 12 % type II asphalt roof binder and 10320 pounds briquetting pressure constitute, the optimum experimental conditions for producing briquettes with desirable drop and abrasion resistances, necessary to withstand handling and transport within the feeding system for recycle at QIT, for crushed or non crushed briquettes produced from anthracite fines.

The successful completion of the laboratory testing has led to the proposal of a flowsheet for briquetting anthracite fines, as illustrated by the schematic flowsheet shown in Figure 2. It is estimated that, a 5 metric tonnes per hour briquetting plant would be more than sufficient for processing the anthracite fines generated at QIT.

TABLE 1

EXPERIMENTAL CONDITIONS FOR BRIQUETTING ANTHRACITE FINES

ROLLS SPEED (RPM)	AUGER RATE (RPM)	BRIQUET. FORCE (LBS)	MOISTURE CONTENT (% WT)	BINDER CONTENT (% WT)	FINES WEIGHT (g)
1.818	32.25	10320	3	5	7077
1.818	32.25	10320	3	7	7077
1.818	32.25	10320	3	9	7077
1.818	32.25	10320	7	5	7000
1.818	32.25	10320	7	7	7000
1.818	32.25	10320	7	9	7000
1.818	32.25	6880	3	12	7077
1.818	32.25	10320	3	12	7077
1.818	32.25	13760	3	12	7077
1.818	32.25	6880	3	10	7077
1.818	32.25	10320	3	10	7077
1.818	32.25	13760	3	10	7077
1.818	32.25	6880	3	12	7077
1.818	32.25	10320	3	12	7077
1.818	32.25	13760	3	12	7077
1.818	32.25	6880	3	14	7077
1.818	32.25	10320	3	14	7077
1.818	32.25	13760	3	14	7077

FIGURE 1
PARTICLE SIZE DISTRIBUTION OF CRUSHED BRIQUETS

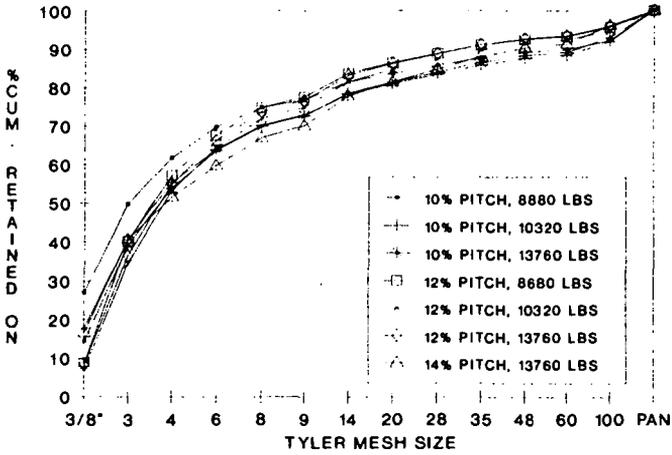
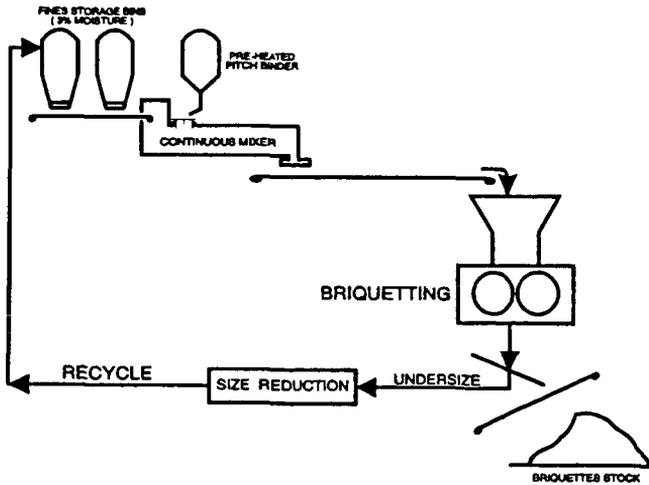


FIGURE 2
ANTHRACITE FINES BRIQUETTING
SCHEMATIC OF PROPOSED FLOWSHEET



ASH UTILIZATION IN WATER QUALITY MANAGEMENT

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ABSTRACT

The potential for water pollution involving heavy metals and organics exists especially when wastewater treatment is either inadequate or non-existent. This paper reviews a number of investigations where coal ashes have been studied for the removal of organic matter (COD), color, organic compounds such as phenol, and heavy metals. Results of experimental studies conducted at the University of Regina, on the adsorption of 1) phenol and 2) heavy metals such as cadmium, chromium, mercury, copper, nickel and zinc by fly ash, are presented. The use of fly ash in sludge management is also examined.

Keywords: coal ash utilization, water treatment, wastewater treatment

INTRODUCTION

Increased reliance on coal as an energy source has led to significant by-product management problems of storage or disposal. These by-products include slag, bottom ash and fly ash. Commercial uses of coal ashes are limited and this paper examines the application of these by-products in water pollution control.

USE OF FLY ASH IN WATER TREATMENT

Ballance *et al.* used fly ash as a coagulant aid in water treatment (1). Fly ash from four sources and in certain proportions was found by the authors to assist in the chemical coagulation of turbid water and in the settling of chemically induced floc. A denser sludge was produced from coagulation with fly ash and alum than with alum alone. Laboratory tests using Neyveli lignite fly ash showed that it aids in the settling of turbid water when used along with alum (2).

USE OF COAL ASHES IN WASTEWATER TREATMENT

The use of bottom ash and fly ash in removing contaminants from wastewater (on-site and municipal) is examined with special reference to removal of COD, color, organic compounds, and heavy metals.

On-site Wastewater Treatment

Bottom ash was considered as an alternative medium for the mound type soil absorption systems used in on-site wastewater treatment. Laboratory work carried out at West Virginia University showed that the bottom ash filter had the ability to reduce BOD and SS (3, 4). Three bottom ash mound systems built in Monogalia County, West Virginia based on this work were reported to be operating well (5). Laboratory studies on four different recirculating filters using pea gravel, medium sand, bottom ash and fly ash-bottom ash mixture showed that there was no significant difference in the performance of different media with respect to reduction in COD and SS (6). A 23-month study examined 11 filters - five bottom ash filters, five sand filters treating septic tank effluent and one bottom ash filter treating aerobically treated effluent. The study data showed that sand media filters resulted in a higher quality effluent; noticeable improvement in the performance of all the filters was observed in the last five-month period with effluent BOD in the 10-14 mg/L range (5). The Southern Illinois Power Co-op used unscreened bottom ash in a single intermittent filter treating septic tank effluent. The filter

operation was monitored from January 1981 to April 1982; the average effluent BOD and SS values were 7 and 8 mg/L respectively (7). Detailed studies on a bottom ash recirculating filter treating septic tank effluent from a residence showed that the system performed consistently and produced an effluent with average BOD and SS less than 12 mg/L (8).

Municipal Wastewater Treatment

Batch tests showed that unsieved fly ash (6% carbon) removed in 24h 19 to 56% of COD, and 0 to 77% of ABS from secondary effluent depending upon the adsorbent dose (9). This study also showed that COD removal increased with an increase in the carbon content of fly ashes tested (9). Deb *et al.* found that the removal of COD is logarithmically related to three parameters - 1) time of mixing, 2) initial COD and 3) concentration of fly ash (10). Nelson and Guarino found that removals of COD, BOD and SS by the addition of fly ash to a municipal plant effluent were not appreciable (11). The investigations by Eye and Basu showed that fly ash was capable of reducing COD of a secondary effluent by about 30 percent at a fly ash concentration of about 1600 mg/L when the initial COD is around 60 mg/L and removal of SS containing fly ash by coagulation with lime was very efficient (12).

Removal of color. The removal of Metomega Chrome Orange GL, a commercial textile dye from wastewater was found to be nearly 99% under optimal conditions (pH = 3.0 and temperature =30°C) using fly ash as an adsorbent (13); the sorption data fitted the Langmuir isotherm model. The removal of Omega Chrome Red ME (a popular chrome dye) from its aqueous solution by adsorption on a mixture of fly ash and coal was studied; a 100% removal of the dye was achieved at 10 mg/L, 30°C, and 2.0 pH, using a 1:1 ratio of fly ash and coal (14). The equilibrium data was reported to fit well with the Langmuir model of adsorption.

Removal of organics. Fly ash was successfully used to recover phenol from industrial wastewater, by lagooning the mixture of fly ash and wastewater; phenol was reduced from 4500 mg/L to 280 mg/L (15). Fly ash was also used to remove TNT in both batch and column systems; in column systems 90% removal of TNT was reported (16). Bhargava *et al.* examined the removal of a detergent in a fixed-bed continuous flow fly ash column and developed a relationship for the design of such systems (17). Using 1000 mg/L of fly ash containing 23.27% carbon, 74% removal of ABS was obtained with a two-hour contact time (18). Khanna and Malhotra examined the kinetics and mechanism of phenol removal by fly ash and provided data for the design of phenol-fly ash adsorption systems (19). Jain *et al.* showed that the adsorption plot of oxalic acid from aqueous solution by fly ash has two linear components each following the Langmuir isotherm (20). Banerjee *et al.* examined the use of fly ash as a sorbent in the treatment of alcohols, aldehydes, ketones and aromatics (21). This study showed that immobilization of organic pollutants is feasible by adsorbing the contaminants onto fly ash. The residual carbon content was found to play a significant role in the adsorption process. Percent reductions of the aromatic compounds were found to be much higher compared to other functional groups such as alcohols, aldehydes and ketones.

Removal of heavy metals. Gangoli *et al.* performed batch tests by contacting 40 g of fly ash with 1 L of an aqueous solution of chromium (22). They concluded that the removal of hexavalent chromium using fly ash involved a chemisorption mechanism associated with the bonding between active alumina sites and the chromate anion. Grover and Narayanaswamy carried out batch experiments to study the effects of contact time, pH and fly ash dosage on the removal of hexavalent chromium (23). They explained the equilibrium data for chromium uptake by fly ash at different pH values on the basis of the Freundlich adsorption isotherm. They found that there was an improved adsorption of chromium at a pH less than 2.5. Yadava *et al.* (24) investigated the removal of cadmium by fly ash at different conditions by varying the

contact time, temperature and pH. They found that the removal of cadmium from aqueous solutions by adsorption on fly ash increased with time and that equilibrium is attained in 2 hours. On studying the kinetics of adsorption of cadmium on fly ash using the Lagergren equation, they concluded the adsorption process to be first order. They found that the adsorption of cadmium on fly ash could be explained by the Langmuir equation. Their results showed that an increase in temperature from 20°C to 40°C decreased the adsorption of cadmium on fly ash from 96.07% to 83.78%. The removal of cadmium by fly ash increased from 11.85% to 89.82% on increasing the pH of cadmium solution from 4.0 to 8.5. The ability of a homogenous mixture of fly ash and wollastonite (1:1) to remove Cr^{6+} from aqueous solution by adsorption was investigated by Panday *et al.* (25). Maximum removal was observed at pH 2.0 and 30°C. Studies were conducted to investigate the removal of copper from the metal cleaning wastes by adsorption on fly ash; these studies showed that adsorption can significantly increase copper removal (26). The removal of Cu^{2+} by adsorption on fly ash was found by Panday *et al.* to be concentration, pH and temperature dependent (27). Adsorption was found to be endothermic; the maximum removal was observed at pH 8.0. Prabhu *et al.* showed that fly ash was a good adsorbent for the removal of zinc from aqueous solutions; maximum removal was obtained in the pH range of 3 to 4 (28). They found that adsorption fitted the Freundlich isotherm. Studies by Gashi *et al.* showed that fly ash showed good adsorptive properties of removal of lead, zinc, cadmium and copper from effluents of battery industry and fertilizer industry (29). Removal efficiencies were greater than 70%. Adsorption studies carried out to estimate heavy metal removal using fly ash on wastewater at Varnasi, India showed that removal was in the following order: $Pb > Zn > Cu > Cr > Cd > Co > Ni > Mn$ (30). Adsorption of Cu^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} and Ag^+ on fly ash was investigated by Weng and Huang and they found that the process was spontaneous and endothermic (31). Sen and De found that fly ash was found to have a good adsorption capacity for Hg^{2+} ; they reported that the adsorption conformed to Freundlich model (32). They found that the equilibrium time for adsorption was three hours and that the optimum pH range was 3.5 to 4.5. Fly ash was found to be a good adsorbent for the removal of lead; an equilibrium time of two hours and a pH of 5.0 was found to be most effective for the removal of lead (33).

USE OF FLY ASH IN SLUDGE MANAGEMENT

Eye and Basu concluded, based on their investigation, that fly ash could be a useful agent in conditioning sludge prior to vacuum filtration (12). Helm *et al.* concluded that mixtures up to 10% wastewater sludge with fly ash appeared suitable for use in highway embankments and other structural fills (34). Kincannon *et al.* showed that an admix of municipal wastewater sludge with fly ash could produce a dry, deodorized and sterile product with a potential for use as a soil conditioner (35).

RESEARCH AT THE UNIVERSITY OF REGINA

Batch studies were conducted to evaluate the use of fly ash in the removal of cadmium, chromium, copper, nickel, zinc, mercury and phenol from municipal wastewater. The fly ash used in the study was obtained from unit #2 of the Poplar River Power Station of the Saskatchewan Power Corporation. The fly ash generated from the combustion of lignite was collected from the first bunker of the power station's electrostatic precipitators. The wastewater used in the study was collected from the City of Regina Municipal Wastewater

Treatment Plant, before the wastewater enters the primary sedimentation tanks. The first study related to cadmium and chromium, the second study was conducted with copper, nickel and zinc; the third study was on mercury removal and the fourth related to phenol. For the studies, the wastewater was spiked with the respective heavy metals to raise their concentrations to approximately 1 mg/L. Batch (kinetic and adsorption isotherm) studies were conducted using a Jar Test Apparatus. Adsorption studies were conducted at various pH values and the best pH for maximum adsorption was chosen. Isotherm studies were conducted at 5°C, 10°C, 15°C and 21°C for heavy metal removal. Methods outlined in "Standard Methods" (36) were followed for the analysis. Batch studies showed that fly ash removed 93% of the cadmium in the wastewater in the pH range 7 to 8, and 44% of the chromium in the wastewater in the pH range 2 to 3 in an equilibrium time of 3 hours (37). The adsorption of cadmium and chromium on fly ash was found to be exothermic. Isotherm analysis of the data showed that the adsorption of cadmium on fly ash was described by the Langmuir isotherm at 5°C, 10°C, 15°C, and 21°C whereas the adsorption of chromium on fly ash followed the Freundlich isotherm at 5°C, 10°C and 15°C and Langmuir isotherm at 21°C. Removals of copper, zinc and nickel attained equilibrium in two hours (38). Removals of the three metals were found to reach maximum values in the pH range 3 to 3.5. It was found that the adsorption capacity of fly ash with respect to these three heavy metals generally decreased with an increase in temperature. Removals of copper, nickel and zinc were approximately 73%, 33% and 59% respectively at 21°C at a pH of 3.0 to 3.5. The adsorption of the three metals on fly ash generally followed the Langmuir isotherm. It was found that a contact time of two hours was necessary for the adsorption of mercury from wastewater to reach equilibrium (39). The optimum pH was found to be between 5.0 and 5.5. The adsorption isotherm data were described adequately by both the Langmuir and the Freundlich models. In the case of the adsorption of phenol from wastewater by fly ash, it was found that the removal of phenol was optimum at a pH of 5.0 in an equilibrium time of five hours. The adsorption data was adequately described by the Langmuir isotherm.

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REUSE OF PRETREATED COAL GASIFICATION WASTEWATER AS COOLING TOWER MAKEUP

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GOALS AND OBJECTIVES

Coal gasification wastewater, containing various high concentrated organic and inorganic contaminants, reuse and recycling is practiced in coal gasification plant for two primary purposes: to reduce wastewater discharge amount and to protect environment. Cooling systems are major consumers in many coal gasification plants. Therefore, reuse of pretreated coal gasification wastewater as cooling tower makeup may bring considerable saving in fresh water consumption and protection of environment.

It is possible to find a feasible approach for the reuse of coal gasification wastewater with large amount discharge and various high concentrated pollutants. Some tests of pretreated wastewater for industrial cooling have been reported [1, 2, 3]. However, the reuse of the wastewater as cooling tower makeup presents both operating and environmental problems, especially in severe biological fouling and organic emissions.

The principal goals of the research project are to develop an advanced process for the treatment and reuse of gasification wastewater. Another object is to test alternative treatment method that may be necessary for

execution of gasification wastewater zero discharge.

WASTEWATER PRODUCTION AND PRETREATMENT

Wastewater tested in this study was the effluent from Lurgi fixed-bed gasification and coal cooking plant. Raw gasification wastewater pretreatment process for removing tar, phenolic compounds and ammonia was performed by a pilot facility⁽⁴⁾. Flotation cell is used to remove residual suspended tars. Phenols and ammonia in the wastewater are reduced by an improved solvent extraction system with steam stripping⁽⁵⁾. In the process, di-isopropyl ether is used as the solvent. 98% (fixed-bed gasification) and 95% (coal coking) phenol removal efficiency and less than 100 mg/l phenol in effluent are obtained at a wastewater-to-solvent ratio of about 10:1. After extraction, the wastewater is directly pumped to steam stripping column. By separating distillate, 98% recovery efficiency of ammonia and 99% recovery efficiency of the solvent dissolved in the wastewater are obtained.

The next step of the pretreatment involves biological oxidation and dualmedia filtration to remove organic contaminants and suspended solids.

Table 1 and 2 show the average composition of the fixed-bed gasification and coal coking wastewater before and after each of these pretreatment respectively. As shown in table 1 and 2, after these pretreatment, the wastewater characterization doesn't meet the national discharge criteria. As shown in the late, it can be reused as makeup in an evaporative cooling tower.

TABLE 1 AVERAGE WASTEWATER CHARACTERISTICS FOLLOWING EACH PRETREATMENT STEP (FIX-BED GASIFICATION)

Constituent*	Raw Wastewater	Solvent Extraction Effluent	Steam Stripping Effluent	Activated Sludge and Filtration Effluent
COD	38500	20600	2900	670
BOD ₅	15600	--	1518	40
Phenol	2450	48	36	0.42
Ammonia	1300	1250	210	163
Sulfide	48	38.4	18.4	14.4
Cyanide	3.5	0.27	0.04	0.013
pH	9.77	9.18	8.7	7.6
Oil	8326	273	40	23
Fatty acid	85	43.7	1.5	0.067

* All concentrations in mg/l except pH

TABLE 2 AVERAGE WASTEWATER CHARACTERISTICS FOLLOWING EACH PRETREATMENT STEP (COAL COKING)

Constituent*	Raw Wastewater	Solvent Extraction Effluent	Steam Stripping Effluent	Activated Sludge and Filtration Effluent
COD	25000	13500	2783	510
BOD ₅	2970	--	1025	36
Phenol	1285	70	45	0.51
Ammonia	1520	1515	190	185
Sulfide	23	14.6	4.87	4.4
Cyanide	9.86	9.36	9.6	6.48
pH	9.08	9.10	8.4	7.18
Oil	300	170	110	74.7
Fatty acid	81.6	38.9	0.24	0.11

* All concentrations in mg/l except pH

COOLING TOWER EXPERIMENTAL PROCEDURES

Two series (phase 1 and 2) were conducted by using fixed-bed wastewater showing in Table 1. A series (phase 3) was conducted by using coal coking wastewater showing in Table 2. The most significant difference between phase 2, 3 and phase 1 was biocide addition which was used to control biological fouling. Another difference between phase 2, 3 and phase 1 was filtration which was used to reduce Suspended Solid in the cooling water. A schematic of the test cooling tower system is presented in Figure 1. The cooling tower design parameters are as the following liquid-to-gas ratio 1:830 m^3/m^3 , flow per unit area of packing sufac: 11.8 m^3/m^2 . The design cooling range of 10 °C to 15 °C and 10 cycles of concentration were maintained in each of the three tests. A 300 l/h cooling water circulation rate, a 6l/h pretreated wastewater makeup rate, and a blowdown rate of approximately 10% of the makeup were kept in order to maintain 10 cycle operation. In addition to hydraulic control, during day-to-day operation of both segments of all phase tests, the cycles of concentration were monitored using the concentration of sodium ions. All three tests were run for 350 hours.

As shown in Figure 1, the blowdown water was pumped into an evaporator, in which the water was futher concentrated by 10 times and condensate was return to the basin. Therefore only approximately 1 % of the wakeup was discharged. Cooling water in the tower basin is pumped through a test heat exchanger wich can be used for measuring the steel corrosion both of carbon and stainless steel and monitoring fouling and heat transfer performance. The test heat exchanger was equipped with carbon stell tube, and operated with tube-side fluid velocity of 1. 0 m/sec. The shell side was heated by steam.

During phase 2 and 3 the biocid (ClO_2) and bypass filtration were added. The biocid was added every six hours with dosage of 20 mg/l (calculated on tatol cooling water volum). The flow rate of bypass filtration was 8 l/h.

COOLING TOWER TEST RESULTS

Characterization of Water. The average makeup and cooling water analysis results for all phase 1, 2 and 3 are presented in Table 3. The most significant difference between phase 1 and phase 2, 3 was the concentration of

suspended solids. TSS of phase 2, 3 was significantly reduced 1/2 comparing with phase 1. This is likely due to the biocide addition which led to reduced bacterial population. In phase 1, without biocide, the counts of total bacteria in the cooling water was 8.2×10^7 /ml. In both Phase 2 and 3, used ClO_2 as biocid, the counts was less 1.5×10^4 /ml. It appears that ClO_2 is a effective biocide for cooling tower operating with pretreated coal gasification wastewater as makeup.

TABLE 3 ANALYSIS RESULTS OF WATER FROM THE TESTS

Constituent*	Fixed-bed gasification				Coal cooking	
	Phase 1		Phase 2		Phase 3	
	Makeup	CW	Makeup	CW	Makeup	CW
COD	697	3767	669	4828	510	4211
BOD ₅	40	88.4	39	249	38	250
Phenol	0.4	1.2	0.42	1.8	0.51	1.7
Ammonia	155	1020	155	1015	185	400
Alkalinity	175	825	195	445	115	325
Calcium	4.16	24.3	19.5	90	12	62.5
Sodium	57.1	588	81.8	563	42.8	423
Magnesium	4.19	8.35	2.56	22.2	3.51	31.6
TSS	46	1640	40	540	110	780
TVSS	0.52	0.53	0.53	0.25	0.52	0.54
TDS	830	5158	916	6718	1448	11942
TVDS	536	3642	548	4242	960	7586
pH	7.1	8.82	7.6	8.7	7.78	8.9
Conductivity	0.0132	0.0676	0.013	0.074	0.034	0.138

* All concentrations in mg/l, conductivity in ms
System Fouling. Figure 2 illustrates the rates of fouling and heat transfer coefficient loss in carbon steel tubes observed in all three test phases. All tests showed that the heat transfer coefficient loss was zero after 200 hours. Figure 2 showed the HTC during first 200 hours for each test. As shown in Figure 2 both the rate of fouling and heat transfer coefficient loss in phase 1 were greater than that in phase 2 and 3. It is indicated that the use of ClO_2 as biocide tested in phase 2 and 3 was beneficial for the reduction of biofouling, because the use of biocide (ClO_2) can control the extent of biological deposition that happened in phase 1. Calculating on the basis of the Kern-Seaton Model⁽⁶⁾, the limit of fouling thermal resistance for phase 2 and 3 tests was 3.324×10^{-4} and 5.86×10^{-4} m² · h · °C /Kcal respectively. The relationship between fouling thermal resistance (R) and time (t) is as following:

For the pretreated fixed-bed gasification wastewater

$$R = 3.324 \times 10^{-4} (1 - e^{-0.0086t}) \text{ m}^2 \cdot \text{h} \cdot \text{C} / \text{kcal}$$

For the pretreated coal coking wastewater

$$R = 5.86 \times 10^{-4} (1 - e^{-0.0078t}) \text{ m}^2 \cdot \text{h} \cdot \text{C} / \text{kcal}$$

Corrosion. Corrosion rates in the cooling tower system were determined using weight loss coupons. Table 4 presents a summary of the corrosion rate during the all three bases tests. As showing in Table 4, the highest corrosion rate always occurred at heat exchanger outline where the temperature of cooling water was the highest. The corrosion rates for carbon steel varied from 0.0036-0.037 mm/y for the various locations, and for stainless steel varied from 0.0002-0.0014 mm/y.

TABLE 4 CORROSION RATES DURING THE TESTS (mm/y)

Metallurgy	Location	Phase 1	Phase 2	Phase 3
Carbon steell	Basin	0.0036	0.0086	0.0078
Carbon steell	HE inlet	0.0184	0.0144	0.0039
Carbon steell	HE outlet	0.0385	0.0182	0.0280
1Cr18Ni9Ti SS	Basin	0.0019	0.0014	0.0014
1Cr18Ni9Ti SS	HE inlet	0.0005	0.0002	0.0010
1Cr18Ni9Ti SS	HE outlet	0.0024	0.0014	0.0014

Based on measuring corrosion rates from each of these tests, corrosion wasn't a significant problem for reusing pretreated gasification wastewater as makeup. These low corrosion rates indicated that the pretreated wastewater from fixed-bed gasification or coking were suitable for makeup to a cooling tower without the addition of corrosion inhibitors. This is likely due to that some organic materials (phenols and cyanide et al.) in the wastewater act as inhibitors.

CONCLUSIONS

Several conclusions can be drawn from the data collected during the three Phases of cooling tower reuse testing with pretreated Lurgi fixed-bed gasification and coal coking wastewater. Use of these wastewater as direct makeup to a cooling tower resulted in a high level of biological activity, which influenced the fouling and heat transfer performance of the equipment in test process. The steel corrosion both carbon and stainless steel in these operations were not high which would be acceptable in a commercial use.

The Phase 2 and 3 indicated that reuse pretreated gasification wastewater was suitable for makeup to a cooling

tower with the biocide (ClO_2) addition. The limit of fouling thermal resistance of the Lurgi fixed-bed gasification and coal coking wastewater was 3.24×10^{-4} and $5.86 \times 10^{-4} \text{m}^2 \cdot \text{h} \cdot ^\circ\text{C} / \text{kcal}$ respectively; the highest carbon steel corrosion was 0.0182 and 0.028 mm/y respectively and the highest stainless steel corrosion were 0.0014mm/y for both. All those results well meet the national criteria of China. These results have led us to conclude that Lurgi fixed-bed gasification and coking wastewater, after removal tar, extraction phenol, stripping ammonia, biological oxidation and dualmedia filtration treatment, will make a suitable cooling tower makeup at ten cycles of concentration with the addition of biocide (ClO_2) and without the addition of corrosion inhibitors. The study also showed that the reuse of this streams were beneficial both for water resource saving and reducing environmental pollution due to the reduction of wastewater discharge.

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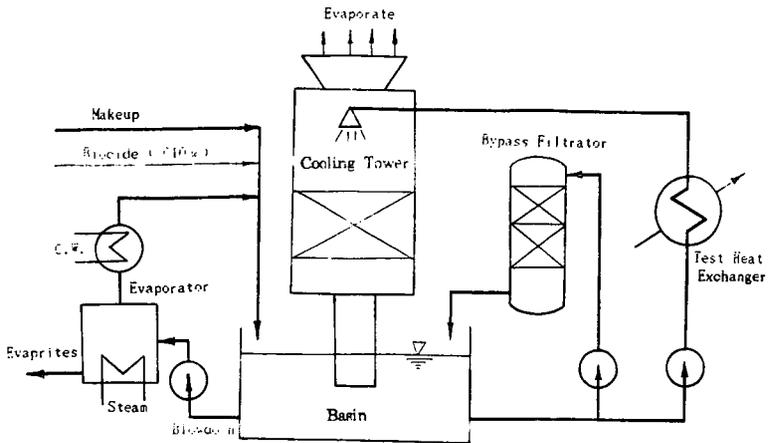


Figure 1 — Schematic of the Test Cooling Tower System

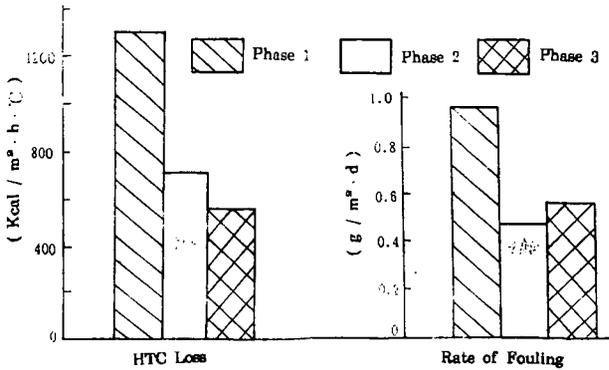


Figure 2 — Results of Average Fouling and Heat Transfer Coefficient Loss in Carbon Steel Tube