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Recycling Possibilities and Applications of Carbon Based Petroleum Ash - A Study Focused on Heavy Oil Based Power Generating Plants

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Abstract— Fossil fuel based thermal energy has been, and still is a major source of electricity generation all across the world. Although renewable energy such as wind, hydro, and solar based photovoltaic sources are becoming more palatable to the public in developed countries, fossil fuel based energy generation still dominates the energy industry. It is estimated that almost 66% of the electricity generation in the U.S. is based on fossil fuel[1]. In this paper, two major types of combustion by-products will be discussed. The first type is the fly and bottom ash product. The second type is carbonic residues. Properties such as chemical and physical characteristics will be explained for both products. Furthermore, feasibility studies of the applications of the products will be considered. The majority of fly and bottom ash is used in the construction industries, specifically in making concrete and asphalt.

Index Terms— Recycling, Carbon Based Ash, Heavy Oil, Power Generation.

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1 INTRODUCTION

1.1 Fossil Fuel Combustion By-Products Overview

Fossil fuel based thermal energy has been, and still is a major source of electricity generation all across the world. Although renewable energy such as wind, hydro, and solar based photovoltaic sources are becoming more palatable to the public in developed countries, fossil fuel based energy generation still dominates the energy industry. It is estimated that almost 66% of the electricity generation in the U.S. is based on fossil fuel[1].

The by-products of the combustion and incineration of fossil fuel is a threat to the environment and to the business of the power plant operation. The residuals from the fossil fuel power plant occupy and increasing number of landfill sites, which strains the logistical ability of the plant to operate profitably. The environmental regulations are becoming tougher in many countries as the public's demand for such regulations and measures are increasing[2,3]. Therefore, the treatment of such residuals is in the interest of both business and environmentally conservative groups.

In this paper, two major types of combustion by-products will be discussed. The first type is the fly and bottom ash product. The second type is carbonic residues. Properties such as chemical and physical characteristics will be explained for both products. Furthermore, feasibility studies of the applications of the products will be considered. The majority of fly and bottom ash is used in the construction industries, specifically in making concrete and asphalt.

Our study has shown that there are numerous solutions that are strongly feasible, which are proven to be successful over time. We will also provide with theoretical, yet thorough solutions to safely dispose the material. This will completely remove the waste and eliminate the need of prolonged usage of landfill sites.

1.2 Conventional Ash Vs. Pure Carbonic Residual

Fly and bottom ash are both captured by-products of fossil fuel incineration. These two ashes are chemically similar in that they both contain SiO_2, Al_2O_3, and Fe_2O_3 [4]. This can also be seen in Figure 1. Studies have shown that the carbon content of the ash varies from 0 to 9% by weight [5 6 7]. Fly ash is captured in the flue stack of the incinerator, where an electrostatic precipitator is used for its collection. Bottom ash is collected at the side walls of a furnace during its operation.

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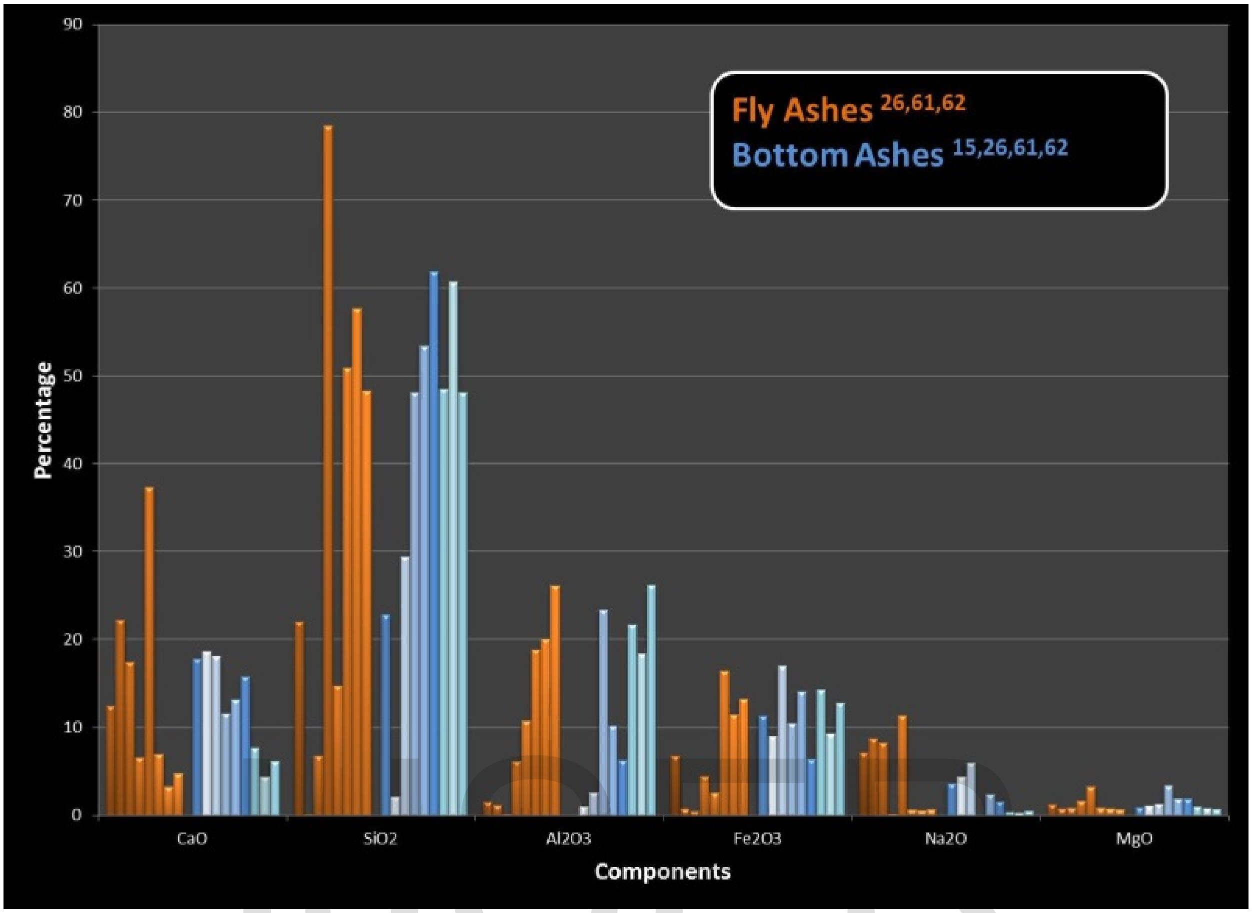


Figure 1: A comparison of the chemical compositions of fly and bottom ash

Due to the nature of the project, the process of the incineration and the resulting residuals were speculated prior to the testing. The residuals were thought as either fly or bottom ash, and thus preliminary research was done in these areas. However, the X-ray diffraction test suggested that the major component of this material is carbon. Loss on ignition (LOI) test also suggested that more than 90% of the material is possibly carbon. This concludes to the fact that the material that is not fly or bottom ash.

In this paper, the carbonic residues are broken down in to three major raw forms. Although carbon is a single element, the material can behave significantly different depending on its crystallographic structure, and other chemical properties. For example, graphite, which is used in pencils, is a far different material than diamond. They are both carbon, but their crystal structure is significantly different to each other. Unfortunately, the visual observation of the sample immediately suggested that it is not in a form of diamond. It is determined throughout the research that graphite, carbon black, and coke are plausible venues of investigation for its applications.

1.3 Feasibility of recycling combustion by-product

Carbonic materials have been used for centuries throughout the history. First use of carbon based product such as graphite dates back to 4000 B.C. [8]. Similar timelines and history are applicable for many other carbon products. There are countless ways to use the product, once its classification and specification is determined. The feasibility of using the residual as a high quality raw material in creating consumer goods is very positive and lucrative. It is theoretically possible to use the residual as a fuel to generate more electricity. The details of the applications will be discussed in later chapters.

CHAPTER 2. LITERATURE REVIEW

2.1 Introduction

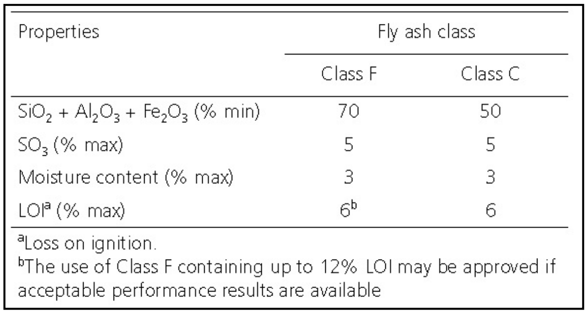
This chapter presents a review of literature and in-depth look at fossil fuel combustion by-products. During the early stages of the research, the focus was to explore the composition and applications of fly and bottom ash. Although the material was determined to be composed mostly of carbon, the results from the earlier research are useful as a reference, as fly and bottom ashes are the major by-products from fossil fuel power generation. Chapter 2.2 will investigate the properties and applications of fly and bottom ash, and chapter 2.3 will cover carbonic residues in detail.

2.2 Fly and Bottom Ashes

2.2.a Properties of Fly and Bottom Ash

Fly ash is most often captured as a product of incineration, generally from that of municipal solid waste, coal, or petroleum coke. It can also be produced by smelting and gasification, leading to the incineration of solid residues [4]. Fly ash is made of particles light enough to escape the combustion by rising with the carbon dioxide and other gaseous exhaust. Before it can escape though, it is captured through either bag filtering [9] or using electrostatic precipitators [10]. The color of the captured product varies by type, where Class C fly ash is typically light or tan colored, while Class F ash is typically dark grey [11]. In either case, the ash has a particle size distribution from 0.5 to 400 µm, with an average size between 12 and 80 µm [4]. The particles are generally spherical in shape, and can be either solid or hollow. The hollow particles can be translucent or opaque, can vary from slightly to highly porous, and can be spherical or elongated [12]. These properties, especially the small size and spherical nature, are useful in the application of fly ash as a pozzolan.

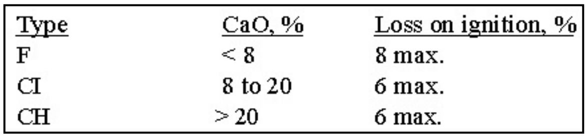
As can be seen from Table 1, the LOI of the fly ashes are generally low, less than 10%. Loss on ignition is an estimate of the carbon content in the ash, and was found by drying the ash, then heating the remaining product till it reaches a constant mass [12]. While not an exact telling of the carbon content, the test gives a good estimate since heating to a constant mass makes the carbon that is in the ash from inefficiencies in combustion burn away, and thus gives an obvious mass difference. This test will be explored with more detail later on in the paper.



Properties	Fly ash class	
	Class F	Class C
$SiO_2 + Al_2O_3 + Fe_2O_3$ (% min)	70	50
SO_3 (% max)	5	5
Moisture content (% max)	3	3
LOI[a] (% max)	6[b]	6

[a] Loss on ignition.
[b] The use of Class F containing up to 12% LOI may be approved if acceptable performance results are available

Table 1: The conventional method of categorizing fly ash [4]



Type	CaO, %	Loss on ignition, %
F	< 8	8 max.
CI	8 to 20	6 max.
CH	> 20	6 max.

Table 2: An alternative method of categorizing fly ash, based on CaO content [12]

There are important benefits to the environment and the economy from the use of ash products in an encapsulated form, such as in wallboard, concrete, roofing materials and bricks, where the ash is bound into products. Environmental benefits from these types of uses include greenhouse gas reduction, energy conservation, reduction in land disposal and reduction in the need to mine/process virgin materials. Government agencies such as Environment Protection Agency in the United States does not have data showing that encapsulated uses pose a problem for human health or the environment [5].

Unencapsulated uses are those where the ash is in a loose or in an unbound particulate or sludge form. EPA has identified concerns with some land-based uses of unencapsulated fly ash, particularly when proper engineering standards have not been met. The EPA considers certain uses, such as fly ash fill in sand and gravel pits, and other large scale fill operations, as disposal and not as beneficial use [5].

MSDS of fly ash from a large scale concrete company states that there are no critical health effects by working with fly ash. It is not considered as carcinogen, and only requires basic protective equipment such as respirators, goggles, and gloves [13].

Bottom ash is usually collected at the bottom of the incinerator, as it is heavier than fly ash. It is also greater in its physical size compared to fly ash [14]. Bottom ash has porous surface, resulting in a lower compressive strength [15]. However, bottom ash has a similar composition to fly ash [14]. Figure 2 shows the general size of the bottom ash.

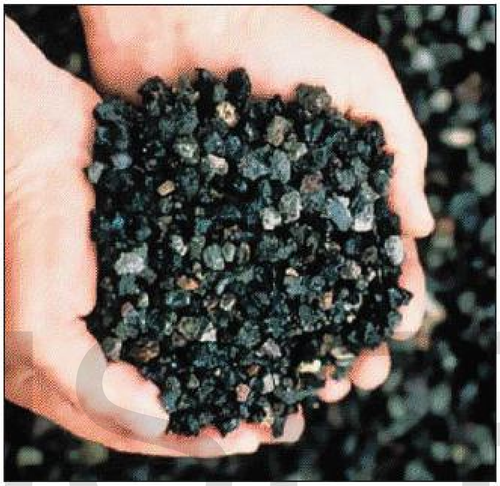


Figure 2: Bottom ash [14]

2.2.b Class C Fly Ash Applications

100% FA Concrete:

Fly ash categorized as Class C varies from its Class F counterpart by being composed of less SiO_2, Al_2O_3, and Fe_2O_3, between 70 and 50%. In its place is CaO, which gives the ash more favorable pozzolanic properties. In fact, the high calcium content leads to a better hydrogen reaction necessary for the solidification of the concrete when water is added [16]. This is such a strong force that some studies have shown it is possible to create concrete without Portland cement, using instead Class C fly ash.

A primary motivator for the use of 100% fly ash concrete is for environmental reasons. Production of ordinary Portland cement (OPC) is an energy intensive process which consists of mining raw materials, crushing, blending and heating said materials to temperatures of 1500 ^{o}C, and finally pulverizing the final product to a fine powder [16]. In fact, the production of 1 kg of Portland cement generates roughly 1 kg of CO_2 [17]. Therefore, it is very appealing for some projects to entirely avoid the use of Portland cement, and instead use 100% fly ash cement.

Three studies in particular have focused on the use of this new cement. Two of these were done by civil engineers at Montana State University (MSU) in 2005, and 2009. The latest study was from 2011 and done by Castle Rock Consultants. This study tested two mixtures. The first was composed of the fly ash, water, and borax to prevent flash solidification, while the second was more conventional, with fly ash, water, and an aggregate larger than fine sand but smaller than gravel [18]. In both cases, the fly ash concrete mixtures offered acceptable or superior strengths in comparison to the ordinary Portland cement, assuming a correct water to fly ash ratio, which turned out to be around 0.23 [18].

Both MSU studies provided equally encouraging results. In the 2005 report, engineers mixed concrete using traditional aggregates, 100% fly ash, and Borax to retard the setting time [19]. In 2009, researchers at MSU used both traditional aggregates, as well as pulverized glass aggregates in their mixture, along with borax [16]. In both cases the water to fly ash ratio was between 0.20 and 0.24, and in both cases good alternatives, in terms of strength and resistivity, to Portland cement were created [16,19].

The benefits of the use of 100% fly ash concrete instead of Portland cement are apparent. As already stated, the manufacture of Portland cement is an energy intensive process, and thus substituting this for recycling what would be a waste material is very environmentally friendly. Furthermore, because of the spherical shape of fly ash, the particles can flow over each other and ensure good workability, with reported slumps of 4 to 6 in [16,19]. This is despite relatively low water to cement ratios, as conventional Portland cement would be unworkable if mixed at a water ratio of 0.23. This in turn leads to the final benefit of 100% fly ash concrete, which is that it requires less water to mix. Less water contributes even more to the fly ash concrete's environmentally friendly nature.

Despite these benefits, there also exist problems with the use of 100% fly ash concrete. The primary issue is due to Class C fly ash's tendency to have high CaO content, generally around 28% [16,18,19]. This leads to flash setting of the cement, which is a big problem for workability and general use [16]. Nonetheless, this problem may be remedied through the addition of a retardant, such as borax, which slows the setting process [19]. Another apparent problem is that the finished concrete tends to have a 15 to 30% lower tensile strength than would be predicted based on its compressive strength [19]. Overall though, the use of 100% fly ash cement is an attractive alternative to using Portland cement, given the right conditions and materials.

Fly Ash as Additive to OPC:

A more traditional use of Class C fly ash in the world of concrete is to use it as an additive, rather than a total replacement, for Portland cement. In general, conventional ratios for concrete mixtures would be used, with a consistent cementitious material to aggregate ratio of 0.18 to 0.21, and the only difference being that a portion of the Portland cement is replaced by Class C fly ash. The degree of replacement varies by study, going from 21% [20] to as high as 70% [11]. Different levels of replacement lead to various compression strengths, drying shrinkage, and workability.

The importance of compressive strength in concrete production cannot be exaggerated. In a Turkish study, researchers found that mixtures containing 40% fly ash replacement yielded the best results for compressive strength, in comparison to their 50, 60, and 70% replacement mixes [11]. Furthermore, all fly ash mixes differed from the conventional control mixtures in that after 28 days, they continued to increase in strength significantly [11]. The Colorado State University study looked into lower percentages of fly ash, and found that in general, replacement of fly ash increases the ultimate strength of the concrete, and that 25-35% replacement provides the optimal strength increase [21]. This test mixed concrete from 0 to 50% fly ash replacement. In contrast to these two studies, research out of Tennessee suggested that 50% fly ash replacement is superior to 25%, as the compressive strengths for the high volume fly ash were slightly higher than those of the 25% replacement concrete [22]. This unconventionally high strength may have been due to the fact that chemical admixtures were used in the Tennessee study to increase workability and strength [22].

Drying shrinkage is the process of water that was not used in the hydrogen reaction seeping out, as it becomes useless. This can lead to cracks in the concrete, and should in general be minimized. Research from Greece shows that a 50% replacement of fly ash in concrete does reduce shrinkage, as can be seen in Figure 3 [23]. This may be the result of the decreased amount of water needed in high volume fly ash concrete, or a decreased need of cementitious paste required [22]. Whatever the cause may be, the results are supported in part by a study from Indiana, which compared 21% fly ash replacement cement to latex modified concrete (LMC) and micro-silica concrete (MSC). Researchers found that the fly ash concrete encountered less shrinkage than the LMC, but more than the MSC [20]. This is likely due to the fact that the LMC mixtures were only moist cured for two days, five fewer than the other two mixtures. Also, MSC and fly ash concrete were composed of larger aggregates than LMC [20]. Whatever the case, it seems like the addition of fly ash may decrease shrinkage, and would have no reason to increase it.

Workability is integral to the use of concrete in practical applications. The addition of water can increase the workability of a mixture without limit, but more important is how workable concrete is with the lowest possible water to fly ash ratio. Fly ash is spherical in nature, so in theory it should not require as much water to maintain high workability. This is demonstrated in the Tennessee study as the 25% fly ash mixture had a water to cement ratio of 0.40, and a slump of 10.8 cm while the 50% fly ash mixture had a ratio of 0.34 and a slump of 13.3 cm [22]. However, this does not seem to always be the case as in the Turkish study the fly ash used increased the required water level for the desired slump [11]. The results are inconclusive, but the theory suggests that, as it was with the 100% fly ash cement, the use of fly ash would decrease the required water for consistent workability.

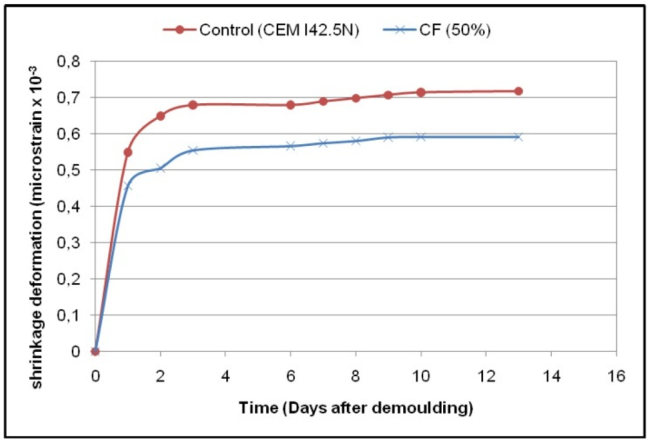


Figure 3: A comparison of the shrinkage of control and fly ash cement [23]

Fly Ash as Additive to Asphalt:

In addition to concrete applications, Class C fly ash may be used as an additive to asphalt. Researchers from Istanbul University tested this by comparing asphalt mixtures containing 5,6,7, and 8% fly ash to mixtures containing the same amount of filler [24]. They observed the greatest differences on two accounts, in stability and in optimal asphalt content. The 5% fly ash mixture maintained the highest stability of the ashes, and all the other ashes demonstrated a higher stability than any of the filler mixtures [24]. However, the filler mixtures each had a lower optimal asphalt content than their respective fly ash mixture, but as the percentage of filler increased, the optimal content also increased, while it decreased when raising the percentage of fly ash addition [24]. This is very significant as a higher optimal asphalt content translates to higher costs in production. The researchers also looked into flow and void values, as well as bulk specific gravity, but in all cases the differences between the filler and ash asphalts were negligible [24].

2.2.c Class F Fly Ash Applications

Fly Ash as Additive to OPC:

Fly ash categorized as belonging to Class F contains a larger ratio of SiO_2, Al_2O_3, and Fe_2O_3 compounds. This means that in turn it contains less CaO, leading to decreased pozzolanic use of the material. Nonetheless, studies have been done concerned with the use of Class F fly ash in Portland cement, replacing it in much the same way as Class C fly ash. The aggregates content was kept the same, and the only difference in design was the replacement of some of the cementitious material with fly ash. The rates of replacement varied from 20% to 50% [22].

Once again, compressive strength is an essential property for the testing and use of cement. In the case of Class F fly ash though, the results are not too promising. In a study from the University of California, a 22% by mass replacement of Portland cement by Class F fly ash yielded an 18, 11, 12, and 3% decrease in strength in comparison to control at 3, 7, 29, and 90 days [25]. These results are mirrored by a study from Italy, which shows concrete made with 30% fly ash demonstrate a lower compressive strength than control throughout the 180 day testing period [26]. In the two above tests, varying amounts of fly ash replacement yield very similar results. This trend seems to continue as a study testing the use of high volume fly ash mixed a 50% replacement concrete and found that its compressive strength throughout the testing period was very similar to 20% replacement cement [22]. Therefore, it seems like the very presence, rather than the amount, of Class F fly ash in cement is affecting the compressive strength of the mixture, and affecting it not in a positive way.

In the world of workability, it seems like Class F fly ash makes little consistent difference in the mixture. In one study, the fly ash mixture had a slump 2 cm greater than the control mixture [25], but in a second study, the fly ash mixture's sump was 4 cm less than control [26]. In both cases, the mixtures had a very similar water to cement ratio, and no superplasticisers were used. Therefore it seems like a similar statement can be made concerning Class F ash as with Class C, where studies conflict in the assertion that fly ash improves the workability of a cement sample. However, according to theory, the “ball bearing” mechanic of the spherical fly ash particles should help improve the workability of a mixture, or at least reduce the amount of water needed [22].

Fly Ash as Additive to Asphalt:

Class F fly ash may also be used as an additive to asphalt. A study from the University of Ohio compared asphalt mixes using fly ash and lime or lime kiln dust to those with cement, mill and fill, and lime kiln dust [27]. The study measured the resilient modulus, the elastic modulus, and the longitudinal and transverse strain of each of the mixes. In the resilient modulus test, results showed that the fly ash mixtures had lower strength values than the concrete mixes till the 10 month mark, but after that their strengths were on par with those mixes [27]. The fly ash mixtures were also far above the lime kiln dust and mill and fill mixtures. Similar results were found with the elastic modulus tests, where fly ash mixtures were compared to mill and fill, and it was found that the fly ash asphalt had a far higher modulus at every stage of the test [27]. These encouraging results continue as the fly ash and lime kiln dust mixture demonstrated minimal longitudinal strain, comparable to the concrete mixture [27]. The fly ash and lime was slightly behind, but still superior to the other mixes. In the transverse strain tests the fly ash and lime kiln dust demonstrated low strain, similar to the concrete mixture, and the fly ash and lime mix had strain similar to all the other mixes [27]. Overall, it seems like the use of Class F fly ash in conjunction with either lime kiln dust or simply lime improves the strength and reliability of asphalt.

Non-OPC Cement:

The production of Portland cement carries with it a heavy environmental toll. For every kilogram of cement, about one kilogram of CO_2 is also produced [17]. Therefore, an option is to shy away from the use of Portland cement, and in its place use geopolymers. A study from Mexico investigated the use of alkali-activated metakaolin in the production of OPC free cement, and the use of Class F fly ash as a cementitious additive to the mixtures [17]. The study also looked into the regulation of the density of the resulting concrete through the use of Al powder. When this powder comes into contact with a hydroxide and water, hydrogen gas is produced, which is entrapped within the cementitious material [17]. This increases the volume and thus reduces density. Lower density translates to lower overall dead weight that concrete adds the mass of a structure.

Compressive strength, flexural strength, and thermal conductivity were measured for all geopolymer mixtures, containing fly ash or not. For compressive strength, high density fly ash was proposed but could not be cured, as gas was lost after the hydrogen bubbles formed [17]. However, the lower density fly ash mixture showed similar strengths between the fly ash and the non-fly ash, and the low density mixture using fly ash had the highest strength after the first day. In the following days the mixtures stabilized to similar strengths [17]. For flexural strength, a similar trend appeared, where the mid-density mixtures had similar strengths, and the low density mix had higher early strengths for fly ash, but increasingly similar as time went on [17]. In thermal conductivity, results showed that overall the mixtures displayed higher values than those typical for these types of concretes, but this may be because of the water content in the concretes, or because of the relatively high amounts of quartz and cristobalite [17]. Overall, it is very possible to create environmentally friendly cement using geopolymers, and fly ash may be used as a partial replacement to maintain strength and even reduce costs.

2.2.d Application of Either Fly Ash

Through the incineration process, metals that would be a waste in combustion are captured in fly ash and appear in small percentages. Common metals found in the ash include Cd, Zn, Cu, and Pb. Various methods exist for the extraction of these metals, but the most popular are through acid leaching, electrolysis, or bacterial colonies. Through these processes, the metals may be removed from the ash, and in some cases the ash may still be used for other processes afterwards, such as an additive to asphalt or cement.

Acid leaching is where ashes are mixed with strong acids, then are filtered and washed to remove the trace metallic elements [28]. This process was tested with Turkish coals and ashes, using sulfuric acid at pH 1.0 for 14 days [28]. The results were mixed, with generally higher success with the ashes than the coals. For example, Cd, Cu, Zn, and Th were extracted to nearly 80% in the ashes, but considerably less from the coals [28]. On the other hand, Co and Ni were also extracted to 60%, and the percentage of extraction from the coals was similar to those of the ashes [28]. Another study from Germany focused exclusively on the recovery of zinc from filter ash. The first step in the process was acid leaching using acidic and alkaline fluids that kept the pH from 3.8 to 4.2 [29]. After this, the ash underwent an electrolysis extraction, which was able to achieve a zinc depletion rate of 99.8% [29].

Electrolysis extraction may be used in conjunction with acid leaching, or on its own as an effective metals recovery method. The process of electrodialytic remediation is shown in Figure 4. The ash is suspended in an aqueous solution in the middle compartment, which is separated from the other two compartments by ion exchange membranes [30]. When current is run through the system, the metallic ions will migrate to either compartment I or III, and from there they may be precipitated or separated by conventional methods [30]. This general process was used in a study from Denmark, with inconsistent results. In successive experiments, the extraction rate of Pb dropped from 8% to 2.5%, and the rate of Zn fell from 73% to 24% [30]. In both tests though, approximately 70% Cd was recovered [30]. Another study from Portugal presented low yields of extraction. The most successful recovery rate was Pb at 30.7%, but all other metals, Zn, Cu, and Cd, had extraction percentages lower than 10% [31]. Despite these discouraging results, an advantage that electrolysis and acid leaching holds is the recovery of ash after the fact. After extraction, the ash may be washed and leached, and then used in other applications [30]. The extraction of metals does not inhibit fly ash's pozzolanic properties, so it may still be used in concrete or in asphalt.

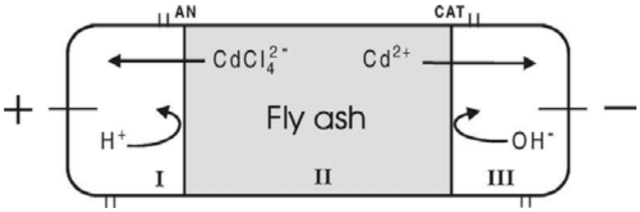


Figure 4: The basic electrolysis process [30]

A final method of extracting metals from ash is through the use of bacterial colonies. A study from Switzerland used a mixed culture of *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* to leach and mobilize metals through redox reaction, formation of inorganic acids, and excretion of organic acids [32]. These three processes coupled together proved to be very effective, with high extraction percentages across a large range of metals. Zn was recovered at 81%, Cu at 89% and Cd was completely extracted [32]. Ni, Al, and Cr yielded slightly lower percentages, at 64, 52, and 12% respectively [32]. It is encouraging to have such a high yield of metals, but using this bacterial extraction, the ash is rendered useless for further recycling. Depending on the situation, one would have to choose between high extraction and continued recycling.

2.2.e Applications of Bottom Ash

Bottom Ash as Additive to OPC:

Bottom ash is distinct in appearance, but not in chemistry to fly ash. The former is far larger, with jagged edged particles while the latter is made up of spherical, far smaller particles. However, because of their similar chemistry, applications of fly ash may be transferred to bottom ash as long as certain modifications are made, such as size reduction. In the world of ordinary Portland cement, bottom ash finds three applications. It may be used as a pozzolanic material, as a fine aggregate, or as a coarse aggregate. Various studies have been done investigating all these applications.

Bottom ash, viewed from a fly ash standpoint, would be classified as Class F fly ash. It has low CaO content, and is made up of over 70% SiO_2, Al_2O_3, and Fe_2O_3 [15,26,33]. In order to be used as a pozzolanic material, the ash is ground to 45um, either through wet or dry grinding [15]. The grinding process not only reduces the size, but also the porosity and finishes with a very jagged, irregular particle [15]. This particle shape leads to reduced workability and a higher optimal water to cement ratio. Another problem encountered through the use of bottom ash as a replacement to Portland cement is dry ground particles would have unreacted particles of aluminum which would react and lead to bubbles of hydrogen gas within the cement [26]. This reduces the concrete's strength and durability. This problem through may be avoided by using wet grinding techniques instead of dry ones [26]. Despite these problems, ground bottom ash is a promising additive to Portland cement. At replacement rates of 30 and 20%, bottom ash was seen to lead to improvements in compressive strengths when compared to the concrete control [15,26]. The bottom ash also reduces the permeability of concrete, even more than when the same amount of fly ash is used [26].

Instead of replacing the cement, bottom ash may also replace the fine aggregate of a concrete mixture. Researchers from Brazil tested this proposition, following replacement rate from 0 to 100% [33]. Because of the ash's high porosity, two addition methods were used, the first being by equivalent volume replacement, and the second through non-equivalent volume replacement, which led to a greater quantity of cement needed and less fine aggregate used [33]. These two mix methods led to significantly different results. The high porosity of the ash meant that water was absorbed internally by the bottom ash and then released to the concrete over time [33]. This led to significant losses in compressive strength for the first mixture, but a decrease in total deformation. On the other hand, the latter mix maintained compressive strengths similar to the concrete control, but had increased plastic shrinkage due to the greater quantity of cement [33]. In both cases there were problems, but overall the tests showed that when using bottom as a fine aggregate, one should use non-equivalent volume replacement.

Due to its large size, bottom ash may also be used as coarse aggregate, replacing 2-32 mm gravel or stones [34]. However, raw bottom ash contains compounds that are harmful to concrete, such as chlorides and sulphates or aluminum [34]. These can harm the concrete and can also prove problematic for recycling. Therefore, the waste materials are removed via various means. Organic compounds and free lime were removed by increased sieving and washing, waste glass was removed by opto-mechanical separation, and the aluminum content was reduced to 0.4%, and chlorides and sulphates almost completely eliminated by lye treatment [34]. After the refining processes, the ash may be used as conventional coarse aggregate. Compressive strength of the bottom ash concrete matches easily that of normal strength concretes, and the positivity is nearly doubled by the use of the new aggregate [34]. Therefore, if the harmful substances can be removed, bottom ash is a very appealing coarse aggregate for normal strength concretes.

Bottom Ash as Additive to Asphalt:

Bottom ash has seen applications in asphalt mixtures. A study from Michigan replaced 9% of the conventional mineral filler with bottom ash, and compared it to a control mixture [35]. They found that the dynamic modulus of the bottom ash mixture was lower than that of the control [35]. Such a lowered dynamic modulus may lead to an increased rutting potential. Researchers also found that because of bottom ash's high absorption, the optimal binder content rose from 5.6 to 9% [35]. To solve these problems, it is recommended that the absorption value of the bottom ash is tested before the production of the asphalt, and lime be added to the mixture to improve its rutting resistance [35]. Despite these setbacks, past studies have suggested that the addition of bottom ash has generally improved structural stability, moisture susceptibility, and skid resistance [35]. These, in addition to the fact that recycling what would be waste bottom ash is both economically and environmentally favorable, put asphalt additions as a very appealing use of bottom ash.

2.3 Properties of carbonic residues

2.3.a Graphite

Graphite is a black, lustrous carbon mineral crystallizing in the hexagonal system, with rhombohedral symmetry [36]. The crystal consists of layers of carbon atoms in the form of fused benzene rings, each atom being symmetrically related to three nearest neighbours in the plane [37]. The planar structure is stabilized by resonance and the mobility of the electrons in the plane results in significant electrical conductivity in the planar directions. In particular, most synthetic graphites contain 10-30% of a slightly less stable rhombohedral form in which the stacking sequence of the layers in ABC rather than AB [38]. Figure 5 shows the layer sequencing in detail.

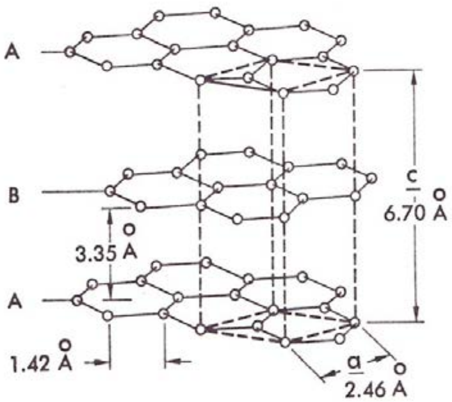


Figure 5: Graphite structure [39]

The specific gravity of graphite is 2.1 to 2.3. Chemically, if one was to heat up a mixture of one part graphite with three parts potassium chlorate and sufficient concentrated nitric acid in hot water bath for several days, the graphite will be converted into golden yellow flakes of graphitic acid [37].

Graphite mineral is easily sectile, flexible but not elastic. It is also greasy to the touch and is a good conductor of heat and electricity. The specific resistivity of natural graphite is 35 to 40, where amorphous carbon is 150 [36]. Graphite is resistant to attack by most chemical reagents. Fusion with alkaline carbonates produces carbon monoxide, which puffs through molten material and ignites as fast as it is formed. Graphite is not affected by dry chlorine gas, hydrochloric or hydrofluoric acids [38].

2.3.b Lamp / Carbon black

Lampblack is known under the names of gloss soot, light soot, flame soot, and flame black. It is the smoke from an unobstructed hydrocarbon flame, the solid particles being deposited in chambers to which the smoke is conducted through flues from the furnaces. Lampblack is carbon of a particular and peculiar kind. Typically less than 60% of the total particle mass of lamp black is composed of carbon. Lampblack is amorphous carbon. The surface structure of the lampblack particle is neutral, free of the complex carbon-oxygen groups found in most pigments. This is understandable since the particle is formed in a vapour containing practically no oxygen. Lampblacks not specially treated have pH values of 2.5 to 5.0 [40]. Early in its history, lampblack was the most important printing ink pigment, but it has not been largely displaced in this particular field by carbon black.

Carbon black is produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions. Its physical appearance is that of a black, finely divided pallet or powder. Carbon black contains greater than 97% elemental carbon arranged as aciniform particulate [41,42]. Carbon black is mainly crystalline with some amorphous particles blended in. The average particle size of carbon black is from 20 to 30 nm. Carbon black is often referred to as gas black, ebony black, jet black, hydro carbon black, satin gloss black, and silicate of carbon. It is shown that the pH of carbon black is from 6 to 9 [43].

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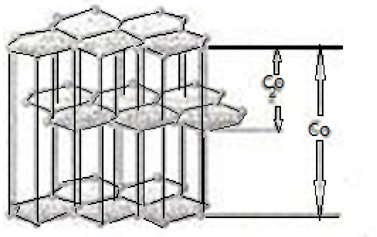
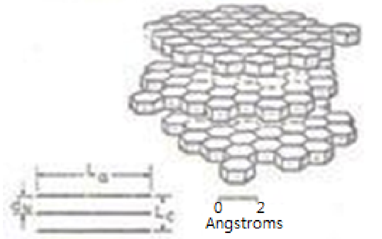


Structure of Graphite



Scale model of carbon black crystallite showing three parallel sheets of hexagonal groupings of carbon atoms

Figure 6: Graphite vs. Carbon Black in crystal structure [44]

The diameter of spherical particles is the fundamental property which largely affects blackness and dispensability when carbon black is mixed with resins or other vehicles. In general, the smaller the particle size is, the higher the blackness of carbon black becomes. Dispersion, however, becomes difficult due to an increase in coagulation force.

Like particle size, the size of the structure also affects the blackness and dispensability of carbon black. Generally, the increase of structure size improves dispensability but lowers blackness. Carbon black with a larger structure in particular shows an excellent conductive property. Various functional groups exist on carbon black's surface. The affinity of carbon black with inks or paint varnishes changes depending on the type and amount of the functional groups. Carbon black, with a large amount of hydroxyl group given with oxidation treatment, has a greatly enhanced affinity to print inks or varnishes, showing excellent dispensability [45].

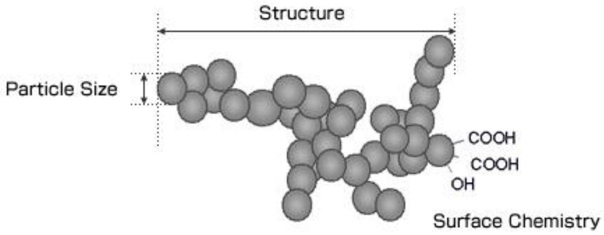


Figure 7: Carbon black under electron microscope [45]

In the simplest terms, carbon black is essentially elemental carbon in the form of extremely fine particles having an amorphous molecular structure. Buried within the amorphous mass is an infrastructure of microcrystalline arrays of condensed rings. These arrays appear to be similar to the layered condensed ring form exhibited by graphite, which is another form of carbon [46]. The orientation of the arrays within the amorphous mass appears to be random, and consequently a large percentage of arrays have open edges of their layer planes at the surface of the particle. Associated with these open edges are large numbers of unsatisfied carbon bonds providing sites for chemical activity. In use, particles remain largely intact and many of the useful properties of carbon black stem from their morphological characteristics while others result from surface activity [47].

All carbon blacks contain carbon-oxygen species that are formed during combustion of the hydrocarbon source. These species can be removed by heating at high temperature in a vacuum or reducing atmosphere, where the oxides are desorbed as CO, CO_2, and H_2O; hence the term "volatiles." The oxide-free carbons are more hydrophobic and have an electronic conductivity much higher than that of the original carbon samples [48].

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It is noteworthy that removal of the surface oxides increases the conductance of the original black by a much greater amount than does the heat treatment to produce graphitization [46]. This indicates that the major component of electrical resistance of carbon powder is the particle to particle contact resistance rather than the bulk resistance of the carbon. The removal of surface oxides is generally irreversible, and reoxidation is extremely slow at room temperature [45]. After formation of the carbon particles, some commercial carbon blacks are oxidized by air at 600C to increase porosity and jetness for use in inks. These carbon blacks may contain up to 15% volatiles, compared to the normal amount which is <5% [48].

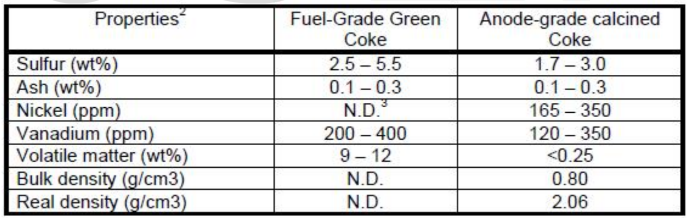
Other than carbon, also present are very small quantities of other elements such as oxygen, hydrogen, and sulfur occurring in various functional groups bound to the carbon mass. In addition, small quantities of condensed hydrocarbons are adsorbed onto the particle surface of most rubber grade carbons [46].

In surface area and particle size, the surface area of carbon blacks may vary from <10 to >500 m²/g, corresponding to particle sizes of >800 to <100 angstrom in diameter [48]. The surface area of carbon blacks is generally determined by gas adsorption and electron microscopy. The agreement between the surface areas obtained by the two methods is seldom good [41]. The gas adsorption measurement takes into account the roughness, porosity, and irregularities in the carbon particle, whereas the surface area obtained from electron microscopy is generally calculated on the assumption that the particles are spherical and nonporous [48]. A chemical and thermal analysis of surface groups on carbon blacks may be found in Appendix 1.

2.3.c Petroleum Coke

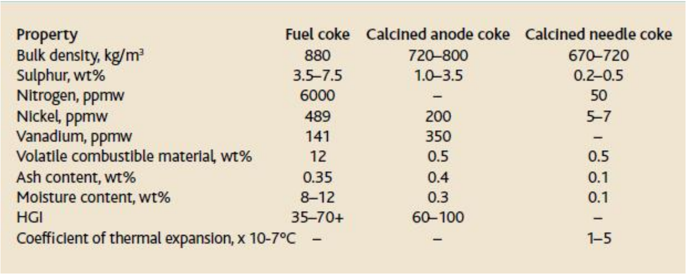
Petroleum coke is formed as the solid residue of the destructive distillation (heating to a high temperature; removing organic materials) of petroleum products whenever these products are heated above their decomposition temperatures [49]. In appearance, petroleum coke is somewhat similar to that made from coal and ranges in color from dark grey to black. Petroleum coke is composed primarily of elemental carbon organized as a porous polycrystalline carbon matrix [50].

Petroleum cokes can be categorized as either green or calcined coke. The initial product of the coking process, green coke, is used as fuel, in gasification and metallurgical processes, or as feedstock to produce calcined coke. Calcined coke is produced when green coke is treated to higher temperatures, from 1200 to 1350°C [50]. Tables 3 and 4 show specifications of different types of petroleum coke. These tables will aid as a reference as further testing on the sample may be conducted in the future.



Properties[2]	Fuel-Grade Green Coke	Anode-grade calcined Coke
Sulfur (wt%)	2.5 – 5.5	1.7 – 3.0
Ash (wt%)	0.1 – 0.3	0.1 – 0.3
Nickel (ppm)	N.D.[3]	165 – 350
Vanadium (ppm)	200 – 400	120 – 350
Volatile matter (wt%)	9 – 12	<0.25
Bulk density (g/cm3)	N.D.	0.80
Real density (g/cm3)	N.D.	2.06

Table 3: Comparison of Green and Calcined Coke Comparison [5]



Property	Fuel coke	Calcined anode coke	Calcined needle coke
Bulk density, kg/m³	880	720–800	670–720
Sulphur, wt%	3.5–7.5	1.0–3.5	0.2–0.5
Nitrogen, ppmw	6000	–	50
Nickel, ppmw	489	200	5–7
Vanadium, ppmw	141	350	–
Volatile combustible material, wt%	12	0.5	0.5
Ash content, wt%	0.35	0.4	0.1
Moisture content, wt%	8–12	0.3	0.1
HGI	35–70+	60–100	–
Coefficient of thermal expansion, x 10-7°C	–	–	1–5

Table 4: Specifications for three grades of coke [50]

CHAPTER 3. LAB ANALYSIS OF THE SAMPLE.

3.1 Introduction

Prior to receiving a sample of the carbon ash, research was done assuming that the ash would be either be in the form of fly or bottom ash. This chapter presents the tests done once the sample was received, and the findings brought about by those tests. Based off of information from the X-ray diffraction and the LOI tests, it was found that the carbon ash was far from bottom or fly ash, and instead was made up mostly of carbon. This opens a new wealth of possibilities to potential applications of the product.

3.2 Microscopic investigation

An examination of the material through an optical microscope is shown in Figure 8 and Figure 9. The general size of the sample is around 100 to 200 µm in diameter. The material is generally spherical and porous. These qualities suggest that the ash may have electrochemical applications.

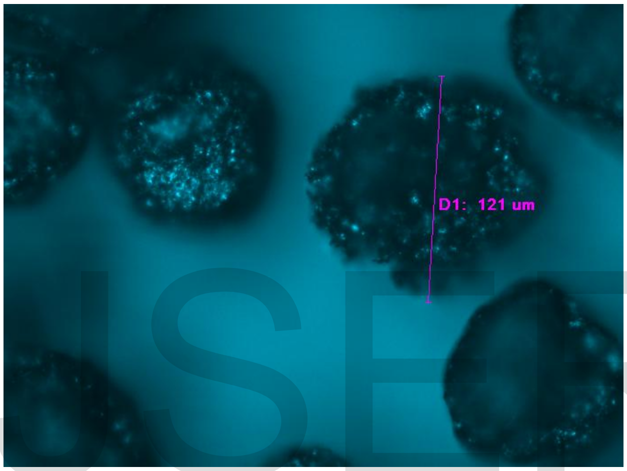


Figure 8: Optical microscope screen capture under 20X magnification

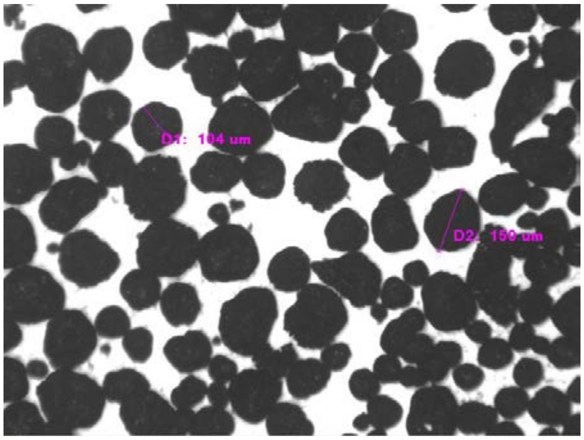


Figure 9: Optical microscope screen capture under 5X magnification

3.3 Moisture and loss on ignition test

Moisture and a loss on ignition (LOI) test were performed following ASTM C311 and CSA A3003-08-9.4 standards [51,52]. The results indicated that the moisture content of the ash was 2.6%, and that 99.9% of the ash combusted after roughly two hours. What remained in the crucible was little enough that it was not detected by the scale, accurate to two decimal places, used. The full results are shown in Figure 10. The mass of ash dips below zero upon conclusion of the test. This is because mass was taken of the hot crucible from the oven. Because of its heat, the air around it rose and made the mass reading less than it actually was. However, after cooling, the mass reached what was originally recorded for only the crucible. It should also be noted that in the LOI test, both the ASTM and CSA procedures suggest the use of a desiccator during cooling to prevent moisture accumulating on the final product [51,52]. During the tests though, this desiccant was unavailable, so the actual mass of the residue may be slightly less than what was recorded. In the end, the loss on ignition test showed a trend that suggests the material contains high percentage of carbon.

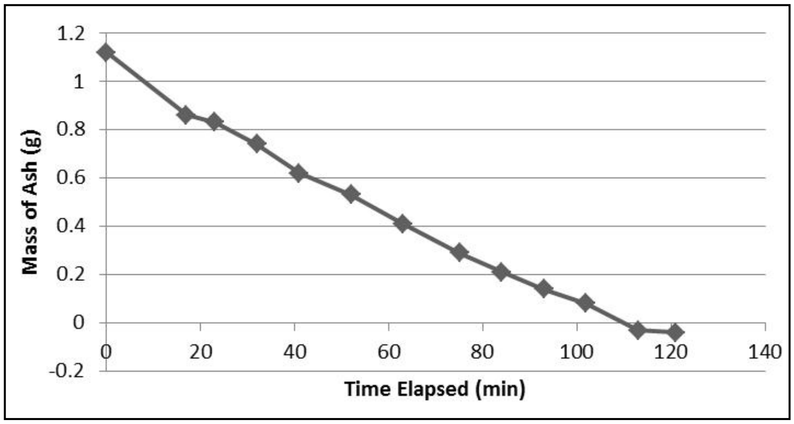


Figure 10: LOI Test

3.4 X-ray diffraction test

The X-ray diffraction (XRD) analysis test result shown on Figure 11 suggests that the material is composed of carbon. There is no evidence of any other crystalline compounds. However, the fact that the (0002) peak is shifted left, and rather broad, indicates a non-graphitic carbon. It is suspected that the material is composed primarily of sp2-hybrid carbon parent material and some degree of graphene layering [53].

It is noteworthy to compare figures 11, 12 and 13. Figure 11 shows the diffraction pattern of the carbon ash sample, and Figures 12 and 13 exhibit very similar patterns to Figure 11. The peak at 002 and the shift of the peak suggest that the material is very similar to unheated carbon black. Furthermore, as suggested from Chapter 2.3.b, the porosity of the material suggests that the material might be closer to carbon black.

3.5 Metal and ammonia analysis.

The metal and ammonia analysis shown on Appendix 1 suggests that the impurities in the sample due to either of these compounds are minimal. In fact, that metal impurities in the sample only make up 0.03% of the ash by weight, and there are only 9.7 parts per million of ammonia. This suggests that the material is potentially high purity carbon, which is highly valued in many industries [54].

The metal analysis shows that the metals in the sample are mostly chromium, iron, magnesium, nickel, and vanadium. The idea of incinerating the ash to attain these metals was raised. However, given the fact that only 0.03% of the mass of the ash is due to the presence of the metals makes said proposition unfeasible. By burning 1 metric ton of the ash, it is theoretically possible to achieve 300 grams of the metal mix. The metal analysis shows that out of 300 grams, there is 141.17 grams of Iron, 50.18 grams of Vanadium, 34.47 grams of Magnesium, 19.96 grams of Nickel, and 18.5 grams of Chromium. It appears that the extra cost involved to extract these metals dominates over the possible profit from the extraction. Therefore, the idea of metal extraction from the ash is not feasible.

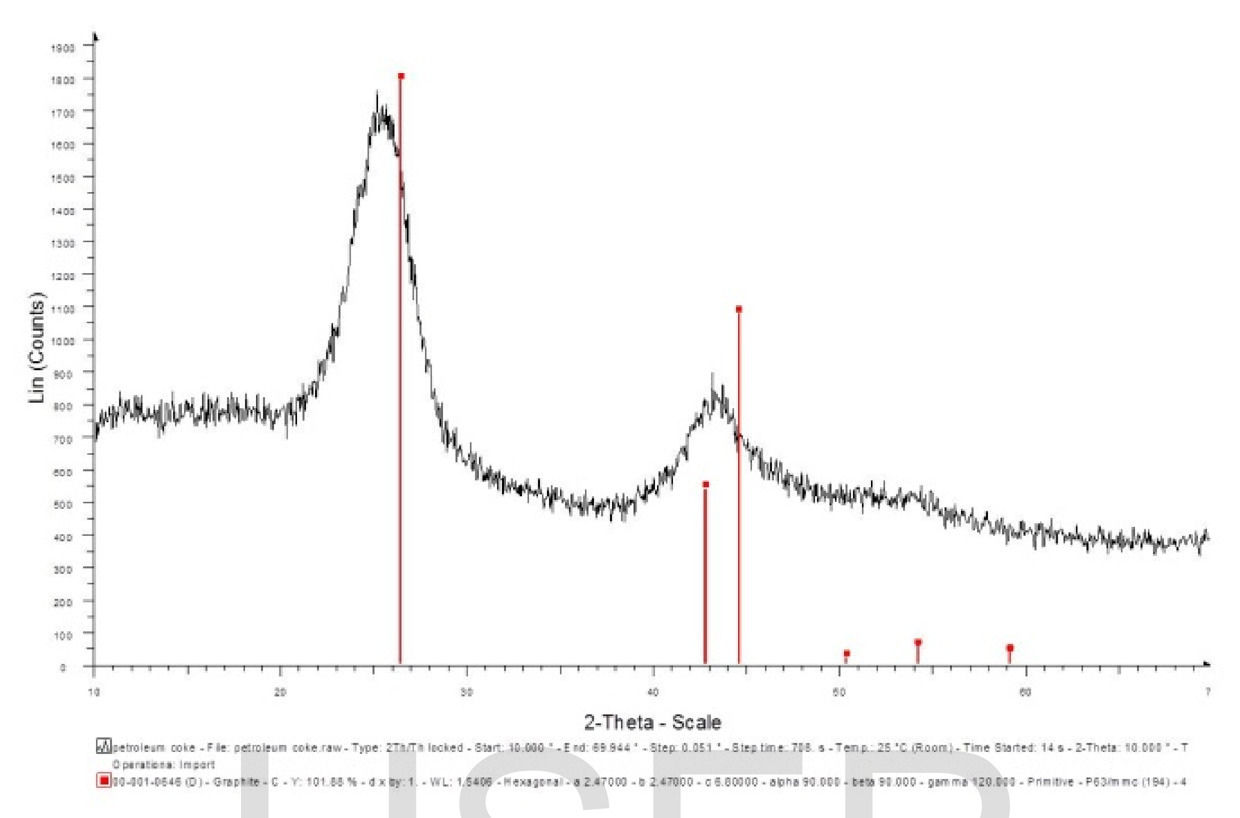
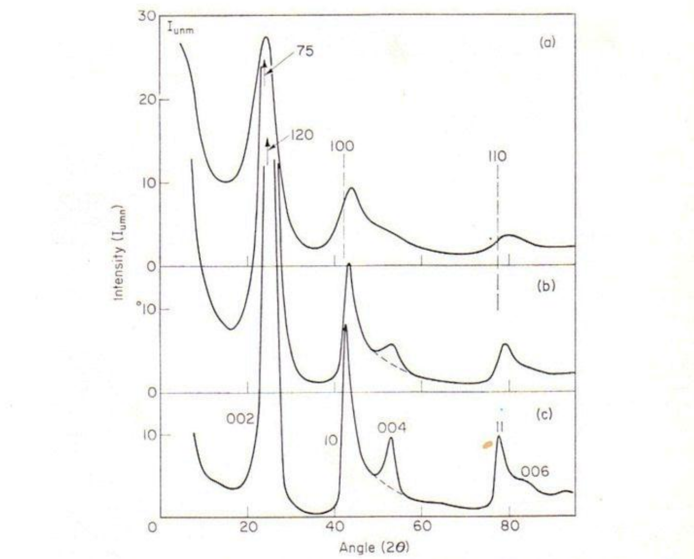
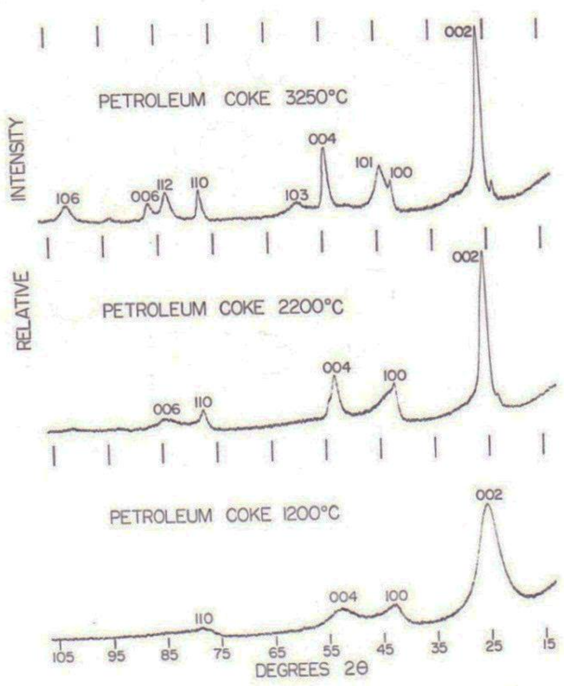


Figure 11: XRD test result



Intensity curves for three carbon black samples. (a) Spheron grade 6 black, unheated; (b) same black, heated 2 hr at 1500°C; (c) same black, heated 2 hr at 2800°C. Radiation Cu *Kα*. For all three curves, the Compton modified scattering has been subtracted.

Figure 12: XRD results of carbon black [36]



Diffraction pattern of a petroleum coke after heating to successive temperatures.

Figure 13: XRD result of petroleum coke [37]

3.6 Conclusion

Although further analysis must be done to concretely determine the material’s classification, an expert from the carbon industry has advised that it is very probable that this material is a highly valuable raw material [53]. Figures 12 and 13, which are XRD results of both valuable carbon products, show significant similarity to the XRD result in Figure 11. Therefore, it is imperative to pay attention to feasible solutions which involves treating the material as high quality raw material such as carbon black, graphite, or petroleum coke.

CHAPTER 4. CHALLENGES IN REUSING BY-PRODUCTS FROM FOSSIL FUEL POWER PLANT

4.1 Problem definition

Fossil fuel power generators leave unavoidable residue from the incineration, and it is becoming increasingly difficult to find landfill sites to dispose of the waste. This has not only become a practical issue, but a serious environmental issue as well. Therefore, a study has been done to look for better ways to recycle or consume the waste material.

4.2 Overview of plausible solutions

4.2.a Graphite

Crucibles:

A good crucible must have strength, refractoriness, heat conduction, the capability of being used for the melting of many metals, and resistance at high temperatures to molten materials. The graphite contributes toward the refractoriness and heat conductivity of the mass, and produces a smooth surface for pouring. The clay is bonding material which makes possible the forming of the crucible and the cementing of the graphite. At the same time it covers them and prevents their oxidation. The particles of the graphite are desired to be smaller than 20 mesh. Larger graphite particulates can be rounded in burr stone mills.

Lubricating Graphite:

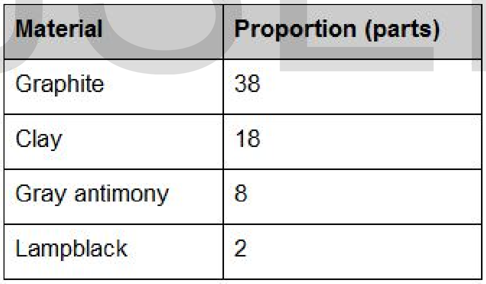
The low coefficient of friction of graphite is retained under practically all working conditions. It is soft and readily adheres to metallic surfaces, even under light pressures. The surfaces of bearings lubricated with graphite acquire with a veneer of the material which reduces the bearing coefficient of friction to that of graphite. The veneer on bearing surfaces tends to protect these from the action of corrosive solutions or vapors. This applies to cylinder lubrication where high pressure steam, oil, or gas is used [37]. Oil and grease lubricants under these conditions tend to lose body or to char or vaporize under the action of the heat and the gases to which they are exposed. In heavy bearings, oils and greases show a tendency to squeeze out from between surfaces [37]. The metal parts come in contact and are subjected to wear. Graphite, forming a coating on both metal surfaces, allows a graphitic contact, instead of metal contact, to be secured [38].

For lubrication in open bearings, slides, gears, and similar places, the graphite is mixed with oil or grease. Many such lubricants are designed for work under conditions such as exposure to salt water, acids, or alkalies, in dredges, winches, and mining machinery, or at different temperatures where varying degrees of viscosity are required [39]. Artificial graphites are purer and more capable of being reduced to an impalpable powder. As a result, they will remain in suspension in oil more easily than the natural flake graphite [37].

Pencils:

Pencils are simply made with a mixture of finely ground graphite and clay, which has a consistency of a thick paste. The paste is molded, and then it is baked. The process makes a much more uniform product than using graphite alone [37]. Changes of the proportions of clay and graphite in the mixture allowed the production of varying degrees of hardness.

Soft amorphous graphites are used in pencil making. They may be more readily ground to a powder of a uniform particle size. Flake graphite, no matter how finely ground, still preserves its flake or lamellar form. The mixture described in table 5 is used for very hard drawing pencils [43].



Material	Proportion (parts)
Graphite	38
Clay	18
Gray antimony	8
Lampblack	2

Table 5: An example of graphite and clay mixture for pencil production

Graphite Packing:

Graphite is employed in engine packing, hard rubber, cord and twine, hat polishing, floor coverings to eliminate static, cordage, ropes, cables, washers, and packing, particularly for piston type machines. Mixed with lead, it forms a suitable high pressure corrosion resistant packing [44].

Graphite slabs are used in flattening window glass. The slab is made by 1 to 2 parts of fire clay, 1 to 2 parts of grog, and 1 to 2 parts graphite. They are mixed dry, screened, and pugged to a stiff paste. The mass is aged for a few days, pugged, and aged. The slabs are molded in a wooded frame, the working surfaces being fine clay place in the bottom of the mold. Filling is continued with coarse material. The slabs are dried, baked and polished successively with we sand, finely ground grog, and pumice stone or talc [36,37].

Electrochemistry:

Graphite also plays significant role in electrochemical industries. Consider the tables in Appendix 1 for its applications and benefits.

For example, consider low temperature fuel cells. The development efforts on fuel cells have focused on five systems, which are often designated by the electrolyte that is employed. These fuel cells are referred to as (a) solid polymer electrolyte (also proton-exchange membrane) fuel cell, (b) alkaline fuel cell, (c) phosphoric acid fuel cell, (d) molten carbonate fuel cell, and (e) solid oxide fuel cell.

The generic list of fuel cell is presented in roughly the increasing order of their operating temperature. Because carbon undergoes rapid chemical reaction at the elevated operating temperatures of molten carbonate (~650 ^{o}C) and solid oxide (~1000 ^{o}C) fuel cells, its use in these system is avoided. The other three fuel cell systems operate with aqueous electrolytes, and at much lower temperatures (<200 ^{o}C), where carbon (or graphite) is an acceptable material of construction for electrode substrates, electrocatalyst supports, bipolar electrode separators, current collectors, and cooling plates [37]. Carbon is a critical material in fuel cells, particularly phosphoric acid fuel cells, since no other practical material has the necessary properties of electronic conductivity, corrosion resistance, surface properties, and low cost, which make an inexpensive fuel cell a reality. The two major electrochemical applications for carbon in fuel cells are (a) electrocatalyst support for electrodes and (b) conductive phase in bipolar electrode separators. Carbon blacks are commonly used in the former application, while graphite powers are commonly used in the latter application. In addition, carbon paper or other porous carbon material is often used for the backing layer on which the catalyzed carbon is placed [36].

4.2.b Carbon black

Tires and Industrial Rubber Products:

Carbon black is added to rubber as both a filler and as a strengthening or reinforcing agent. For various types of tires, it is used in inner liners, carcasses, sidewalls and treads, depending on the specific performance requirements. Carbon black is also used in many molded and extruded industrial rubber products, such as belts, hoses, gaskets, diaphragms, vibration isolation devices, bushings, air springs, chassis bumpers, and multiple types of pads, boots, wiper blades, fascia, conveyor wheels, and grommets [41].

Plastics:

Carbon blacks are now widely used for conductive packaging, films, fibers, moldings, pipes and semi-conductive cable compounds in products such as refuse sacks, industrial bags, photographic containers, agriculture mulch film, stretch wrap, and thermoplastic molding applications for automotive, electrical/electronics, household appliances and blow-molded containers [41].

Electrostatic Discharge (ESD) Compounds:

Carbon blacks are carefully designed to transform electrical characteristics from insulating to conductive in products such as electronic packaging, safety applications, and automotive parts [41]. Carbon black particles have the graphite-type crystalline structure, providing an excellent electric conductivity. Therefore, carbon black is widely used as conductive filler, being mixed in plastics, elastomer, paints, adhesives, films, and pastes. Fuel caps and fuel-introducing pipes of automobiles, for example, are required of electric conductivity for preventing static. Therefore, carbon black is used as an excellent antistatic agent [45]. Carbon black also provides stable resistance, and therefore is used as electronic equipment related material in various display components, magnetic recording materials, and OA rolls.

High Performance Coatings:

Carbon blacks provide pigmentation, conductivity, and UV protection for a number of coating applications including automotive (primer basecoats and clearcoats), marine, aerospace, decorative, wood, and industrial coatings [41].

Resin and Film Coloring Agents:

Carbon black has high tinting strength and is thermally stable, and therefore it is suitable for coloring resins and films that are heat-formed. It is also excellent for absorbing ultraviolet light, providing both a superb resistance against ultraviolet rays and a coloring effect when just a small amount is mixed with resins. Carbon black is widely used for general coloring for resins and films. Resins with carbon black are used in automobile bumpers, wire coverings and steel pipe linings which require weather resistance in particular [45].

Toners and Printing Inks:

Carbon blacks enhance formulations and deliver broad flexibility in meeting specific color requirements [41].

Carbon black has higher tinting strength compared to iron black or organic pigments, and is widely used for newspaper inks, printing inks, India inks, and paints. Carbon black is also used as black pigment for inkjet ink or toners [45].

4.2.c Petroleum Coke

Batteries:

Petroleum coke used for battery filler is a selected grade having low ash content, with objectionable metallic impurities absent. It is calcined to various degrees to bring the resistivity to the required point by partial or complete graphitization. The carbon content of the battery filler acts as an extension of the positive electrode, carrying the current through the depolarizing agent to the negative pole [49]. Several manufacturers of dry-cell batteries in the United States purchase the necessary electrodes and battery filler from the various carbon or graphite companies. Petroleum coke, calcined and milled, is sold as battery filler at prices ranging from $50 to $60 a ton [49].

Active Carbon:

Active carbons are high-surface area, high porosity carbons that are produced by two principal methods: thermal activation and chemical activation. Thermal activation involves heating a previously charred material at high temperature in the presence of an oxidizing gas such as steam. Chemical activation involves heating a mixture of the raw material and dehydrating agent to temperatures from 200 to 650 ^{o}C. After carbonization, the dehydrating agent is leached out and reduced. The three dehydrating agents that are most commonly used are H_3PO_4, $ZnCl_2$, and H_2SO_4.

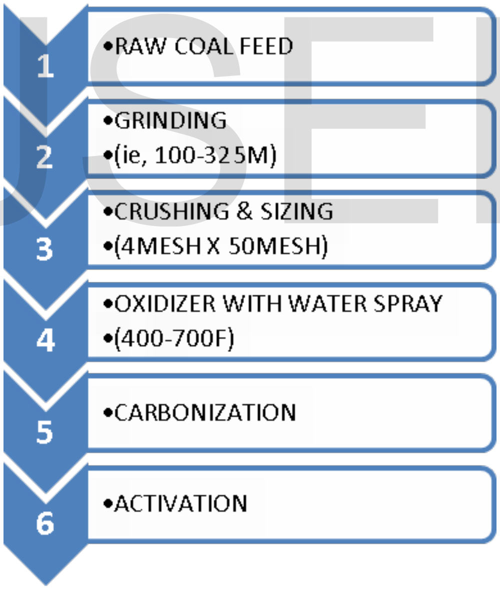


Figure 14: Process for making activated carbon [55]

The raw materials for active carbons are principally sawdust, coconut shells, black ash, charcoal, lignite bituminous coal, and petroleum coke. Charcoals are produced by heating wood or other solid organic matter in the absence of oxygen. Activated charcoals are prepared by heating the carbonized materials in the steam at 900 ^{o}C followed by exposure to air at 400 ^{o}C to produce surface oxides similar to that found in carbon blacks [48]. This method produces an amorphous carbon that is not graphitized to any extent, and it may not even be completely carbonized since charcoals contain rather high hydrogen content, approximately 5%. Depending on the source of the raw material, the ash content of active carbons can be quite high (15 to 20%) [48]. The ash is often water soluble, but active carbons from lignite, wood, or coal contain ash consisting mainly of silica and insoluble silicates that are removed by treatment with hot, strongly alkaline solutions [56].

The surface area of active carbons may be extremely high, ranging from 450 to over 1000m^2/g, in the case of activated charcoals. The pore structure of activated charcoals can be quite well defined, and the pore distribution can be very narrow. For instance, in coconut charcoal almost the entire pore volume is in pores with diameters from 10 to 20 angstroms [56].

An important difference between active carbons and carbon blacks is their agglomerate structure. Carbon-black agglomerates are formed during the manufacturing process by fusion of smaller particles, whereas charcoal agglomerates are formed by grinding larger particles to a finer particle size. The typical agglomerate size of charcoals may be 2 µm or greater, which is considerably larger than that for carbon blacks [56].

The major applications for active carbon involve its excellent properties as an adsorbent. They are used for solvent recovery, gas refining, air purification, exhaust desulfurization, deodorization, and gas separation and recovery. Active carbons are also used extensively for liquid-phase adsorbents in water treatment, decolourization of solutions, and collection and recovery of solutes. A third major use for active carbons is for catalysts and catalyst supports [48].

4.2.d Carbon as fuel

Much like the combustion of petroleum, through which the carbon ash is a by-product, the carbon itself may undergo combustion to generate energy. The oxidation of carbon is an exothermic process, and follows the chemical formula $C + O_2 \rightarrow CO_2$. The spontaneity of the reaction may be determined by using standard equations to determine enthalpy and entropy change. These calculations may be seen in Equation 1, and the standard enthalpies and entropies of formation may be seen as a table in Appendix 1.

$$\begin{aligned}\Delta H^\circ &= \sum H^\circ{}_f(products) - \sum H^\circ{}_f(reactants)\\ &= \left(-393.5\frac{\mathrm{kJ}}{\mathrm{mol}}\right) - \left(0\frac{\mathrm{kJ}}{\mathrm{mol}}\right)\\ &= -393.5\frac{\mathrm{kJ}}{\mathrm{mol}}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \sum S^\circ(products) - \sum S^\circ(reactants)\\ &= \left(213.7\frac{\mathrm{J}}{\mathrm{K\cdot mol}}\right) - \left(5.74\frac{\mathrm{J}}{\mathrm{K\cdot mol}} + 205.1\frac{\mathrm{J}}{\mathrm{K\cdot mol}}\right)\\ &= 2.86\frac{\mathrm{J}}{\mathrm{K\cdot mol}}\end{aligned}$$

Equation 1: Enthalpy and entropy changes by standard equations

Since the enthalpy is negative, and the entropy is positive, the reaction is always spontaneous. In order to start the reaction, 188.28 kJ/mol must be supplied as an activation energy, but once the reaction starts, it will continue to completion without the need for any more energy [57].

As the heat of the reaction increases, the activation energy drops. In fact, if the temperature passes 800 ^{o}C, the activation energy is only 96.29 kJ/mol [57]. This is due to pore diffusion theory, where the oxygen is able to penetrate the particles and initiate internal combustion [57]. This property is very useful in the world of coal combustion, as conventional burners run at 1100 ^{o}C [58]. Traditional coal-fired plants burn bituminous coals for their low cost, but some burn the high carbon anthracite coals instead [59]. These coals have a carbon percentage up to 98%, and thus are most similar to the carbon ash sample. The activation energy of anthracite coal is 75.38 kJ/mol, which is less, but still similar to the predicted activation energy of the carbon at high temperatures [59]. Also coal, when burned in plants, is ground to sizes at or below 75 µm, which matches well with the size of the carbon ash particles. Overall, it seems that while not entirely on par with anthracite coal, the carbon ash would be able to be burned in said coal-fired plants. This coupled with the high carbon content leading to a maximum energy output makes this application very appealing.

Petroleum power plants are in the same family as coal-fired power plants, and thus work in much the same fashion. The obvious difference is that instead of anthracite or bituminous coal, petroleum is used in the combustion chamber to create the energy that is later captured. However, like the carbon plant where the substance is pulverized to maximize surface area, as petroleum enters the combustion chamber, it is sprayed as a mist [58]. This is an essential step of the process as it enables the petroleum to burn quickly and efficiently, thus maximizing the energy output. The carbon ash may be used in a petroleum plant so long as it undergoes some modifications to make it more similar to petroleum.

In order to supply the necessary activation energy for the combustion of the carbon ash in a petroleum-fired power plant, the proposed technique is to mix the ash with gasoline, which has an activation energy low enough that it can be ignited through conventional means. In order to find the enthalpy of combustion for gasoline, the enthalpy of combustion was determined for four major components of gasoline. This was done using the same technique as in Equation 1, and the results are shown in Equation 2.

Isooctane

$$C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O \qquad \Delta H = -5063.6\ \mathrm{kJ/mol}$$

Butane

$$C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O \qquad \Delta H = -2656.7\ \mathrm{kJ/mol}$$

3 – ethyltoluene

$$C_9H_{12} + 12O_2 \rightarrow 9CO_2 + 6H_2O \qquad \Delta H = -4990.5\ \mathrm{kJ/mol}$$

2 – methoxy – 2 – methylpropane

$$C_5H_{12}O + 7.5O_2 \rightarrow 5CO_2 + 6H_2O \qquad \Delta H = -3133.3\ \mathrm{kJ/mol}$$

Equation 2: The enthalpies of combustion of four major components of gasoline

In order to ignite the graphite, the energy output of the reactions in Equation 2 must match or exceed the activation energy requirement of the graphite. This was done through the use of ratios, as can be seen in Equation 3. To ensure that there is sufficient energy, ratios where twice the required activation energy needed is generated were found.

$$\frac{2(\Delta H_{\mathrm{ash}})}{\Delta H_{\mathrm{component}}} = \frac{M_{\mathrm{ash}}}{M_{\mathrm{component}}} \cdot \frac{1}{x}$$

with the mass ratio of ash: component being x: 1

Isooctane:

$$\frac{-376.56\frac{\mathrm{kJ}}{\mathrm{mol}}}{-5063.6\frac{\mathrm{kJ}}{\mathrm{mol}}} = \frac{\frac{12\mathrm{g}}{\mathrm{mol}}}{114.23\frac{\mathrm{g}}{\mathrm{mol}}} \cdot \frac{1}{x}$$

$$x = 1.41$$

Equation 3: The ratio method for determining the necessary mass of component

This ratio method was repeated for all the other compounds, and the following ratios were found:

1.41:1
1.45:1
1.32:1
1.13:1

Therefore, a mass ratio of 3:2 of carbon ash to gasoline would ensure that sufficient energy will be supplied through gasoline combustion to ignite the ash. This process would not only generate usable energy, but would also significantly reduce the waste that needs to be disposed of. The LOI test demonstrated that less than 1% of the ash will remain after complete combustion, meaning that tonnes of ash might be reduced to mere kilograms of waste.

In order to have a complete picture of the efficacy of ash combustion, it must be compared to conventional petroleum combustion. The petroleum burned at the Rabigh Electricity Company is listed as being heavy crude oil. This means that it has an API gravity of 10 to 20, which correlates to a specific gravity from 0.93 to 1 [60]. This information is implemented into Equation 4, which gives an estimation of the combustion energy of petroleum, based on specific gravity.

$$Q_v = -12400\frac{\mathrm{cal}}{\mathrm{g}} + \left(2100\frac{\mathrm{cal}}{\mathrm{g}}\right)d^2$$
$$\text{where d is the specific gravity}$$

Equation 4: An estimation of the combustion energy of petroleum

This equation was implemented using both the upper and lower limits of specific gravity, generating a range from 43.095 kJ/g to 44.280 kJ/g.

The energy generated from the petroleum is compared to that of the mixture assuming a 3:2 ratio of carbon ash to gasoline. Equation 5 calculates the energy generated by the combustion of one gram of gasoline, where the molar mass and enthalpy of combustion are found by adding the respective values of the four gasoline components.

$$\begin{aligned}\Delta H_{\mathrm{gasoline}} &= n_{\mathrm{gasoline}} \cdot \Delta H_{T_{\mathrm{gasoline}}} \\ &= \left(0.4\ \mathrm{g} \cdot \frac{1\ \mathrm{mol}}{380.7\ \mathrm{g}}\right)\left(-15844.1\frac{\mathrm{kJ}}{\mathrm{mol}}\right) \\ &= -16.647\ \mathrm{kJ}\end{aligned}$$

Equation 5: The combustion energy of 0.4 g of gasoline

The energy generated by the combustion of the carbon ash is somewhat more complex, as the activation energy must be taken into consideration. Thus, first the activation energy for 0.6 g of carbon was found, then the energy output of burning 0.6 g of carbon was found. Finally, all the energies are added together to find a total energy output of the mixture combustion. All this is shown in Equation 6.

$$\begin{aligned}E_a &= n_{\mathrm{carbon}} \cdot E_{a_{\mathrm{carbon}}} \\ &= \left(0.6\ \mathrm{g} \cdot \frac{1\ \mathrm{mol}}{12.1\ \mathrm{g}}\right)\left(188.28\frac{\mathrm{kJ}}{\mathrm{mol}}\right) \\ &= 9.336198\ \mathrm{kJ}\end{aligned}$$

$$\begin{aligned}\Delta H_{\mathrm{carbon}} &= n_{\mathrm{carbon}} \cdot \Delta H_{T_{\mathrm{carbon}}} \\ &= \left(0.6\ \mathrm{g} \cdot \frac{1\ \mathrm{mol}}{12.1\ \mathrm{g}}\right)\left(-393.5\frac{\mathrm{kJ}}{\mathrm{mol}}\right) \\ &= -19.5123\ \mathrm{kJ}\end{aligned}$$

$$\begin{aligned}\Delta H_T &= \Delta H_{\mathrm{gasoline}} + \Delta H_{\mathrm{carbon}} + E_a \\ &= -16.647\ \mathrm{kJ} - 19.5123\ \mathrm{kJ} + 9.336198\ \mathrm{kJ} \\ &= -26.82\ \mathrm{kJ}\end{aligned}$$

Equation 6: The combustion of carbon and the final energy output of the mixture

One is able to compare the petroleum and the mixture through simple percentages. This is shown in Equation 7, which includes the lower and upper bound of the petroleum energy.

$$\mathrm{Percent}_{\mathrm{energy}} = \frac{\Delta H_{\mathrm{ash\ and\ gas}}}{\Delta H_{\mathrm{petroleum}}}$$

$$= \frac{26.82\frac{\mathrm{kJ}}{\mathrm{g}}}{43.095\frac{\mathrm{kJ}}{\mathrm{g}}} = 62.23\% \qquad\qquad = \frac{26.82\frac{\mathrm{kJ}}{\mathrm{g}}}{44.280\frac{\mathrm{kJ}}{\mathrm{g}}} = 60.56\%$$

Equation 7: The calculation of the percent energy generated by the mixture compared to petroleum

Thus, for equal masses of petroleum and the gas-ash mixture, the latter produces roughly 61% the amount of energy as the petroleum.

It should be taken into consideration the diminished energy generation is at a fraction of the cost of petroleum. In Saudi Arabia, the current cost of gasoline is roughly \$0.16/litre, and the ash can be acquired free of charge. In the case of the coal-fired power plant, the replacement coal needs no alterations or additions, and thus would also be very cost effective. Overall, this seems to be a very appealing use of the waste carbon ash.

4.3 Use in road construction

Using the ash product in road construction might be a simplest solution to dispose and recycle the material. Soil is used extensively in the road construction as it acts as a binding agent to glue aggregates together. Therefore, the structural stability of the road increases as proper mix of soil is implemented in the construction. The soil can be used in road embankment and for road base. With further testing, the material can be used in various parts in the road including subgrade.

A stable base material contains suitable proportions of gravel, sand, silt and clay. Occasionally, deposits of such material occur naturally, e.g. the desert and estuarine sand-clay deposits in Egypt and Nigeria, and the wall-ballasts and Higgins of the Thames valley and Hampshire basin. More often though, it is necessary to combine two or more soils in suitable proportions, a process sometimes referred to as mechanical stabilization [64].

Experience suggests that almost any material that is resistant to weathering will be suited for use as aggregate in a mechanically stabilized road; all kinds of natural rock, gravel and sand, and artificial materials (such as slag, burnt shale, etc.) have been used with success [64]. Low-grade material such as laterite, coral and lime rock are also known to give dense, mechanically stable roads.

The sample ash consists of spherical particles ranging from 100 to 200 µm which fits with mesh 72. Therefore, up to 40% of the mix can be replaced with the ash [64] [65]. Given its porous properties, it will aid as frost and weather resistant material, giving more longevity for the base and surface layer of the road [65]. Figure 15 shows the proportion of the soil mix for road construction..

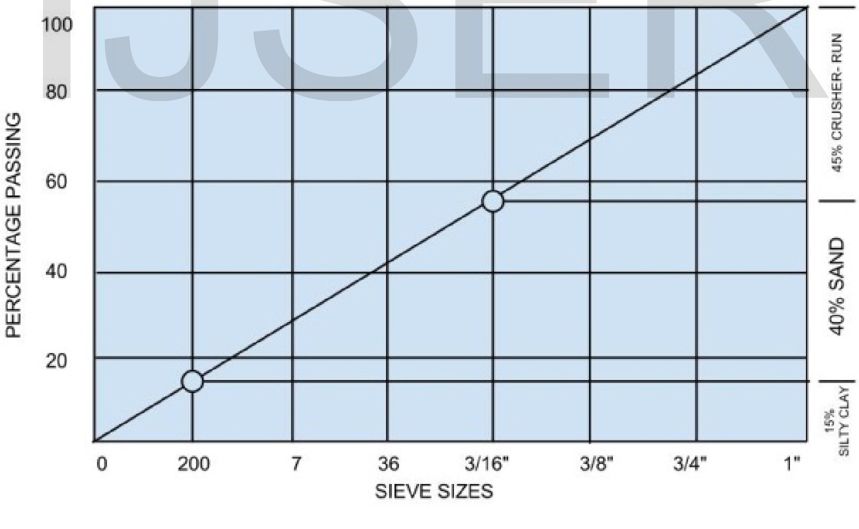


Figure 15: Mixtures for stabilized surfacing [64]

4.4 Conclusion

A great wealth of applications has been proposed in this chapter, spanning from pencils to batteries to energy generation. Further practical tests of the carbon ash sample will bring to light the feasibility of the proposed solutions, as more information will bring into focus the type of carbon that will be used. For now though, the possibilities are very broad and exhibit the vast amount of options that may be found in the use of what is considered merely a waste material.

CHAPTER 5. CONCLUSIONS AND FUTURE PLANS

5.1 Research summary

The objective of this research was to understand the incineration by-product from the supplier, and generate feasible solutions, such as using the by-product as a high quality raw material. X-ray diffraction and LOI tests suggest that the material mostly consists of carbon. However, there are multiple constraints in this research. This includes the amount of sample on hand, and the lack of other key lab services to concretely determine its classification. With that in mind, the solutions were generated in broad spectrum, including three major types of carbon and one post processed carbon. Furthermore, using the by-product as fuel was also considered assuming the product is 99% or higher in Carbon by weight. Since the fundamental basis of the application is creating something from what is considered as nothing, the profitability and feasibility of it is extraordinary.

5.2 Future plans

Presented above are a wide range of potential applications for the carbon ash that is left as waste following petroleum combustion. Based on testing of the material, futures in electrochemistry, graphite manufacturing, carbon black creation, and combustion may be seen. However, there is still work to be done before profit may be made off of this waste. This project is currently in a purely research stage. Tests were done on the material itself, but testing applications has not yet come to pass. Therefore, in order for this study to continue, this practical testing must begin. The following are suggested tests in each of the fields presented in this research.

- Determine oxygen reduction reaction activity of the material as a Pt catalyst support
- Measure its true density, electrical resistivity, tactile lubricity, and take SEM imaging to determine graphitic nature of carbon ash
- Test similarities to carbon black, and procedures required to convert material to carbon black
- Create mixture of gasoline and ash, and measure energy output, residue, and relative power generation to petroleum combustion
- Measure the energy output of burning the carbon ash in an environment similar to an anthracite coal-fired power plant

The possibilities to make good use out of this waste material are bright, and with continued research it is highly likely that a profitable solution will be found. With additional time and resources, this study will yield and economically and ecologically friendly solution.

REFERENCES

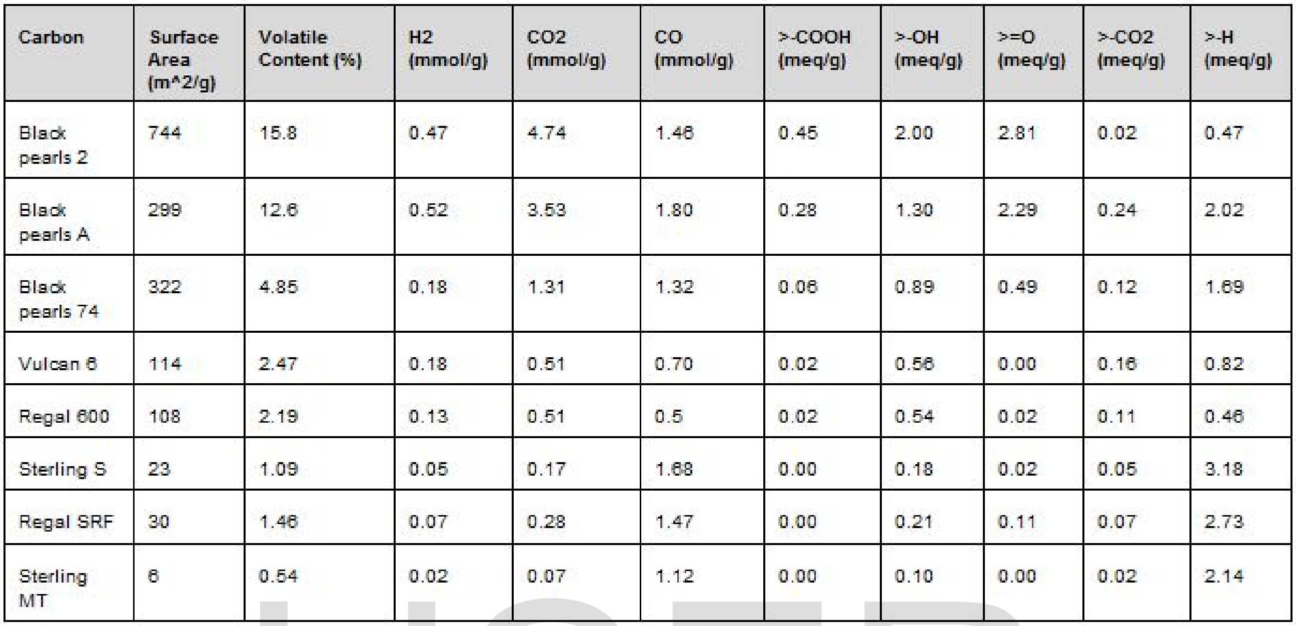
1. USEIA. Electric Power Monthly. U.S. Department of Energy (2012) ES1.B
2. Kridel, C. *Encyclopedia of Curriculum Studies*. Sage Publications, Inc. p. 341, (2010).
3. Sinsel, J . Earth Day Activities. *Lesson Planet*. (2010)
4. Gonzalez, A., Navia, R., and Moreno, N. Fly ashes from coal and petroleum coke combustion: current and innovative potential applications. *Waste Management & Research*. 27(10), 976-987 December (2009).
5. Environmental Protection Agency. Fly ash. *USEPA* (2010).
6. Shibaoka, M. Carbon content of fly ash and size distribution of unburnt char particles in fly ash. *Fuel.* 65(3), 449-450 (1986).
7. LaCount, R.B., and Kern, D.G. Economical Treatment of High Carbon Fly Ash to Produce a Low Foam Index Product with Carbon Content Retained. *Waynesburg.* (2000).
8. Boardman, J. The Neolithic-Eneolithic Period. *The Cambridge ancient history.* 3(1) (1973).
9. Zhang, F.S., and Itoh, H. Extraction of metals from municipal solid waste incinerator fly ash by hydrothermal process. *Journal of Hazardous Materials*. 136(3), 663-670 August (2006).
10. Pedersen, A.J., Ottosen, L.M., and Villumsen, A. Electrodialytic removal of heavy metals from different fly ashes - Influence of heavy metal speciation in the ashes. *Journal of Hazardous Materials*. 100(1-3), 65-78 June(2003).
11. Felekoglu, G. Utilisation of Turkish fly ashes in cost effective HVFA concrete production. *Fuel*. 85(12-13), 1944-1949 September 2006.
12. ACI 232.2R-03 (2003), "Use of Fly Ash in Concrete," American Concrete Institute, Farmington Hills, MI, www.concrete.org.
13. Lafarge. LaFarge Fly ash and Bottom ash MSDS. *LaFarge Corp* (2009).
14. CIRCA. Origin & Applications of Bottom Ash Technical Fact Sheet #9. *Association of Canadian Industries Recyling Coal Ash.* (2010).
15. Jaturapitakkul, C., and Cheerarot, R. Development of bottom ash as pozzolanic material. *Journal of Materials in Civil Engineering*. 15(1), 48-53 January(2003).
16. Berry, M., Cross, D., and Stephens, J. Changing the Environment: An Alternative “Green” Concrete Produced without Portland Cement. *World of Coal Ash Conference*. May (2009).
17. Aguilar, R.A., Diaz, O.B., and Garcia, J.I.E. Lightweight concrete of activated metakaolin-fly ash binders, with blast furnace slag aggregates. *Construction and Building Materials*. 24(7), 1166-1175 July (2010).
18. Caires, W.S., and Peters, S. Class C Mixtures as Alternates to Portland-cement-based Foundation Concrete. *World of Coal Ash Conference*. May (2011).
19. Cross, D., Stephens, J., and Vollmer, J. Structural Applications of 100 Percent Fly Ash Concrete. *World of Coal Ash Conference*. April (2005).
20. Alhassan, M.A., and Ashur, S.A. Sustainable Fly Ash Bridge Deck Concrete Overlay. *Journal of the Chinese Ceramic Society*. 39(10), 77-83 May (2011).
21. Namagga, C., and Atadero, R.A. Optimization of Fly Ash in Concrete: High Lime Fly Ash as a Replacement for Cement and Filler Material. *World of Coal Ash Conference*. May (2009).
22. Crouch, L.K., Hewitt, R., and Byard, B. High Volume Fly Ash Concrete. *World of Coal Ash Conference*. May (2007).
23. Papayianni, I., and Anastasiou, E. Development of Self Compacting Concrete (SCC) by using High Volume of Calcareous Fly Ash. *World of Coal Ash Conference*. May (2011).
24. Celik, O. Influence of Fly Ash on the Properties of Asphalt. *Petroleum Science and Technology*. 26(13), 1571-1582 (2008).
25. Mehta, P.K., and Gjorv, O.E. Properties of Portland Cement Concrete Containing Fly Ash and Condensed Silica-Fume. *Cement and Concrete Research*. 12(5), 587-595 (1982).

26. Bertolini, L., Carsana, M., Cassago, D., Curzio, A.Q., and Collepardi, M. MSWI ashes as mineral additions in concrete. *Cement and Concrete Research*. 34(10), 1899-1906 October(2004).
27. Wolfe, W., Butalia, T.S., Walker, H. Full-Depth Reclamation of Asphalt Pavements Using Lime-Activated Class F Fly Ash: Structural Monitoring Apects. *World of Coal Ash Conference*. May(2009)
28. Seferinoglu, M. et al. Acid leaching of coal and coal-ashes. *Fuel*. 82(14), 1721-1734 October(2003).
29. Schlumberger, S., Schuster, M., Ringmann, S., and Koralewska, R. Recovery of high purity zinc from filter ash produced during the thermal treatment of waste and inerting of residual materials. *Waste Management & Research*. 25(6), 547-555 December(2007).
30. Peterson, A.J., Ottosen, L.M., and Villumsen, A. Electrodialytic removal of heavy metals from different fly ashes - Influence of heavy metal speciation in the ashes. *Jounal of Hazardous Materials*. 100(1-3), 65-78 June(2003).
31. Ferreira, C., Jensen, P., Ottosen, L., and Ribeiro, A. Removal of selected heavy metals from MSW fly ash by the electrodialytic process. *Engineering Geology*. 77(3-4), 339-347 March(2005).
32. Brombacher, C., Bachofen, R., and Brandl, H. Development of a Laboratory-Scale Leaching Plant for Metal Extraction from Fly Ash by *Thiobacillus* strains. *Applied and Environmental Microbiology*. 64(4), 1237-1241 April(1998).
33. Andrade, L.B., Rocha, J.C., and Cheriaf, M. Influence of coal bottom ash as fine aggregate on fresh properties of concrete. *Construction and Building Materials*. 23(2), 609-614 February(2009).
34. Rubner, K., Haamkens, F., and Linde, O. Use of municipal solid waste incinerator bottom ash as aggregate in concrete. *Quarterly Journal of Engineering Geology and Hydrogeology*. 41, 459-464 November(2008).
35. Goh, S.W., and You, Z.P. A preliminary study of the mechanical properties of asphalt mixture containing bottom ash. *Canadian Journal of Civil Engineering*. 35(10), 1114-1119 October(2008).
36. Blackman, L.C.F . *Modern Aspects of Graphite Technology*. Academic Press INC, (1970) London and New York.
37. Mantell, C.L. *Carbon and Graphite Handbook*. Interscience publishers, (1968), New York.
38. Donath, D.G. *Eine Chemisch-technische Monographie*. Deuticke (1904).
39. Spence, L. *Report No. 511. Graphite*. Canadian Mines Branch (1920).
40. Mattiello, J. *Protective and Decorative Coatings*. John WIley Sons, Inc. (1942), New York.
41. ICBA. *What is Carbon Black?* International Carbon Black Association (2012).
42. CCCRL. *The Particle Size and Shape of Carbon Black as Revealed by the Electron Microscope*. Columbian Carbon Company Research Laboratories (1940), New York.
43. Kemp, A.R., and Herrmann, D.B. *Rubber Chem*. Tech (1939).
44. Clark, G. L. *Applied X-rays*. McGraw-Hill Book Company, Inc., (1932), New York.
45. Mitsubishi Chemicals. *Three Main Properties of Carbon Black*, (2006). http://www.carbonblack.jp/en/cb/tokusei.html
46. Arnal, C. Experimental and Kinetic Study of the Interaction of a Commercial Soot Toward NO at High Temperature. *Chia Laguna Cagliara.* (2011).
47. Norman, D.T. Rubber Grade Carbon Blacks. *Continental Carbon* (2012).
48. Kinoshita, K. *Carbon Electrochemical and Physicochemical properties.* Wiley-Interscience Publication. (1988), New York.
49. Swanson, E. B. *Petroleum coke : an economic survey of its production.* (1893).
50. API (The American Petroleum Institute). *Petroleum Coke Category Analysis and Hazard Characterization*. US EPA (2008).
51. ASTM Standard C311 - 11b, 1953 (2012), "Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete," ASTM International, West Conshohocken, PA, 2012, DOI: 10.1520/C0311-11b, www.astm.org.
52. CSA Standard A3003 - 1998 (2008), “Cementitious materials compendium,” CSA Group, Toronto, ON, 2008, www.csa.ca.
53. Tamashausky, A. "Petroleum Based Carbon." Message to Perry Ham. 230062012. E-mail.
54. Verlag, S. *Steel A Handbook for Material Research and Engineering Volume 1: Fundamentals*. Berlin, Mercedes-Druck GmbH, (1965).
55. Yahaskel, A. *Activated Carbon: Manufacture and Regeneration* (Chemical Technology Review No. 117; Pollution Technology Review No. 51). NDC (1978).

56. Schwod, Y. *Chemistry and Physics of Carbon, Vol. 15*. P.L. Walker and P.A. Throwerd, Eds., Dekker, (1979) New York.
57. Froberg, R.W., and Essenhigh, R. Reaction order and activation energy of carbon oxidation during internal burning. *Symposium (International) on Combustion*. 17(1), 179-187 (1979).
58. Kim, J.K., and Lee, H.D. Combustion Possibility of Dry Sewage Sludge Used as Blended Fuel in Anthracite-Fired Power Plant. *Journal of Chemical Engineering of Japan*. 44(8), 561-571 (2011).
59. Korytnyi, E. et al. Sub-Bituminous Coals Fired in Boiler Designed for Bituminous Coals. *Proceeding of the Asme Power Conference 2008*. 31-36 July(2008).
60. Boduszynski, M.M., Rechsteiner C.E., Shafizadeh A.S.G., and Carlson R.M.K. Composition and Properties of Heavy Crudes. *UNITAR Centre for Heavy Crude and Tar Sands*. (1998).
61. Chang, F.Y., and Wey, M.Y. Comparison of the characteristics of bottom and fly ashes generated from various incineration processes. *Journal of Hazardous Materials*. 138(3), 594-603 December(2006).
62. Liu, G.J., Zhang, H.Y., Gao, L.F., Zheng, L.G., and Peng, Z.C. Petrological and mineralogical characterizations and chemical composition of coal ashes from power plants in Yanzhou mining district, China. *Fuel Processing Technology*. 85(15), 1635-1646 October(2004).
63. ACS (American Chemical Society). *Rubber Chem*. Technol. (1963) 36, 729.
64. RRL (Road Research Laboratory)- *Soil Mechanics For Road Engineers*.(1951).
65. Radford, Thomas – *The Construction of Roads and Pavements 5Th Edition,* (1940).

APPENDIX 1: TABLES

Chemical and Thermal Analysis of Surface Groups on Carbon Blacks [63]

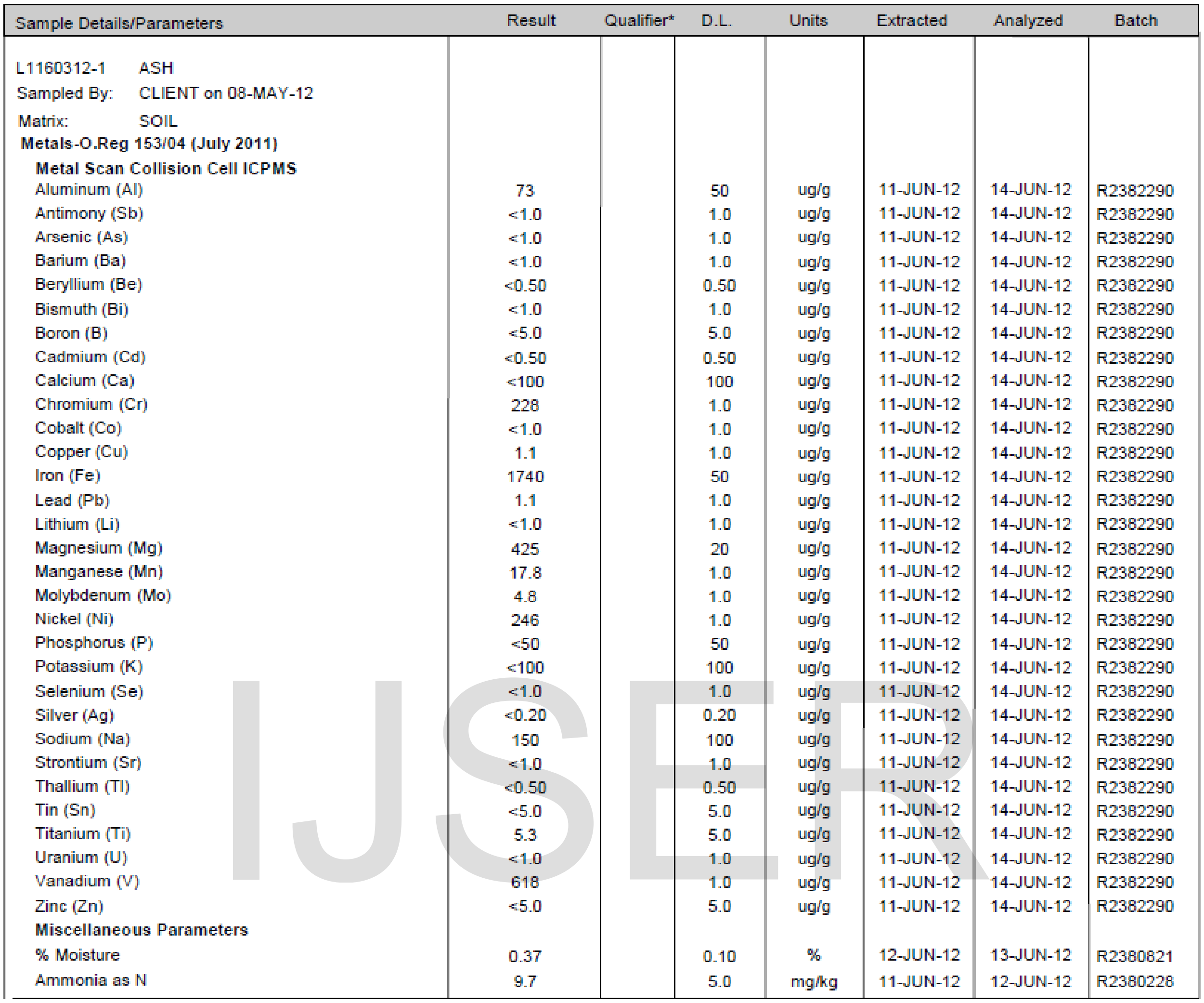


Carbon	Surface Area (m^2/g)	Volatile Content (%)	H2 (mmol/g)	CO2 (mmol/g)	CO (mmol/g)	>-COOH (meq/g)	>-OH (meq/g)	>=O (meq/g)	>-CO2 (meq/g)	>-H (meq/g)
Black pearls 2	744	15.8	0.47	4.74	1.46	0.45	2.00	2.81	0.02	0.47
Black pearls A	299	12.6	0.52	3.53	1.80	0.28	1.30	2.29	0.24	2.02
Black pearls 74	322	4.85	0.18	1.31	1.32	0.06	0.89	0.49	0.12	1.69
Vulcan 6	114	2.47	0.18	0.51	0.70	0.02	0.56	0.00	0.16	0.82
Regal 600	108	2.19	0.13	0.51	0.5	0.02	0.54	0.02	0.11	0.46
Sterling S	23	1.09	0.05	0.17	1.68	0.00	0.18	0.02	0.05	3.18
Regal SRF	30	1.46	0.07	0.28	1.47	0.00	0.21	0.11	0.07	2.73
Sterling MT	6	0.54	0.02	0.07	1.12	0.00	0.10	0.00	0.02	2.14

The Entropies and Enthalpies of Formation of Relevant Compounds

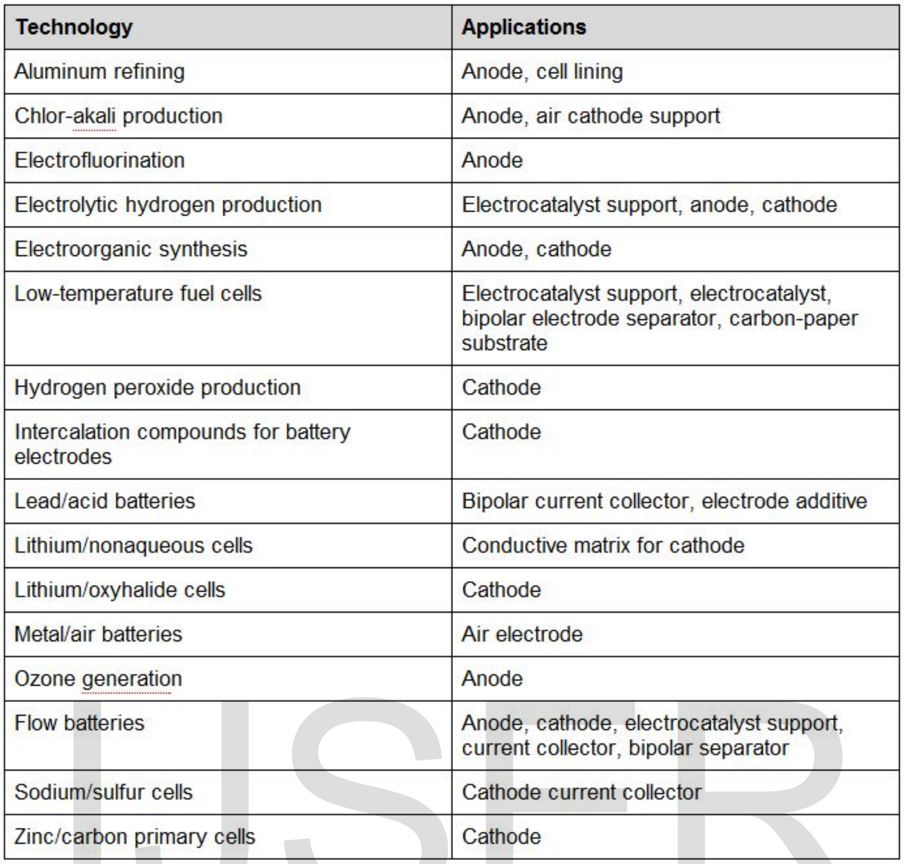
Compound	**Standard Enthalpy of Formation (kJ mol^{-1})**	**Absolute Standard Entropy (J mol^{-1} K^{-1})**
CO_2	-393.5	213.7
O_2	0	205.1
C (graphite)	0	5.74
H_2O	-241.8	-
C_4H_{10}	-126.3	-
C_9H_{12}	-1.8	-
$C_5H_{12}O$	-285.0	-

Results of the Metals and Ammonia tests



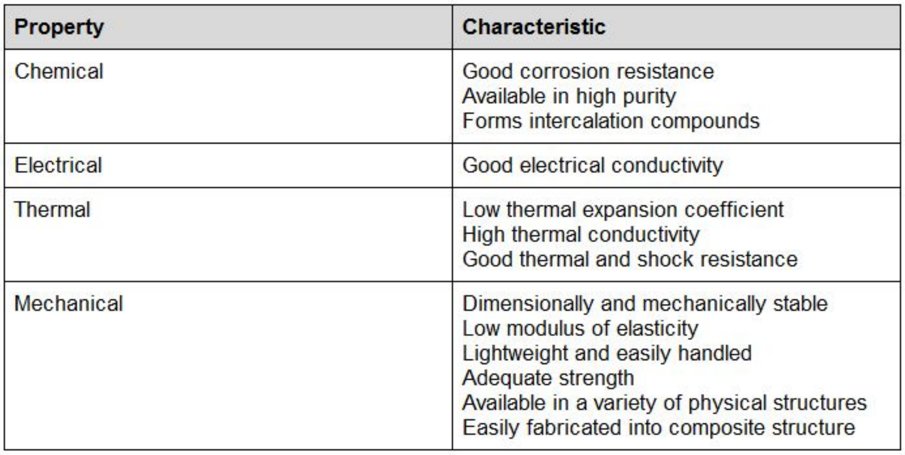
Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L1160312-1 ASH							
Sampled By: CLIENT on 08-MAY-12							
Matrix: SOIL							
Metals-O.Reg 153/04 (July 2011)							
Metal Scan Collision Cell ICPMS							
Aluminum (Al)	73		50	ug/g	11-JUN-12	14-JUN-12	R2382290
Antimony (Sb)	<1.0		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Arsenic (As)	<1.0		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Barium (Ba)	<1.0		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Beryllium (Be)	<0.50		0.50	ug/g	11-JUN-12	14-JUN-12	R2382290
Bismuth (Bi)	<1.0		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Boron (B)	<5.0		5.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Cadmium (Cd)	<0.50		0.50	ug/g	11-JUN-12	14-JUN-12	R2382290
Calcium (Ca)	<100		100	ug/g	11-JUN-12	14-JUN-12	R2382290
Chromium (Cr)	228		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Cobalt (Co)	<1.0		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Copper (Cu)	1.1		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Iron (Fe)	1740		50	ug/g	11-JUN-12	14-JUN-12	R2382290
Lead (Pb)	1.1		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Lithium (Li)	<1.0		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Magnesium (Mg)	425		20	ug/g	11-JUN-12	14-JUN-12	R2382290
Manganese (Mn)	17.8		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Molybdenum (Mo)	4.8		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Nickel (Ni)	246		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Phosphorus (P)	<50		50	ug/g	11-JUN-12	14-JUN-12	R2382290
Potassium (K)	<100		100	ug/g	11-JUN-12	14-JUN-12	R2382290
Selenium (Se)	<1.0		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Silver (Ag)	<0.20		0.20	ug/g	11-JUN-12	14-JUN-12	R2382290
Sodium (Na)	150		100	ug/g	11-JUN-12	14-JUN-12	R2382290
Strontium (Sr)	<1.0		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Thallium (Tl)	<0.50		0.50	ug/g	11-JUN-12	14-JUN-12	R2382290
Tin (Sn)	<5.0		5.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Titanium (Ti)	5.3		5.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Uranium (U)	<1.0		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Vanadium (V)	618		1.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Zinc (Zn)	<5.0		5.0	ug/g	11-JUN-12	14-JUN-12	R2382290
Miscellaneous Parameters							
% Moisture	0.37		0.10	%	12-JUN-12	13-JUN-12	R2380821
Ammonia as N	9.7		5.0	mg/kg	11-JUN-12	12-JUN-12	R2380228

Application of Carbon and Graphite in Electrochemical Technologies [37]



Technology	Applications
Aluminum refining	Anode, cell lining
Chlor-akali production	Anode, air cathode support
Electrofluorination	Anode
Electrolytic hydrogen production	Electrocatalyst support, anode, cathode
Electroorganic synthesis	Anode, cathode
Low-temperature fuel cells	Electrocatalyst support, electrocatalyst, bipolar electrode separator, carbon-paper substrate
Hydrogen peroxide production	Cathode
Intercalation compounds for battery electrodes	Cathode
Lead/acid batteries	Bipolar current collector, electrode additive
Lithium/nonaqueous cells	Conductive matrix for cathode
Lithium/oxyhalide cells	Cathode
Metal/air batteries	Air electrode
Ozone generation	Anode
Flow batteries	Anode, cathode, electrocatalyst support, current collector, bipolar separator
Sodium/sulfur cells	Cathode current collector
Zinc/carbon primary cells	Cathode

Beneficial properties and characteristics of carbon and graphite for electrochemical technologies [37]



Property	Characteristic
Chemical	Good corrosion resistance Available in high purity Forms intercalation compounds
Electrical	Good electrical conductivity
Thermal	Low thermal expansion coefficient High thermal conductivity Good thermal and shock resistance
Mechanical	Dimensionally and mechanically stable Low modulus of elasticity Lightweight and easily handled Adequate strength Available in a variety of physical structures Easily fabricated into composite structure