Chapter 2
Literature review

2.1 Introduction

Coal is the most abundant fossil fuel with reserves all over the world. Through extensive research and development, various coal conversion processes have been developed for the purpose of extracting various useful compounds which arise from chemical processes that involve breaking of various bonds in the macromolecular structure of coal. Some of the conversion processes currently being used for the transformation of coal include coal combustion, liquefaction, coal gasification and coal pyrolysis or destructive distillation.

The destructive distillation of coal yields various products and by-products. The process involves the heating of coal in coking ovens in the absence of air yielding coke as the main product and coal tar (CT), ammonia and light oils as by-products.

CT has many applications that range from road construction, medical and clinical applications, pharmaceutical applications, production of refined chemicals such as creosote, anthracene oils, fuel in open hearth furnaces and the carbon industries. In the carbon industry, CT is further processed through the process of distillation to produce coal tar pitch (CTP), which can be used as a binder or impregnation pitch during the manufacture of graphite electrodes, or anodes used in the aluminium industry.

CT and CTP both contain numerous and complex hydrocarbon compounds [Conroy et al., 1975]. To understand the behaviour, properties and composition of CT and CTP, various analytical techniques and methods, which include chromatography, spectroscopy and thermal analysis, have been developed and applied to obtain as much information as possible. When CTP and coke are mixed and subjected to heat treatment at temperatures ranging between 2500 and 3000 °C, a new product (synthetic graphite) is produced. Synthetic graphite is a material that has excellent physical, chemical, thermal and mechanical properties. These properties are essential for industries involved in the manufacturing of anodes used in many electrochemical processes, such as aluminium production and graphite electrodes used in different ferroalloy industries.

Graphite electrodes are designed to carry large amounts of current into electric arc furnaces. They can be divided into two main categories, namely prebaked electrodes, as well as Söderberg electrodes. These two types of electrodes have similar applications, but they differ in the way in which they are manufactured. The synthesis, properties and applications of electrodes are discussed in section 2.4.

2.2 Coal tar (CT) and tar

CT is an oily, viscous dark coloured mixture consisting of a wide range of aromatic hydrocarbons, such as phenols, poly-aromatic hydrocarbons (PAHs) and heterocyclic compounds of varying composition. It is obtained as a by-product during pyrolysis or destructive distillation of coal. Tar can also be obtained from other organic materials such as biomass and waste lubricating oils [Enzminger and Ahlert, 1987; Yu et al., 1997; Purevsuren et al., 2004; Li and Suzuki, 2009; Li et al., 2010]. Typical coal pyrolysis reactions are illustrated in Figure 2.1.

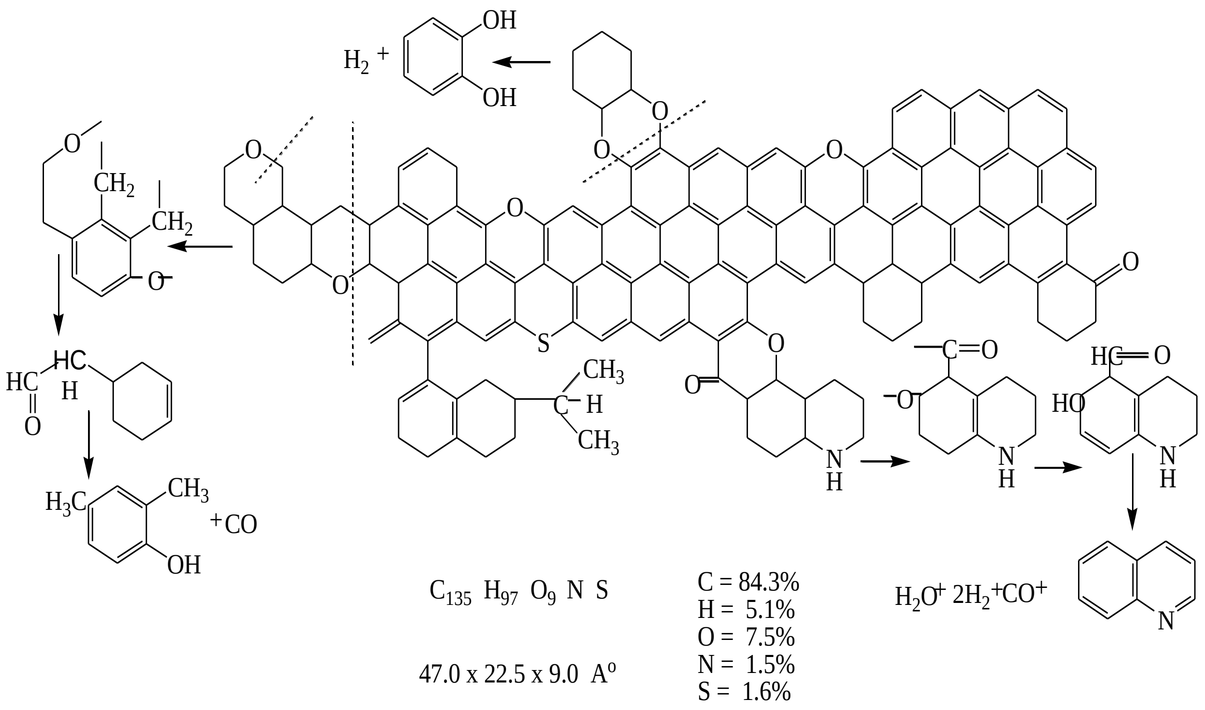


Figure 2.1 Typical coal pyrolysis reactions [Fuchs and Sandoff, 1942]

During the destructive distillation of coal, volatile components evolve. These evolved gases comprise ammonia, CT vapours and many other products, which can be recovered through a number of processes [Fuchs and Sandhoff, 1942; Codd et al., 1971]. The gas formed during the destructive distillation, entrained liquid and solid particles pass upwards into the collecting main. As the gas leaves the oven, it is sprayed with ammonia [Austin, 1945]. The ammonia condenses some of the tar and ammonia from the gas into liquid. Other essential by-products that can be obtained include ammonium sulphate, light oils and other gaseous products [Austin, 1945] . Lowry et al. [1945] reported that the chemical and physical characteristics of CT depend largely on the carbonisation temperature, kind of coal used and carbonising equipment. The yield of CT depends mainly on the rank of the coal.

2.2.1 Classification of CT

CT can be divided into two main different categories depending on the temperature range in which it is obtained, i.e. low temperature (primary) and high temperature CT.

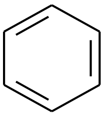
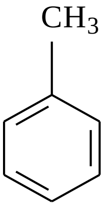
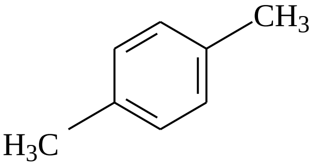
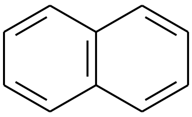
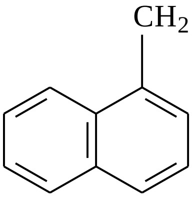
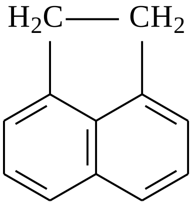
2.2.1.1 Low temperature CT

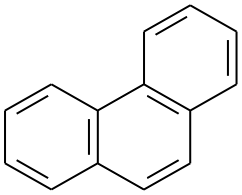
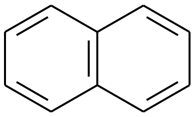
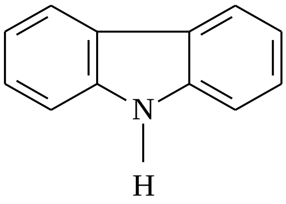
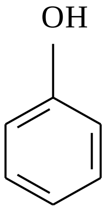
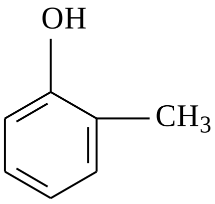
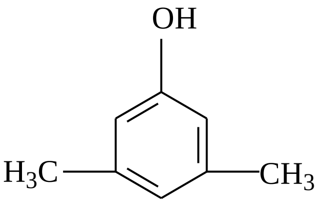
Primary or low temperature CT is obtained from the initial decomposition/pyrolysis of coal at temperatures ranging between 400 and 700 °C [Bergeim and Leonia, 1937; Arnold, 1997]. The composition of the primary CT obtained depends on the characteristics of the coal used in the pyrolysis stage [Fuchs and Sandhoff, 1942; Casal et al., 2008]. Gas chromatography-mass spectrometry (GC-MS) characterisation of low temperature CT carried out by Islas et al. [2003] showed the existence of unsubstituted alkanes and alkylated aromatics. It is also reported that low temperature CTs have a high content of phenols in addition to the tar acids [Arnold, 1997]. Watt et al. [1996] reported that the use of low temperatures in the production of low temperature CT inhibits the possibility of side reactions taking place; therefore, there will be a slight difference between the parent material and the CT.

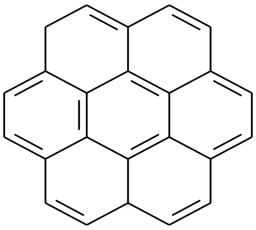
2.2.1.2 High temperature CT

High temperature CT is produced when the destructive distillation of coal takes place within a temperature range of 900 to 1200 °C [Lowry, 1945; Speight, 1998]. The properties of high temperature CT are influenced by the temperature, at which it is obtained, with high temperatures resulting in the chemical decomposition and rearrangement of materials. CT produced at high temperature is significantly different from that produced at low temperature [Bergeim and Leonia, 1937]. Li and Suzuki [2010] reported that high temperature CT is a complex black liquid oil that is made up of several components with a wide range of molecular weights. The characterisation of high temperature CT showed the presence of linear alkanes ranging from C_{14} to C_{31} in addition to aromatic compounds such as naphthalene and anthracene [Arnold, 1997; Liu et al., 1998;]. Some of the main constituents of CT are presented in Table 2.1 and Figure 2.2.

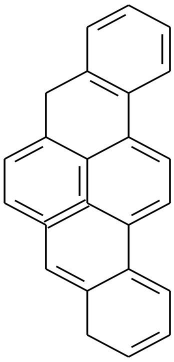
Table 2.1 Different compounds found in CT [Lowry et al., 1945]

Compound	**Chemical Structure**
Light oils	
Crude benzene	
Toluene	
Xylenes	
Middle and heavy oils	
Naphthalene	
Methylnaphthalene	
Acetanapthene	

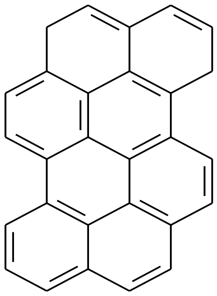
Anthracene oils	
Phenanthrene	
Anthracene	
Carbazole	
Phenols	
Phenol homologs	 



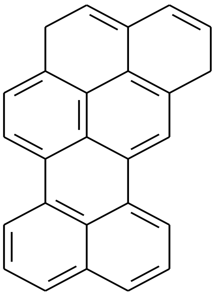
Coronene



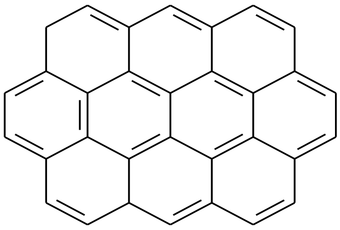
Benzo[rst]pentaphene



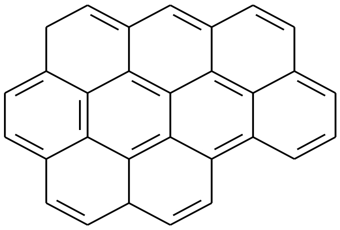
Benzo[pqr]naphtho[8,1,2-bcd]
perylene



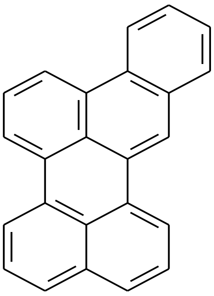
Naphto[8,1,2-bcd]perylene



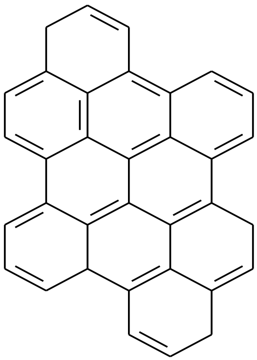
Ovalene



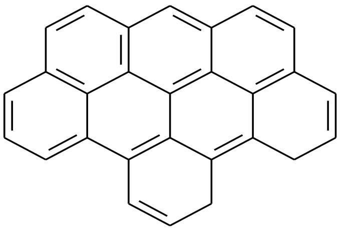
Naphtho[8,1,2-bcd]peryelene



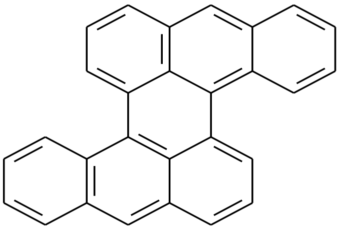
Benzo[b]perylene



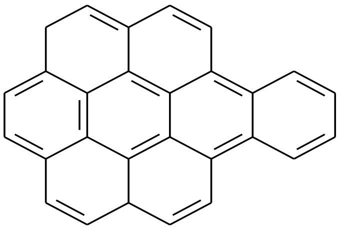
Peryleno[3,2,1,12-pqrad]peryelene



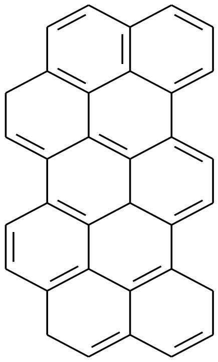
Phenathro[5,4,3,2-efghi]perylene



Dibenzo[a,j]perylene



Benzo[a]coronene



Benzo[rst]dinaphtho[2,1,8,7-defg:
2',1',8',7'-ijkl]perylene

Figure 2.2 PAHs found in CT and CTP [Fetzer and Kershaw, 1995]

2.3 Coal tar pitch (CTP)

CTP is obtained as a conversion product from the distillation of CT and its commercial application was first discovered in the 14th century [Matsumoto, 1986; Menendez and Granda, 2007]. The separation of components during the distillation of CT is attained through variations of temperature. During the fractionation of CT, fractions of higher boiling point compounds such as tar acid oils and naphthalene oils will be removed and this leaves behind a solid residue known as CTP [Conroy et al., 1975]. The distillation of CT can be carried out at temperatures ranging from 140 to 275 °C [Radasch, 1937]. CTPs act as precursors in reactions that involve the manufacture of various carbon compounds [Cebolla et al., 1996; Blanco et al., 2000; Perez et al., 2004]. CTP appears as a solid material at room temperature that softens on heating [Rocha et al., 2002]. CTPs mainly comprise several condensed aromatic rings and PAHs having at least three to eight aromatic rings that are joined together. Mashau. [2007] reported that CTP mainly consists of the following compounds, PAHs, alkylated PAHs, carbonyl compounds, partially hydrogenated PAHs and polycyclic hetero-aromatic compounds. The average molecular weight of CTP ranges from 300 to 400 amu [Matsumoto, 1986; Fitzer et al., 1987]. The high aromaticity and low aliphatic carbon content in the CTP give exceptional results when it is carbonised. CTPs have good affinity as well as binding properties to other carbon products such as petroleum coke and calcined anthracite, resulting in its wide application as a binder in the manufacture of graphite electrodes, carbon anodes and carbon matrices used in manufacture of composites [Conroy et al., 1975; Bermejo et al., 1997; Diaz and Blanco, 2003; Mora et al., 2003]. The popularity of CTP as a binder in the carbon industry is also due to its relatively low cost in comparison with other binders. In addition, it spreads easily over a solid carbon surface (good wettability to carbons) and can generate matrices with different microstructures upon graphitization [Mashau, 2007].

2.3.1 Reaction pathway during thermal treatment of CTP

Carbonisation is a polymerisation reaction that involves the thermal conversion of organic materials to only carbon-containing compounds and this conversion depends on the chemical composition of the CTP. Major reactions that take place during this process include the cleavage of C-H and C-C bonds, rearrangement of molecules, thermal polymerisation, aromatic condensation and the elimination of side chains [Matsumoto, 1986; Mendez et al., 2001].

When CTP is heated to between 400 and 500 °C in an inert atmosphere, it softens and undergoes polymerisation and condensation reactions that lead to the development of an intermediate phase known as a mesophase (liquid stage). The mesophase stage of CTP has properties such as a high softening point, good carbon yield and excellent graphitisability properties [Perez et al., 2002]. Heating of the CTP results in the agglomeration of aromatic components to form a solid material with several aromatic spheres joined together. Further heating will result in the joining together of the spheres to form a hard infusible solid carbon material (coke) [Matsumoto, 1986]. Figure 2.3 below is a summary of the transformation reactions that take place when CTP is subjected to thermal treatment.

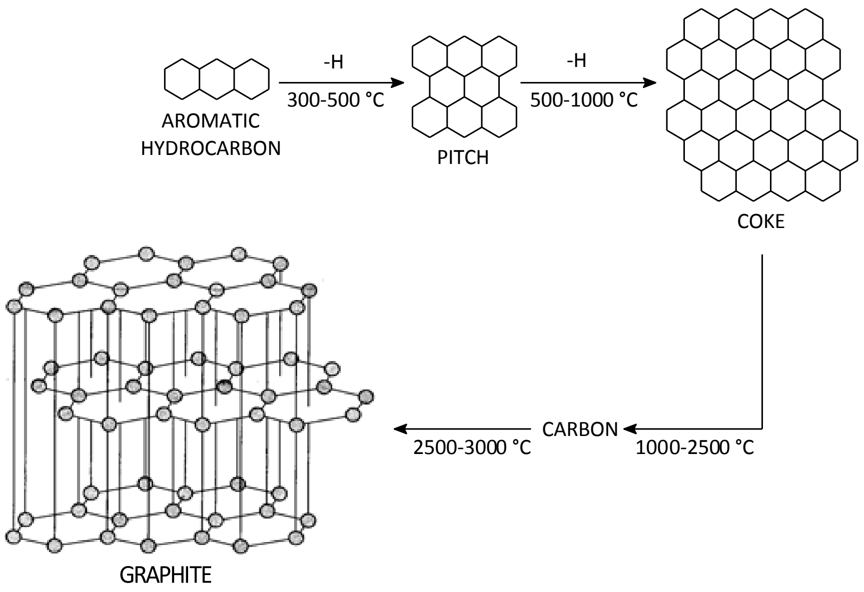


Figure 2.3 Structural transformations and reactions that take place during carbonisation of CTP [Matsumoto, 1986]

2.4 Graphite

2.4.1 Occurrence

Carbon naturally occurs in a number of different forms, which include graphite, diamond and carbon black [Chung, 2002; Wissler, 2006]. The various forms of carbon differ in their structure, properties and applications. Graphite can be divided into two main types, namely natural and synthetic graphite.

2.4.1.1 Natural graphite

Natural graphite is a form of graphite that occurs as a mineral with reserves spread all over the world. It occurs in three different physical forms, namely flake graphite, vein graphite and amorphous graphite [Wissler, 2006]. The major component in natural graphite is carbon with the remainder being mineral matter or inorganic material such as oxides and sulphides of iron, gypsum and clay minerals [Codd et al., 1971]. Different processing techniques such as floatation can be used to remove impurities and concentrate the graphite. The main uses of natural graphite include applications in refractories, steelmaking, expanded graphite, brake linings and foundry lubricants.

2.4.1.2 Synthetic graphite

Synthetic graphite in the carbon industry has a wide range of applications [Stiller et al., 1998]. It is manufactured on a commercial basis through the reorientation of the disordered layers of carbon by heating up to temperatures of about 3000 °C in graphitization furnaces. The properties of the final synthetic graphite depend on factors such as raw materials used, as well as the heat treatment procedures [Chung, 2002; Salvatore, 2003]. Prior to the manufacture of synthetic graphite, ash and other impurities are removed from the carbon source. This is aimed at improving the properties of graphite. Graphite electrodes are widely used in electric arc furnaces for the production of different ferroalloys. Synthetic graphite is obtained from the processing of graphitizable carbons and, as mentioned earlier, this results in the reorientation of the disordered layers into an orderly arrangement. Most compounds that have carbon precursors can be subjected to thermal treatment at high temperatures above 900 °C, and this process produces three main types of carbons, namely graphitizable, non-graphitizable and partially graphitizable carbon [Marsh, 1989]. Non-graphitizable carbon is a carbonaceous material that, when subjected to heat treatment, produces a rigid disordered structure. Partially graphitizable carbon is a material whose properties lie in between graphitizable and non-graphitizable, i.e. the layers are partially arranged in an orderly arrangement. Graphitizable carbon is the type of a carbonaceous material that possesses the ability to have a systematic hexagonal arrangement of carbon-carbon networks that are arranged in a three-dimensional order after high temperature heat treatment [Matsumoto, 1986]. It can be converted into a graphitic material through the reorientation of crystals in an orderly arrangement (graphitization). The hexagonal structure of graphite is presented in Figure 2.4.

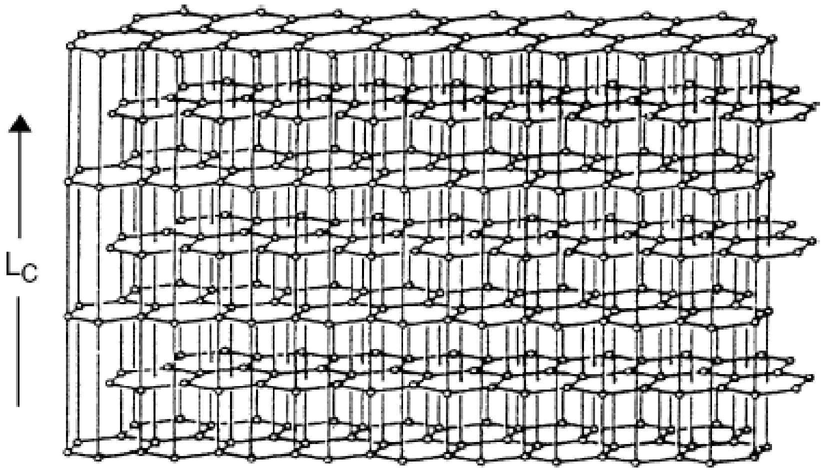


Figure 2.4 Hexagonal or layered structure of graphite [Wissler, 2006]

2.4.2 Manufacture of synthetic of graphite

2.4.2.1 The graphitization process

Graphitization is a process of heat-treating carbon precursors in an inert environment at temperatures ranging from 2000 to 3500 °C [Gray et al., 1976] with the aim of improving its thermal and mechanical properties. As previously mentioned, the process of graphitization results in the rearrangement of disordered layers into a very organised structure. Graphite has improved high Young’s modulus, strength, electrical and thermal conductivity, as well as thermal shock resistance [Karagoz et al., 1994]. These properties are essential for graphite that will be used for industrial applications in which there are significant thermal and mechanical stresses, e.g. as electrodes in submerged arc furnaces.

2.4.3 Properties of graphite

The graphite obtained from the blending and graphitization of CTP and coke or calcined anthracite has to meet certain specifications [Purevsuren et al., 2004; Li et al., 2009]. The properties of graphite produced depend on the quality and nature of the coke or calcined anthracite used as filler, as well as the CTP binder [Salvatore, 2003]. As reported by Codd et al. [1971], the graphitization temperature applied during thermal treatment also plays a significant role in determining the physical, chemical, mechanical and thermal properties of graphite.

2.4.3.1 Physical properties

The physical properties of graphite depend largely on the arrangement of layers that make up the crystal structure, raw materials used, as well as the graphitization temperature [Codd et al., 1971]. Essential physical parameters that are measurable on the graphite include electrical conductivity, thermal conductivity, density, mechanical strength and Young’s modulus [Rocha et al., 2002; Perez et al., 2004; Purevsuren et al., 2004]. Typical values for these specifications of baked carbon and graphite are shown in Table 2.2.

Table 2.2 Typical specifications of thermally treated graphite and baked carbon [Codd et al., 1971]

	Baked carbon	Electrode graphite
Density(g/ml)	1.3 -1.8	1.5 - 2.0
Young's modulus (kg/mm^2)	12 - 35	12 - 40
Electrical resistivity (Ω cm)	0.0036 - 0.009	0.0006 - 0.0013
Thermal conductivity (cal/cm s °C)	0.01	0.38
Coefficient of linear expansion(per °C)	0.65 - 2.3 x 10^{-6}	1.1 - 4.6 x 10^{-6}
Elasticity	300 - 660	470 - 980

2.4.3.2 Chemical properties

Raje et al. [2009] reported that the chemical properties of graphite have an influence on its performance when used as electrodes. Under normal circumstances, graphite is an inert material, although it can still be susceptible to chemical processes such as oxidation and reactions with metal solutions to form carbides at high temperature [Currie et al., 1955].

2.4.3.3 Mechanical properties

The mechanical properties of graphite are essential as they determine the correct usage of the material, as well as any pre-treatment that might be necessary before the material is used. According to Miyazaki and Ikeda [1982], good graphite is characterised by a low modulus of elasticity and very good tensile, compressional and flexural strength.

2.4.3.4 Thermal properties

The effect of temperature on graphite and related materials is normally studied by means of thermal analysis [Raje et al., 2009]. Synthetic graphite is characterised by a good thermal conductivity, good electrical conductivity, as well as a low coefficient of thermal expansion

[Miyazaki and Ikeda, 1982]. These properties make it the material of choice for use in different ferroalloy processes, as well as electric arc furnaces.

2.4.4 Industrial applications of graphite

Synthetic graphite is widely used to manufacture anodes that are used in the aluminium industry, graphite electrodes used in ferroalloys processes (e.g. ferrochrome, ferrosilicon and calcium carbide), nuclear reactor applications, electric motors and generators. Figure 2.5 shows the origin of carbon materials and some of their industrial applications.

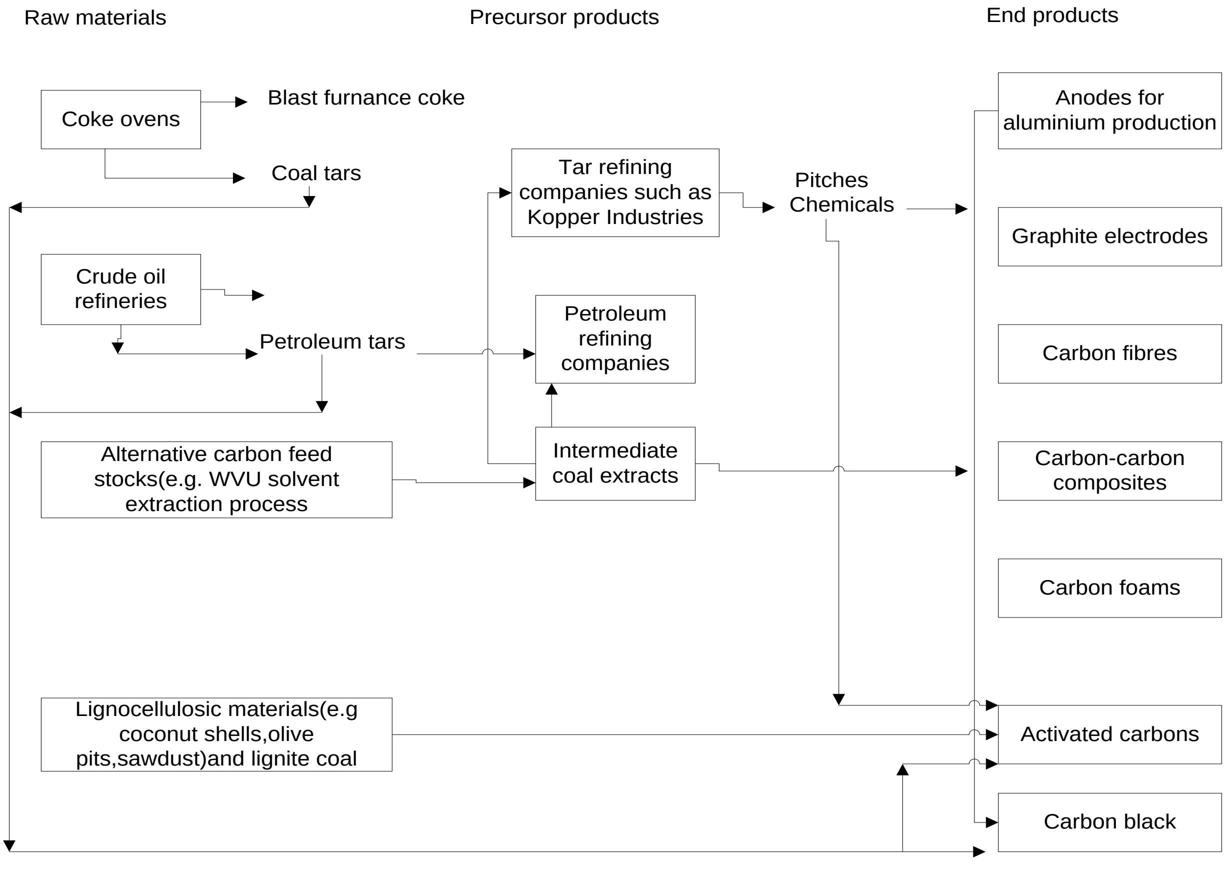


Figure 2.5 Material flows in the carbon industry [Codd et al., 1971; Irwin et al., 1998].

2.5 Graphite electrodes

Graphite electrodes have a wide range of industrial applications such as in reduction furnaces in ferroalloy processing, in aluminium smelters and in the calcium carbide industry. The electrodes are designed in such a way that they conduct electrical energy necessary for chemical reactions to take place [Bermudez et al., 2002; Visser, 2006] in submerged arc furnaces. Essential graphite electrode properties include good electrical conductivity, mechanical strength and thermal conductivity [Karagoz et al., 1994; Chung, 2002].

2.5.1 Synthesis of graphite electrodes

The first step in the production of graphite electrodes involves calcined anthracite or coke to be crushed and mixed with a binder such as CTP or petroleum pitch [Cross et al., 1964; King, 1967; Coutinho et al., 2000; Rocha et al., 2002]. External factors such as the quantity of binder added, as well as mixing period affect the final properties of the graphite artefact [Pappano et al., 2006]. The mixing of the binder and the coke/calcined anthracite allows the binder material to form a coating over the filler material. Therefore, the CTP binder should be in liquid state [Lewis and Howard, 1995]. The mixing of the binder and CTP can be done at temperatures of around 200 °C [Meyer zu Reckendorf, 1997]. After thoroughly mixing the binder and the coke/calcined anthracite, the mixture will be moulded into the desired shape and it is then ready for baking [Kortovich and Micinski, 1985]. This unbaked electrode is often referred to as a green electrode. The different process steps required during the production of graphite electrodes are discussed in more detail in sections 2.5.1.1 to 2.5.1.4.

2.5.1.1 Calcination of coke and anthracite

The manufacture of graphite electrodes for various metallurgical processes requires that the coke used in the process be graphitizable, anisotropic and should have needle-like crystals in conjunction with low impurity levels. These properties will improve the graphite electrode characteristics such as thermal shock resistance, which correlates to a low coefficient of thermal expansion, electrical and thermal conductivity [Gray et al., 1976; Karagoz et al., 1994]. Calcined anthracite can also be used as solid filler instead of coke. In fact, calcined anthracite is used much more commonly in South Africa for the production of Söderberg electrode paste for use in the ferroalloy industry, than coke [Beukes et al., 2013].

2.5.1.2 Grinding and mixing

The product from the coke or anthracite calcination stage is ground into smaller pieces, to the desired particle size depending on the size of the product to be manufactured.

2.5.1.3 Baking of green electrodes

Baking is the first heat treatment step of the green electrodes and is related to the partial graphitization that converts the pitch binder into a coke [Lewis and Howard, 1995]. During the baking process, the mixture of coke and binder is baked at a temperature of 500 to 1000 °C. This heat treatment ensures the removal of volatile components that may still be in the filler material. If these volatiles are not removed, it will lead to the cracking of the graphite artefact manufactured. The heat treatment will also lead to changes in the physical and chemical properties of the manufactured artefact [Codd et al., 1971; Meyer zu Reckendorf, 1997; Coutinho et al., 2000]. Further thermal treatment of the graphite artefact leads to the formation of a polycrystalline material; this also carbonises the binder material thereby imparting the essential electrical and physical properties to the electrodes [Stiller et al., 1998].

2.5.1.4 Graphitization

The carbon artefact formed during baking has moderate electrical and thermal properties. The treatment of this material at higher temperature produces a material that has excellent electrical and thermal properties. The process of graphitization involves a gradual increase in the temperature up to around 2500 to 3000 °C for a period ranging from 0.5 to 20 hours [Lewis and Howard, 1995]. This slow heat treatment leads to a significant change in the physical (growth of the crystalline structure) and chemical properties of the carbon material. Metallic impurities together with carbon and sulphur will be eliminated from the material. The different processes and stages involved in the manufacture of graphite artefacts are summarised in Figure 2.6.

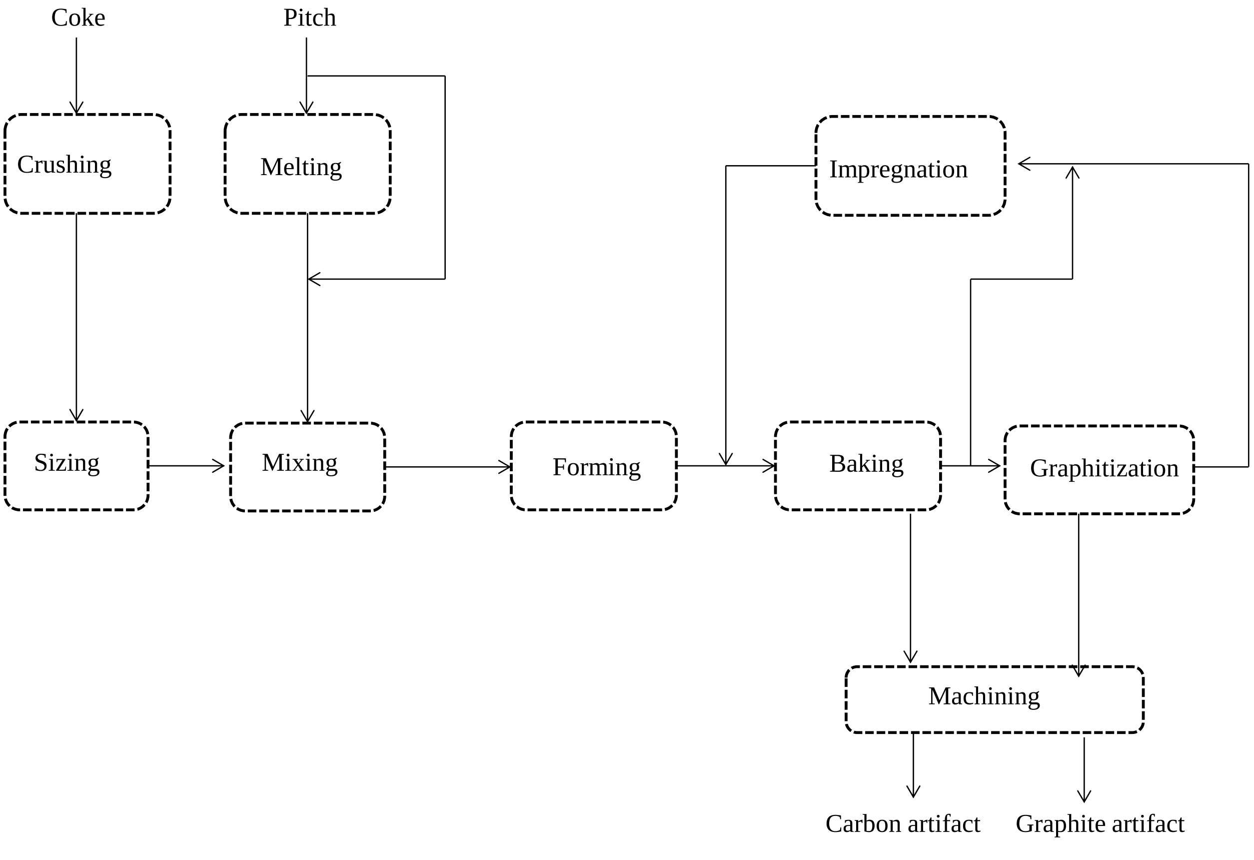


Figure 2.6 Processes involved in the manufacture of graphite artefacts [Meyer zu Reckendorf, 1997]

2.5.2 Types of graphite electrodes

There are two classes of graphite electrodes, namely prebaked electrodes and Söderberg electrodes [Tucker, 1981; Habashi, 2004]. The main differences lie in the manner in which they are manufactured. The properties and applications of baked specimens of these two types of electrodes are similar.

2.5.2.1 Prebaked electrodes

The process of making prebaked graphite electrodes is outlined in Figure 2.6 above. In the process, binder (coal tar or coal tar pitch/petroleum pitch) is mixed with a carbonaceous material such as calcined anthracite or petroleum coke. The paste made from the binder and filler materials is pressed in hydraulic presses [Sem, 1954]. The moulded paste is then heated up to 1000 °C after which it is transferred to a separate furnace where it is graphitized at temperatures ranging from 2500 to 3000 °C [Hamister, 1953]. Thereafter it will be transported to a plant where it will be used. The process of prebaking these electrodes makes them much more expensive in comparison to self-baking electrodes [Toromanhoff and Habashi, 1990; Bermudez, 2003].

2.5.2.2 Söderberg electrodes

Söderberg electrodes were first developed by Carl Wilhelm Söderberg. They first came into effect in beginning of the 19th century and were developed for the purpose of conducting electricity into smelting furnaces [Fitt and Howell, 1998]. Söderberg electrodes are made *in situ* in metallurgical furnaces where they are used. They have reasonably larger diameters and are less expensive to make compared to prebaked electrodes [Innvaer, 1992]. Söderberg electrodes are made from steel casings that are joined together in such a way that they form a cylindrical hollow cylinder into which electrode paste is continually introduced [Bruff et al., 1985; Habashi, 2004; Nelson and Prins, 2004; Visser, 2006]. The electrode paste consists of a mixture of solid filler (coke or calcined anthracite) and a CTP binder. Electrode paste is usually moulded into either paste cylinders of smaller blocks. The electrode paste cylinders typically used in Söderberg electrodes are shown Figure 2.7.

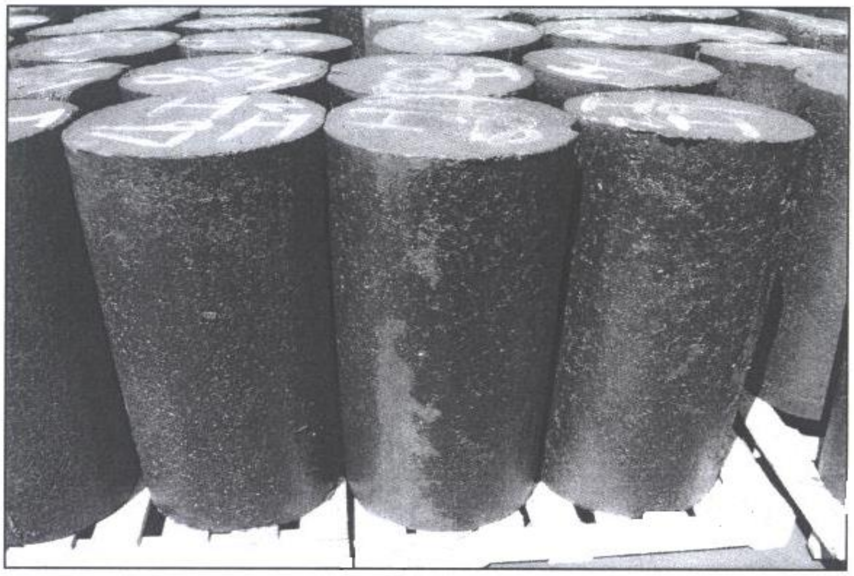


Figure 2.7 Electrode paste cylinders [Dall, 2008]

Good quality electrode paste is characterised by excellent flowing characteristics that allow the electrode paste to flow once heated, to fill the entire diameter of the electrode casing uniformly without causing segregation of the material. The baking of the electrode paste in the baking zone drives off volatile components, which, if not driven off, will result in the cracking of the electrodes while in operation [Sem, 1954]. The thermal treatment of the electrode paste transforms it into a solid material that is characterised by good electrical conductivity, as well as excellent mechanical properties. Furthermore, after baking, the electrode can support itself.

The electrode paste is solid at room temperature but softens at 60 °C when heated and starts flowing at around 80 °C [Innvaer, 1992], depending on the SP. Carbonisation of the electrode paste occurs at temperatures of around 400 to 500 °C [Innvaer and Olsen, 1980; Walker, 1986; McDougall et al., 2004; Meyjes et al., 2010]. This temperature is commonly referred to as the baking isotherm temperature. The Söderberg electrode baking isotherm is an extremely important temperature in electrode management. If the electrode is grown (extended) so that the baking isotherm is below the contact shoes it could have disastrous consequences. The electrode is extremely vulnerable to breakage if the baking isotherm is below the contact shoes, since the liquid/soft electrode paste does not contribute to the mechanical strength of the electrode column. Furthermore, if a hole is arced into the metal casing, liquid/soft paste could run into the furnace. This is usually termed a green electrode break. A green electrode break could result in an explosion due to the liquid/soft electrode paste being exposed to the very high temperatures inside the furnace. It is therefore vital for continuous, safe and profitable operation that the Söderberg electrode baking isotherm is kept above the contact shoe level under normal furnace operational conditions. As the carbonised electrode moves deeper into the burden material being smelted, increased temperatures result in *in situ* conversion to graphite. Temperatures at the arc of the furnace could be as high as 3000 °C; therefore, full graphitisation is achieved *in situ.*

During operation, electrical energy will be supplied through the contact shoes and this electrical energy results in the baking and evolution of volatile organic compounds [Arnesen, 1979; Visser, 2006]. The continual heating of the filler and binder will result in it being transformed into a good, solid carbon conductor [Bermudez et al., 2003]. Figure 2.8 presents the cross-sectional view of a typical Söderberg electrode system.

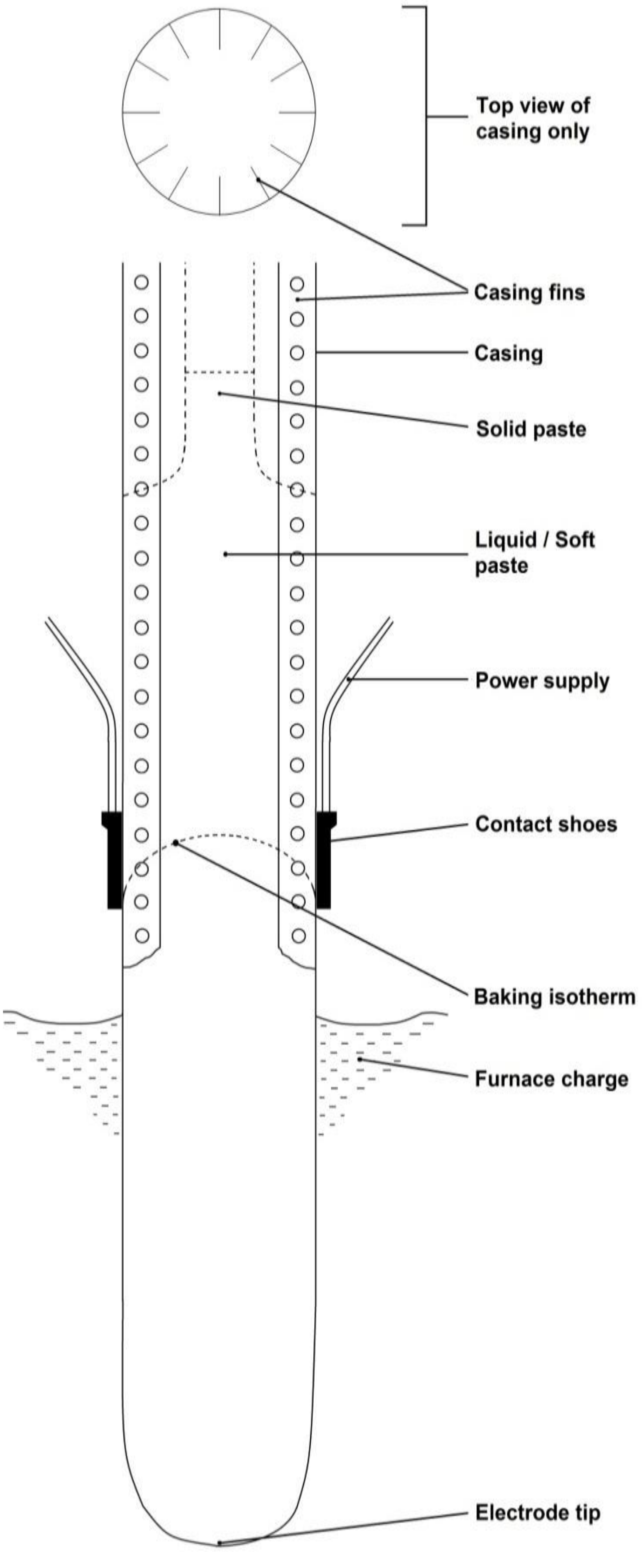


Figure 2.8 Structure of a Söderberg electrode [Beukes et al., 2013; Shoko et al., 2013].

The management of Söderberg electrodes is considered one of the most critical operational aspects in the operation of submerged arc furnaces [Arnesen, 1979]. For efficient production processes, it is essential that the electrode system operates smoothly. Proper electrode operation largely depends on the equipment used, as well as the quality of the electrode paste [Sem, 1954].

In the smelting furnaces in which Söderberg electrodes are used, conditions are very harsh with severe mechanical and thermal stresses. These stresses may lead to the wear of the electrode along the column, which may eventually lead to electrode breaks [Montgomery, 1981]. It is therefore essential that electrodes be designed in such a way that they can withstand these forces.

2.5.3 Essential properties of graphite electrodes

The graphite obtained from the blending and graphitization of CTP and coke or calcined anthracite has to comply with certain characteristics required [Purevsuren et al., 2004; Li et al., 2009]. Some of these essential characteristics are discussed in subsequent paragraphs.

2.5.3.1 Mechanical properties

The mechanical strength of graphite electrodes gives them the ability to withstand compressive, flexural and tensile forces.. Electrodes used in electric arc furnaces should have high flexural strength [Kortovich et al., 1985; Miller et al., 2010]. When the graphite electrodes are in operation, they are subjected to various stresses; therefore, it is important that electrodes have good mechanical properties so as to minimise the chances of the electrodes breaking [Bullon and Perez, 2010].

2.5.3.2 Thermal properties

2.5.3.2.1 Electrical and thermal conductivity

The thermal and electrical conductivity of electrodes should be good enough so that they are able to conduct currents to the tip of the graphite electrodes [Bullon and Perez, 2010].

2.5.3.2.2 Coefficient of thermal expansion

The coefficient of thermal expansion is a measure of the increase in dimension of a material with an increase in temperature. The differences in the temperature gradient endured by electrodes when in operation builds up thermal stresses that may lead to the breaking or failure of electrodes [Janes, 1969]. Electrodes used in electric arc furnaces should have a low coefficient of thermal expansion so as to reduce the risk of cracking of electrodes when in operation [Janes, 1969; Tucker, 1981; Kortovich et al., 1985; Miller et al., 2010]. The coefficient of thermal expansion of electrodes depends on factors such as the raw material used, particle size, binding material, methods of mixing, as well as the graphitization temperature [Coutinho et al., 2000].

2.5.3.2.3 Thermal shock resistance

The thermo shock resistance of graphite electrodes relates to the cracking or rupturing of the electrodes incurred as a result of sudden changes in temperature. This is one of the most vital characteristics of graphite electrodes and depends largely on the quality of the electrode paste used in the preparation of the electrodes. Thermal shock comes as a consequence of the uneven thermal gradient that occurs when a material expands in different directions by different amounts [Lewis and Howard, 1995]. Graphite is characterised by a high degree of thermal shock resistance of approximately 150 x 10^3 W/m. The thermal shock resistance of a material is given by the equation below [Sato et al., 1975],

$$\text{Thermal shock resistance} = \frac{Ks}{\alpha E}$$

Where:

K is the thermal conductivity of the material (W/mK);

S is the tensile strength of the material (psi);

E is Young’s modulus (psi); and

α is the coefficient of thermal expansion (ppm/°C).

2.5.3.3 Corrosion resistance and chemical inertness

Corrosion of graphite electrodes occurs as a result of chemical or electrochemical reactions taking place between the environment and the electrodes; therefore, it is essential that graphite electrodes used in corrosive, oxidative and high temperature environments should be corrosion resistant [Currie et al., 1955]. The inability of the graphite electrodes to resist corrosion has a wide range of implications, such as contamination of products during processing, environmental effects, loss of production as result of decommissioning of equipment and replacement of broken electrodes.

2.5.3.4 Bulk density

With respect to graphite electrodes, good mechanical properties are a reflection of higher bulk density, which is essential for the electrode to resist the mechanical stresses endured during operation in electric arc furnaces.

2.5.3.5 Ash content and harmful elements

Graphite electrodes should have low levels of elemental impurities such as boron, titanium and vanadium. In the alloy-making processes, the presence of impurities could interfere with the process, as well as contaminate the final product. Quantitative determination of harmful elements can be determined using Atomic Absorption Spectrometry (AAS) and/or Inductively Coupled Plasma (ICP) analysis.

2.5.3.6 Specific resistance (electrical resistivity)

The specific resistance (resistivity) of a material is the electrical resistance of a unit length of the material. It is also inversely proportional to the electric conductivity [Codd et al., 1971]. A graphite electrode is a good current conductor and it is vital that its resistivity should not change much as a function of temperature.

2.5.4 Söderberg electrode breakages

There are two major types of electrode breakages, namely soft paste breakage and hard breakage. The soft paste breakage occurs as a result of the steel casing not being able to conduct the full electrical load or holes being arced into the steel casing. This occurs mainly due to poor welding of the electrode casings [Innvaer et al., 1984] or to too high currents being passed through unbaked electrodes. This type of electrode breakage is considered to be extremely dangerous because it can lead to explosions due to the presences of volatile components. Hard breakages are the most common type of breakages in submerged arc furnaces and they are mainly due to high thermal and mechanical stresses and sudden changes in temperature [Innvaer, 1992; Innvaer et al., 1984]. Bailey. [1950] reported that major sources of deterioration in graphite electrodes emanate from various mechanical and thermal shocks that electrodes are subjected to while in use.

2.5.4.1 Causes of Söderberg electrode failures/breakages

During normal operations in electric arc furnaces, the electrodes undergo wear-and-tear. Some of the major causes of electrode fracture, as reported by Yarushina et al. [2007], are due to the oxidation of carbonaceous components by slag and hot gases, thermal shock cracking, corrosive wear and cleavage in the slag zone. Innvaer et al. [1984] also stated that conditions that contribute to electrode breakage include high temperatures at the electrode tip, sudden temperature changes, low temperatures due to cooling water on the contact clamps and chemical and mechanical wear. The water-cooled contact shoes will lead to a temperature difference within the electrode system and the temperature difference leads to thermo shocks that can ultimately lead to the electrode being broken in parts where the electrode paste has not been baked [Ord et al., 1995**]**. Factors that contribute significantly towards electrode breakages include uneven operating temperature conditions, long down times, bad welding on electrode casings, high temperature gradients, electrode paste segregation, and dust and dirt that lead to inhomogeneity of the electrode system. The combination of thermal stresses and general electrode wear leads to small tips of electrodes loosening [Innvaer and Vatland, 1984]. The nipple joint failures are normally attributed to a combination of both mechanical and thermal stresses being applied to the electrode. Kuznetsov and Korobov. [2000] identified four different types of wear in electrodes and these are oxidation, burning of the lateral surface, end wear, breakage of the nipple joint and cracking of the working tips of the electrodes. There are at least four characteristic electrode breaks, which are shown in Figure 2.9.

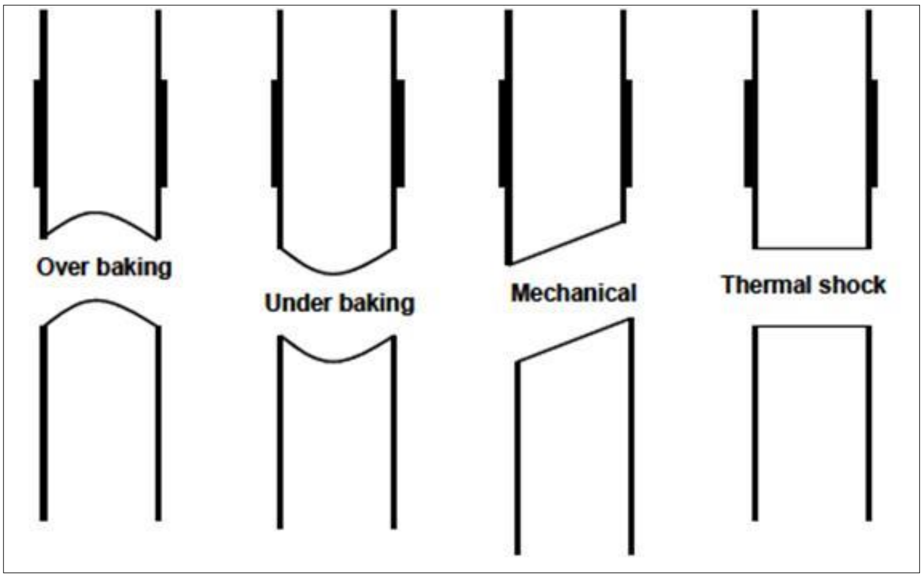


Figure 2.9 Characteristic electrode breaks and their main causes [Nelson and Prins, 2004].

2.6 Analytical techniques used to characterise CT, CTP and graphite

The chemical composition of CT, CTP and graphite can be determined by various analytical techniques. In the characterisation of CT and CTP, some of the widely applicable analytical techniques include ultimate/elemental analysis, proximate analysis, Nuclear Magnetic Resonance Spectroscopy (NMR) and Fourier Transform Infra-red Spectroscopy (FT-IR) [Lewis, 1982; Snape, 1989; Guillen et al., 1996; Meyer zu Reckendorf, 1997]. These combined analytical methods provide essential information that can be used to distinguish between different CT and CTP materials [Alcañiz-Monge et al., 2001], as well as understanding their behaviour when they undergo reactions such as carbonisation and thermal treatment at higher temperatures. Zander [1987a, 1987b] reported that the efficient and accurate characterisation of CTP allows for the prediction of different CTP properties, which can be related to the different applications in the carbon industry. The structure of graphite can be characterised by X-ray diffraction spectroscopy (XRD) and Raman spectroscopy, while Thermomechanical analysis (TMA) can be used to establish the change in dimensions as a function of temperature. Brief background information on the different analytical methods is described in sections 2.6.1 to 2.6.6. Further details on the techniques that were used in this study will be provided in Chapter 3.

2.6.1 Proximate analysis

The proximate analysis of CTP involves the determination of moisture, volatile matter and ash content. The fixed carbon (FC) content of CTP is calculated by difference (100 - moisture (%) – ash content (%) – volatile matter (%)). The procedure involves heating the sample under standard conditions.

2.6.2 Ultimate/elemental analysis

The ultimate/elemental analysis of CTP involves the determination of the percentages of carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) as found in the gaseous form after complete combustion of the carbonaceous material. Oxygen (O) is determined by difference. Ultimate analysis usually confirms C as the main constituent in CTP samples [Blanco et al., 2000; Alcañiz-Monge et al., 2001]. From the ultimate analysis data, the ratio of carbon to hydrogen (aromaticity) can be calculated. The aromaticity of CTP can be defined as the ratio of aromatic to aliphatic carbons in a carbonaceous material [Manabile, 2009]. The C/H ratio gives an indication of the degree of aromaticity in CTP. CTPs with a high aromatic content are characterised by a high carbon residue during the process of carbonisation [Mason, 1970].

2.6.3 C and H - Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR is a very valuable and non-destructive technique that is widely used to determine the distribution of hydrogen among various functional groups in different carbonaceous materials by making use of techniques such as cross polarisation magic angle spinning (CP MAS) and dipolar decoupling (DD) [Solum et al., 1989; Speight, 2005]. Other essential information that can be obtained from NMR analysis includes the aliphaticity and the aromaticity, the extent of alkyl substitution, as well as the configuration of aromatic rings in carbonaceous materials

[Dreeskemp et al., 1989; Diaz and Blanco, 2003]. McMurry. [1992] and Cerny. [1991] indicated that the NMR analysis gives the C-H structural outline of a given molecule.

The principle of NMR analysis revolves around the interaction and behaviour of the nuclei on application of an external magnetic field. NMR analysis has the unique ability of differentiating between aromatic (f_a) and aliphatic/non aromatic (f_{al}) carbons in organic materials [Dreeskemp et al., 1989, McMurry, 1992].

NMR analysis for carbon-related materials can be divided into ^{1}H NMR, which provides information on the distribution of hydrogen types in carbonaceous materials [Speight, 2005], and ^{13}C NMR, which focuses on the identification of carbon atoms in carbonaceous materials [Snape et al., 1998]. ^{1}H and ^{13}C have different NMR absorption bands and this makes it easier for the C-H skeletal structure determination in carbonaceous materials. The ^{13}C NMR is the most widely used in the characterisation of fossils fuels [Solum et al., 1989].

The NMR spectrum is characterised by chemical shifts that give an indication of the exact place where a nucleus absorbs energy and the spectra are reported in ppm chemical shift [McMurry, 1992], with the resonances of a given chemical shift being related to the structural features of the pitch samples or any other carbonaceous material [Diaz and Blanco, 2003]. Through the NMR analysis of carbonaceous material, different structural parameters found in CTP can be evaluated [Snape, 1989].

2.6.4 FT-IR spectroscopy

Fourier Transform Infra-red spectroscopy (FT-IR) is an analytical technique that can be used to provide qualitative and quantitative information about the existence of different functional groups within a given sample. During thermal treatment, CTP undergoes structural transformations and FT-IR can be used for the purpose of getting a much deeper understanding of the changes that take place when CTP is subjected to thermal treatment at different temperatures [Guillen, 1992]. The IR spectrum refers to the output from the FT-IR instrument and it is expressed as intensity versus a wavenumber scale with units of cm^{-1} [Stuart, 1996]. Correct interpretation of the FT-IR spectrum allows for the identification of different functional groups within a given sample [McMurry, 1992; Griffiths and de Haseth, 2007]. Alcañiz-Monge et al., 2001 et al. [2001] indicated that the successful identification of different functional groups in CTP and other carbonaceous materials is achieved by considering the characteristics of C-H bands within the structure. The introduction of modern sampling techniques such as attenuated total reflectance has made FT-IR much simpler. The spectrum is characterised by three essential spectral regions, namely far infrared (FIR), which is in the range 400 to 0 cm^{-1}, mid infrared (MIR), which is in the range of 4000 to 400 cm^{-1}, and near infrared (NIR), which is in the range of 14000 to 4000 cm^{-1}. The MIR is the most widely used spectral region [Stuart, 1996; Griffiths and de Haseth, 2007]. FT-IR analysis is based on the interaction of molecules with electromagnetic radiation. Output from the FT-IR instrument can be expressed as % transmittance (T) or % absorbance (A) versus wavenumber (cm^{-1}). %T is mainly used in qualitative FT-IR, while % A is mainly used for the quantitative analysis of samples [Stuart, 1996]. In their normal state, molecules contain some energy and this energy allows them to bend, stretch and vibrate [McMurry, 1992]. Each molecular species absorbs radiation within a given range of the FT-IR spectrum. The vibrational modes of molecules are unique implying that it can be used to identify functional groups present in the molecule. However, compounds of a similar class, such as carbonaceous (coal and CTP) materials, are characterised by similar sets of bands in their IR spectra. The only notable difference is the difference in their intensities, which is due to varying quantities of functional groups [Guillen, 1995; 1996].

2.6.5 Thermomechanical analysis (TMA)

Thermomechanical analysis (TMA) is a technique that is used to measure changes in dimensions of a sample when the sample is subjected to a load. The changes that occur can also be expressed as a function of temperature [Brown, 1988]. TMA can be used to determine the morphological, chemical and physical properties of coal ash, as well as slag if the degree of penetration into a sample is measured when the sample is subjected to thermal treatment [Bryant et al., 1998; Liu et al., 2007]

2.6.6 XRD analysis

The XRD technique is widely used in the characterisation of crystallinity of a wide range of materials such as coal and coal-related products. In carbonaceous materials, XRD can be used to establish a number of parameters, such as the degree of graphitization in graphitic materials, crystallinity or amorphous nature of carbon-related materials, as well as the interlayer spacing of materials (d_{002}) and the lateral size (L_a) [Hussain and Qadeer, 2000; Manoj and Kunjomana, 2012]. The different parameters that can be evaluated by XRD analysis on carbon and graphitic materials are represented in Figure 2.10.

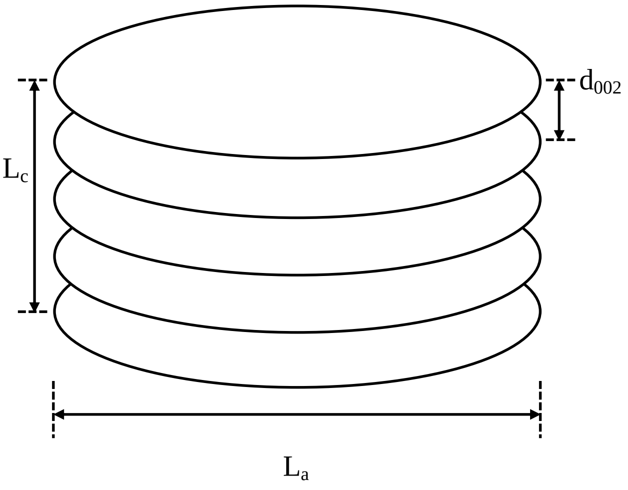


Figure 2.10 Parameters that can be determined by XRD in graphitic materials [Belekov, 2001]

The crystallinity is usually expressed as (L_c) and is calculated from the Scherrer equation below [Feret, 1998; Van Niekerk et al., 2008; Manoj and Kunjomana, 2012]

$$L_C = \frac{0.89\lambda}{\beta Cos\theta}$$

Where

0.89 is the Scherrer Constant;

λ is the radiation wavelength; and

β is $2\Theta_1$- $2\Theta_2$ (scattering angles).

During the process of graphitization of carbonaceous materials, there is a shift and reorganisation of molecules, which leads to the formation of a three-dimensional structure. The thermal treatment also results in the loss of impurities and this leads to an increase in the crystallinity of carbon-related materials [Hussain and Qadeer, 2000]. The degree of ordering also increases with an increase in the graphitization temperature and this is due to the growth in the crystallite sizes [Hussain and Qadeer, 2000; Belekov, 2001]. The changes that take place during graphitization are reflected in the changes that take place in lateral size and stacking height. The interplanar distance between the different graphene layers can be used to calculate the degree of graphitization (g) according to the equation below [Feret, 1998; Zou et al., 2003; Makgato et al., 2009]

$$g = \frac{3.44 - d002}{3.44 - 3.354} = \frac{3.44 - d002}{0.086}$$

where:

g is the degree of graphitization;

3.345 Å is the interlayer distance for pure graphite (nm);

d_{002} is the interlayer spacing derived from XRD (nm); and

3.440 Å is the interlayer spacing of fully non-graphitized carbon (nm).

2.7 Summary

Both CT and CTP are complex organic materials. Different analytical techniques can be used to establish the chemical composition as well as structural changes during the thermal treatment of CT and CTP. CT and CTP can be used as binders in the manufacture of graphite electrodes. The thermal treatment of CTP and CT results in the occurrence of thermal polymerisation, aromatic condensation reactions, as well as the elimination of side chains (Section 2.3.1). Graphite electrodes formed from the mixing of CTP and calcined anthracite or coke are classified into two main categories, which are prebaked and Söderberg electrodes. Söderberg electrodes are widely used in different ferroalloy processes and proper electrode management is required for their successful operation.