Open book: 2003

Photochemical smog's comprise of primary and secondary pollutants.

Primary pollutants are released directly into the atmosphere, through combustion of fuels in car engines and power stations. The main primary pollutants produced because of motor vehicle combustion are; Nitrogen oxides, carbon monoxide and various hydrocarbons.

Secondary pollutants are produced by a further chemical reactions taking place with primary pollutants. Secondary pollutants comprise of O_3, NO_2, H_2O_2, HNO_3, partially oxidised VOC's and PAN peroxyacetyl nitrate. (Illustrated below in figure 1.1)

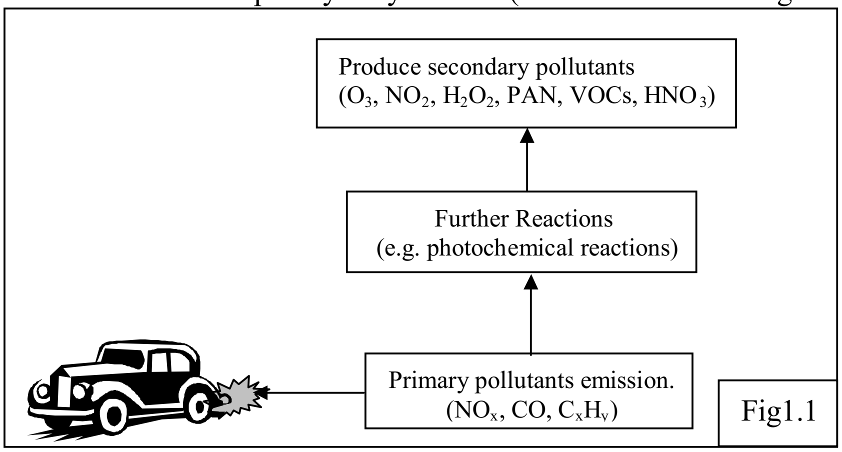

Fig1.1

Formation of the ozone (secondary pollutant) summarised in figure 1.2

Firstly NO_2 dissociates to form: $\mathbf{NO_2 \rightarrow NO^{\cdot} + O^{\cdot}}$ **STEP (1)**
The ozone then reacts with NO: $\mathbf{O_3 + NO^{\cdot} \rightarrow O_2 + NO_2}$ **STEP (2)**
Then the products react to form: $\mathbf{O_2 + O_3 \rightarrow O_3}$ **STEP(3)**
These reactions result in the production of the secondary pollutant ozone derived form the photochemical reaction of NO_2 a primary pollutant.

Fig1.2

Coal is a fossil fuel (made from the decomposition of living material). All living organisms contain sulphur and therefore when coal burns, the sulphur compounds are oxidised to form sulphur oxides.

Organisms store nitrogen as protein and therefore it is present in the coal, therefore when coal is burnt the nitrogen compounds are oxidised to form NO_x. Also because of the high temperature of combustion the nitrogen and oxygen in the atmosphere combine to form thermal NO_x.

CO_2 is a waste product of most combustion reactions, as the carbon in the organic material in the decomposed organisms oxidises it may partially oxidise to form carbon monoxide (summarised in figure 1.3) 200

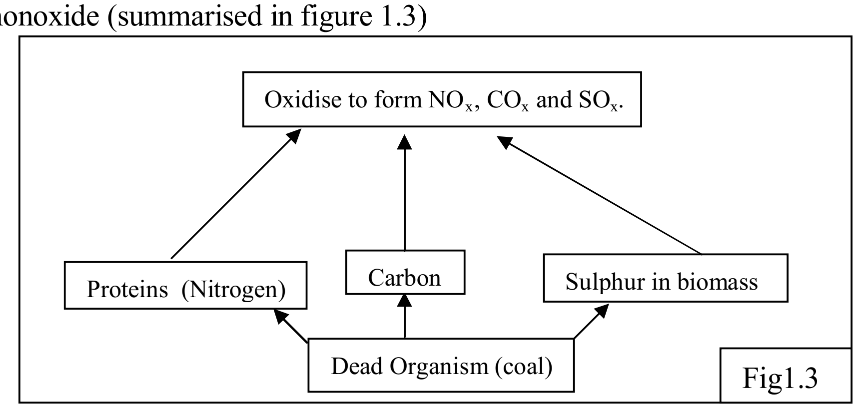

Fig1.3

The best conditions for photochemical smog formation are during the summer. High levels of sunshine allow increased photodissociation of chemicals such us NO_x producing secondary pollutants. The light winds and high atmospheric pressure keep the stagnant air mass of pollution from dispersing and therefore pollution levels remain in high concentrations. Pollutants stay closer to ground level and mix more easily and light prevailing winds are able to transport the pollutants close to the grounds surface to other regions (Summarised in figure 1.4)
High concentrations of hydrocarbons and nitrogen oxides are also required as they are primary pollutants, which will be able to initiate the smog formation. These pollutant concentration levels can be achieved in areas of large mass of traffic and combustion processes in industrial regions.

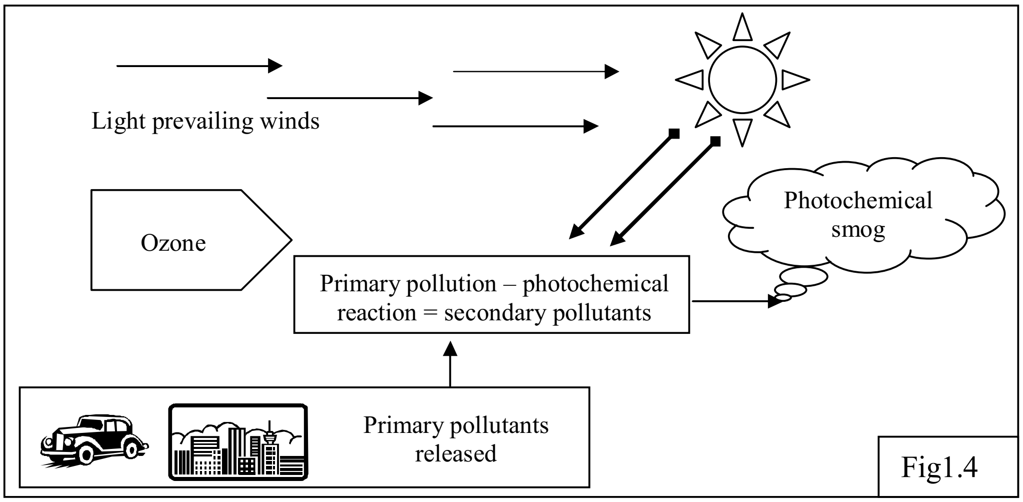

Fig1.4

High ozone concentrations are attained in the troposphere because even though the dissociation of the primary pollutant NO_2 to form NO and O initiates the breakdown of O_3 (as shown in figure1.2). The two products of the two reactions react to reform the ozone layer. As a result the ozone being depleted is being reformed. Also within the reaction when more NO_2 is formed in STEP (2) this makes more NO_2 available to dissociate and form more oxygen atoms, which can then make more ozone.

The high ozone concentration in the troposhphere is also maintained by the breakdown of hydrocarbons in the atmosphere to produce more NO_2, which can be depleted to produce oxygen atoms needed to make the ozone layer. (Refer to figure 1.5)

RCH_3 stands for the hydrocarbon
Hydrocarbon reacts with a hydroxyl radical: $\mathbf{RCH_3 + OH \rightarrow RCH_2 + H_2O}$ STEP(1)
The product of the previous reaction reacts with oxygen in the atmosphere:
$\mathbf{RCH_2 + O_2 \rightarrow RCH_2O_2}$ STEP (2)
The peroxy radical reacts further: $\mathbf{RCH_2O_2 + NO \rightarrow RCH_2O + NO_2}$ STEP (3)
NO_2 can then dissociate again as shown in figure 1.1
Fig1.5

Because of the equilibrium achieved between the depletion of the ozone and its reformation through the dissociation of NO_2 the concentration of the ozone does not 400
fall overall. However the peroxy radical reacts faster with nitrogen oxide to form nitrogen dioxide compared to the reaction between nitrogen oxide radical and ozone

(depletion). Therefore there is a faster rate of ozone production compared to ozone destruction therefore concentration of ozone overall increases as smog forms.

Methods chosen by BPEOs (Best Practical Environmental Option) for minimising sulphur dioxide and nitrogen oxide emissions are described below:

- To reduce sulphur dioxide emissions the 'Sea water scrubbing' Process is used:
  The flue gases are passed through seawater, which is naturally alkaline. The sulphur dioxide dissolves in the alkaline solution forming sulphite ions. The water produced is then aerated to oxidise the sulphite ions into a more 600
  harmless sulphate. This is then passed back into the sea, the pH change of the water is from 7.5 to 6; however as the water returns back to the sea the pH change becomes negligible. Process is summarised in figure 1.6

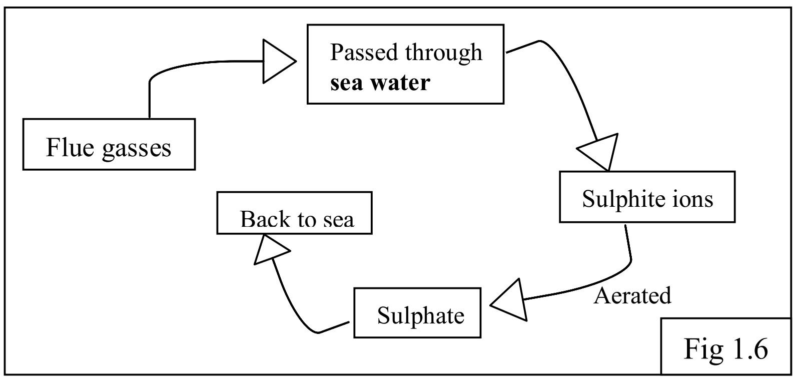

Fig 1.6

At Longannet the management has opted to use the sea water scrubbing process because it does not produce any solid wastes that needs to be disposed of and it does not have any by-products that need to be sold, such as the gypsum produced by the limestone process and so they do not need to compete for price and efficiency for the by-product. Also the site is located near the sea and a result has access to a large resource of water, this makes the process environmentally friendly and cheap for Longannet to use. Also because the sulphur is returned to sea in a quick and less harmful way as it cuts short the sulphur oxides cycle.

- To reduce the nitrogen oxide emission the reburn furnace process is used in this process the furnace is split into three different zones.
  The first zone PRIMARY COMBUSTION ZONE powered by coal is where 800
  the nitrogen oxidise forms as the coal combusts, but in less air than usual, this leads to less NO_x formation. In the REBURNING ZONE natural gasses are added, the NO_x reacts with the alkanes to produce nitrogen, carbon dioxide and water vapour (figure1.7).

$$CH_{4(g)} + 4NO_{(g)} \rightarrow 2N_{2(g)} + CO_{2(g)} + 2H_2O_{(g)}$$

Fig1.7

  Any unreacted fuel and carbon monoxide is burnt in the BURNING ZONE. Oxidation of the natural gases is exothermic and as a result additional heat is given off, this contributes to the generation of electricity. Figure 1.6 shows the furnace structure.

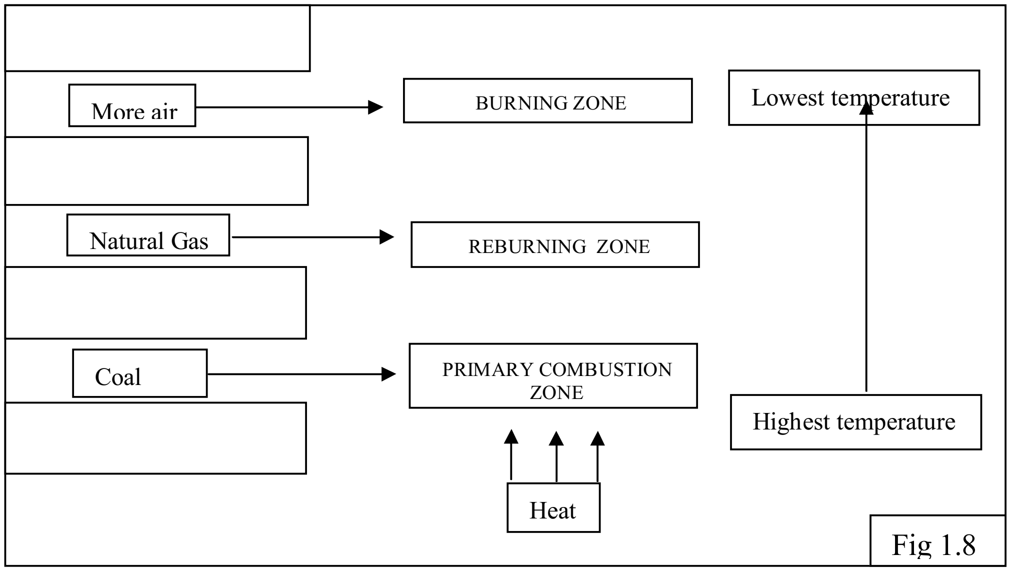

Fig 1.8

For lowering Nitrogen Oxide emission the company has adapted the reburning furnace, this choice was made after a large scale testing investigation which showed better cost efficiency and that the process was environmentally friendly.

Chemists are currently developing their understanding into the pollutants present in the troposphere and their concentrations, as well as the conditions which encourage the deterioration of the atmosphere. Chemists are also trying to model and replicate conditions and reactions in labs to develop their understandings and develop methods to reduce atmosphere destruction, as they will know more precisely the causes of the depletion. It is important for chemists to develop this understanding so that they can prolong the life of the atmosphere, as we know it now. 1000

Bibliography: