CHEMISTRY IN THE COAL INDUSTRY

The main role of chemistry in the coal industry today is analysis. Coal from differnt mines varies enormously and users need to know accurately the composition of the product they are buying.

Coal Research Ltd. is an independent coal testing laboratory (funded by the Coal Research Association of New Zealand and the Foundation for Research, Science and Technolgy) which analyses coal produced from New Zealand mines for:

Total Moisture - Calculated from the weight loss of the coal (as sampled at the mine) when heated to 105^{o}C in nitrogen until constant weight.

Ash - The weight percent of material remaining after the coal sample is completely incinerated in a furnace at 815^{o}C.

Volatile Matter - The weight percent loss when the coal sample is heated in a reducing atmosphere (out of air contact) for seven minutes at 900^{o}C.

Fixed Carbon - Calculated by subtracting the sum of moisture, ash and volatile matter from 100 percent.

Gross Calorific Valve (Specific Energy) - Calculated from the measured amount of heat released when the coal is burnt in excess oxygen in a bomb calorimeter under standard conditions.

Sulfur - Calculated from the measured amount of SO_2 released when the coal is combusted in excess oxygen in a tube furnace set at 1350^{o}C.

Crucible Swelling Number - Assigned by comparing the shape of a coke button produced when the coal is heated in a lidded silica crucible at 820^{o}C for a minimum of 2.5 minutes against a standard set of profiles. 0 = no swelling, 9 = high swelling.

Ash Fusion Temperature - Hemi (AFT) - The temperature at which controlled heating under reducing conditions causes sufficient softening to change to change a moulded pyramid shaped ash pellet to a hemispherical shape (height equal to half the base).

INTRODUCTION

Coal is defined in the Concise Oxford Dictionary as " a hard black or blackish rock, mainly carbonised plant matter, found in underground seams, and used as a fuel and in the manufacture of gas, tar etc". Coal is the result of the geological metamorphosis of plant material. The process of metamorphosis leads to a reduction in moisture, oxygen and hydrogen and an increase in percentage carbon. The degree of metamorphosis is termed "rank". High rank coals have low moisture and high carbon. The highest rank coals in New Zealand (bituminous) are all from the West Coast of the South Island. North Island coals are sub-bituminous (intermediate rank), while most Southland coals are lignite (low rank). Only high rank coals are exported as with lower rank coals one would be paying transport costs for water.

New Zealand has moderate reserves of coal of the types given above. The use of coal as the raw material for household gas supply ceased in the 1970's (Volume 1 contained an article on Dunedin town gas, but the plant had closed by the time of publication.) Today it is used as a fuel for heating, occasionally for electricity generation (Huntly power station, but this is normally fired by natural gas), and as a reductant of iron sands in the steel industry at Glenbrook. About one third is exported from the West Coast to Japan and Korea as a coking blend. The carbon required to make the anodes for the aluminium smelter in Southland is derived from oil and is imported.

There are currently about fifty coal mines, owned by twenty-four different companies, producing coal in New Zealand. However at least 90% comes from mines in the Waikato and Buller regions owned by the SOE Solid Energy, and the vast majority of this from five mines, Huntley East No.1 (286 000 tonnes) and Rotowaro (888 000 tonnes) in the Waikato, Stockton (1 097 000 tonnes) in the Buller region, Strongman No.2 (301 000 tonnes) near Greymouth, and Wairaki, Ohai (158 000 tonnes) in Southland. The figures are for 1997 production. The two biggest producers other than Solid Fuel are Glencoal Energy Ltd. in the Waikato (136 000 tonnes) and New Vale Coal Co. Ltd. in Southland (136 000 tonnes).

Coal is considered from the analytical viewpoint to consist of three distiguishable components, coal substance, minerals and moisture. Coal substance contains besides carbon, hydrogen and oxygen other elements such as sulfur, nitrogen, calcium, boron and aluminium. The metallic elements contribute to the coal ash. The structure of coal is very variable and complex with carbon, the ingredient of use, present as giant hydrocarbon molecules. The major role of the chemist in New Zealand's coal industry is to analyse the coal produced from the mines. This is of utmost importance in the marketing of coal as customers must know that what they are buying meets their specifications.

COAL ANALYSIS

Coal Research Ltd. is an independent coal testing laboratory in Lower Hutt , jointly funded by the Coal Research Association of New Zealand Inc. and the Foundation for Research, Science and Technology. The Association is made up of coal producers, coal suppliers and users, and others connected with energy industries.. The laboratory is accredited by International Accreditation New Zealand, the national accreditation authority for laboratories and operates in accordance with ISO/IEC Guide 58:1990 and accredits to ISO/IEC Guide 25:1990.

Sampling is done at the point of production at the mines. The sample is ground to reduce particle size and sub-sampled and then analysed for: Total Moisture, Ash, Volatile Matter, Fixed Carbon, Gross Calorific Value, Sulfur, Crucible Swelling Number and Ash Fusion Temperature - Hemi (AFT). These analyses are discussed below. Commercial coal normally has a lower moisture content than as mined coal unless it has been exposed to wet weather. Coal with lower moisture will have corresponingly higher calorific value, volatile matter and ash.

Total Moisture

As the equilibrium moisture content will vary with temperature and humidity the coal is conditioned by placing it in a humidity controlled room at 20^{o}C and 70% humidity prior to weighing. The total moisture is then calculated from the weight loss of the coal (from the mine sub-sample) when heated to 105^{o}C in nitrogen until constant weight. Care must be taken in cooling the dried sample for weighing as it readily reabsorbs moisture from the atmosphere.

The range in total moisture content of as-mined coal in 1997 was 6.4 - 44.7%. Southland coals have overall a high moisture content, while Stockton coal, most of which is exported, has a low value of 8%.

Ash
The ash content is the weight percent of material remaining after the coal is completely incinerated in a furnace at 815^{o}C. Initial heating too rapidly creates problems, so a standard method used is to raise the temperature of the sample to 400^{0}C over 30 minutes, then to 815^{o}C during a further 30 minutes and then holding it at that temperature for two hours.

The 1997 range for as-mined samples was 1.5 - 12.4%

Volatile Matter
This is the weight percent loss when the coal is heated in a reducing atmosphere (out of air contact) for seven minutes at 900^{o}C. The weight loss of a sample is critically dependent on almost every variable in the test, temperature, time, rate of heating, sample size, particle size, and the shape and material of the containing vessel. The method adopted is to place a 1 g sample in a silica crucible on special lightweight stand, inserted in to a furnace at 910^{o}C on a mineral wool pad, and left for seven minutes. The temperature drops to 885^{o}C and then recovers to 900^{o}C.

The 1997 range was for as-mined coal 19.3 - 42.0%.

Fixed Carbon
This is calculated by subtracting the sum of moisture, ash and volatile matter from 100 percent. It contains the errors and scatter of the other three measurements and is regarded as an approximate figure.

The 1997 range for as-mined coal was 23.8 - 66.7%.

Gross Calorific Value (Specific Energy)
This is the most important quantity required of coal analysis. It is calculated from the measured amount of heat released when the coal is burnt in excess oxygen in a bomb calorimeter under standard conditions. It includes the heat of combustion of the mineral content. The moisture in the coal and frequently the minerals supply a heat loss, the latter because clays and carbonates require heat to decompose them. The gross calorific value assumes that the water formed ends up as a liquid. The net calorific value is obtained by subtracting the enthalpy of vaporisation of water. (When the coal is burned as a fuel the water is given of as vapour and the heat which would be given out on condensation is not available.)

Isothermal or adiabatic bomb calorimeters may be used. The former involves the application of a cooling correction to the temperature readings to derive the initial heat output. Computers are of great help in making this correction. No such corrections are requires with the latter as an external water jacket is heated to the same temperature as the inner jacket by a thermistor controlled device. The results have to be corrected for the heat involved in the combustion of the cotton used to ignite the coal, and for the heat given out by the electricity passed through the small length of platinum wire used to fire the cotton.

The heat obtained by the calorimeter readings assumes sulfur ends up in the form of sulfur dioxide and nitrogen as dinitrogen gas. In the calorimeter the SO_2 is converted to sulfuric acid and some nitrogen to nitric acid. A correction is needed for the heat of dilution of these acids. This can involve determining the amounts of the acids present in the bomb calorimeter. This is done by titration with barium hydroxide to obtain total acidity, the sulfate formed precipitating as barium sulfate. Excess sodium carbonate is added to precipitate the remaining barium as barium carbonate and the excess found by back titrating with hydrochloric acid.

The 1997 range for as-mined coal was 13.87 - 32.08 MJ kg^{-1}.

Sulfur
This is calculated from the measured amount of SO_2 released when the coal is combusted in excess oxygen in a tube furnace set at 1350^{o}C. An approximate 0.5 g sample is weighed into an unglazed porcelain boat and covered with aluminium oxide. A stream of purified oxygen passes over it at 1350^{o}C in the furnace and the oxides of sulfur formed are absorbed into neutral hydrogen peroxide which oxidises SO_2 to sulfuric acid. The sulfuric acid is determined volumetrically.

The 1997 range for as-mined coal was 0.15 - 4.67%.

Crucible Swelling Number
This is assigned by comparing the shape of a coke button produced when the coal is heated in a lidded silica crucible at 820^{o}C for a minimum of 2.5 minutes against a standard set of profiles. 0 = no swelling, 9 = high swelling. Swelling coals form coke when carbonised. Carbonising is heating the coal to drive off volatiles. The coal becomes fluid and evolves gas. On cooling the product, coke, is porous. NZ high swelling coals from the West Coast are exported tro Japan and Korea to form parts of coking blends for steel manufacture.

The 1977 range was 0 - 9+.

Ash Fusion Temperature - Hemi (AFT)
The temperature at which controlled heating of the ash under reducing conditions causes sufficient softening to change a moulded pyramid shaped ash pellet to a hemispherical shape (height equal to half the base). Ash with low fusion temperature can cause problems during combustion.

The 1997 range was 1550 - 1080^{o}C.

Written by John Packer and Dr Vincent Gray with information from

"Coal Research Analysis Update", Coal Research Association of New Zealand Inc., 1998.