"THE CHEMICAL CHARACTERISTICS OF VICTORIAN BROWN COAL"

G. J. Perry, D. J. Allardice and L. T. Kiss*

Victorian Brown Coal Council, 151 Flinders Street, Melbourne, 3000 Australia,
*State Electricity Commission of Victoria, Herman Research Laboratory, Howard Street, Richmond, 3121 Australia.

1. INTRODUCTION

Extensive deposits of soft brown coal exist in Tertiary age sediments in a number of areas in Victoria and the largest single deposit occurs in the Latrobe Valley, about 150 kilometers east of Melbourne. In this region the coal seams often exceed 150 metres in thickness, with an overburden to coal ratio usually better than 1:2 making the coal ideally suited for large-scale open-cut mining.

A recent study (1) has estimated the State's brown coal resources to be almost 200,000 million tonnes with approximately 52,000 million tonnes defined as usable reserves. About 85% of this coal is located in the Latrobe Valley.

Since 1920 Latrobe Valley brown coal has been developed for power generation. The State Electricity Commission of Victoria (SECV) wins coal from two major open cuts at Yallourn and Morwell and operates coal fired power stations which presently consume approximately 35 million tonnes per annum. In addition to power generation, small quantities of brown coal are used for briquette manufacture and char production.

Brown coal accounts for about 95% of Victoria's non-renewable energy reserves and it is now recognized that with suitable up-grading, primarily drying, it has the potential to become the basis of the supply of energy in a variety of forms. Currently various studies for major conversion projects proposed by Australian, Japanese and German interests are being undertaken with the co-operation of the Victorian Brown Coal Council, the most advanced project being a 50 tonne per day hydrogenation pilot plant currently under construction at Morwell funded by New Energy Development Organization (NEDO) of Japan.

The chemical characteristics of Latrobe Valley brown coals have been extensively studied over the last twenty-five years, primarily in relation to the effect of coal quality on combustion for power generation. More recently a research project was initiated with the objective of determining the characteristics and suitability of the State's brown coal resources for uses other than power generation, primarily conversion to liquid fuels.

This paper outlines the chemical characteristics of Victorian brown coal and discusses the variability of the coal both between fields and within a seam. The importance of chemical properties in relation to coal quality and the implications for utilization are also briefly addressed.

2. PROPERTIES OF VICTORIAN BROWN COAL

The development and adaptation of modern analytical techniques for analysis of Victorian brown coal was pioneered jointly in the 1960's by the Commonwealth Scientific and Industrial Research Organization and the State Electricity Commission of Victoria. As a result the total coal analysis time was halved and the determination of the ash forming constituents directly on the coal took one sixth of the time of conventional ash analysis. More importantly brown coal analysis was put onto a rational basis taking its unique properties into account; and providing more pertinent information concerning the genesis, occurrence and use of Victorian brown coal.

Moisture

One of the most important chemical measurements made on brown coal is the bed moisture content which is also a good measure of physical rank; the greater the degree of compaction of the coal and its degree of coalification, the lower is the moisture content. To obtain meaningful results the sampling and sample preparation have to be carried out quickly to avoid moisture loss. The choice of the method of determination is important as thermal decomposition of functional groups can result in loss of CO_2 as well as H_2O. The preferred methods therefore involve direct measurement of the water released either by azeotropic distillation or adsorption from an intert carrier gas rather than by weight loss of the coal.

It is important to realize that the bed moisture content of soft brown coals is significantly higher than the equilibrium moisture holding capacity, a parameter which is used to characterize higher ranks coals. This is illustrated in Table 1 for a range of Victorian brown coals.

In terms of moisture the economic value of high rank coals is best indicated by the moisture holding capacity because it reflects the condition of the coal for utilization. In the case of Victorian brown coal the bed moisture content is the critical value, since the coal is used directly from the open cut.

Mineral and Inorganic Content

Ash content has been traditionally used to assess the magnitude of combustion residue and to derive the so called "coal substance" by difference which allows meaningful comparisons of different coals. In this context the ash is used as an approximation of the mineral matter content. The tacit assumption made, of course, is that the ash is derived solely from coal minerals, and this is certainly not the case for Victorian brown coal where the bulk of the ash forming material occurs as inherent inorganic matter in the form of exchangeable cations, associated with oxygen containing functional groups. This is also the case with many other low rank coals.

Using a combination of X-Ray fluorescence (XRF) on coal pellets and Atomic absorption (AA) techniques on acid extracts, direct chemical analyses of the ash forming elements in Victorian brown coal has been performed. Arising from this, a method of expression of results has been developed (2) which is based on classifying the mineral matter in brown coal into mineral and inorganic matter fractions and expressing each in a way which reflects their occurrence in the coal.

The Inorganics are a group of exchangeable cations and water soluble salts, analysed by AA on dilute acid extracts from the coal and expressed in terms of chemical analysis on a coal basis as -

$$\text{Inorganics} = Na + Ca + Mg + Fe + (Al) + (Si) + NaCl$$

where Fe refers to the non-pyritic iron and (Al) and (Si) to the acid soluble aluminium and silicon respectively. This expression is complicated by the fact that some iron and aluminium can be present as acid soluble hydroxides, but these are not usually significant.

The group named Minerals, which occurs as discrete particles principally of quartz, kaolinite and pyrite/marcasite is expressed in terms of chemical analysis as -

$$\text{Minerals} = SiO_2 + Al_2O_3 + TiO_2 + K_2O + FeS_2$$

This expression ignores the water of constitution of clays which is usually of negligible magnitude for Victorian brown coals.

The total weight of Minerals and Inorganics expressed on a dry coal basis gives the best estimate corresponding to "mineral matter" in high rank coal technology. In the case of Latrobe Valley coals the Inorganics are far more important than Minerals both in quantity and from a utilization point of view.

From a knowledge of the chemical constitution of the mineral matter it is possible to calculate and predict the composition of the ash or inorganic residue remaining after most technological processes. Table 2 illustrates the comparison between mineral matter content and ash content and the successful calculation of ash content from mineral matter data for a number of typical Victorian brown coals. Table 3 illustrates the futility of predicting the quantities of ash produced in modern, pulverized fuel fired power stations from the empirical ash test results. It illustrates for Morwell and Yallourn coals the quantities of ash produced in a boiler as opposed to the ash test; and it compares the laboratory ash composition with the precipitator ash actually produced. The mineral matter composition is also given as a guide. Both the laboratory and precipitator ash compositions can be calculated from the composition of the mineral matter by allowing for the difference in the degree of sulphation of the Inorganics. By extending this approach it should also be possible to calculate the composition of the inorganic residue obtained in hydrogenation processes.

It should also be noted that oxygen can only be estimated by difference if the mineral matter is known; using the ash value will yield misleading results.

Oxygen Functional Groups

Oxygen is one of the major elements present in the organic substance of Victorian brown coal. For Latrobe Valley brown coals oxygen generally comprises over 25% on a dry mineral and inorganic free (dmif) basis and about half of this oxygen can be accounted for in the acidic functional groups -phenolic hydroxyl, free carboxylic acid and carboxylate. The 40-50% of the oxygen not accounted for as acidic oxygen is primarily contained in carbonyl groups, ether linkages and heterocyclic ring structures.

3. VARIATION OF CHEMICAL PROPERTIES WITHIN A SEAM

The variation of chemical properties in a brown coal seam is attributable to the influence of two independent variables, namely coal rank and coal type. Rank variations are due to the burial history of the coal, that is the time, temperature and pressure it has undergone since its deposition. However, type (or lithotype) variations also significantly influence brown coal properties. Lithotypes arise from variations in the prevailing botanical communities, in the depth and nature of the swamp water and in the conditions of decay and decomposition of plant material. In Victorian brown coal these lithotypes are macroscopically recognizable bands or layers within a coal seam which become readily apparent on partially dried and weathered faces of open cuts. The basic factors on which lithotypes are classified are colour and texture in air dried coal , with degree of gelification, weathering pattern and physical properties used as supplementary characteristics which varies from pale to dark brown. In the case of Latrobe Valley coals, the colour of the air dried coal as measured by its diffuse reflectance and expressed as a Colour Index gives a numerical value related to lithotype.

The variation in rank with depth in the Morwell Open Cut is illustrated by the yearly weighted averages for each operating level. The gradation in rank is clearly illustrated in Figure 1 by the increase in carbon content, and the associated increase in gross dry specific energy; the volatile matter also decreases slightly with depth. These samples were not selected on a lithotype basis and the gradual changes in these coal properties are presumed to arise primarily from the increase in rank with depth.

The variation of coal properties with lithotype has been examined within continuous sequences of samples taken from five Latrobe Valley coal fields (3). The results indicate that the coal properties related to the organic coal substance, eg: volatile matter, hydrogen, carbon, oxygen and specific energy vary with lithotype layers in the coal seam. The dependence of carbon and hydrogen on lithotype (as measured by colour index) is illustrated in Figure 2 for a typical bore. All the major constituents of the organic coal substance are lithotype dependent and their variation within a seam is a direct consequence of the changes in depositional environment which occurred during formation of the seam.

The occurrence of organic sulphur and organic nitrogen is independent of lithotype although the concentration of nitrogen is influenced by the presence of wood in the coal.

Generally speaking, the concentration of minerals in the coal is highest near the overburden and the interseam sediment layers. Because of the discrete nature of the minerals their sporadic distribution in a seam cannot be accurately assessed from a single traverse of sampling through the seam.

The concentration of inorganics, particularly sodium, magnesium, calcium and non-pyritic iron show no relationship to lithotype (Figure 2) although some depth related concentration gradients are apparent. Sodium and magnesium often show a concentration increase near the top of a bore whilst the aluminium concentration tends to increase near the bottom. This is believed to be due to diffusion of aluminium into the coal from the clay containing sediments below the coal seam. On the other hand calcium in the Morwell open cut has the highest concentration near the middle of the profile.

The lack of correlation between these inorganic species and lithotype indicates that the inorganics are probably post-depositional in origin. This is consistent with their diffusion through the water of the coal giving rise to concentration gradients.

4. VARIATION IN CHEMICAL PROPERTIES BETWEEN COALFIELDS

In addition to the variation of chemical properties within coal seams, significant variation also occurs between different coalfields in Victoria. An extensive research programme in which this variation was investigated has been conducted by the State Electricity Commission of Victoria on behalf of the Victorian Brown Coal Council.

In this Brown Coal Evaluation Programme a sampling philosophy was adopted that would highlight the natural variability of the coal and indicate the range of coal qualities which may be encountered during mining and utilization of the deposits.

The programme commenced in the Latrobe Valley coalfields by sampling open-cut faces and 220 mm diameter bore cores and was later extended to include major coal deposits in Victoria. Lithotype logs were prepared using quarter core sections laid out to dry, and selected lithotype samples from each core were analysed for a variety of chemical, physical and petrographic characteristics and utilization parameters; 144 parameters in all. To date, a total of 219 coal samples have been analysed from three open cut faces and twenty 220 mm diameter bore cores, representing 11 coalfields throughout Victoria. Coal samples from a further six bores are presently being characterized.

The data generated from these analyses and tests was evaluated by statistical methods and correlation coefficients have been determined between all pairs of variables. Analysis of this data has revealed significant differences in the chemical properties of the coal from different fields and enables the selection of coal with specific properties for particular applications. Table 4 illustrates

some of these differences by showing the range of values determined for selected coal properties from 219 samples (11 coalfields). Typical values from the two open cut mines currently operating in the Latrobe Valley are shown for comparison. These differences in chemical properties between the different coalfields are generally more significant than lateral variations within a particular field (ie: between different bores within a field) and they are primarily related to rank.

5. EFFECT OF CHEMICAL PROPERTIES ON UTILIZATION

As a result of the Brown Coal Evaluation Programme, the understanding of the variability of Victorian brown coals and its implications for utilization have improved substantially. It has become apparent that certain chemical properties can have important consequences for utilization of the coal for power generation, liquefaction and other applications.

A number of examples will be briefly described -

Carbonate Formation During Hydrogenation

The formation of carbonate minerals during hydrogenation of low rank coals can cause serious operational difficulties in the reactor systems. A good correlation has been found between the calcium content of a number of Victorian brown coals and the carbonate formed during hydrogenation. However, the results indicated that cations other than calcium were involved in the formation of carbonate.

XRD analysis has revealed the presence of several different types of carbonate minerals in residues from a number of coals. Minerals identified included vaterite and calcite (two polymorphs of $CaCO_3$) dolomite ($CaMg[CO_3]_2$) and in the residue from a high sulphur (2.26% db) coal anhydrite, ($CaSO_4$) was identified. The types of mineral deposits formed depend not only on the coal but also on the reaction conditions. Our data indicates that whilst vaterite forms at low temperatures (380°C) as the temperature increases the vaterite becomes progressively converted to calcite, the more stable form. After further increases in temperature, particularly at long reaction times, dolomite begins to form.

The reaction to form anhydrite, in the case of the high sulphur coal, must compete for calcium with the formation of calcium carbonate, and this may have a beneficial effect.

Clearly the types of inorganic precipitates which form during hydrogenation of Victorian brown coal are dependent on the nature of the exchangeable cations and to some extent the available coal sulphur.

Sodium and Boiler Fouling

The concentration of sodium in coal is regarded as the most significant factor in the formation of troublesome ash deposits during combustion. Although Victorian brown coals are generally low in ash forming constituents, coals with a high proportion of sodium can form ashes which contain of large amounts of low melting point, sodium sulphate compounds. These are formed during combustion from the inorganic sodium and organic sulphur in the coal.

The sodium sulphate condenses on the surface of boiler tubes and together with fly-ash particles forms sticky deposits, which can consolidate on heating and lead to extremely dense hard-to-remove deposits. The presence of high sodium sulphate content ash thus requires special consideration during the design and operation of boilers.

Aluminium and Precipitator Ash

In some Victorian brown coals significant quantities of acid soluble aluminium are found. This is believed to be present as aluminium hydroxide which is dispersed throughout the water phase of the coal. During combustion of this coal the refractory aluminium oxide formed takes the shape of the relics of the plant material present in the coal, thus forming an extremely low density ash (approximately 100 kg/m³). Whilst the collection of these particles by lectrostatic precipitation is possible, the problem of reentrainment on rapping has necessitated the use of larger sized units than would otherwise be required. It is therefore important to determine the acid soluble aluminium fraction in the coal to determine if precipitation of fly ash is likely to be a problem.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

1. Victorian Brown Coal Resource Development Study, Kinhill Pty Ltd. 9 Volumes. December 1982.

2. Kiss LT and King TN. Fuel 56, 340 (1977).

3. King TN, George AM, Hibbert WD and Kiss LT. Variation of Coal Properties with Lithotype Pt 2. SECV Report No. SO/83/55 (1983).

TABLE 1. **BED MOISTURE AND MOISTURE HOLDING CAPACITY FOR SELECTED VICTORIAN COALS**

Coal Field (Selected Values)	Bed Moisture (As Received)		Moisture Holding Capacity % (Equilibrium Moisture)*
	Kg/Kg Dry Coal	Weight Percent	
Yallourn-Maryvale	1.82	64.2	38.4
Morwell-Narracan	1.54	60.5	38.2
Loy Yang	1.63	61.9	42.1
Flynn	1.76	63.5	41.2
Yallourn North Ext	.98	49.5	41.2
Coolungoolun	1.19	54.4	35.0
Gormandale	1.27	56.0	39.0
Gelliondale	1.83	64.6	35.3
Stradbroke	1.41	58.4	37.1
Anglesea	.87	46.6	32.9
Bacchus Marsh	1.53	60.4	31.2

* Determined at 97% humidity and 30°C

TABLE 2. **COMPARISON OF ASH CONTENT AND MINERAL MATTER FOR SELECTED VICTORIAN BROWN COALS**

Coal Field (Selected Values)	% Ash, Coal Dry Basis		% Mineral Matter, Coal Dry Basis
	Determined	Calculated	
Yallourn-Maryvale	2.3	2.4	1.7
Morwell-Narracan	2.4	2.6	1.5
Loy Yang	1.0	1.1	0.8
Flynn	1.4	1.5	0.1
Yallourn North Ext	4.3	4.5	3.0
Coolungoolun	2.3	2.4	2.2
Gormandale	1.6	1.6	1.3
Gelliondale	5.8	5.8	3.4
Stradbroke	3.9	3.6	2.0
Anglesea	3.9	3.4	2.2
Bacchus Marsh	7.4	7.4	3.5

TABLE 3. **COAL-ASH CHEMISTRY : MORWELL OPEN CUT**

Coal % Dry Basis		Ash%	Laboratory	Boiler Precipitator
Minerals				
FeS_2	0.13	-	-	-
SiO_2	0.19	SiO_2	6.2	8.0
Al_2O_3	0.04	Al_2O_3	1.3	1.7
Inorganics				
Fe	0.32	Fe_2O_3	17.6	22.7
Ca	0.70	CaO	32.0	41.2
Mg	0.24	MgO	13.1	16.8
Na	0.08	Na_2O	3.6	4.6
Cl	0.04	-	-	-
Organic S	0.25	SO_3	26.1	5.0
Total Ash			3.1	2.6

TABLE 4. **VARIATION IN SELECTED CHEMICAL PROPERTIES BETWEEN VICTORIAN BROWN COALFIELDS**

Property	Yallourn Open Cut	Morwell Open Cut	Range of Values (219 Samples)
Moisture (wt %)	66.4	60.2	43.7 - 71.0
Net wet specific energy (MJ Kg^{-1})	6.87	8.95	5.24 - 13.87
Ash (wt %)	1.3	3.5	0.5 - 12.8
Minerals and Inorganics (wt %, db)	1.3	2.7	0.3 - 12.8
Volatile Matter (wt%, dmif)	52.1	49.2	43.3 - 67.8
H/C Atomic Ratio	0.86	0.86	0.77 - 1.16
Oxygen (wt%, dmif)	26.2	24.2	17.4 - 30.0
Nitrogen (wt%, dmif)	0.52	0.62	0.36 - 0.85
Sulphur (wt%, dmif)	0.27	0.34	0.14 - 5.36
SiO_2 (wt% db)	0.38	0.14	0.01 - 7.6
Calcium (wt% db)	0.04	0.74	0.01 - 2.07
Magnesium (wt% db)	0.18	0.23	0.02 - 0.85
Sodium (wt% db)	0.06	0.13	0.02 - 0.47
Iron - total (wt% db)	0.18	0.19	0.01 - 1.80
Phenolic - OH (meq/g)	3.72	3.70	1.91 - 4.44
-COOH (meq/g)	2.21	1.90	0.90 - 2.94
$-COO^-$ (meq/g)	0.49	0.59	0.03 - 1.66

dmif - dry, mineral and inorganic-free basis db - dry basis

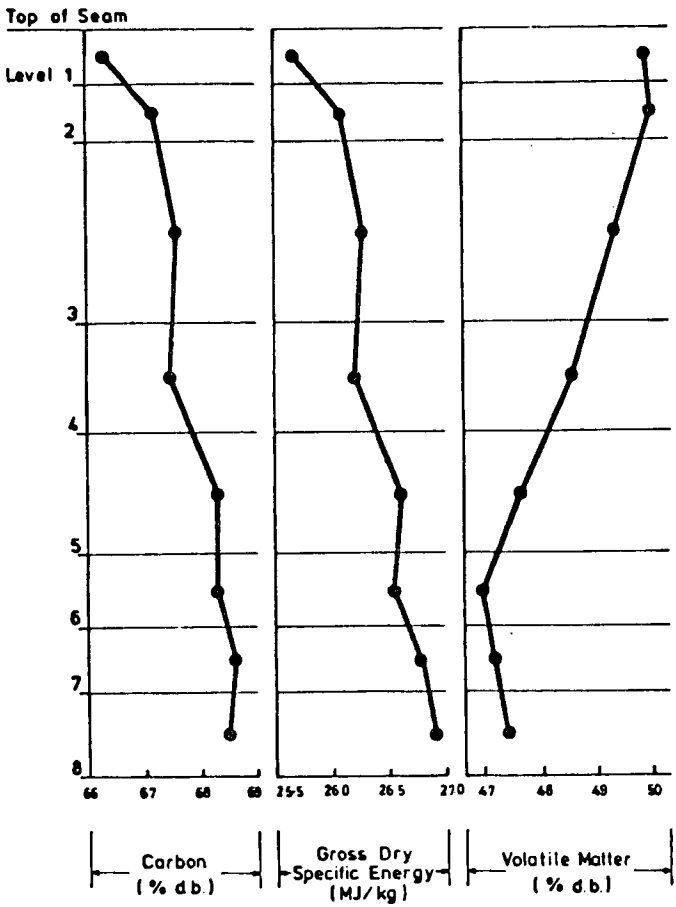

Fig. 1. Variation in selected coal properties with depth in the Morwell Open Cut.

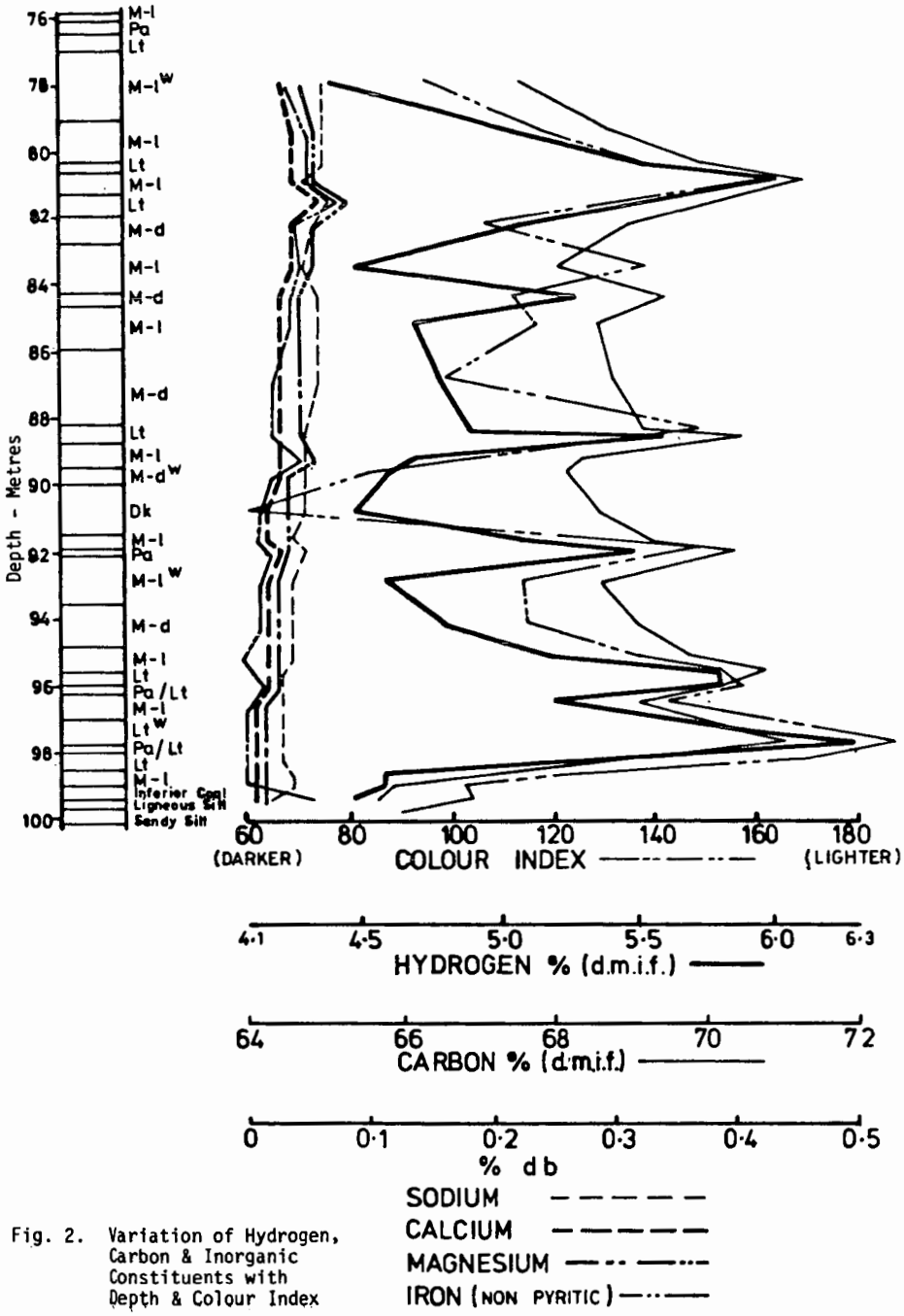

Fig. 2. Variation of Hydrogen, Carbon & Inorganic Constituents with Depth & Colour Index