

THE CHEMICAL COMPOSITION OF THE MAKERWAL COAL AND ITS ASH

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Introduction

Due to the anomalous behaviour of Makerwal coal under superheated steam treatment at 300°C.¹ and also due to its high ash content, it was considered necessary to have an insight into its composition which is responsible for this strange behaviour. In order to make a systematic approach to this problem, ultimate and proximate analyses of coal² and quantitative analysis³ of its ash were carried out by applying macromethods. The results of the quantitative analysis of ash thus obtained were further confirmed by spectrographic analysis.

The difficulty in the quantitative analysis of ash was encountered in the determination of alkali metals. For their determinations all the other metallic ions were removed by precipitation and subsequent filtration and washings. This, however, does not give a very effective separation.

Experimental

The analysis of coal was carried out using coal ground to pass through a 72-mesh B. S. sieve and was air-dried (cf. Tables 1 and 2).

The wide variation in the high percentages of humidity rendered it difficult to weigh the coal sample accurately. To overcome this, coal sample was allowed to remain in contact with atmosphere for 24 hours, the temperature and humidity being 31°C. and 90%, respectively. The sample thus obtained was termed as air-dried coal.

Various minor changes were made in the usual methods of analysis³ to conform to the nature of Pakistan coals and to make the analysis more easy and practicable.

The two spectrums of the sample were taken with the help of Hilger medium quartz spectrograph using Hartman's diaphragm. Each spectrum consists of 2 subspectrums, which in spectrum No. 1 are from (a) iron arc, (b) unknown coal ash sample, and (c) standard coal ash sample (exposure time—2 sec.); in spectrum No. 2 are from (a) carbon arc, (b) unknown coal ash sample and (c) standard coal ash sample (exposure time—3 secs.).

TABLE 1.—ULTIMATE ANALYSIS OF MAKERWAL COAL.

Determination	% (on dry basis)	% (on ash-free dry basis)
Carbon	59.4	71.765
Hydrogen	5.4	6.524
Nitrogen	1.066	1.288
Sulphur	5.102	6.164
Oxygen (by difference) ..	29.032	14.259

TABLE 2.—QUANTITATIVE ANALYSIS OF MAKERWAL COAL ASH.

Determination	Amount
Silica, SiO ₂	.. 41
Iron oxide, Fe ₂ O ₃	.. 19.5
Aluminium oxide, Al ₂ O ₃	.. 21.7
Calcium oxide, CaO	.. 1.2
Magnesium oxide, MgO	.. 0.1
Mangano-manganic oxide, Mn ₃ O ₄	.. 0.2
Alkali oxides, Na ₂ O & K ₂ O	.. 7.1
Sulphur trioxide, SO ₃	.. 11.3

TABLE 3.

Analysis	Si%	Fe%	Al%	Ca%
Spectrographic	17	13	14	2
Chemical	19.16	13.67	11.49	0.86

The standard sample contained SiO₂ 40%, Fe₂O₃ 20%, Al₂O₃ 25%, and CaCO₃ 40%.

The intensities of the lines of elements present in the standard ash sample were compared with the intensities of the lines of elements present in the unknown coal ash sample. The results thus obtained were well in order with those of chemical analysis as is shown in Table 3.

Conclusion

The quantitative chemical analysis of the original Makerwal coal ash, though it provides some data necessary for the composition and characterization of coal, still do not give a comprehensive account of the changes involved when superheated steam is passed through it. For the complete characterization of the coal and its strange behaviour, the ash analysis of steam treated Makerwal coal and mineral concentrate of Makerwas coal are under progress.

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PREPARATION OF ALLYL CYANIDE

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Introduction

Allyl cyanide is an important starting material for a number of syntheses. It has been prepared for this purpose by the interaction of aqueous potassium cyanide and allyl chloride,¹ allyl bromide,² and allyl iodide,³ and also by heating a mixture of dry cuprous cyanide and allyl bromide,⁴ and allyl chloride.⁵ The present method is based on the report of Breckpot,⁶ and appears to represent the optimum condition of favourable yield and convenient procedure for the preparation of allyl cyanide.

Procedure

Caution.—This preparation must be carried out in a good hood, or with a gas absorption trap (Note 1), because hydrogen cyanide is evolved.

In a 1-l round-bottomed flask equipped with an efficient reflux condenser (Note 2) under a hood, or with a gas absorption trap (Note 1) are placed 174 g. (205 ml.; 3 moles) of allyl alcohol, 277 g. (3.1 mole) of cuprous cyanide (Note 3), and 350 ml. of aqueous hydrochloric acid (sp. gr. 1.17; 34.5%). The mixture is shaken thoroughly and then heated gently when a vigorous reaction starts. Soon the speed of the reaction slows down and the mixture is heated under reflux on an oil bath maintained at 80°C. for 2.5 hours with occasional shaking when the reaction is substantially complete as indicated by cessation of refluxing. Heating is continued for a further 1 hour with the bath temperature raised to 110°C.

The reaction mixture is allowed to cool to 80°C. the reflux condenser replaced by a distilling head fitted to a condenser (Note 4), a few boiling chips added, and the mixture distilled from the oil bath kept at 130°C. until the temperature of vapour reaches 100°C. and 375-385 cc. of distillate collected (Note 5), or as long as organic material passes over. This is taken up in a separatory funnel; the lighter ally cyanide layer separated, dried with anhydrous sodium sulphate, and collected by filtration. Upon distillation, the yield of allyl cyanide is 150-160 g. (75-80%), b.p. 116-121°C., n_D^{30} 1.40082-1.40086. The process gives equally satisfactory yield with smaller or larger amounts of starting material.

Notes

1. Hydrogen cyanide is evolved in this reaction, and must be led into a good suction draft in a fume cupboard, or removed by gas absorption trap (*Org. Syntheses*, Coll. Vol. 1, Fig. 7, p. 97, 1951).
2. A double jacketed condenser about 90 cm. long is satisfactory.
3. Commercial cuprous cyanide, containing 69-71% copper, gives the same result as that dried in an oven at 110°C. for 72 hours, and was therefore used in the preparation.
4. Distilling head with fused-on Mohr condenser is preferable.
5. The residue in the flask is mostly cuprous chloride together with a liquid mixture. This is drained with liberal flow of tap water, and is easily cleaned.

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