FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

TECHNICAL MEMORANDA NOS. 21(a) AND 21(b) OF 1963.

# (a) DETERMINATION OF COKING PROPERTIES.

# (b) THE FLUORINE CONTENT OF SOUTH AFRICAN COALS AND ITS CONTRIBUTION TO THE VOLATILISATION OF BORON DURING COMBUSTION.

by

F. KUNSTMANN.

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

Technical Memorandum No. 21(a) of 1963.

PROGRESS REPORT: DECEMBER, 1962 TO MARCH, 1963.

## DETERMINATION OF COKING PROPERTIES.

### 1) The Bonding Index:

The determination of the Bonding Index, as described in the last Annual Report, proved to be a useful test of the coking ability of a coking coal. Unfortunately, all attempts to lay down specifications for the standard anthracite, which determine its behaviour in this test, failed. Investigations indicated a weak influence of the ash content of the anthracite (in the range of 2 - 15% studied) and a somewhat stronger influence of the volatile matter content on the value of the bonding index. Comparing different anthracites, no clear correlation between the ash content or the volatile matter content on the one hand, and the bonding index on the other hand, could be found. Apparently in this test the physical properties of the surface of the anthracite particles have greater significance than in the Roga test.

TABLE I.

BONDING INDEX AND ROGA INDEX OF WATERBERG COAL DETERMINED WITH VARIOUS SPECIFIC GRAVITY FRACTIONS OF "ROGA ANTHRACITE".

| Sample | % Yield | % Ash | % Vol. Matter | Bond. Index | Roga Index |
|---|---|---|---|---|---|
| Original Anthracite | 100 | 5.36 | 5.52 | 12.3 | 72 |
| Float 1.430 | 19.1 | 2.22 | 5.73 | 13.8 | 67 |
| Sink 1.430 | 80.9 | 6.10 | 5.43 | 11.4 | 70 |
| Float 1.445 | 39.1 | 2.78 | 5.39 | 12.4 | 65 |
| Sink 1.445 | 60.9 | 7.04 | 5.24 | 11.2 | 67 |
| Float 1.459 | 62.3 | 3.42 | 5.48 | 12.0 | 68 |
| Sink 1.459 | 37.7 | 8.58 | 5.29 | 11.4 | 65.5 |
| Float 1.475 | 79.4 | 4.09 | 5.32 | 11.3 | 67 |
| Sink 1.475 | 20.6 | 10.58 | 5.28 | 11.1 | 67 |

From the above table, showing the bonding index and the Roga index of Waterberg coal carried out with various specific gravity

fractions/...

fractions of "Roga anthracite", it can be seen that the influence of the ash content on both indices is fairly weak.

The difficulties in determining specifications for a standard anthracite suggested the use of "standard" sand instead of anthracite. Experiments carried out with standard sand, as used for the determination of the Agglutination Index, showed that the test also gives reasonable results with sand. A definite disadvantage, compared with anthracite, is, however, the higher S.G. of sand, which causes a greater breakage when sieving off the unbonded material and reduces the reproducibility of the values somewhat.

Searching for material having a lower S.G. than sand and more reproducible surface characteristics than the anthracite, it was decided to try pitch-coke. It was obvious that the conditions under which pitch-coke is manufactured would influence its properties, therefore it had to be established, first of all, whether pitch of different origin (e.g. ex Iscor or Waschbank) when carbonised under the same conditions, would yield pitch-coke with sufficiently constant characteristics to give reproducible bonding index results.

The production of pitch-coke from Iscor pitch is in progress. To make the carbonisation easier, the pitch as received was preheated in an open vessel until it turned into a viscous mass.

(signed) F. KUNSTMANN

Senior Technical Officer.

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA

Technical Memorandum No. 21(b) of 1963.

PROGRESS REPORT: DECEMBER, 1962 TO MARCH, 1963.

## THE FLUORINE CONTENT OF SOUTH AFRICAN COALS AND ITS CONTRIBUTION TO THE VOLATILISATION OF BORON DURING COMBUSTION.

In the course of this investigation it was found, as already mentioned in the Annual Report for 1962, that boron trioxide can be volatilised as such from a boiler grate. This finding is not contradictory to Osborn's* statement that boron is volatilised in the form of boron trifluoride, but it is in disagreement with conclusions resulting from his statement, namely, that the fluorine content of coal limits the amount of boron volatilised. As also mentioned in the Annual Report, it is unlikely that the reaction proposed by Osborn for the formation of $BF_3$ (see below) really does take place on a boiler grate.

$$CaSiF_6 + 2B_2O_3 = CaO \cdot B_2O_3 \cdot SiO_2 + 2BF_3 \quad \ldots\ldots\ldots\ldots\ldots (1)$$

It seems more likely that boron trifluoride is formed according to equation (2) below, on which the commercial production method of Baldeschwieler (Standard Oil)** is based:

$$7B_2O_3 + 3CaF_2 = 3CaB_4O_7 + 2BF_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

As far as Osborn is concerned, equation (2) could not represent a true reflection of the reaction in the fuel bed because of the fact that, according to it, only 1/7 of the boron present in coal is volatilised, while a boiler test, carried out by him, showed that half of the boron was volatilised. The finding that boron trioxide as such can be volatilised from the boiler grate may explain this discrepancy.

A clear proof for the fact that boron is also volatilised in the absence of fluorine, was furnished by the following experiments: In the one case, boric acid was heated with $CaF_2$ at about 1400°C to a constant weight; in the other case, the same amount of boric acid was heated with an amount of $CaCO_3$ equivalent to the $CaF_2$ used in the first experiment. In both cases the same

residue/...

* Osborn, D.W., J.S.A. Inst. Mech. Eng., Vol. 4, 4, 99-123 (1954).
** Baldeschwieler, E.L., A.P. 216323 (1937).

residue was obtained, which means that in both cases, with and without fluorine, the same amount of $B_2O_3$ was volatilised.

A further confirmation of the assumption that boron trioxide can be volatilised as such at the temperature on a boiler grate, was supplied by another experiment: Calcium tetraborate, made in the laboratory, was heated to about 1400°C. At first $B_2O_3$ was volatilised from the salt at a high rate; later the volatilisation slowed down and finally the salt turned into the orthoborate.

$$3CaB_4O_7 = Ca_3(BO_3)_2 + 5B_2O_3$$

The ratio between CaO and $B_2O_3$ in the heating residue depends, as further experiments showed, upon the temperature to which the salt is heated.

It seemed to be obvious that the amount of boron volatilised was dependent, not only on the temperature on the grate, but also on the ratio between basic and acid components in the ash. To study this problem, coals rich in calcium and low in calcium were ashed at 1000°C and the boron in the ash was determined. It was found that the boron losses were too low at 1000°C to allow a definite conclusion to be made. The experiments are being repeated at higher temperatures.

In further experiments, coals low in calcium were ashed with and without an addition of $CaCO_3$, the ashes heated to about 1400° and their boron content determined. This investigation is in progress. The small boron content of the coal samples on the one hand, and the low accuracy of the micro-determination on the other, allow conclusions only when the determinations are done at least in triplicate.

(signed) F. KUNSTMANN

Senior Technical Officer.