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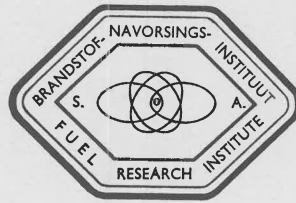
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**BRANDSTOFNAVORSINGSINSTITUUT
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**FUEL RESEARCH INSTITUTE
OF SOUTH AFRICA
REPORT NO. 35 OF 1976**

A PRELIMINARY REPORT ON INVESTIGATIONS INTO THE PROBLEM

ONDERWERP:
SUBJECT:

OF PHOSPHATIC DEPOSITS IN COAL FIRED BOILERS

ENGINEERING

AFDELING:
DIVISION:

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GATIONS INTO THE PROBLEM OF
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FIRED BOILERS

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SECTION : COMBUSTION

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A PRELIMINARY REPORT ON INVESTIGATIONS INTO THE PROBLEM
OF PHOSPHATIC DEPOSITS IN COAL FIRED BOILERS.

1. SYNOPSIS

A literature survey has been carried out. Investigations into the growth of phosphatic deposits, using the Institute's experimental boiler plant, are reported.

PART 1. LITERATURE SURVEY

2. INTRODUCTION

Phosphatic deposits constitute a serious problem, and are associated with the burning of medium and high phosphorus coals. The deposits are hard, they are insoluble in water, and have thermal expansion characteristics of the same order as that of boiler steel; hence they can be removed only with difficulty. Much general literature on fused boiler deposits, and sulphatic deposits is available, mainly from overseas. Particular literature devoted to phosphatic deposits is, however, sparse, and is concerned with the combustion of South African coals of high phosphorus content.

3. THE ORIGIN OF PHOSPHATIC DEPOSITS

A number of authors (4, 11, 12, 15) postulate that the major factors concerned in the creation of phosphatic deposits are the presence in the coal of phosphorus, boron and fluorine. Kunstmann and co-workers (4) claim that the fluorine content of the coal is not the decisive factor.

In the fuel bed, phosphorus pentoxide is liberated from fluorapatite, and combines with water vapour in the flue gases to form meta-phosphoric acid.

Osborne (11), further assumes that calcium silicofluoride is formed in the fuel bed, and that this reacts with boron oxide liberated from the coal, to form boron trifluoride. Kunstmann and co-workers (4) however, claim that the presence of fluorine is not necessary in order to volatilise boron oxide, as it is able to volatilise itself.

Boron oxide and boron trifluoride, volatilised from the fuel, react with the phosphoric acid which has been deposited on the tubes, to form boron phosphate, the principal component of phosphatic deposits together with fly ash.

The extent of volatilisation of phosphorus, boron and fluorine which occurs in the fuel bed, is decided by many factors. The inorganic constituents of coal constitute an extremely complex chemical system, and together with the presence of both oxidising and reducing conditions and differences in temperature between the various zones in the fire bed, make it almost impossible to predict the course of all the reactions which take place.

4. FACTORS SUGGESTED AS INFLUENCING THE VOLATILISATION OF PHOSPHORUS, BORON AND FLUORINE

- (i) The percentage of phosphorus, boron and fluorine in the coal.
- (ii) Both the overall temperature of the fuel bed, and the local temperatures at various parts.
- (iii) The velocities and composition of air and combustion gas which are present within the fuel bed.
- (iv) The ratio between acidic and basic oxides present in the coal ash.
- (v) The nature of conditions within the fuel bed - whether oxidising or reducing.

5. THE ALLEVIATION OF PHOSPHATIC DEPOSITS

There are a number of ways by which phosphatic deposits may be at least partially prevented, some of which are economic and practical, and some of which are not.

(NOTE: Pulverised coal fired boilers are relatively free of phosphatic deposits, because the fuel is burned in oxidizing conditions.)

Some of the ways are:-

- 5.1 By increasing the quantity of air blown through the fuel bed, in order to decrease the CO₂ content of the flue gases, decrease

the combustion chamber temperature, also to increase the oxidizing nature of the fire bed conditions. All of these factors help in decreasing the volatilisation of phosphorus, boron and fluorine. There would, it is true, be some increase in the volume of flue gases and hence heat loss, but this can be offset against better heat transfer through deposit free tubes, and better boiler availability due to less frequent shut-downs for tube cleaning.

- 5.2 By decreasing the thickness of the fuel bed and increasing the speed of the grate; provided that the required steam output and coal quality will permit this to be done. This would promote more oxidizing conditions in the fire bed. Further, ash fusion temperatures in reducing conditions are 100 - 150°C lower than in oxidizing conditions; this is rendered more extreme by high iron contents.
- 5.3 By decrease of the fuel bed temperature, this can be done in a number of ways (2, 9, 14):-
- A. Theoretically this could be done by injecting steam into the air supplied to the fuel bed. (The endothermic reaction between carbon and steam would help reduce the temperature).
 - B. By recirculating flue gas (+ 10%) into the air supplied to the fuel bed.
 - C. By fitting water cooled side blocks in place of the lower part of the ignition arch. (2, 9). This would of course create possible problems with coals which are difficult to ignite.
- 5.4 By decreasing the temperature of the gases in the combustion chamber.
- (A) By the injection of steam into the furnace and/or combustion chamber. In this way, the gases would be cooled and the turbulence increased, so that stratification in the furnace would be avoided and combustion completed more quickly. (9).
 - (B) By injecting surplus air (+ 10%) into the combustion chamber. Again, here the argument is that the greater waste gas heat loss would be balanced by deposit free tubes and better boiler availability.

- (C) By recirculation of waste gas into the combustion chamber to achieve the effect described in (B).
 - (D) By the insertion of baffles into the furnace (9), in order to promote turbulence and mixing in order to burn the gases more fully before the combustion chamber is reached, and hence reduce the combustion chamber temperature.
- 5.5 By changing the ratio of basic and acidic oxides in the ash, in order to change the ash fusion characteristics. Kunstmann and co-workers (4) suggest that this ratio might influence the volatilisation of phosphorus, boron and fluorine from the fuel bed. The addition of dolomite or silica would alter the ratio in either direction.
- 5.6 By the use of various additives (5, 6, 7, 14). This is suggested either via the air blower as inorganic smoke, or by direct addition to the coal. The aim here is to influence the growth and composition of the deposits. For example Kiss and co-workers (5) suggest the use of copper oxychloride, which is said to render the deposits friable and easily removable.
- 5.7 By the re-allocation of different coals to different firing systems, (i.e. so that susceptible firing systems are given the least sensitive coals).
- 5.8 By better combustion control. Sensitive approach to boiler operation is said to minimise the build-up of deposits. These include frequent soot blowing, avoidance of overload conditions, and the use of slightly lower combustion chamber temperatures. The use of coal of close size distribution would also help - segregation of coal on the grate results in uneven particle size distribution which in turn impairs the air distribution. Adjacent to large particles, forge like conditions occur with local very high temperatures, which give rise to increased volatilisation of phosphorus, boron, and fluorine. In patches of fine coal, strong reducing conditions will exist, which also support the volatilisation of phosphorus, boron and fluorine, despite the lower temperatures (9).

6. THE REMOVAL OF PHOSPHATIC DEPOSITS

The main difficulty in the removal of phosphatic deposits is that boron phosphate is insoluble in water, extremely hard, and as its coefficient of thermal expansion is similar to that of boiler steel, it does not crack as a result of alternate heating and cooling. Deposits are normally removed by scraping and brushing. There is also a chemical method by which the tubes are treated alternately with hydrochloric acid and caustic soda, followed by a final water wash. (11)

7. GENERAL COMMENTS ON METHODS SUGGESTED FOR ALLEVIATION

The problem with most of the methods is that although logical, they are extremely difficult to use on a practical boiler installation.

The idea of using closely graded coal for example should be seen against South Africa's current coal supply position. Smalls (25 mm - 0) are now of necessity being used in place of the hitherto used peas (25 mm - 6 mm). Further, suggestions regarding better standards of boiler control, probably involve both operator education and better supervision, factors which are not always easily achieved. Avoidance of over-running is of course logical, but production schedules cannot always wait on equipment down time, further in some cases, boiler plant can be actually inadequate for the duty required. The idea of water cooled blocks at the base of the ignition arch would undoubtedly help, but where low volatile high-ash coals are burned, this would aggravate an already difficult ignition problem. Generally, also companies operating coal fired boilers, are not always willing to install modifications.

Despite the available literature, more information is required as to the origins and causes of phosphatic deposits when using South African coals.

PART 2

PRELIMINARY INVESTIGATIONS CARRIED OUT INTO THE ORIGIN AND CAUSE OF PHOSPHATIC DEPOSITS.

8. FUEL

It had been intended to use Koornfontein peas, the fuel that was used in previous FRI work, but this coal is no longer generally available. Further, an early trial using Delmas peas proved abortive. Hence the coal finally chosen was Tavistock peas, a fuel known to have caused serious trouble on a local factory boiler. The phosphorus content of this coal is medium to high (0,028% P).

8.1 ANALYSIS OF COAL

Calorific value	27,9 MJ/kg
H ₂ O	3,0%
Ash	12,9%
Volatile matter	26,8%
Fixed carbon	57,3%
Total sulphur	0,75%
Ash fusion temperature +1400/+1400/+1400	
Boron as B ₂ O ₃	0,008%
Phosphorus as P	0,028%
Fluorine as F	0,004%

ANALYSIS OF ASH PREPARED IN LABORATORY

Basic oxides		Acidic oxides	
Al ₂ O ₃	34,0%	SiO ₂	45,00%
Fe ₂ O ₃	4,10%	P ₂ O ₃	0,51%
TiO ₂	1,74%	SO ₃	2,24%
CaO	8,20%	<hr/>	
MgO	1,50%	Total	47,75%
K ₂ O	0,48%	Ratio $\frac{\text{basic oxides}}{\text{acidic oxides}} = 1,05$	
Na ₂ O	0,19%		
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Total	50,21%		

8.3 SIZE ANALYSIS OF COAL

>25,4 mm	0,9%
>19,05 mm <25,4 mm	16,0%
>12,7 mm <19,05 mm	33,5%
>6,35 mm <12,7 mm	38,0%
>3,12 mm <6,35 mm	6,8%
>1,59 mm <3,12 mm	0,8%
<1,59 mm	<u>4,0%</u>
	100,0%

9. EXPERIMENTAL PROCEDURE

9.1 THE TEST BOILER

The boiler on which the work has been carried out is an Adamson Triple Pass Economic Boiler, fitted with a Bennis Chain Grate Stoker, and has a rated output of 1800 kg/hr of saturated steam.

Three consecutive steaming periods were carried out. Each period comprised 6 x 4 hours at the rated output. (This does not include the periods spent in reaching full output and the rated pressure of 100 psig). The combustion chamber temperature was restricted to 900 - 950°C, due primarily to fuel and boiler conditions; and the CO₂ content of the flue gases was \pm 12,0%.

After each of the steaming periods, the boiler was cooled down, the deposits were inspected, photographs were taken, and samples removed for analysis.

9.2 DEPOSIT COLLECTION

A preliminary attempt was made to collect a deposit on two probes, one air cooled and one not, which were inserted into the combustion chamber. The degree of deposition was negligible, hence their use was discontinued. Instead samples were taken from the side wall of the combustion chamber, from the end of the fire tubes, from the back wall of the combustion chamber and from the ceramic thermocouple sheath.

10. RESULTS

Analyses of deposits are referred to the series of photographs (1 - 12), which illustrate the growth of the various deposits.

Table 1

Accumulated steaming period	Location of deposit, and photographic reference				% P ₂ O ₅	Fusion temperature °C	Remarks
	Side wall photo No.	Tubes photo No.	Back wall photo No.	Thermocouple photo No.			
24 hours	1	4	7	10	3,12	1280/1310/1400	Friable
48 hours	2	5	8	11	2,89	1320/1350/1390	Friable
72 hours	3	6	9	12	2,33	1310/1330/1400	Friable
Ashes removed from boiler					0,43	1340/1390/1400	
Coal					0,068	1400+/1400+/1400+	

Table 2 Analysis of deposits taken from thermocouple surface

	% P ₂ O ₅	Fusion temperatures °C	Remarks
Outer layer	3,63	1300/1320/1380	Friable
Inner layer	12,55	1160/1180/1270	Hard thin layer

11. DISCUSSION

It can be seen from Table 1, that the P₂O₅ contents of the deposits are considerably higher than the P₂O₅ content of the ashes which were removed from the boiler during the test. Also as might be expected, the P₂O₅ content of the ashes removed during the test is slightly lower than that of the ash prepared from the coal in the laboratory. The deposits are rather friable. (This is probably partly due to the relatively high basic ash fusion temperature of the coal.) In previous work carried out at the Institute (10), combustion chamber temperatures of the order of 1000 - 1100°C were achieved, but this was possibly due to the high volatile content of Koornfontein coal. This may be the cause of the unexpectedly low P₂O₅ content of the deposits. It is interesting to note that as the steaming period grew longer, the P₂O₅ content of the outer deposits decreased. It is in fact postulated by Garner (16) that as

the deposits are laid down, the inner layers are richer in basic constituents, in this case boron phosphate. This might be due to fly ash adhering to the sticky early deposit, or might be due to reactions occurring within the deposit, which cause migration of boron phosphate inwards. This same effect is shown in much more extreme fashion in Table 2, which deals with the deposits on the thermocouple sheath.

Generally as might be expected, as the P_2O_5 content of deposits is increased, so the fusion temperature is decreased.

During the test work there was no progressive growth of the deposit on the sides of the combustion chamber, (photos 1, 2 and 3). Deposits on the tubes increased, but due to their friable nature, showed a tendency to fall off. (Photos 4,5 and 6). The deposits at the back of the boiler, started growing first, but later became extremely friable. (Photos 7-8-9) The most striking deposit was that on the thermocouple, where the early hard layer and later friable layer can be easily distinguished. (Photos 10, 11 and 12).

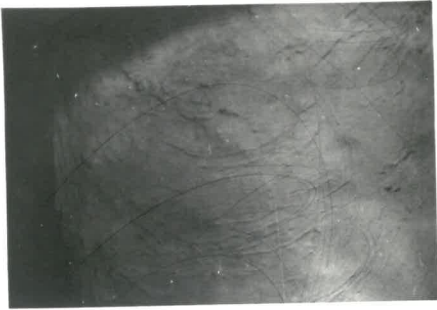
12. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

In testing, data have been obtained relative to the growth and chemical composition of phosphatic deposits. It is suggested that analytical coverage be extended to include a study of the parts played by boron and fluorine in the coal; also a study of chemical reactions which possibly take place within the deposits themselves.

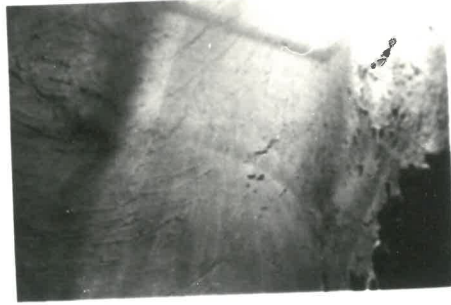
It is further suggested that some of the more realistic methods of alleviation of the deposits, which have been discussed in literature, are tried out. In particular here, methods which might create additional problems with South African coals, or which involve impracticable boiler modifications, should be avoided.

D CLARK - CHIEF RESEARCH OFFICER
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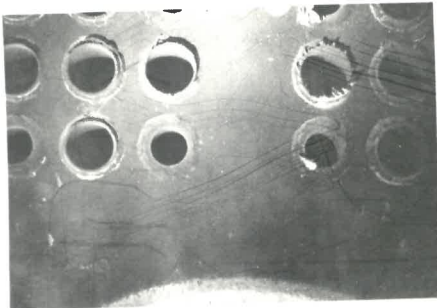
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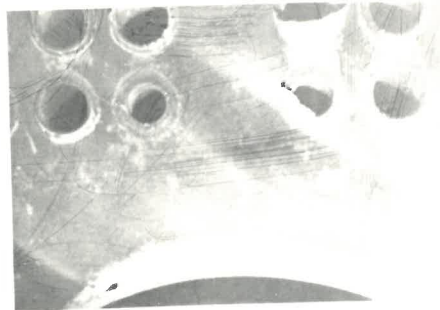
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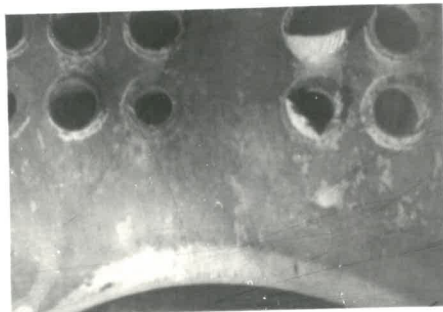
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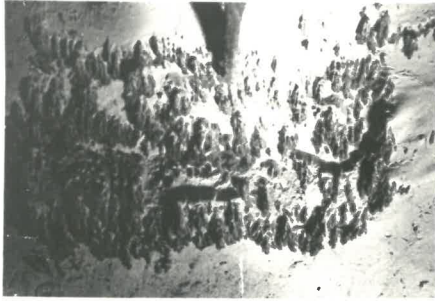
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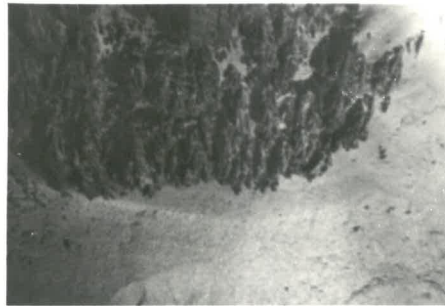
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NO. 11



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