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CONTROL OF ACID RAIN PRECURSORS

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Combustion and Carbonization Research Laboratory

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BY

H. Whaley\*, E.J. Anthony\* and G.K. Lee\*

## ABSTRACT

Research sponsored under an International Energy Agency Agreement between Canada, Denmark and Sweden has shown that  $\text{NO}_x$  and  $\text{SO}_x$  emissions from pulverized coal flames can be reduced significantly by staged combustion concepts. An evaluation of 45 coals, determined that much of the fuel nitrogen in the volatile matter can be transformed to  $\text{N}_2$  instead of  $\text{NO}$ . The conversion of fuel nitrogen to  $\text{NO}$  was from 30 to 40% in conventional flames but only 7 to 14% in staged flames. Nitrogen retained in the char showed about 20% conversion to  $\text{NO}$  and appeared to be relatively independent of local oxygen concentration. Reductions in sulphur emissions of 50% by sorbent injection into tertiary combustion air were achievable with a Ca/S molar ratio of 2. These research results have been incorporated into two field demonstrations involving retrofits of staged combustion systems in a front-wall-fired and a tangentially-fired boiler.

An alternative to conventional boilers is provided by fluidized bed combustion systems. These units operate at temperatures below that at which the nitrogen in the air is fixed and are inherently low producers of  $\text{NO}_x$ . Considerable work has been carried out in Canada under the auspices of CANMET/EMR on a number of pilot- and full-scale FBC units in Canada burning a wide range of Canadian fuels. The results suggest that typically only 10 to 25% of the fuel nitrogen is actually converted to  $\text{NO}_x$ , which results in low  $\text{NO}_x$  emissions (typically less than 258 ng/J), while removing 90% of the  $\text{SO}_2$  produced when burning high sulphur fuels. By adroit use of secondary air  $\text{NO}_x$  emissions can be kept to even lower levels in staged bubbling bed combustors, while circulating fluidized bed combustors achieve staging by the nature of their design, and are also associated with extremely low  $\text{NO}_x$  emissions.

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## INTRODUCTION

One of the major concerns associated with the expanded use of coal for heat and electricity is the emission of acid rain precursors,  $\text{NO}_x$  and  $\text{SO}_x$ , to the atmosphere. In 1980, North American utility boilers, most of which are coal fired, emitted over 5.9 million tonnes of  $\text{NO}_x$  and 16.6 million tonnes of  $\text{SO}_x$  with Canadian utility sources accounting for about 5% of both the  $\text{NO}_x$  and  $\text{SO}_x$  emissions.

Current developments on abatement technology indicate that these pollutants can be controlled by flue gas scrubbing, by combustion system modifications or by the use of novel combustion technologies, such as fluidized bed combustion (FBC). Flue gas scrubbing generally has proven energy intensive, expensive and complex. For this reason, increased emphasis has been placed on combustion modification, or the development of novel combustion technologies. Combustion modification now appears to be the most cost effective method for controlling  $\text{NO}_x$  and/or  $\text{SO}_x$  from pulverized coal-fired boilers.

This paper reviews some of the fundamental aspects of  $\text{NO}_x$  and  $\text{SO}_x$  control in flames and describes two Canadian initiatives to suppress simultaneously the generation of  $\text{NO}_x$  by staged-burner aerodynamics and sorbent injection respectively. The results of both bubbling and circulating fluidized bed combustion pilot- and full-scale work with a wide range of Canadian fuels are also described.

## THEORETICAL CONSIDERATIONS

Flame generated  $\text{NO}_x$  is produced from two sources:

1. thermal  $\text{NO}_x$  formed by high temperature reaction of atmospheric oxygen and nitrogen;
2. fuel  $\text{NO}_x$  formed by the reaction of fuel nitrogen with available oxygen during combustion.

Thermal  $\text{NO}_x$ , although a major source of the total  $\text{NO}_x$  generated when low nitrogen fuels are burned, is a minor source of  $\text{NO}_x$  when high nitrogen fuels are burned in suspension firing systems or when FBC technology is employed. Typical high nitrogen fuels include residual oil, coke and many coals.

Thermal  $\text{NO}_x$  forms fairly slowly and is favoured by flame temperatures above  $1400^\circ\text{C}$ , low rates of heat extraction, high excess air levels with intense air/fuel mixing, and high volumetric heat release rates.

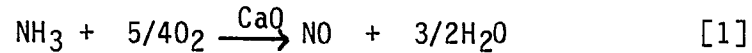
Fuel  $\text{NO}_x$ , on the other hand, appears to be only weakly dependent on temperature and forms very rapidly. Formation is promoted by fuel-lean stoichiometry during pyrolysis, a large evolution of volatile nitrogen species, and low rates of heat extraction.

Burners with physical staging of combustion air are being widely studied as a cost effective means of minimizing the oxidation of fuel nitrogen. One popular technique has been to design burners, combustion chambers, or combinations of both with a fuel-rich primary stage followed by controlled additions of secondary air and injections of tertiary air to complete combustion slowly as shown in Fig. 1.

During coal combustion, upwards of 70% of the total  $\text{NO}_x$  emissions is derived from fuel nitrogen which forms  $\text{N}_2$ , HCN, NO and  $\text{NH}_3$  during devolatilization and sub-stoichiometric combustion. About 20 to 35% of the fuel nitrogen can be retained in the char, but only about 20% of this char nitrogen is converted to  $\text{NO}_x$  regardless of stoichiometry or mixing intensity. Good char burnout can therefore be achieved under high excess air conditions without increasing significantly the  $\text{NO}_x$  levels entering the tertiary combustion zone.

A secondary method under study employs "fuel reburning" to chemically reduce NO formed in the initial combustion stage. In this method, also shown in Fig. 1, the fuel is burned in the lower furnace under slightly air-rich conditions. Then additional fuel is added downstream of the first zone to reduce or "reburn" most of the NO generated in the first stage under slightly sub-stoichiometric conditions, converting it to  $\text{N}_2$ . Finally, tertiary air is injected into the fuel-rich products leaving the reburning zone to complete the combustion process under slightly air-rich conditions. It is also possible to employ reburning in individual burners (1).

Recent work (2-4) has suggested that the limestone used for sulphur capture can augment the formation of  $\text{NO}_x$  in circulating fluidized bed combustors by catalyzing reactions of the type:



This effect has not been reported in normal bubbling bed units, although it had been observed with a two-staged unit (5). For circulating fluidized beds, however, it appears that changing the Ca/S molar ratio from 0 to 3 can cause the  $\text{NO}_x$  emissions to double (3,4). This process is not well understood and will require further study, but in principle it would suggest that  $\text{SO}_x$  and  $\text{NO}_x$  control are competing objectives for this technology. However, circulating fluidized bed boilers are well able to achieve  $\text{NO}_x$  emissions below the limits suggested by the National Guidelines for Stationary Sources (6), i.e. less than 258 ng/J, while ensuring sulphur captures of 90% or more. This augmentation of  $\text{NO}_x$  by limestone addition has not been reported with conventional boilers equipped with limestone injection, multi-staged burners (LIMB).

### $\text{SO}_x$ Emissions

Sulphur in fuel, regardless of the form, generates  $\text{SO}_x$  during combustion. Some of this sulphur may react with indigenous alkaline ash constituents, or be trapped and sometimes enriched in unburnt char in the case of FBC systems, but the balance is emitted as gas phase  $\text{SO}_x$ .

Most flame sulphur capture systems use calcium-based minerals to react with and convert  $\text{SO}_x$  to solid sulphates. Other less developed concepts utilize sulphur capture with a calcium sorbent under reducing conditions to produce calcium sulphide, which must then be either rendered inert to prevent decomposition of the sulphide, or oxidized to sulphate during the final combustion stage under excess air conditions. Therefore, the effectiveness of sulphur neutralization, with simultaneous  $\text{NO}_x$  reduction, will depend strongly on sorbent injection into a furnace region with the desired stoichiometry, temperature and residence time.

In FBC systems, sulphur is trapped by means of either a bubbling or circulating bed of calcined limestone or dolomite. The primary

Limitation with this technology is the relatively low sorbent utilization which is normally in the order of 30%. Recent results suggest that more advanced fluidized bed designs may be capable of achieving utilizations approaching 50%. Since this technology is likely to be used with higher sulphur fuels (3% S) than pulverized-coal combustion technology, optimizing the efficiency of the sorbent capture process to reduce both sorbent use and disposal costs for the waste residues is a major consideration to the economics of the process.

Small amounts of sulphides have also been found in the residues produced by these processes (typically  $\leq 0.5\%$ ). These amounts do not appear to limit significantly fluidized bed combustion technology.

When injected into an oxidizing flame zone or a fluidized bed, the sulphur/sorbent reactions are as follows:



For pulverized-coal combustion, calcination must occur via reaction 2 above 1000°C and below 1350°C. If the calcination does not occur above 1000°C it is too slow and the unreacted  $\text{CaCO}_3$  is swept out of the combustion zone. However, above 1350°C, the  $\text{CaO}$  is rapidly deactivated by dead burning via bulk diffusion of ions within the crystal lattice of the  $\text{CaO}$ . This reduces significantly the specific surface for reaction with sulphur. Overheating of the  $\text{CaSO}_4$  end product is also undesirable because above 1350°C,  $\text{CaO}$  and  $\text{SO}_2$  are regenerated. The best capture will occur when the sorbent is injected into an oxidizing region which allows calcination without deactivation. Sulphation can then occur at reaction temperatures from 750°C to 1200°C, see (Fig. 2).

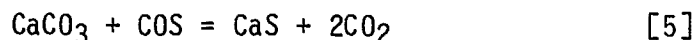
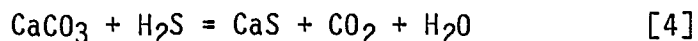
In FBC systems, the residence times are inherently long for solids, typically minutes or hours, compared with seconds in pulverized coal-fired systems. Thus they can be operated between 800°C and 900°C, which appears to be the optimum temperature range for the sulphation reaction for these systems. The calcination reaction can be regarded as going to completion and as effectively instantaneous for FBC systems unless they are operated at pressure, i.e. pressurized fluidized bed combustion.



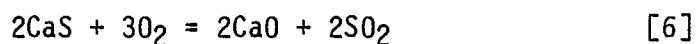
In that case, dolomite is often employed as a sorbent since the calcination temperature of the  $MgCO_3$  component is several hundred degrees lower than that of the  $CaCO_3$  component. The  $MgCO_3$  component will thus calcine producing a porous and reactive sorbent, regardless of whether the  $CaCO_3$  component calcines. This allows the sulphation reaction to proceed directly with the  $CaCO_3$ , in a reaction analogous to reaction 3. At this time pressurized fluidized bed combustion is still an experimental technology.

At the temperatures employed for fluidized bed combustion, reaction 2 dominates, and the primary reasons for sorbent utilization inefficiency are elutriation of unreacted sorbent from the FBC or pore plugging of the sorbent by the  $CaSO_4$  which has a significantly larger molar volume than that of the original  $CaCO_3$  or the  $CaO$  produced by calcination. These low temperatures also minimize  $NO_x$  formation and slagging and fouling problems.

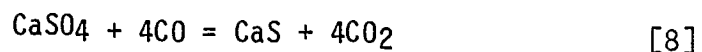
The mechanism for the sulphur reaction in reducing atmospheres is less clear, but may occur by means of the two endothermic reactions below:



The  $CaS$  formed may then if required, be sulphated or oxidized as follows:



In FBC systems sulphide formation does not seem to occur via reactions 4 or 5, or the analogous reactions with  $CaO$ . Detailed measurements of sulphide concentrations in the lower region of a pilot-scale circulating FBC unit indicated quite low concentrations of sulphide in the reducing region (beneath the region where secondary air enters the combustor). Instead the highest levels of sulphides are found in regions where the char components are concentrated, i.e. secondary cyclone and baghouse. A possible mechanism is reduction of the sulphate via reactions of the type:



though other possible mechanisms exist. In any case it appears that sulphide contamination of residues from FBC systems is not a serious problem.

During sulphation any sulphur in char that escapes the reducing zone, in a pulverized-coal combustion unit, must be captured in the subsequent oxidation stage. Application of physical-staged combustion systems, which are in the embryonic stage of development, will depend on further elucidation of critical process parameters, such as mixing, stoichiometric ratios of the primary and secondary combustion zones, sorbent injection points, volumetric heat release rates and char carryover from each stage.

Sulphur capture is also enhanced by increased thermal loading of the reaction zone, increased sorbent fineness down to about 50  $\mu\text{m}$ , Ca/S molar ratios above 2, and the presence of halogens.

Three important factors that are strongly system dependent but which have not yet been fully investigated are:

- (a) the slagging and fouling propensity of the fuel ash and sorbent in the various combustion and downstream heat transfer zones;
- (b) the amount of char emitted into the post flame gases and dust collectors; and
- (c) the flame shape with respect to furnace temperature gradients and geometry.

Research data indicate that 50% sulphur capture is possible with a Ca/S molar ratio of 2 for sorbent injection.

#### CURRENT CANADIAN PROJECTS FOR SIMULTANEOUS REDUCTION OF $\text{NO}_x$ AND $\text{SO}_x$ IN PULVERIZED COAL FIRED SYSTEMS

Two major Canadian initiatives in the simultaneous reduction of  $\text{SO}_x$  and  $\text{NO}_x$  from pulverized coal flames have been sponsored by the Canada Centre for Mineral and Energy Technology (CANMET). The first was an International Energy Agency (IEA) research project, co-funded by Canada, Denmark and Sweden with United States guidance and participation on the validation and optimization of advanced burner concepts. The second is a

demonstration project in cooperation with the Canadian Department of National Defence (DND) at Canadian Forces Base Gagetown, New Brunswick to accelerate the application of state-of-the-art LIMB technology to operating boilers. In addition to the above two projects, Energy, Mines and Resources (EMR) Canada collaborates with the Flue Gas Desulphurization Panel of the Canadian Electrical Association on utility R&D programs for reducing  $\text{NO}_x$  and  $\text{SO}_x$  emissions from flames.

#### INTERNATIONAL ENERGY AGENCY PROJECT

The IEA project, which has been conducted by the Environment Energy Research Corporation in the USA was planned in three stages (7). Stage one consisted of small-scale furnace trials on 45 coals, including 9 from Canada, to elucidate the mechanism of  $\text{NO}_x$  formation from fuel nitrogen under premixed and staged-combustion conditions. Illustrations of the small-scale furnace and burners are given in Fig. 3.

Highlights from this research indicate that for unstaged flames with 5%  $\text{O}_2$  in the exhaust gases:

- (a) more fuel nitrogen was converted to NO from premixed flames than from axial diffusion flames, with the difference in NO production between the two systems decreasing from high-volatile bituminous to lignite to medium-volatile bituminous coals (Fig. 4);
- (b) conversion of fuel nitrogen with premixed flames ranged from 30 to 45% regardless of the total fuel nitrogen content (Fig. 5); and
- (c) high-volatile coals produced lower NO emissions from coarse particles with premixed flames than with axial flames. Evidently, fuel nitrogen, which is evolved early in the flames from fine particles, is available for conversion to NO if oxygen is present (Fig. 6).

For staged flames, i.e., a sub-stoichiometric first stage and an air-rich second stage with 5% oxygen in the exit gases:

- (a) all high-volatile coals, bituminous and lignite, produced minimum NO emissions at a stoichiometric ratio of about 0.6 in the first stage; the

- medium-volatile coals yielded progressive increases in NO as the first stage stoichiometry increased;
- (b) fuel nitrogen conversion ranged from 7 to 14% with the lowest NO emissions coming from high volatile coals (Fig. 7);
  - (c) fine particles produced less NO than coarse particles for a high-volatile coal;
  - (d) the lower rank coals, lignite and subbituminous, produced large amounts of NH<sub>3</sub> and HCN at stoichiometric ratios below 0.6. These species appeared to favour transformation to N<sub>2</sub>, rather than NO, during second stage burnout; and
  - (e) heat extraction lowered NO emission from low-rank coals, particularly for first-stage stoichiometric ratio above 0.7.

#### GAGETOWN PROJECT

This project involved retrofitting LIMB burners on a 17 MW(th) frontwall-fired heating boiler at Gagetown, New Brunswick, to reduce simultaneously emissions of SO<sub>x</sub> and NO<sub>x</sub>. The boiler had been previously fired with two conventional pulverized coal burners each having its own pulverizer. Figure 8 illustrates the new installation.

The staged burner design concept shown in Fig. 8, was installed in the spring of 1984 with commissioning and evaluation scheduled for the following heating seasons (8). The retrofitted burners are designed to achieve a 50% reduction in both NO<sub>x</sub> and SO<sub>x</sub> emissions, at full load, with:

- (a) 3% high-volatile bituminous coal;
- (b) Ca/S molar ratios of 2.5 or less
- (c) combustible in ash of 7% or less;
- (d) no flame impingement on walls;
- (e) boiler efficiency of 82% or more; and
- (f) no furnace slagging with routine soot blowing.

The unit had completed commissioning trials at the time of writing and is now operated routinely by DND.

## CANADIAN ELECTRICAL ASSOCIATION PROJECT

A research project to study the feasibility of retrofitting a 350 MW<sub>e</sub>, lignite-fired utility boiler in Western Canada with a lower NO<sub>x</sub>/SO<sub>x</sub> burner system was also concluded. The tangentially-fired system was modified with staged burners designed to provide a flame zone with a sub-stoichiometric core and an oxidizing outer annulus. The sulphur sorbent was injected through the lower coal burners to maximize residence time and to provide the optimum temperature for calcination (9).

At full load, with 3% O<sub>2</sub> in the flue gas, NO<sub>x</sub> levels were reduced from 425 to 200 ppm, with about 40% reduction in sulphur emissions at a Ca/S molar ratio of 2.5 (10). Although lignite typically contains less than 1% sulphur on a moisture free basis, Western Canadian utilities now generate over 5500 MW of electricity from low-sulphur, low-rank coals and are major regional sources of NO<sub>x</sub> and SO<sub>x</sub> emissions.

The IEA research program indicates that staged-combustion concepts, together with sorbent injection, can be used to reduce simultaneously SO<sub>x</sub> and NO<sub>x</sub> emissions in boiler furnaces. Staged combustion may however be only marginally effective in reducing NO<sub>x</sub> emissions from coals in which most of the fuel nitrogen is present in the fixed carbon.

The demonstration projects involving burner retrofits are directed at accelerating the transfer of research results to commercial application and in validating staged burner concepts, together with sorbent injection, for reducing NO<sub>x</sub> and SO<sub>x</sub> emissions under operational conditions.

## FLUIDIZED BED COMBUSTION

In 1976 CANMET started a program of research on FBC technology which simultaneously achieves low SO<sub>2</sub> and NO<sub>x</sub> emissions. It is the most mature of all the novel combustion technologies and is being increasingly used across North America. The combustion efficiency associated with FBC systems is somewhat lower than that of pulverized combustion systems (95 to 99% compared with 99% plus). Typically the technology is also more

expensive per MW of power, although costs are strongly site and fuel specific, and if the pulverized combustion system must be used in conjunction with flue gas desulphurization technologies such as scrubbers, the costs per MW become similar. However, FBC systems can operate with fuels which are outside the range of conventional combustion systems, such as extremely unreactive fuels, e.g., oxidized coals, high ash or moisture fuels, e.g., washery rejects which may contain up to 70% ash, or 50% moisture and high sulphur fuels (above 3%, where sorbent techniques would demand an excessively high solid loading in a conventional burner). The technology therefore offers the possibility of extending Canada's energy base in an environmentally benign way.

CANMET commenced its program by building or sponsoring the construction of pilot-plant facilities both in-house and externally. Subsequently as the number of units increased in Canada, CANMET performed or sponsored combustion research on a wide range of fuels including oxidized coals, washery rejects, petroleum coke, pitches and high sulphur coal, in order to generate a database on Canadian fuels. Mathematical modelling work was also supported under an IEA agreement on atmospheric fluidized bed combustion and the CANMET model for bubbling bed FBC is currently used as the basis for modelling of bubbling FBC systems amongst the membership of the agreement.

As the pilot-plant work became more mature, CANMET supported the development of the first industrial bubbling bed boilers at Summerside, Prince Edward Island (two 15 MW(th) boilers) and subsequently the first utility demonstration of circulating FBC (22 MW<sub>e</sub>) at Chatham, New Brunswick. Both units were used to study the combustion of high sulphur maritime coal.

### Summerside Boilers

Canada's first bubbling fluidized bed heating plant was installed in 1982 at the Canadian Forces Base Summerside in Prince Edward Island. The demonstration project was jointly funded by Department of National Defence, and Energy, Mines and Resources Canada, at a cost of about \$18 million.

Foster Wheeler Ltd. of St. Catharines, Ontario was the prime contractor for supplying a turnkey heating plant including two boilers each rated at 18 tph of steam. The units were successfully commissioned during the 1984/85 heating season and have operated successfully since.

The units were designed to burn a 5.5% S high-volatile bituminous Eastern Canadian coal, while maintaining emissions below 705 ng/J SO<sub>2</sub> and 516 ng/J NO<sub>x</sub>. These limits were easily achieved and NO<sub>x</sub> emissions below 258 ng/J were also achieved, although the unit had to be operated with about 10% O<sub>2</sub> in the flue gas rather than the design value of 3.6%, in order to prevent bed overheating and clinkering.

In a series of tests on five high sulphur (4 to 11% S) Maritime coals, sulphur captures of 76 to 84% were obtained with Ca/S molar ratios from 1.7 to 3.3 while NO<sub>x</sub> emissions were consistently below 250 ng/J for all loads (10). In 1986, Energy, Mines and Resources Canada collaborated with the US Environmental Protection Agency to study the behaviour of these units in a series of tests to maximize sulphur capture at boiler loads of 70% or more (11). These tests included a 30-day trial to establish the Ca/S molar for 90% capture. Operating data averaged over the 30 days yielded a boiler load of 70.6% while burning a 5.9% sulphur coal. Average flue gas analyses indicated that 93% capture could be achieved with a Ca/S molar ratio of 4. This corresponded to emissions of 258 ng/J for SO<sub>2</sub> and 267 ng/J for NO<sub>x</sub>. In other shorter tests, carried out during this series of trials, SO<sub>2</sub> captures up to 99.4% were achieved. The units have thus demonstrated their ability to cope with high-sulphur fuels while meeting the most stringent SO<sub>2</sub> capture requirements. They can also meet NO<sub>x</sub> emission guidelines of 258 ng/J providing combustion conditions are optimized, despite design problems which forced the units to operate with higher excess air than originally planned.

### Chatham Boiler

Canada's first industrial-scale circulating fluidized bed boiler was constructed at New Brunswick Power's Chatham Generating Station. The boiler system was supplied by Combustion Engineering Superheater Ltd., Canada, using technology developed by Lurgi of West Germany. The new boiler supplies steam to the existing 22 MWe turbine generator. The \$38 million plant expansion was funded largely by EMR Canada.

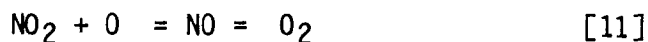
Construction of the plant started in 1985, and despite some delays the unit was ready for commissioning trials in 1987. Initially test work was carried out on a high-sulphur (7% S) bituminous coal from New Brunswick (Minto) using a blend of Albert County oil shale and limestone for sulphur capture. Subsequently the unit has been used to burn a high-sulphur (5% S) Nova Scotia coal and a petroleum coke. The unit has been shown to be able to achieve 90% sulphur capture with Ca/S molar ratios of about 2.5. The NO<sub>x</sub> emissions have proven to be very low indeed with values of as low as 60 ppm for 3.5% O<sub>2</sub> in the flue gas, which corresponds to emissions below 100 ng/J. Work is continuing with this unit in order to optimize the sulphur capture performance. It is planned to burn a wide variety of fuels including coal wash plant tailings, high ash coals, and other high-sulphur coals. The unit has nevertheless been shown to be able to achieve emission guidelines for SO<sub>2</sub> capture and to easily meet the guidelines for NO<sub>x</sub> emissions.

#### NITROUS OXIDE EMISSIONS

This gas is not normally thought of as an atmospheric pollutant. However, it appears to be a major source of NO in the stratosphere by means of the following reaction:



The NO so formed can then destroy ozone by means of the cyclic reactions:



This gas appears to be increasing on a global basis at about 0.2% /a (12). The causes of this increase are almost certainly anthropogenic, and man-made nitrogenous fertilizers and combustion systems have been identified as likely contributors.



There are very few studies on N<sub>2</sub>O emissions from combustion systems and estimates of their overall contribution to N<sub>2</sub>O production are somewhat uncertain. This situation has recently been worsened by the realization that N<sub>2</sub>O can be produced from NO<sub>x</sub> during attempts to measure N<sub>2</sub>O emissions. Specifically, it has been shown that zeolite materials which are often used in molecular sieves in gas chromatography, can convert NO<sub>x</sub> to N<sub>2</sub>O (13) via the reaction:



Gas chromatography is the standard technique for measuring N<sub>2</sub>O formation.

It has also been shown that in the presence of moisture and SO<sub>2</sub>, NO can react to produce N<sub>2</sub>O in significant concentrations (up to several hundred parts per million by volume) over periods as short as 2h, where none had originally existed. Even complete drying of the gas does not completely eliminate this effect (14). It seems likely that many of the previous studies of N<sub>2</sub>O, which relied on taking grab samples of combustion gases for subsequent analysis from combustion sources, have been affected by these phenomena. It is probable that the contribution of combustion sources to N<sub>2</sub>O formation has been overestimated in the literature.

As a result of these uncertainties, Environment Canada undertook an extensive sampling program of N<sub>2</sub>O emissions from boilers across Canada, the results of which are not yet available. In addition CANMET is also supporting research to study the formation of N<sub>2</sub>O from circulating fluidized bed combustion.

## CONCLUSIONS

Studies of 45 coals undertaken in laboratory furnaces using premixed and diffusion flames in staged and unstaged modes indicate:

- a) For unstaged flames, more fuel nitrogen was converted to  $\text{NO}_x$  in premixed compared with diffusion flames. The conversion of fuel nitrogen was between 30 and 45% for premixed flames regardless of the coal nitrogen content. High-volatile coals produced lower  $\text{NO}_x$  emissions from coarse grinds with premixed flames than with diffusion flames.
- b) For staged flames, all high-volatile coals produced minimum  $\text{NO}_x$  levels at a stoichiometric ratio of 0.6, and medium volatile coals produced progressively more  $\text{NO}_x$  as the stoichiometric ratio was increased. The fuel nitrogen conversion was between 7 and 14% with the lowest  $\text{NO}_x$  produced from high volatile coal. Finer pulverized coal grinds produced less  $\text{NO}_x$  than coarser grinds.
- c) High heat fluxes from the flames lowered  $\text{NO}_x$  levels for low-rank coals, particularly at higher stoichiometric ratios.

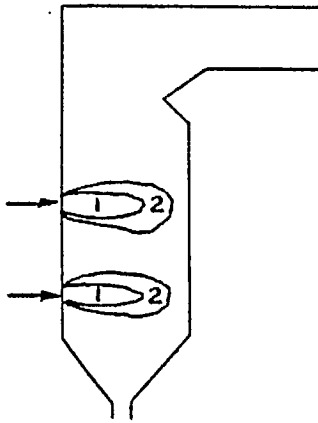
Investigations conducted on a wide range of high-sulphur coals using bubbling and circulating fluidized bed combustion technology have indicated that it is possible to achieve  $\text{NO}_x$  emissions below 258 ng/J without difficulty while achieving over 90% sulphur capture. Conversions of fuel nitrogen to  $\text{NO}_x$  range from 5 to 25%, with circulating fluidized beds producing lower  $\text{NO}_x$  emissions than bubbling beds.

The issue of  $\text{N}_2\text{O}$  emissions from combustion systems is now being addressed. It seems likely that many combustion studies in the past overestimated the emissions of this species from both conventional and fluidized bed combustion systems. This is an area however, that merits further study.

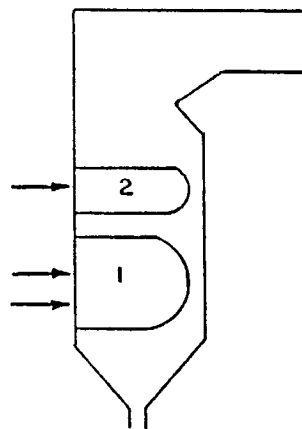
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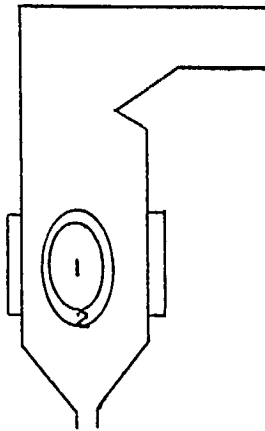
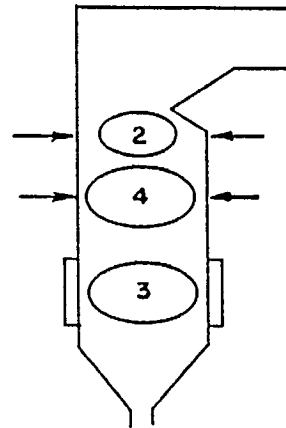
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WALL-FIRED FURNACES

A) BURNER STAGING



B) FURNACE STAGING

TANGENTIALLY-FIRED FURNACESC) STAGED BURNER  
AND FURNACED) STAGED FUEL  
REBURNING

1 = 65 % TOTAL AIR  
2 = 25 % TOTAL AIR

3 = 110 % TOTAL AIR  
4 = 95 % TOTAL AIR

Fig. 1 - Staged combustion: burner, furnace and fuel reburning

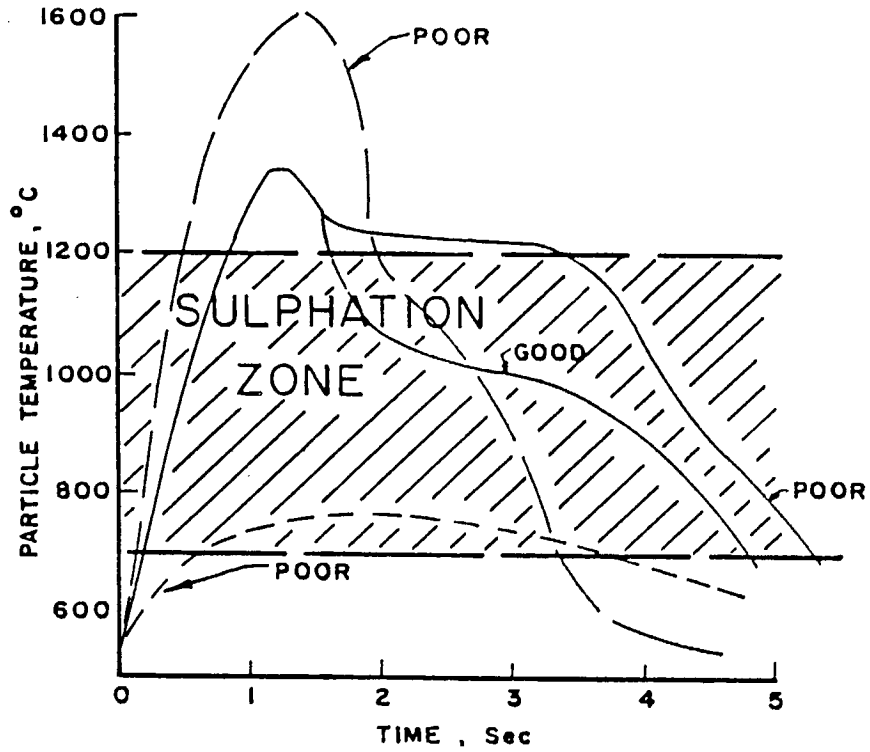
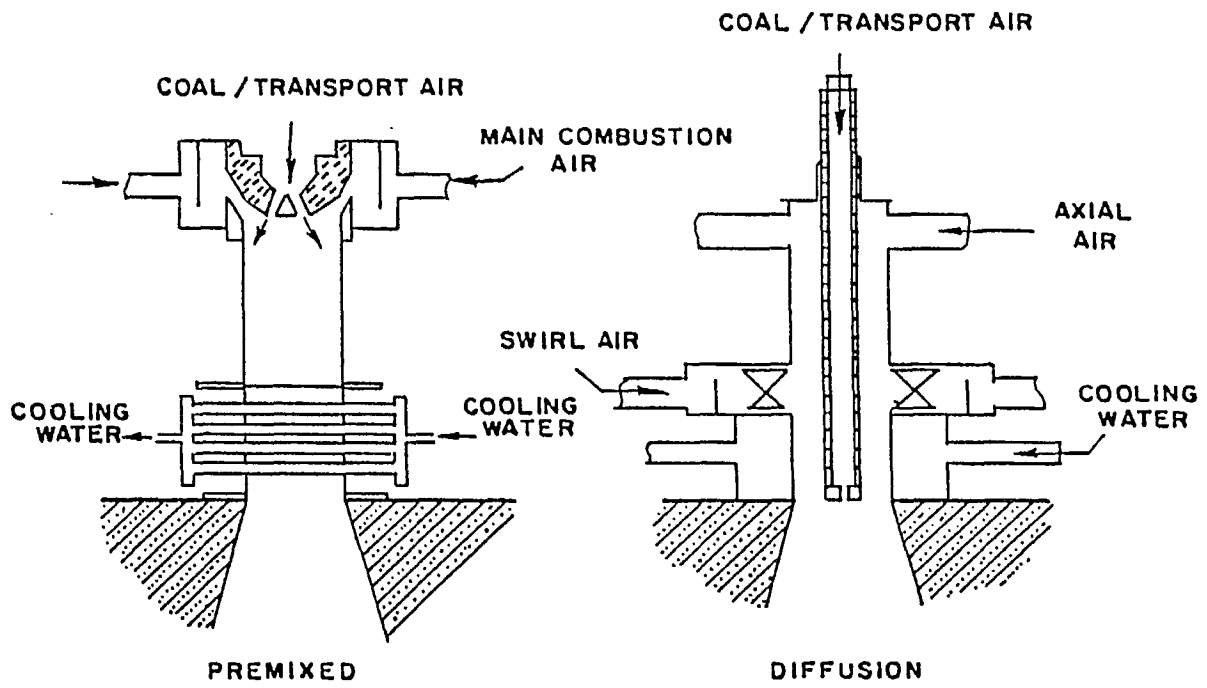
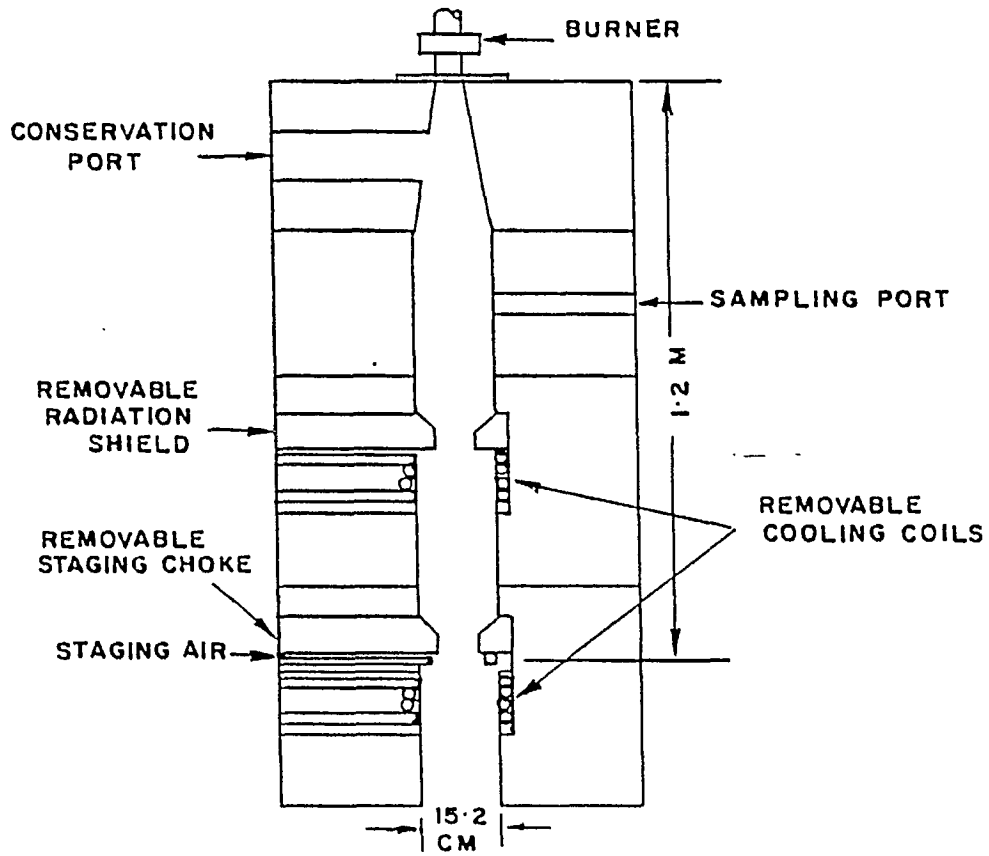


Fig. 2 - Time-temperature effect on limestone calcination



(a) BENCH-SCALE BURNERS.



(b) FURNACE SECTIONS

Fig. 3 - Modified furnace and burner sections for staged combustion studies

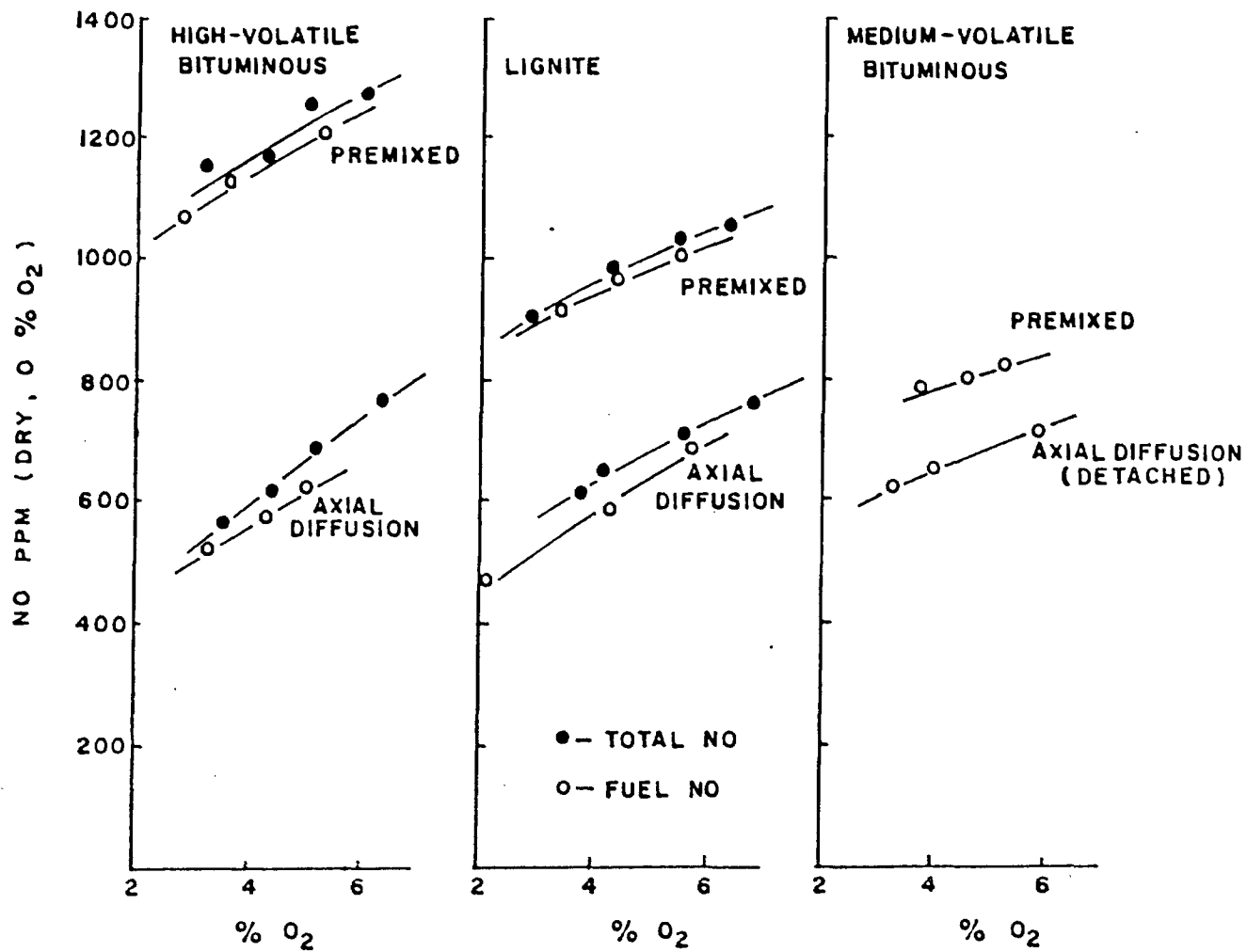


Fig. 4 - Fuel NO/total NO for premixed and axial diffusion flames



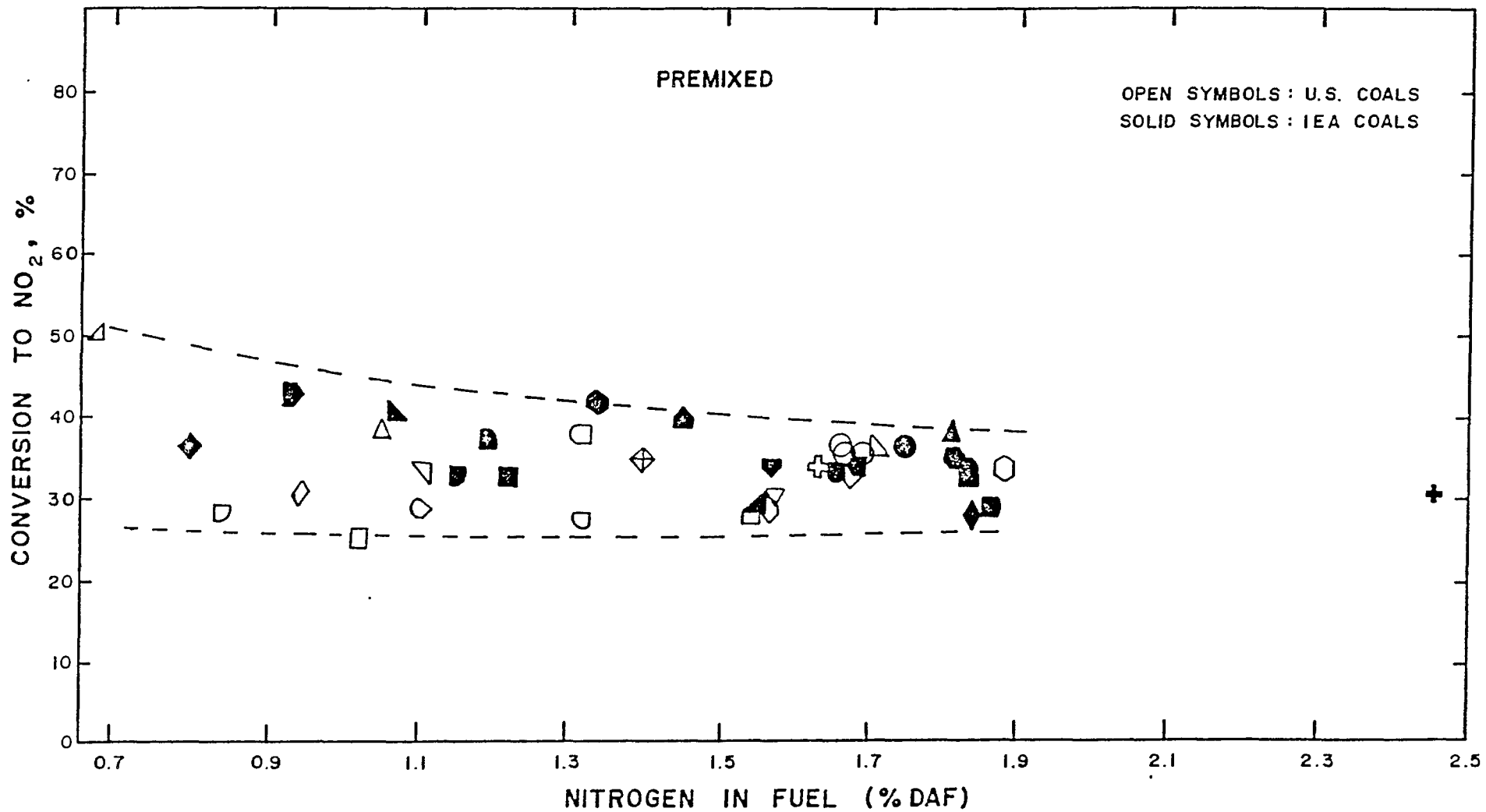


Fig. 5 - Fuel nitrogen conversion in premixed flames

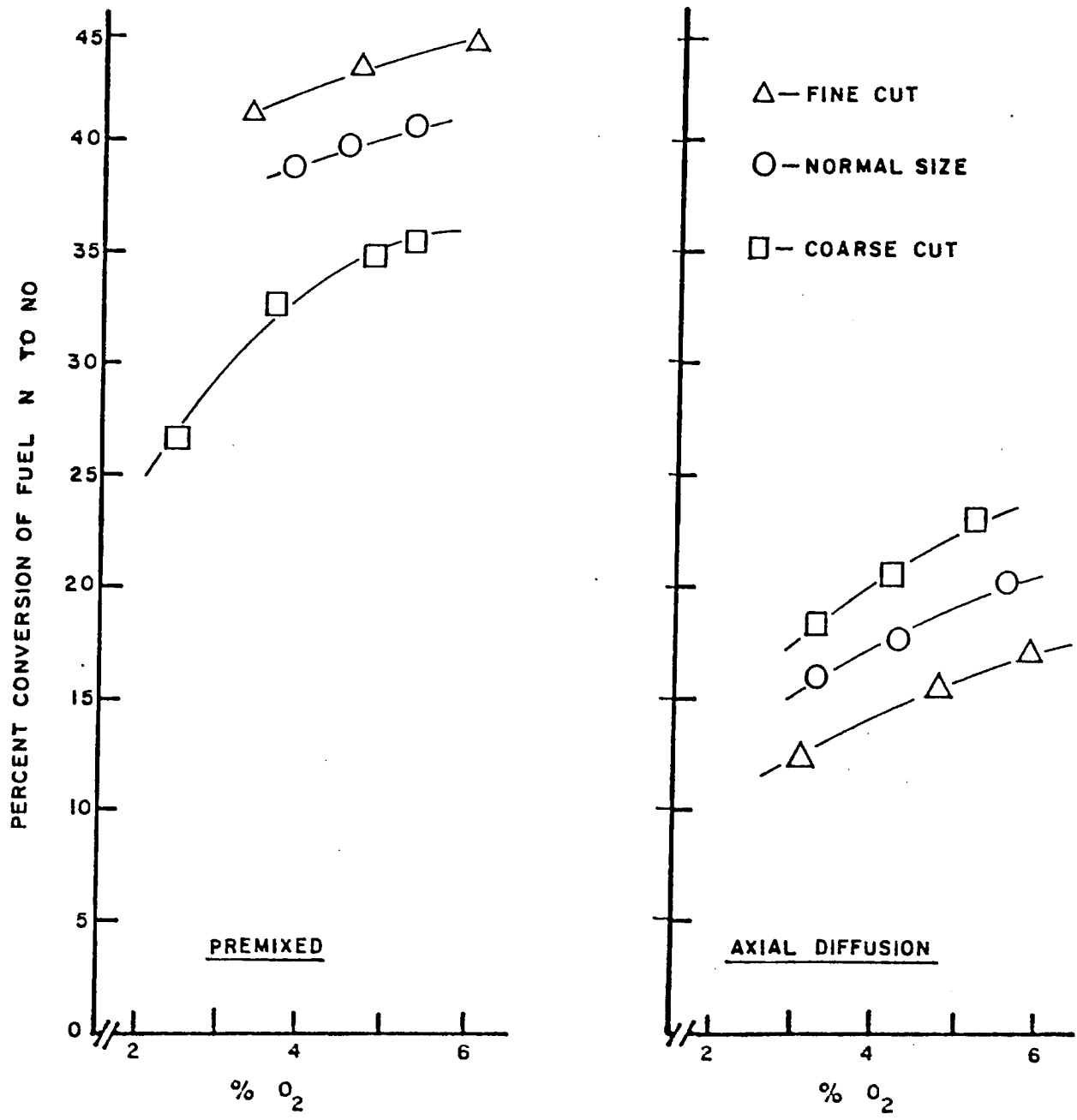


Fig. 6 - Influence of particle size, high-volatile bituminous coal

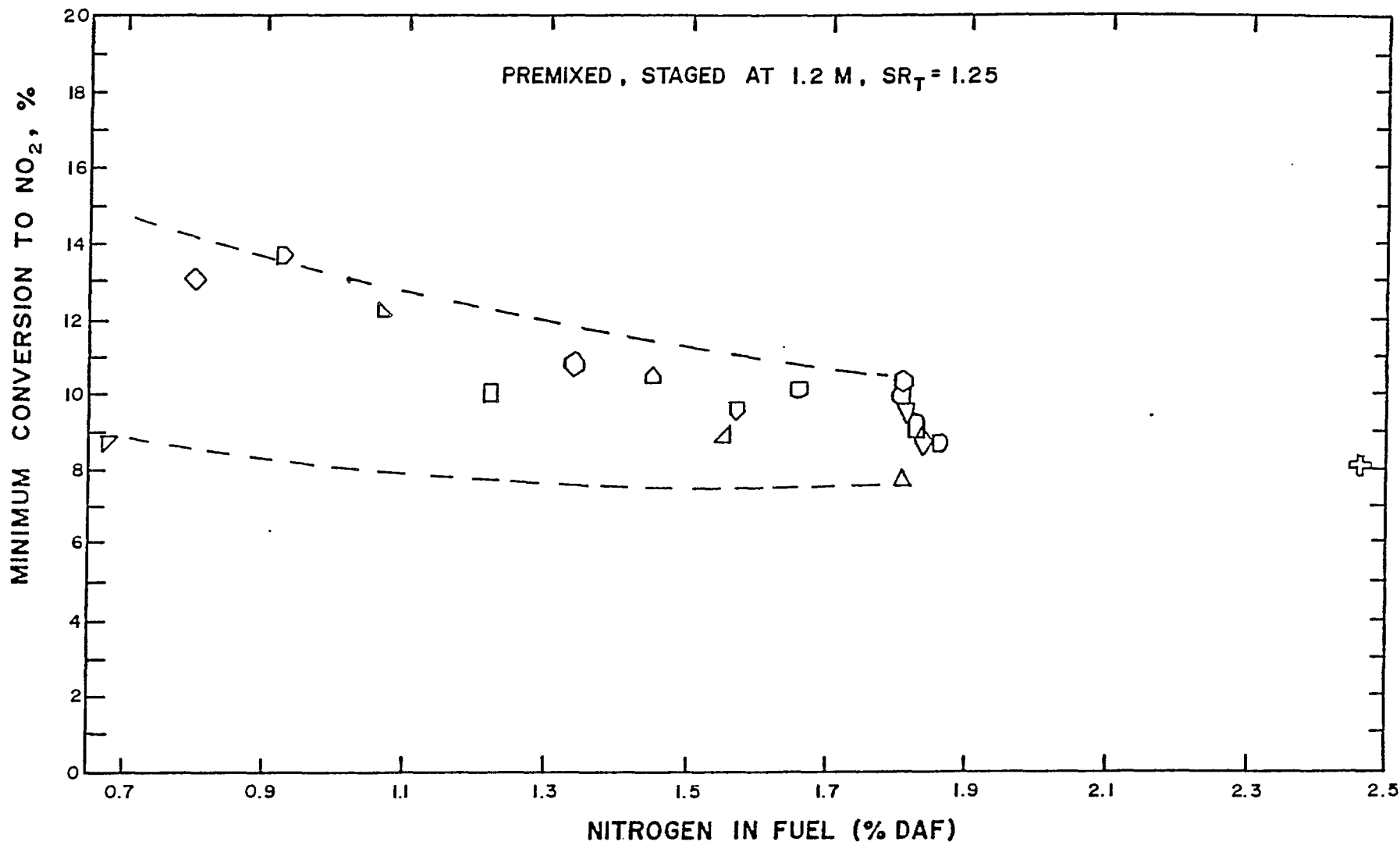
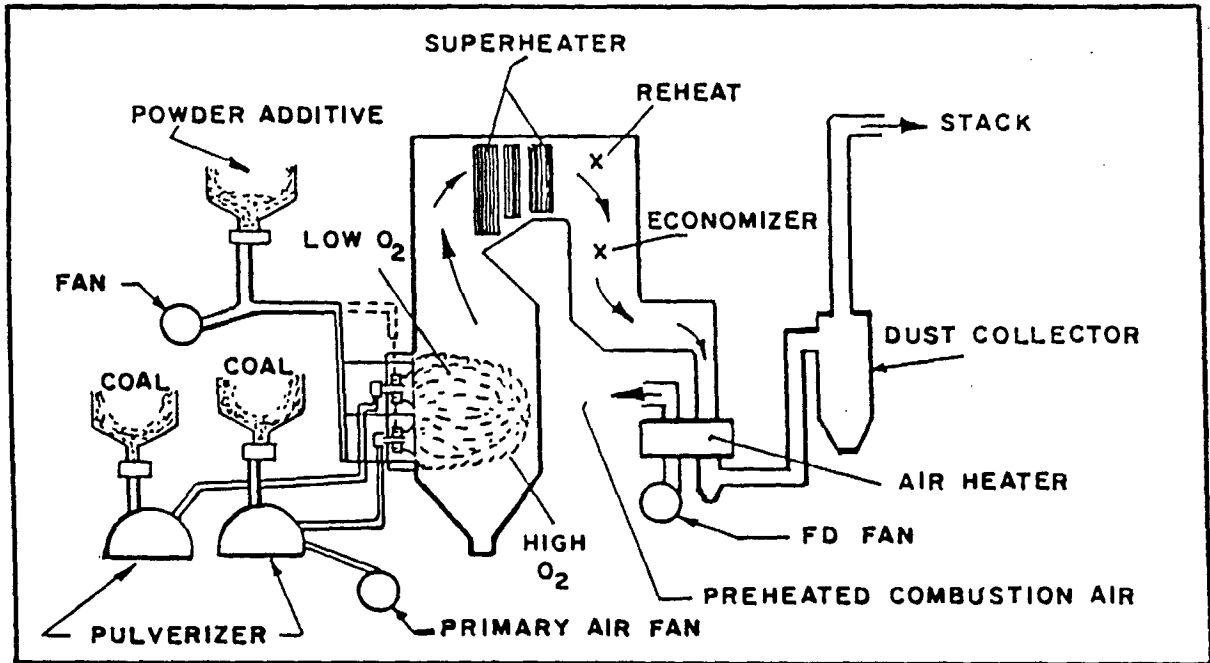
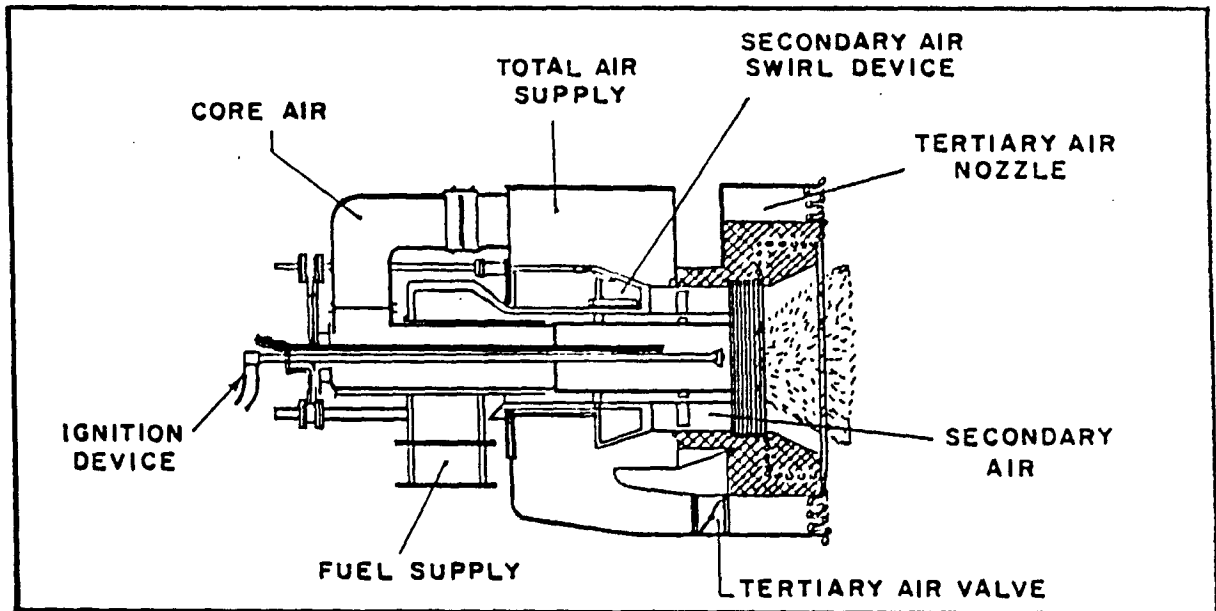


Fig. 7 - Minimum conversion of fuel nitrogen to  $NO$  under staged combustion conditions



a) Schematic of Gagetown boiler system



b) Staged mixing burner (SM burner)

Fig. 8 - Schematic of boiler and burner systems for Gagetown, NB.