

Research Strategies  
Relevant to Heating Fuel Oil Specifications:  
Fuel Sulphur Aspects  
Literature Review

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## EXECUTIVE SUMMARY

On February 17, 2001, the Federal Minister of Environment published the agenda for cleaner vehicles, engines and fuels as a Notice of Intent in Part I of the Canada Gazette.

Measures to reduce the levels of sulphur in light and heavy fuel oils used in stationary combustion facilities are one of the planned actions outlined in the Notice of Intent. Scoping studies of the benefits to the health of Canadians and the environment began in 2001. Among these studies is a literature review of relevant information that would complement the quality of science and prior knowledge as applied to policy formulation.

Natural Resources Canada and CANMET Energy Technology Centre (CETC) actively participate in the integrated federal clean air strategy. As a federal research organization, CETC participates in a variety of programs focusing on clean and efficient use of Canada's abundant but not unlimited energy resources.

This literature review was done to examine the impact of sulphur content in petroleum based fuels on the research strategies relevant to fuel oil specifications, fuel oil combustion in stationary combustion equipment and associated gaseous and particulate emissions. It was undertaken by the Advance Combustion Technology (ACT) laboratory of CETC under contract with Oil, Gas and Energy Branch of Environment Canada's Air Pollution Prevention Directorate.

Burning heavy fuel oils releases to the environment a range of gaseous oxides of sulphur, nitrogen and some of the metals present in the fuel. Carbon particulate matters from incomplete combustion or particulates containing a range of sulphate compounds are also released. Depending on the firing conditions they could be supplemented by other pollutants such as Volatile Organic Compounds (VOC), Polyaromatics Hydrocarbons (PAH) and occasionally chlorine such as HCl. Lowering the sulphur content in the heavy fuel oils will lead directly to overall reduction in stack gas emissions of sulphur dioxide. Lower sulphur content in the fuel oil will also lower the risk of high temperature corrosion within the combustion chamber.

To gain boiler efficiency, it is desirable that the flue gas leaving the combustion system be as close in temperature as possible to that of ambient air. This is achieved by adding convective heating surfaces in the boiler. As flue gas temperature is lowered, however, some tail-end boiler metal surfaces may be cooled below the dew point of the system. When fuel containing sulphur is combusted, sulphur trioxide present in the flue gas may initiate formation of condensate containing sulphuric acid. Corrosion of exposed metal surfaces will start, if they are not protected. The low temperature corrosion phenomenon is complex and governed by the level of sulphur trioxide in the flue gas. One path to generate sulphur trioxide is during heterogeneous oxidation of sulphur oxides in the presence of metals such as iron. Without special measures, even small amounts of

sulphur present in heavy fuel oil will lead to production of sulphur trioxide in the combustion system. Therefore the boiler acid dew point might be reached as the flue gas is cooled. Just lowering the fuel sulphur content will not lead to direct gains in boiler efficiency.

If acid dew point is reached during boiler operation and low temperature corrosion is not controlled equipment damage can be catastrophic. Tail-end boiler corrosion is also greatly accelerated in the presence of chlorine. Traces of chlorine could enter the furnace with burner combustion air if the boiler is located near the ocean or sea. The risk of reaching the acid dew point for boiler tail-end surfaces can be lowered either by reducing the levels of excess air at the burner (as is the case with some modern low-NO<sub>x</sub> burners) or by injection of Ca or Mg (or of their oxides) at a strategic temperature window within the furnace envelope. Alternatively, tail-end boiler surfaces must be protected with special Teflon-type coatings capable of withstanding acid attacks.

Residual fuel oils usually contain ash perhaps as much as 0.25% by weight. For heavy fuel oil much of the ash consists of compounds of metals such as vanadium, sodium and nickel. These metals, especially vanadium, present a danger of high temperature corrosion of superheater and reheater boiler tube surfaces. High temperature corrosion phenomena are numerous and complex. The role of vanadium is that of a catalyst during the formation of low melting point sulphates. These sulphates together with other sodium and/or chlorine compounds can attack high temperature mild-steel tube surfaces. For this reason during the boiler design stage the high temperature superheater and reheater tubes are typically selected and made of expansive alloys of Cr and Mo.

Heavy oil must be preheated for proper burner atomization and spray droplet sizes of 50 microns or less in order to achieve efficient combustion. Fuel atomization is done either mechanically by increasing fuel pressure at the burner or by use of saturated steam which is mixed with the fuel oil at the burner tip. If fuel atomization at the burner is poor combustion of heavy oils can generate particulates in the form of unburned carbon called soot. These particulates are typically larger than 10 microns. Large soot particles after they leave the stack are likely to contain condensed sulphuric acid as a result of reaction with moisture in the air. They are called acid soot. Acid soot is unsightly and corrosive to the environment and to exposed metal surfaces. These acid soot particles are too heavy to travel long distances with the plume. They are easily controlled by proper burner selection and by a well-tuned boiler control system.

Numerous other particulate emissions from combustion of heavy fuel oil may pose greater problems than acid soot. These may be very small carbon particles combined with compounds of sulphur and the various ash metals that residual oils typically contain in trace quantities. Particulate emissions especially those in the smaller size ranges (less than 2.5 microns) contain most of the sulphur chemically bound with the other heavy metals present in the fuel ash. When firing heavy fuel oil 30 to 50% of the particulates is likely to be less than 1.8 micron size.

Important work on emissions from combustion of heavy fuel oil has been conducted at Research Triangle Park, North Carolina, under the auspices of the U.S. Environmental Protection Agency (EPA). The EPA studied the emissions of particulates and hazardous air pollutants from a range of fuels having different sulphur contents. The results are presented below:

Emission	Fuel oil grade			
	No. 2 S = 0.41 %	No. 5 S = 1.42 %	No. 6 S = 0.49 %	No. 6 S = 1.66 %
Total particulates, g/m <sup>3</sup>	0.0061	0.0529	0.0148	0.1074
Antimony, lb/10 <sup>12</sup> Btu	0 (0)	4.96 (0)	17.6 (33)	15.5 (28)
Arsenic, lb/10 <sup>12</sup> Btu	0 (0)	8.48 (16)	2.84 (5)	3.61 (7)
Beryllium, lb/10 <sup>12</sup> Btu	0 (0)	0 (0)	0 (0)	0.066 (0)
Cadmium, lb/10 <sup>12</sup> Btu	0 (0)	0 (0)	0.934 (20)	7.22 (51)
Chromium, lb/10 <sup>12</sup> Btu	3.80 (148)	6.61 (31)	9.57 (42)	22.6 (39)
Lead, lb/10 <sup>12</sup> Btu	1.15 (56)	25.4 (45)	102 (48)	513 (45)
Manganese, lb/10 <sup>12</sup> Btu	6.11 (1110)	9.33 (43)	11.0 (70)	39.4 (80)
Nickel, lb/10 <sup>12</sup> Btu	2.96 (115)	896 (57)	508 (61)	1570 (67)
Selenium, lb/10 <sup>12</sup> Btu	0 (0)	3.46 (6)	0.687 (1)	2.68 (5)
Vanadium, lb/10 <sup>12</sup> Btu	2.72 (88)	5870 (82)	401 (108)	6020 (76)
Total metals, lb/10 <sup>12</sup> Btu	16.7	6820	1050	8190

EPA findings show that lowering the sulphur content in the heavy No.6 fuel oil will lead to lower particulate emissions. When sulphur in heavy fuel oil is reduced, its ash content and heavy metal compounds are also reduced in the process as shown by the same EPA work:

Element	Fuel oil grade			
	No. 2	No. 5	No. 6	No. 6
Ash, wt %	0.01	0.05	0.06	0.23
Sulphur, wt %	0.41	1.42	0.49	1.66
Chlorine, wt %	0.03	0.02	0.03	0.05
Arsenic, ppmw	<1	<1	<1	<1
Antimony, ppmw	<1	<1	<1	<1
Beryllium, ppmw	<0.5	<0.5	<0.5	<0.5
Cadmium, ppmw	0.01	0.08	0.09	0.26
Chromium, ppmw	0.05	0.41	0.43	1.06
Lead, ppmw	0.04	1.04	4	21
Manganese, ppmw	0.01	0.40	0.30	0.91
Mercury, ppmw	0.11	0.02	0.02	0.02
Nickel, ppmw	0.05	29.0	15.7	43.0
Selenium, ppmw	<1	<1	<1	<1
Vanadium, ppmw	0.06	132	7	146

Organic emissions also appear to be influenced by sulphur levels in the fuel oil. Extensive measurements by EPA of 195 organic compounds during combustion of low-sulphur No. 6 oil and high-sulphur No. 6 oil indicate an increase of total PAH with higher sulphur No. 6 oil as shown in the table below. However, refined oils show higher emissions of PAH due to a higher percentage of volatile components.

<b>Grade of oil</b>	<b>No. 2</b>	<b>No. 5</b>	<b>No. 6</b>	<b>No. 6</b>
Sulphur content	0.41	1.42	0.49	1.66
<b>PAH</b>	<b>Emission rate, lb/ 10<sup>12</sup> Btu</b>			
Acenaphthene	0.019	0	0	0.036
Acenaphthylene	0.018	0.078	0	0.062
Anthracene	0	0.043	0.031	0
Benzo(a)anthracene	0.348	0.037	0.095	0.044
Benzo(a)pyrene	0.695	0	0	0
Benzo(b)fluoranthene	0.859	0	0	0
Benzo(g,h,i)perylene	0.042	0.0287	0.027	0.066
Benzo(k)fluoranthene	0.745	0	0	0
Chrysene	0	0	0	0.029
Dibenz(a,h)anthracene	0.430	0.093	0.038	0
Fluoranthene	0.882	0	0.052	0.049
Fluorene	0.098	0.042	0.041	0.072
Indemo(1,2,3-cd)pyrene	0.129	0.033	0.028	0
Naphthalene	0.042	0.640	0.218	2.36
Phenanthrene	1.10	0.056	0.118	0.132
Pyrene	0.148	0	0.022	0.052
<b>Total PAH</b>	<b>5.93</b>	<b>1.05</b>	<b>0.669</b>	<b>2.90</b>

One possible way of lowering the ash and sulphur content in heavy fuel oil is by subjecting the crude oil to hydrodesulphurization prior to refining. This could have added advantages by reducing typical problems encountered in the refinery such as equipment corrosion, plugging and catalyst poisoning. Hydrodesulphurization is just one possible way of treating crude oil prior to refining which will ultimately lead to lower sulphur content in the residual heavy fuel oil downstream.

A study by Halkos (1995) compares pre-combustion, during-combustion and post-combustion technologies for desulphurization for both coal and oil. For oil two types of pre-combustion desulphurization, direct and indirect, are discussed. In the direct method the residue from initial distillation is reacted with hydrogen in the presence of a catalyst to form H<sub>2</sub>S which later is removed and converted to elemental sulphur. The

desulphurized product is then re-blended with the distillates and perhaps processed further. Sulphur removal is accomplished by treating the crude oil or a sulphur-enriched portion of the refinery stream with hydrogen at high pressure in the presence of a catalyst. The process is admittedly sensitive to peculiarities of the feedstock and may require prior demetallization of itself desirable. But the technology exists, is widely used, and doubtless can be improved in terms of effectiveness and economy.

Methods exist that can remove up to 90% of the input sulphur with an associated fuel loss of about 8%. In the indirect method the light oils produced from atmospheric distillation of crude oil are re-distilled under vacuum, hydrotreated to remove the sulphur, then blended with the heavy oil to produce a lighter, lower-sulphur fuel oil. This method can achieve a sulphur reduction of about 40% with an associated fuel loss of about 5 %.

Halkos (1995) observes that costs of desulphurization can vary widely depending on the size of the refinery, degree of desulphurization, nature of the crude oil and its cost. He cites one study which estimates the cost of desulphurization in 1985 \$U.S.:

Reducing heavy fuel oil from 2.15 to 1.0% S \$333/t of SO<sub>2</sub> removed.

Reducing heavy fuel oil from 1.0 to 0.7% S \$722/t of SO<sub>2</sub> removed.

Processes for removing sulphur during combustion, such as fluidized-bed combustion or limestone injection require high-efficiency particulate cleanup systems and so are not usually applied to oil-fired boilers. Post-combustion desulphurization by means of flue gas scrubbers is estimated to add 15 to 20% to the total cost of a power plant. Operating costs for oil-fired plants are between 610 and 720 \$U.S./t of sulphur removed.

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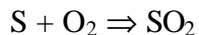
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## INTRODUCTION

Petroleum fuels have been in common use for about a century and in that time we have become increasingly dependent upon them. In terms of cost and availability they have remained competitive with other fuels; in terms of flexibility of application, energy density and versatility for distribution they have clear advantages; as fuels for transport, i.e., motor vehicles, aircraft, locomotives and ships they have little competition. But they have disadvantages as well, primarily in the pollutants they emit, which not only affect human health but also contribute to acid rain and often cause corrosion of combustion equipment such as steam generators.

The emissions of major concern are the sulphur oxides  $\text{SO}_2$  and  $\text{SO}_3$ , nitrogen oxides, generally referred to as  $\text{NO}_x$ , and particulate matter comprised of carbon, soot and small quantities of fuel oil contaminants such as vanadium and nickel. Of serious concern are also emissions of carbon monoxide (CO), volatile organic compounds (VOC), and polyaromatic hydrocarbons (PAH). The emission during oil combustion of greatest magnitude, water vapour and carbon dioxide ( $\text{CO}_2$ ), formerly considered harmless but now believed to be contributors to climate change, are not discussed here because current practicable technologies do not provide a means for dealing with them.

Sulphur dioxide ( $\text{SO}_2$ ) is an expected and predictable emission resulting from the combustion of sulphur-bearing fuels. Its primary mechanism of formation is simple enough:



although other mechanisms may also be active. Its role as a precursor to acid rain is now well-understood and much has been learned about the many mechanisms by which it can be involved in wastage of metals surfaces in steam generators subjected to high temperatures ( $>500^\circ\text{C}$ ). The higher oxide of sulphur,  $\text{SO}_3$ , which also forms in combustion processes, has less direct environmental impact mainly because the emission rate is only about 1% that of  $\text{SO}_2$ . However,  $\text{SO}_3$  readily reacts with water to form  $\text{H}_2\text{SO}_4$  and thus has been a major cause of corrosion at relatively low temperatures ( $<200^\circ\text{C}$ ) in boilers and water heaters.

Early in the twentieth century Johnstone (1929) noted that sulphuric acid in flue gas had the effect of raising the dewpoint and therefore the temperature at which condensation could occur and corrosion could begin. However, with the inefficient combustion equipment of the times, i.e. high flue gas exit temperatures, cold-end corrosion remained a minor problem. Then, in the mid twentieth century, utility boiler efficiency was improved via the use of air heaters, economizers and other heat recovery devices. Efficient heating and power generation systems employing high temperature water became common and low-temperature corrosion was suddenly a widespread problem that stimulated much research.

Within a couple of decades much had been learned about minimizing the formation of  $\text{SO}_3$  and mitigating low-temperature or cold-end corrosion. The understanding of high-temperature corrosion mechanisms involving sulphur was also advanced although these are many and complex. In combination with chlorine, a common trace element in coal and municipal waste, high-temperature corrosion by sulphur compounds continues to challenge metallurgical science.

But as corrosion problems have been reduced concern about atmospheric emissions has increased with  $\text{SO}_2$  being a component of major concern. Here two solutions present themselves. One is to remove, via scrubbers, the  $\text{SO}_2$  from the flue gas before it leaves the stack. The other is to remove the sulphur from the fuel. Both have been implemented to a degree dictated by economics - scrubbing becomes uneconomical for all but large installations; sulphur removal at the fuel source is also costly but may benefit from economies of scale, advances in research, and perhaps a broadly based cost/benefit analysis.

As precursors to acid rain, emissions of nitric oxide and nitrogen dioxide (collectively,  $\text{NO}_x$ ), rank with  $\text{SO}_2$ . They are formed during combustion both from atmospheric nitrogen and from organic nitrogen compounds present in fuel oil. They can be reduced by various means, least successfully in residual oils with relatively high concentrations of organic nitrogen compounds.

As for particulate emissions, research in the last half of the twentieth century has demonstrated potential negative health effects of particulates in the micron and sub-micron range. Obviously some materials are more toxic than others but few are neutral. Concurrent research has shown that combustion of petroleum fuels results in significant emissions of respirable particulates. These comprise mostly carbon in the case of refined products such as gasoline, diesel fuel and light fuel oil. However, of a barrel of crude oil, about half to two-thirds is converted to refined products, and the remainder, containing most of the contaminants, is utilized as residual fuel oil. When burned the residual oils emit particulates of carbon combined with the contaminants that in varying quantities are part of the ash content of crude oil.

The present review addresses a representative sample of the pertinent literature over the last half-century. The aforementioned contaminants and emissions are discussed in terms of quantity, the mechanisms of formation, major mechanisms of corrosion, and current technology for emissions control. Finally, current technology for eliminating contaminants at the refining stage is discussed and this, it is suggested, may be the most fruitful route for further advances.

## SO<sub>2</sub>, SO<sub>3</sub> AND DEWPOINT

Early recognition of the impact of H<sub>2</sub>SO<sub>4</sub> on dewpoint of flue gas has already been mentioned (Johnstone, 1929). Among the first research into the mechanisms involved was that conducted by the British Coal Utilization Research Association. For example, in 1949 Whittingham (1949), reporting on previous work (Taylor, 1942; Dooley and Whittingham, 1946; Whittingham, 1948), presented the relationship shown below in Fig. 1 of dewpoint vs. H<sub>2</sub>SO<sub>4</sub> in dust-free flue gas containing various amounts of water. Dewpoint was determined by a dewpoint meter consisting of an internally air-cooled glass thimble containing two electrodes, one of which was also a thermocouple measuring the surface temperature of the thimble. A low-voltage DC potential was applied across the electrodes and as increasing airflow cooled the thimble condensation would form an electrical bridge. The thimble temperature at which current flow was first detected was taken as the dewpoint. Wet chemistry was used to measure SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>. Concentrations of SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> can be considered equal in the presence of even slight amounts of moisture. Figure 1 thus shows that 50 to 100 ppm of SO<sub>3</sub> can raise dewpoint by 50°C to 80°C.

Whittingham went on to demonstrate that oxidation of SO<sub>2</sub> by atomic oxygen,



is a major formation mechanism for SO<sub>3</sub>. Addition of species such as H<sub>2</sub>, Pb(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, and Fe(CO)<sub>5</sub>, more likely than SO<sub>2</sub> to react with atomic O, indeed reduced SO<sub>3</sub> formation and dewpoint.

Since, in the manufacture of H<sub>2</sub>SO<sub>4</sub>, ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) was once used to catalyze SO<sub>2</sub> to SO<sub>3</sub>, it was recognized that the large area of oxidized metal in a boiler might generate SO<sub>3</sub> in the same way. This was shown to be true by Tolley (1948) using mild steel at 600°C. However, Crossley (1946) determined that sulphur-related corrosion was not a problem in British power boilers fired with high-sulphur coal, and Barkley et al. (1947) showed that the more fly ash, the less SO<sub>3</sub> was present, suggesting that the former absorbed the latter.

Hedley (1962) undertook study of SO<sub>3</sub> formation using a small furnace designed to produce a flame with a controlled mixing history. The fuel was kerosene with carbon disulphide added to raise sulphur content to about 2%. He found that:

- under sub-stoichiometric conditions no SO<sub>3</sub> formed;
- with excess air SO<sub>3</sub> formation in the flame reached 70 ppm, even though the flame temperature, as high as 1500 °C, could be expected to encourage breakdown of SO<sub>3</sub> to SO<sub>2</sub>;

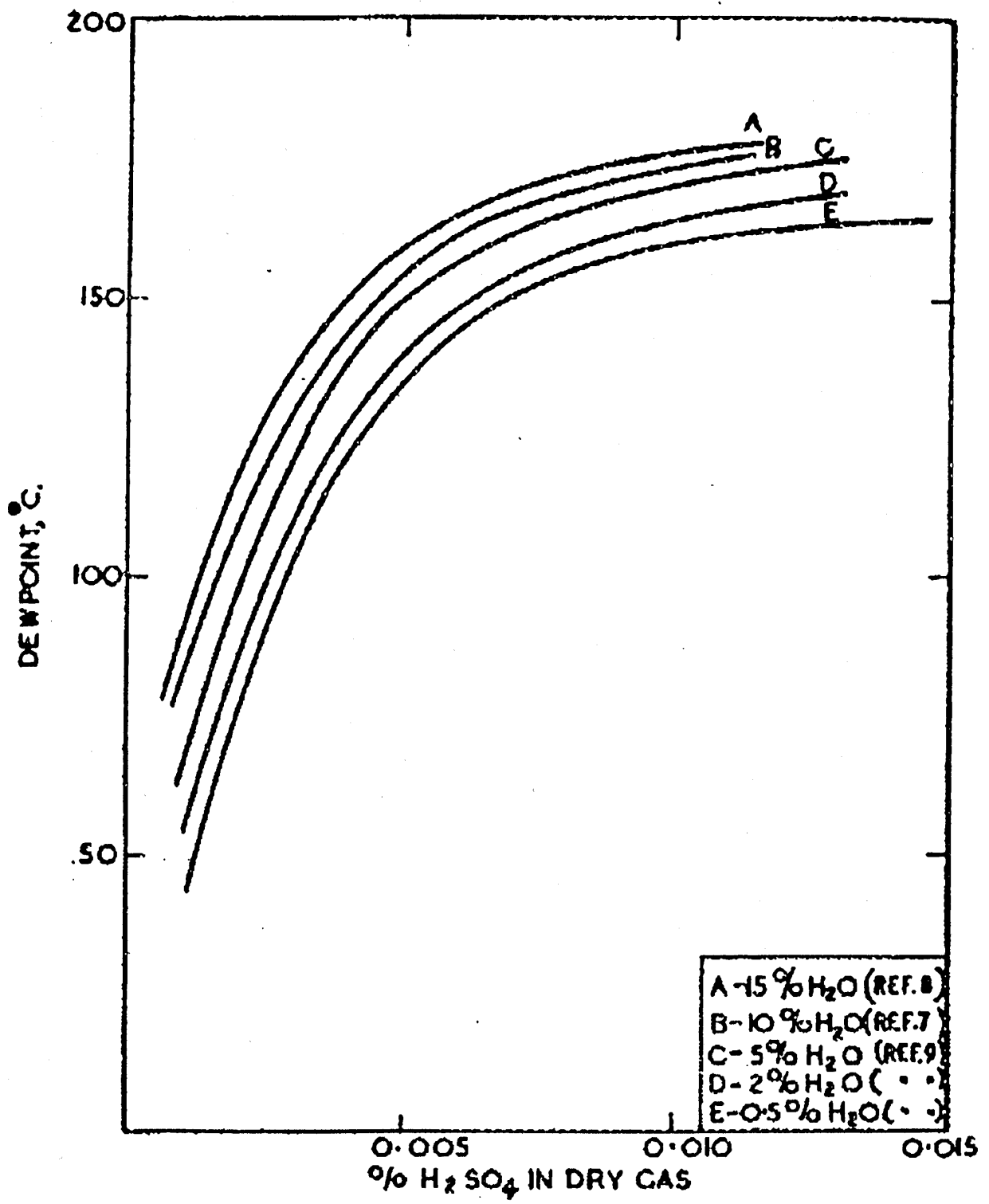


Fig. 1 - Variation of dewpoint with H<sub>2</sub>SO<sub>4</sub> content gases having different water vapour content

- under excess air conditions SO<sub>3</sub> concentration rose sharply from the point of ignition, peaked at a point downstream equivalent to a residence time of 0.03 s, and then declined gradually.

Hedley concluded that the amount of SO<sub>3</sub> formed depends more upon the availability of atomic oxygen than upon sulphur concentration and that formation of SO<sub>3</sub> in the flame is substantially more important than subsequent formation by catalysis.

Further work on acid dewpoint by various researchers, conveniently summarized by Lisle and Sensenbaugh (1965), called into question the reliability of dewpoints as determined by dewpoint meter. Müller (1959) had used thermodynamic relationships to calculate the dewpoints of flue gas with very low concentrations of sulphuric acid and these showed a different relationship from those obtained by dewpoint meter (see Figure 2 below). Lisle and Sensenbaugh measured SO<sub>3</sub> and SO<sub>2</sub> using apparatus developed by Goksøyr and Ross (1962) in synthetic flue gas made up of nitrogen, oxygen, carbon dioxide and sulphur dioxide. Concentration of SO<sub>3</sub> was varied by feeding known quantities of dilute H<sub>2</sub>SO<sub>4</sub> into an evaporator in the flue gas stream. Then, by varying the temperature of the SO<sub>3</sub> condenser and measuring SO<sub>3</sub> captured vs. SO<sub>3</sub> passing through the condenser, it was possible to establish the temperature at which a given concentration of SO<sub>3</sub> saturated the flue gas i.e., the acid dewpoint. The results of this work, shown in Figure 3, confirm the accuracy of Müller's calculations based on thermodynamic equilibrium.

Work at Battelle Memorial Institute by Levy and Merryman (1965) on combustion of H<sub>2</sub>S in a one-dimensional flame indicated that H<sub>2</sub>S is first oxidized to SO (H<sub>2</sub>S + O<sub>2</sub> ⇒ H<sub>2</sub>O + SO) then to SO<sub>2</sub> (SO + 1/2 O<sub>2</sub> ⇒ SO<sub>2</sub>). Then oxidation to SO<sub>3</sub> may occur via atomic oxygen (SO<sub>2</sub> + O ⇒ SO<sub>3</sub>) or molecular oxygen (SO<sub>2</sub> + 1/2 O<sub>2</sub> ⇒ SO<sub>3</sub>). Formation of SO<sub>3</sub> was greatly enhanced by the presence of platinum as a catalyst, particularly at temperatures above 600 K. V<sub>2</sub>O<sub>5</sub> and copper oxides were less effective as catalysts but still produced about 500 ppm SO<sub>3</sub>, far higher than normally encountered in conventional flames.

In a study of SO<sub>3</sub> reduction by low excess air and a magnesium additive in a 185 MWe boiler fired with residual oil Reese et al. (1965) found that SO<sub>3</sub> formation depended on boiler load as well as excess air level. For example, when operating with 2% excess oxygen and without additive, SO<sub>3</sub> concentration at the air heater inlet was 56 ppm at 185 MWe output, 39 ppm at 110 MWe output, and 12 ppm at 55 MWe output. In all cases, SO<sub>3</sub> concentration dropped as excess oxygen was reduced below 2%. The increase of SO<sub>3</sub> with load may be due to the greater availability of atomic oxygen one might expect at the higher furnace temperatures that prevail at higher load, but the authors later found that SO<sub>3</sub> concentration was very low e.g., 3 ppm at the furnace outlet but had increased ten-fold at the air heater inlet. This infers formation by catalysis involving the convection surfaces.

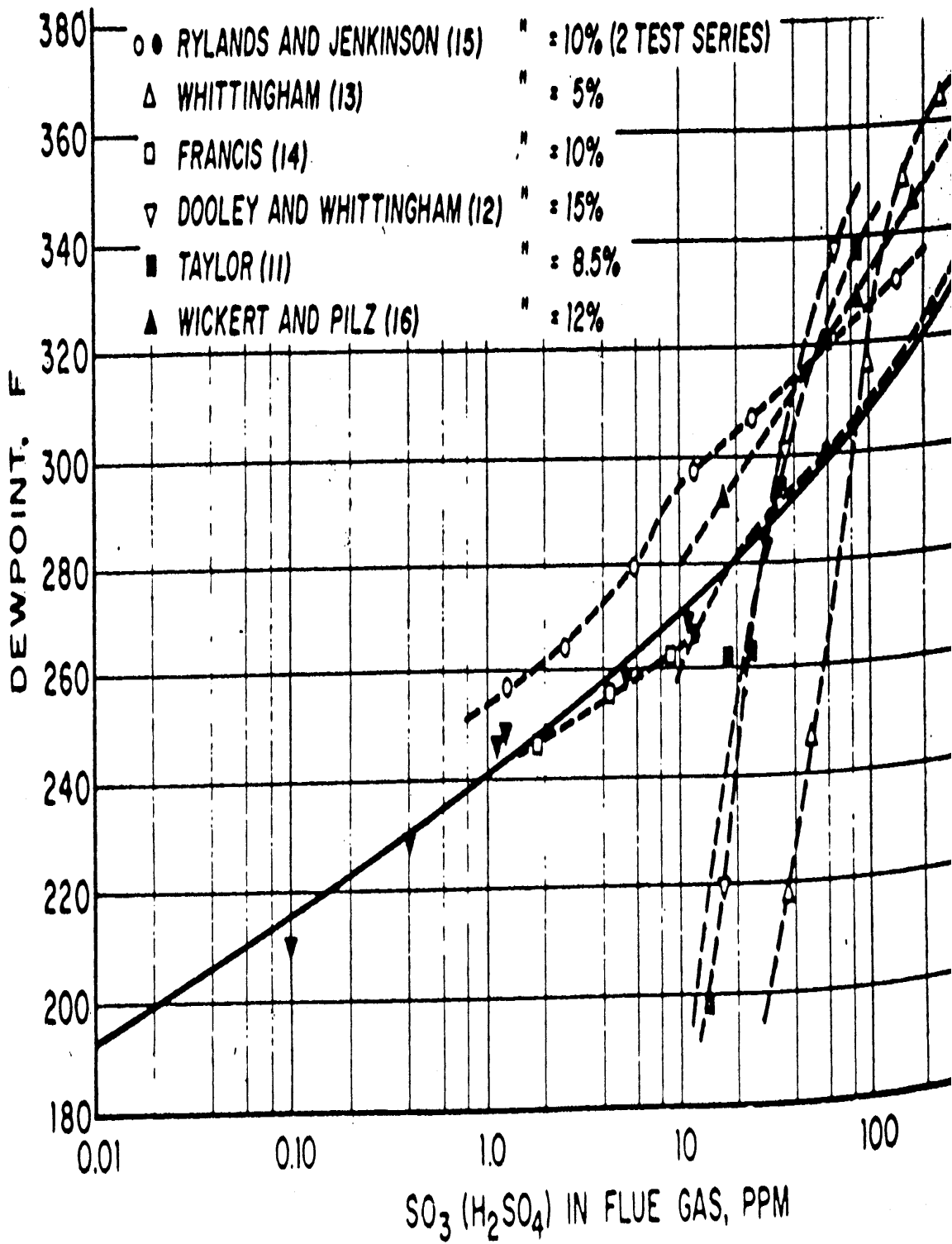


Fig. 2 – Comparison of data on the relationship between acid dew and flue gas H<sub>2</sub>SO<sub>4</sub> concentration



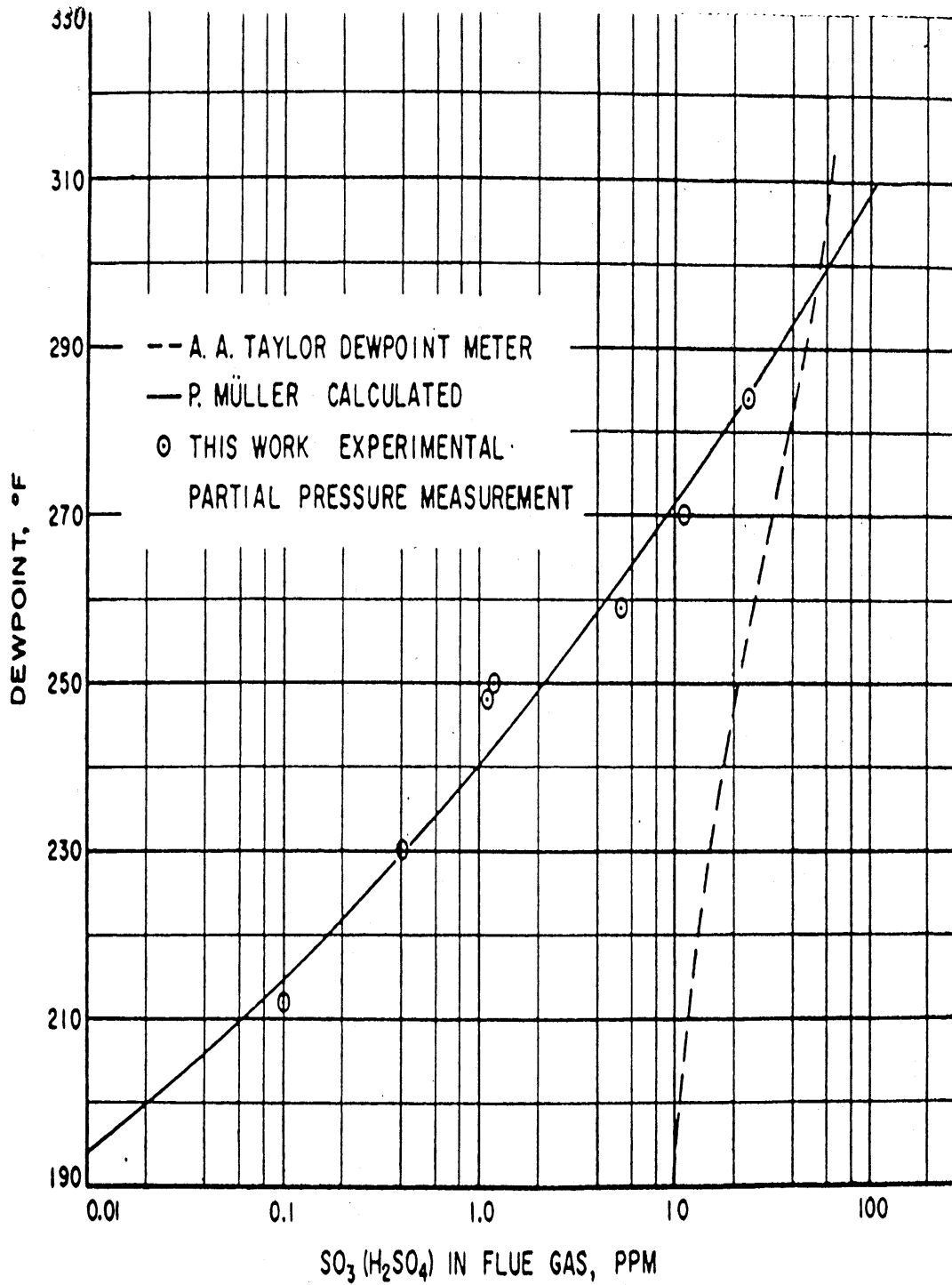


Fig. 3 – Acid dewpoint as a function of H<sub>2</sub>SO<sub>4</sub> concentration in flue gas

About the same time, extensive research was conducted at CANMET using a well-instrumented pilot-scale boiler. In one test program Lee et al., (1967) reported test results from two very high sulphur Eastern Canadian coals (6.3 and 7.3% S, dry basis) and Western Canadian lignite (containing 0.7% S, dry basis) which were pulverized fired in CANMET pilot-scale research boiler. Test conditions ranged from near stoichiometric to 8% oxygen in the flue gas. Figures 4 and 5 respectively show  $\text{SO}_3$  and acid dewpoint for coal with 6.3% S. Figure 6 shows the relationship of  $\text{SO}_3$  to acid dewpoint, compared with the calculated data of Müller. Lee et al. (1967) concluded that when firing high sulphur coals, relationship among sulphur content,  $\text{SO}_3$  level, acid dewpoint and corrosion potential becomes unpredictable. This may be due to the effects of ash which ranged from 10 to 17%. However,  $\text{SO}_3$  and acid dewpoint consistently dropped to low values when excess air was reduced below 1% oxygen in the flue gas.

Subsequently the same CANMET team used the pilot-scale boiler to study  $\text{SO}_3$  formation in combustion of No.6 oil (Lee et al. 1969).  $\text{SO}_3$  levels in the flue gas were found to be anomalously low. The cause was traced to the role of soot. In the vicinity of the coal-walled furnace, any soot which forms is likely to be deposited on the walls and, being sticky and porous, becomes a condensation site for  $\text{H}_2\text{SO}_4$  formed when chilling effect of the walls drop  $\text{SO}_3$  below the acid dewpoint.

The acid may condense on the soot before the soot deposits on the furnace walls but in either case the metal of the furnace walls is then subject to attack. As expected, firing with low excess air reduced acid dewpoint formation. More important, addition of MgO to the oil in a ratio of 1/1000 resulted in successful neutralization of the acid at any excess air.

This groundbreaking research at CANMET led to wide implementation of MgO injection technique in large power stations firing heavy fuels. As a result, utility power plants can operate safely, reliably and with significantly reduced operating and maintenance cost using high sulphur heavy oils.

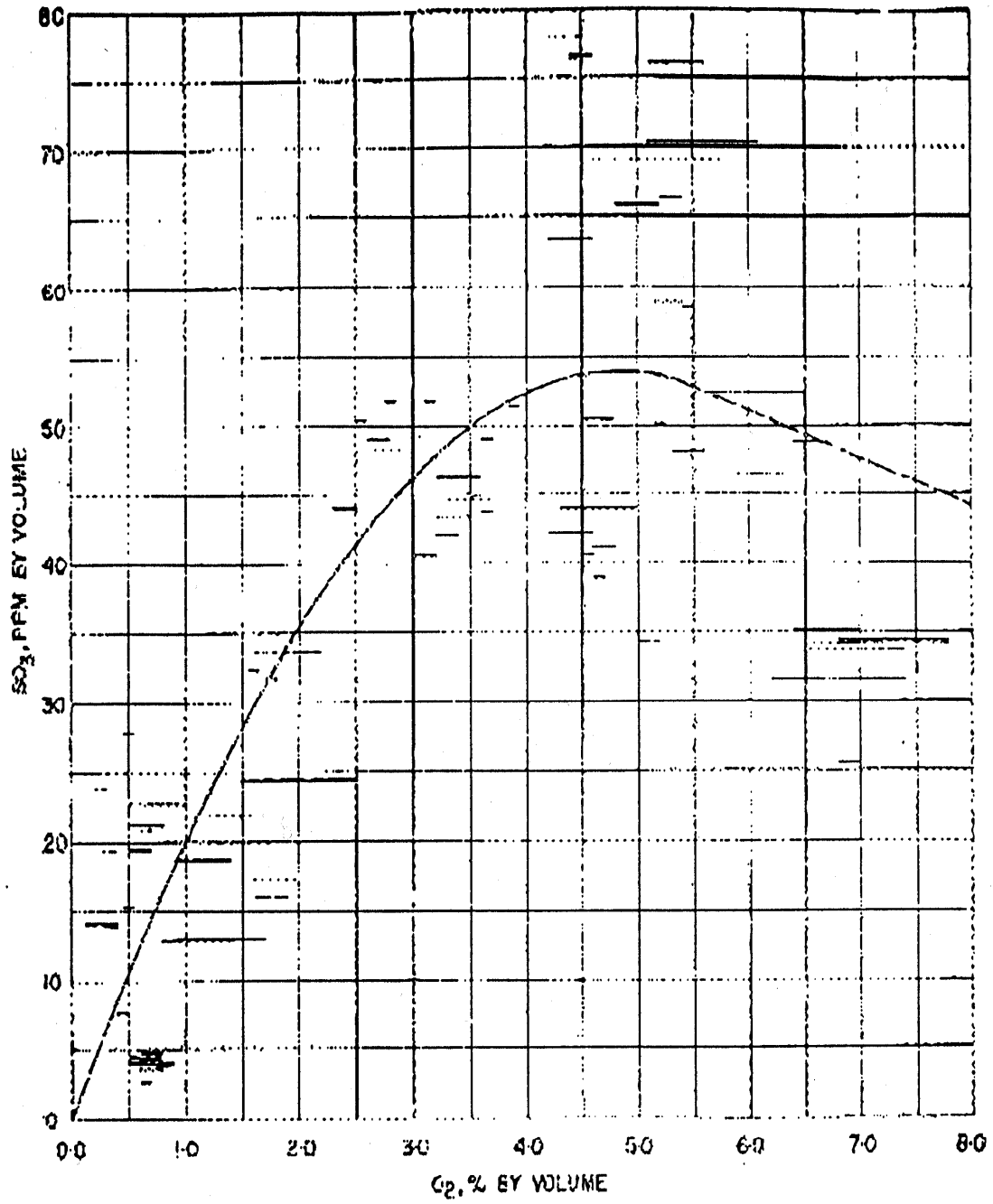


Fig. 4 - SO<sub>3</sub> concentration plotted against oxygen in flue gas for Four Star coal

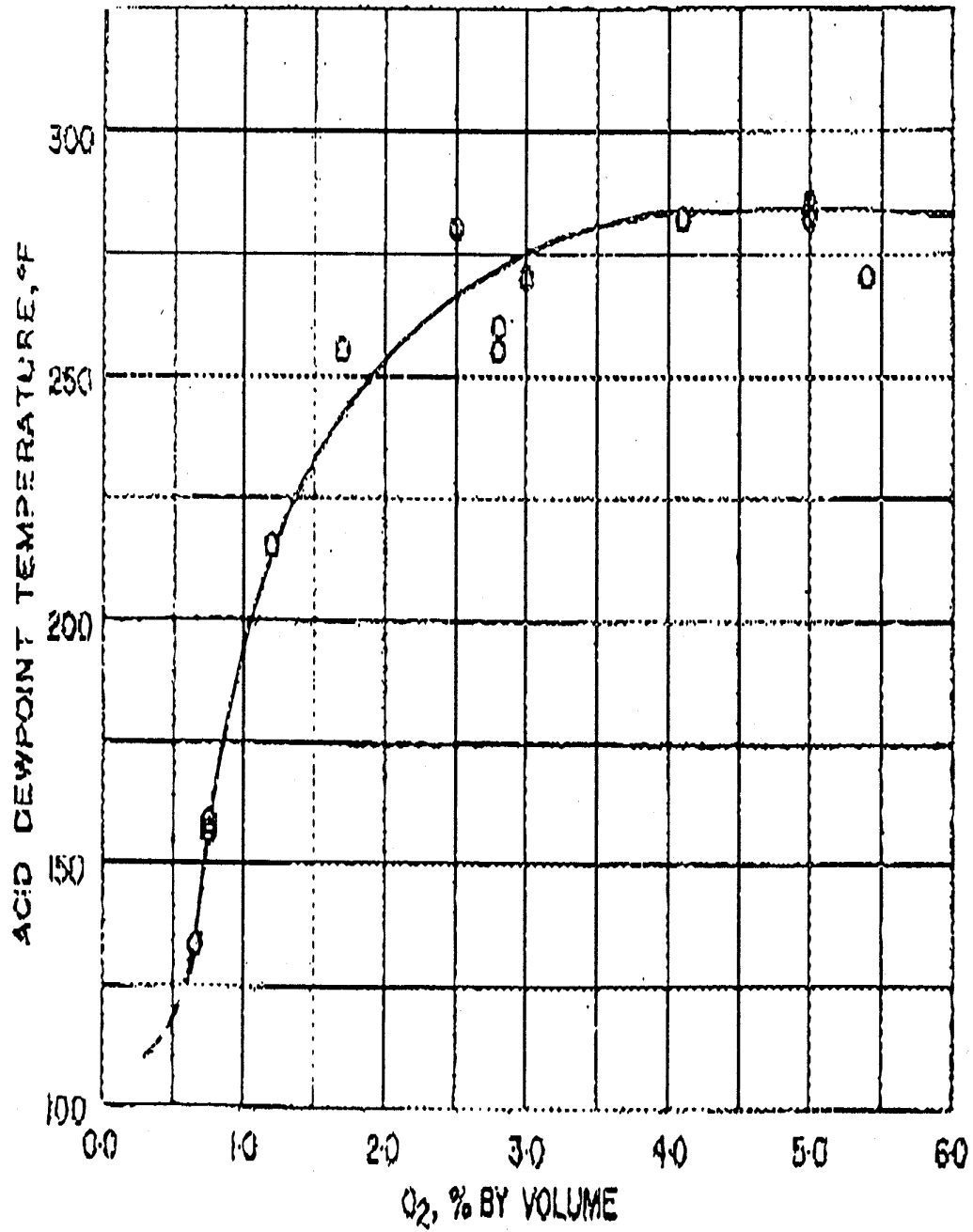


Fig. 5 - Acid dewpoint temperature plotted against oxygen in the flue gas for Four Star coal

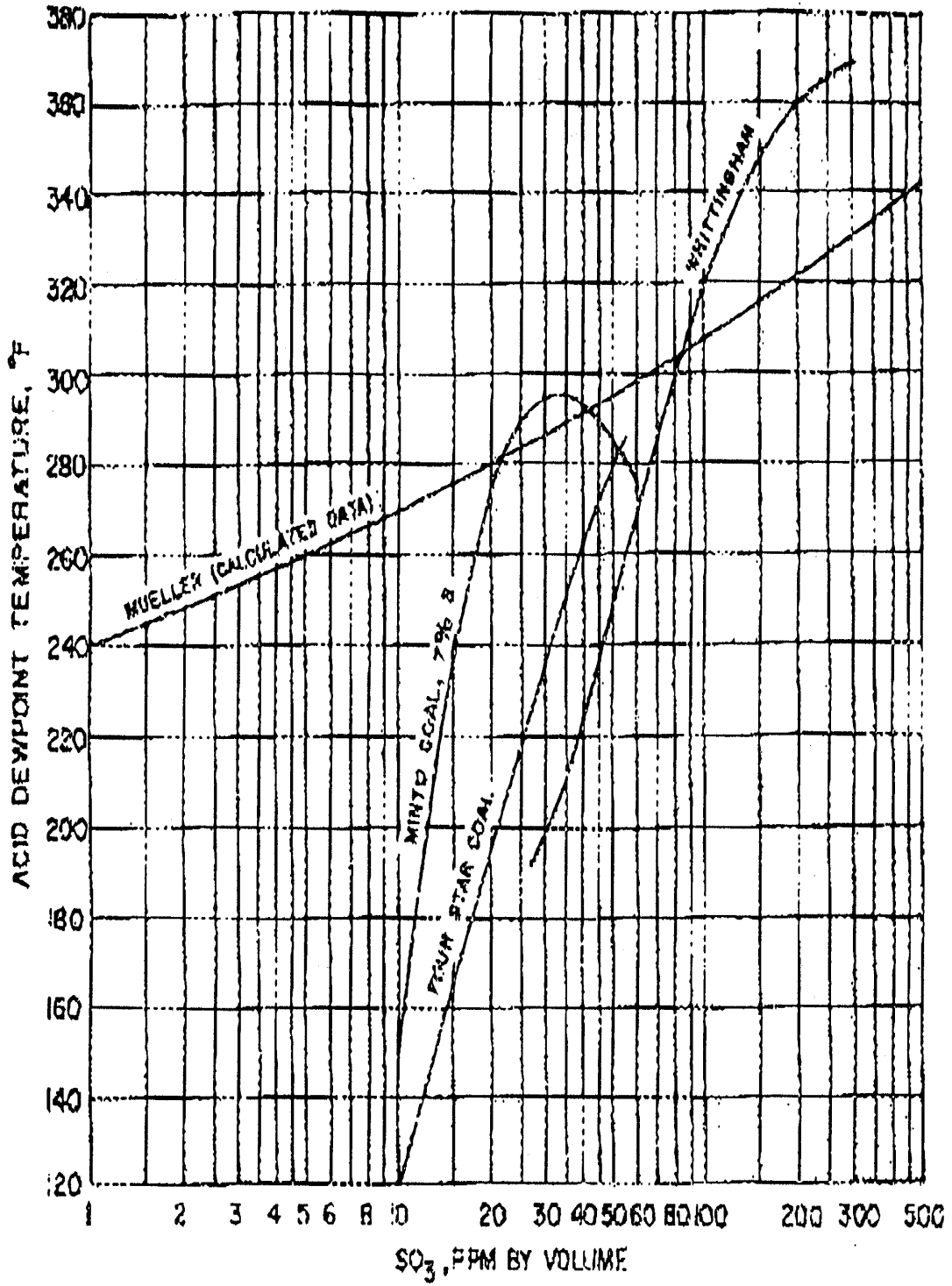


Fig. 6 - Acid dewpoint temperature plotted against SO<sub>3</sub> concentration in flue gas

## CORROSION

It has already been stated that the role of fuel sulphur in wastage of steam generators was recognized and extensively researched in the latter half of the twentieth century. Syrett (1994) claimed that in fossil-fuel-fired utility steam generators corrosion is responsible for 50% of forced outages and adds 10% to the cost of electricity. Of course, sulphur is not the only agent. Compounds of oxygen, nitrogen, calcium, chlorine, sodium, potassium and vanadium may also play a role sometimes in very complex relationships. This is particularly true of high-temperature corrosion, i.e., steam generator tubes operating at temperatures of 400°C to 650°C, in the presence of molten ash and oxides. Under these conditions even highly alloyed steels may suffer catastrophic corrosion. In cold-end or low-temperature corrosion, i.e., at temperatures below acid dewpoint,  $\text{H}_2\text{SO}_4$  formed from fuel sulphur is the primary agent although in some circumstances HCl and  $\text{H}_2\text{CO}_3$  may play some role. Vanadium can also play a significant role in high-temperature corrosion and is of interest to this literature review because it is a major constituent in the ash of residual oils. Chlorine, another element with catastrophic potential for corrosion at elevated temperatures, is of great concern to combustion systems firing municipal waste because of the chlorine introduced via polyvinyl chloride. However, chlorine is not a common contaminant of fuel oil and so is not discussed extensively here.

### Sulphur Corrosion

Sulphur, a common contaminant of most coals and fuel oils, is the most widespread elemental cause of fireside corrosion. There seem to be several mechanisms by which it attacks tube metal, depending on fuel ash composition, flue gas composition, tube alloy and temperature, and the presence of other elements such as chlorine and vanadium. Electron microprobe analyses of attacked tubes typically show sulphides at the corrosion front as well as in outer layers of deposits (Kirsch and Reuchel, 1977; Brandel and Moussel, 1973; Kautz and Kirsch, 1973; Kung and Eckhart, 1993).

Once atomic oxygen was established as a major precursor to  $\text{SO}_3$  and hence  $\text{H}_2\text{SO}_4$ , it seemed logical to address low-temperature corrosion by operating combustion systems with minimal excess air to minimize the formation of atomic oxygen. The success of this approach was first reported by Glaubitz (1963A; 1963B) and it quickly became standard operating procedure where cold-end corrosion was a problem. Reese et al. (1965) in extensive work on a 185 MWe utility steam generator firing heavy oil showed that  $\text{H}_2\text{SO}_4$  in the flue gas dropped from 52 to 20 ppm as  $\text{O}_2$  in the flue gas was reduced from 1.5% to 0.5%. Stelliga and Burnett (1970) presented the data shown in Figure 7, indicating great reductions in corrosion rate as excess air is reduced in an oil-fired boiler.

An alternative approach to controlling low-temperature corrosion has been the application of protective coatings to the affected areas. Johnson et al. (1994) describe the use of

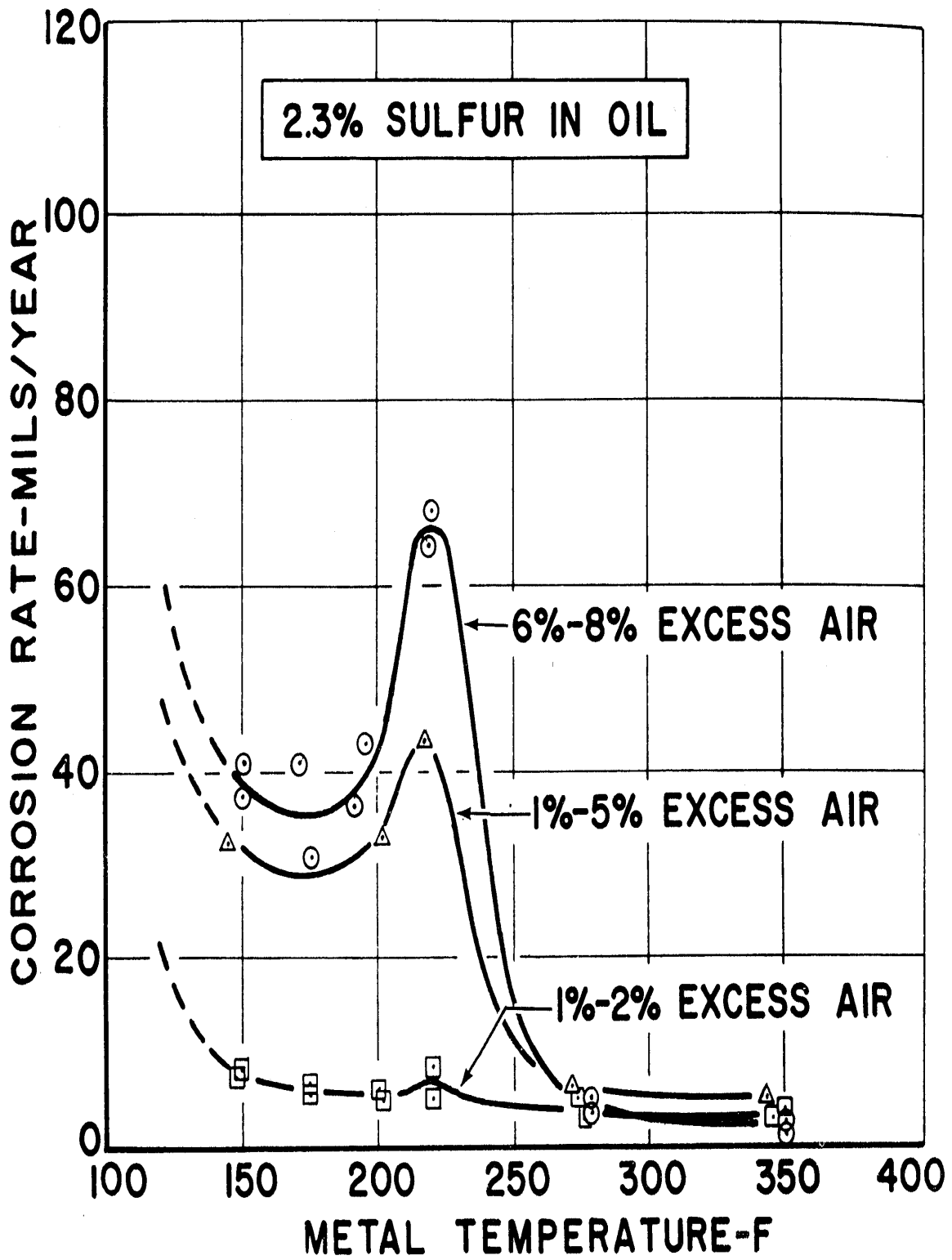


Fig. 7 - Effect of excess air on low-temperature corrosion of carbon steel

Teflon-coated tubes for condensing heat exchangers, also the use of an integrated scrubber and condensing heat exchanger to substantially remove  $\text{SO}_2$ ,  $\text{SO}_3$ , particulates and condensable contaminants from the flue gas stream. To avoid thermal damage to the protective coatings, gas inlet temperatures are limited to  $260^\circ\text{C}$ . Presumably the condensate effluent requires neutralizing treatment. Oil-fired condensing boilers have also been protected against low-temperature corrosion by means of phenolic resin coatings on the cold-end tubes as reported by Faller et al. (2001).

Operation with low excess air has been found advantageous for another reason. It reduces emissions of nitrogen oxides ( $\text{NO}_x$ ), another precursor to acid rain. Accordingly, even equipment fired with natural gas which contains only minute traces of sulphur is operated with minimal excess air. However, there are disadvantages. Imperfect mixing of fuel and air can lead to localized sub-stoichiometric conditions, which in turn may lead to increased emissions of CO and soot and increased corrosion. For example, Schneider et al. (2000) attempting to reduce severe cold-end corrosion in the air heater of a heavy-oil-fired boiler by experimenting with various parameters of fuel atomization, found that  $\text{SO}_3$  was reduced only by reducing excess air. Unfortunately this led to higher CO emissions and soot formation.

Means by which sulphur reaches the tube metal may vary. Baumann (1975) noted that under reducing conditions, e.g., 6.5% CO, as sometimes measured in slag-tap boilers, significant quantities of fuel sulphur may convert to  $\text{H}_2\text{S}$  instead of  $\text{SO}_2$ . This resulted in a very corrosive environment as is well known in gasification processes. The mechanism is one of gas-phase attack, forming metal sulphides from the tube metal.

Baumann (1975), in a discussion of fouling, observed that solid carbon only burns by converting to CO. Thus every fuel particle is enveloped in CO gas. This extremely localized reducing condition promotes the release of sulphur as  $\text{H}_2\text{S}$  but also the reaction with mineral components forms sulphides such as  $\text{CaS}$ ,  $\text{Na}_2\text{S}$  and  $\text{FeS}$ . They generally have lower melting points than their corresponding oxides thus may deposit on the tubes in a sticky state and then gradually convert, under more oxidizing conditions, to hard oxides or sulphates. The point is that the deposit found on a tube is not necessarily what arrived there; it may have a history that would be very helpful if it were better understood.

A recent study of the evolution of gaseous sulphur and chlorine species during temperature-controlled pyrolysis and combustion used a quadruple gas analyzer and a thermal gravimetric analyzer integrated with Fourier Transform Infrared – FTIR - spectroscopy (Illinois State Geological Survey, 1992). It found that under reducing combustion conditions gaseous COS and  $\text{H}_2\text{S}$  were formed along with  $\text{SO}_2$ .

To obtain data more representative of boiler practice, Kung and Eckhard (1993) exposed samples of ferritic and austenitic steels to simulated flue gas containing 0.05 to 0.5%  $\text{H}_2\text{S}$ . They obtained corrosion products that were multi-layered scales, the outer layer being iron sulphide, under which were layers of iron oxide and iron sulphide in the case



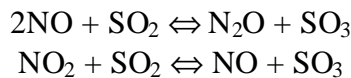
of the ferritic alloys, chromium oxide in the case of the austenitic alloys. The rate of corrosion depended on alloy composition, temperature and H<sub>2</sub>S concentration, generally in that order of importance.

Somewhat similar work had been carried out earlier by Levy and Merryman (1966). They coated coupons of low-carbon steel or Vycor with ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and mixtures of these oxides with sodium hydroxide. The coupons were then exposed to various gas mixtures containing SO<sub>2</sub>, SO<sub>3</sub> and H<sub>2</sub>S along with nitrogen and oxygen. Gas temperature was 600°C. They concluded that Fe<sub>3</sub>O<sub>4</sub> reacts directly with sulphur oxides to yield sulphates whereas Fe<sub>2</sub>O<sub>3</sub> is less reactive in this respect. SO<sub>3</sub> produced more sulphate than SO<sub>2</sub>; on the mild-steel coupons adding O<sub>2</sub> to the gas or NaOH to the coatings increased sulphate formation. Formation of ferrous sulphide (FeS) was maximized on the metal coupons when O<sub>2</sub> was absent, and formed a layer next the parent metal. Both SO<sub>2</sub> and SO<sub>3</sub> proved capable of reacting with the metal whether it was coated with FeO, Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>.

While SO<sub>2</sub> provides a ubiquitous means for a sulphur form to contact boiler tubes it is considered to be not nearly as corrosive as SO<sub>3</sub>. The higher oxide is much more aggressive and is believed to play a significant role in promoting formation of metal sulphides or sulphates even though it represents a small portion of the total sulphur forms particularly under low excess air operating conditions. Brandel and Mousset (1973) concluded that SO<sub>3</sub> reacts with tube metal to form Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> and FeS. Cutler et al. (1974) established that SO<sub>3</sub> may sulphate hematite as follows:

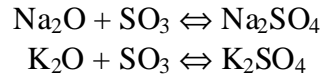


They note that the solubility of the metal oxides in molten sulphate deposits must be relatively low in the equilibrium partial pressures typical for SO<sub>3</sub> in combustion systems. However, they also indicate that vanadium compounds in deposits on the superheater tubes of oil-fired boilers may act as catalysts in the conversion of SO<sub>2</sub> to SO<sub>3</sub>, thus raising the partial pressure of SO<sub>3</sub> adjacent to the tubes. Also, Wahnschaffe (1971) states that nitrogen oxides and SO<sub>2</sub> in the flue gas can react to form SO<sub>3</sub> as follows:

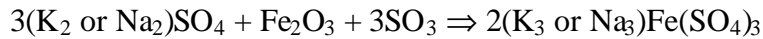


Probably the most common mechanism of superheater and reheater corrosion is one involving alkali trisulphates (Dooley and McNaughton, 1994; Singer, 1981; Baumann, 1975; Kirsch and Reichel, 1977; Kautz and Kirsch, 1973). It is a high temperature phenomenon; Baumann (1975) states that it can lead to severe corrosion at temperatures above 550°C. Because furnace tubewall temperatures are usually less than that Dooley and McNaughton (1994) rank this mechanism as a less common cause of furnace waterwall corrosion than reducing atmospheres. However, any circumstance, which permits sulphur-bearing molten slag to contact tube metal, can lead to rapid corrosion, even of superalloys.

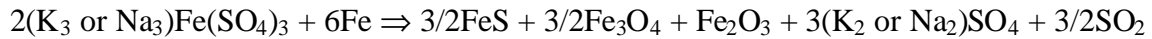
Singer (1981) in Chapter 3, presents the following mechanism for the formation of alkali pyrosulphates: during combustion, pyrite and organic sulphur in the fuel are oxidized to  $\text{Fe}_2\text{O}_3$ ,  $\text{SO}_2$  and  $\text{SO}_3$ . Concurrently, alkalis in the clay and shale oxidize to  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . These then react with  $\text{SO}_3$ , either in the gas stream or after deposition, to form the corresponding sulphates:



A further reaction with iron oxide and  $\text{SO}_3$  then produces the complex sulphate:



The molar ratio of the alkalis determines the temperature range over which the complex sulphate is molten; a 1:1 ratio corresponds to a molten range of about  $550^\circ\text{C}$  to  $700^\circ\text{C}$ . The molten phase readily attacks the tube metal as follows:



While the reaction products slow down the corrosion rate, spalling of the deposits permits renewed attack. Chromium and nickel can be attacked by the same or similar mechanisms albeit at a slower rate.

It is also possible that the alkalis form sulphides in the flame and then oxidizes to sulphate form after deposition as postulated by Baumann (1975). The end result would be the same.

The precise mode of transportation of sulphur and iron across the metal/oxide interface of a tube is not well understood. Kautz and Kirsch (1973) point out that  $\text{O}^{2-}$  ions and  $\text{S}^{2-}$  ions, having respective diameters of 2.6 and  $3.5\text{\AA}$ , can be expected to have more difficulty diffusing inward through the oxide layer than  $\text{Fe}^{2+}$  ions (with a diameter of  $1.7\text{\AA}$ ) have in diffusing outward.

An early attempt to mitigate corrosion via additives to the flame or gas stream was that of Reese et al. (1965). They added small amounts of powdered magnesium metal, 20 to 50 mesh, at various levels in the furnace of a tangentially-fired 185 MWe boiler burning heavy oil. This formed a thin layer of MgO on the exposed furnace and convection surfaces and was found to significantly reduce  $\text{SO}_3$  formation probably by inhibiting the catalytic effect of these surfaces. The authors surmized that the layer of MgO would also beneficially influence high-temperature corrosion. This proved to be true. Work by many researchers including Lee et al. (1966) led to widespread use of MgO as a combustion additive to reduce high-temperature corrosion. Also, Levy and Merryman (1966) exposed mild steel coupons coated with MgO to high concentrations of  $\text{SO}_3$  obtained from combustion of  $\text{H}_2\text{S}$ . They found that initially  $\text{SO}_3$  concentration dropped sharply then gradually regained or exceeded the original value as shown in Figure 8. From this they concluded that the protecting effect of MgO is primarily through its ability to

remove  $\text{SO}_3$  from the gas stream, and only to a lesser extent through its ability to mask the iron surface physically.

The complexity of interactions between sulphur and chlorine in combustion processes can be highlighted by reference to two papers. Krause et al. (1975) as part of an extensive study of corrosion in municipal incinerators found that adding sulphur to the municipal waste substantially reduced high-temperature corrosion of carbon and stainless steels. The mechanism appears to be one in which metal chlorides react with  $\text{SO}_2$  in the gas stream to produce metal sulphates and HCl. The sulphates, as deposits on the tubes, are less aggressive than chlorides would be and the HCl, provided temperatures remain above dewpoint, escapes via the stack. In a recent study Lin and Hsieh (1995) investigated the effects of air containing sodium chloride, i.e., a marine environment on combustion of No. 2 oil. Several unfavourable effects were noted. Flame temperature was reduced somewhat, CO and  $\text{SO}_2$  concentrations increased, and combustion efficiency was reduced. Perhaps on the positive side formation of nitrogen oxides was reduced. All these effects are in accord with chlorine's known properties as a combustion inhibitor.

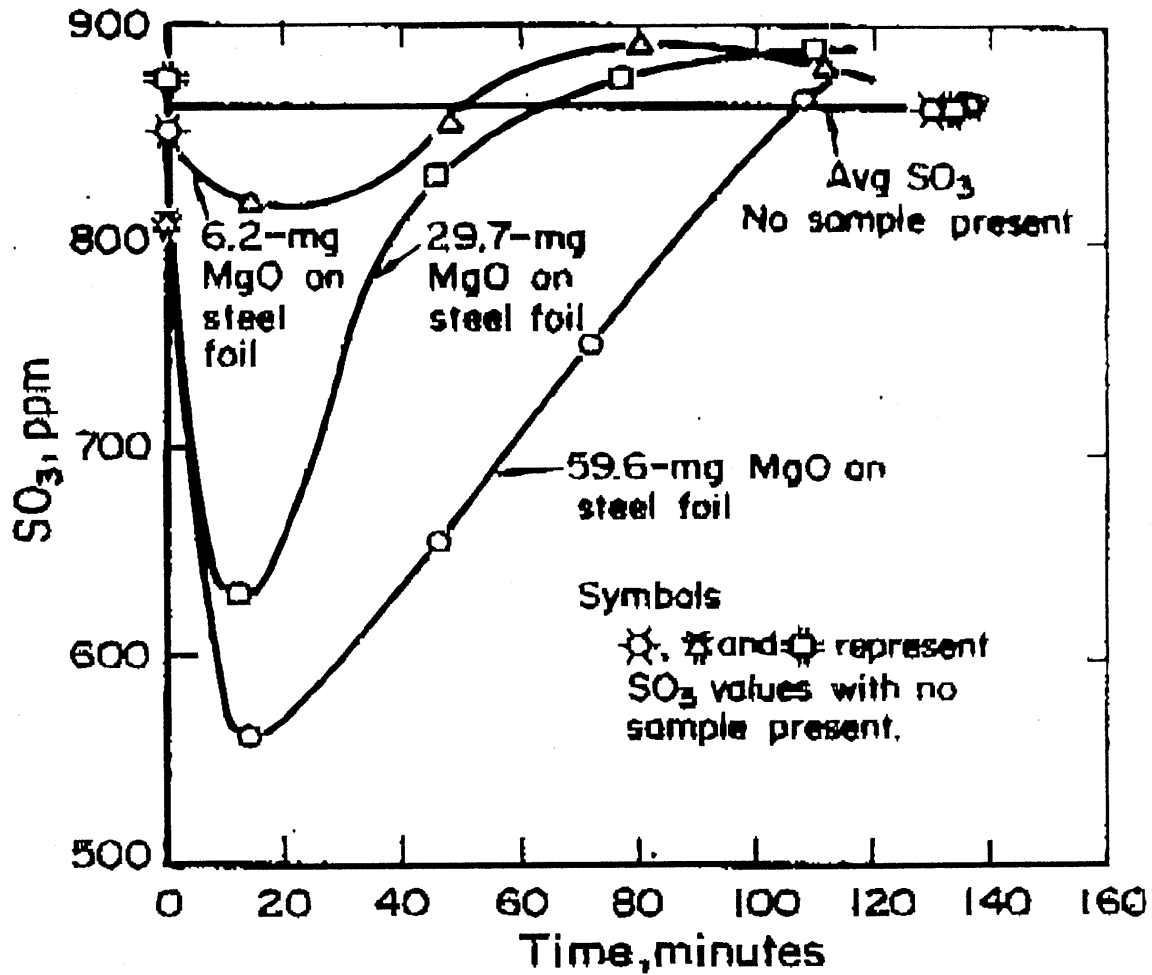


Fig. 8 -  $\text{SO}_3$  profiles in the presence of MgO coatings

## Vanadium Corrosion

Corrosion related to compounds of vanadium is usually associated with superheaters and reheaters in boilers fired with heavy oil, the ash of which is the source of the vanadium. Early work in this area indicated that sodium vanadyl vanadate is the main agent for corrosion, possibly with the presence of sodium sulphate and  $\text{SO}_3$  facilitating partial melts (Cutler et al. 1974; Balajka, 1973; Coats, 1969; Pollman, 1965). However, Brandel and Mousset (1973) using electron microprobes to examine high-temperature corrosion specimens from both coal- and oil-fired boilers found only oxides and sulphides at the corrosion front. Vanadium compounds first appeared some hundreds of microns distant. They established that complex sulphates with a low melting point or  $\text{SO}_3$  could be responsible for the wastage via a mechanism in which sulphate ions ( $\text{SO}_4^-$ ) or  $\text{SO}_3$  react with the tube metal to form  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3$  and  $\text{FeS}$ . The role of vanadium compounds might simply be to catalyze the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ .

Kautz and Kirsch (1973) conducted an experiment in which a probe of “Material 10 Cr Mo 910” (similar to alloy T22) was exposed for four months at the outlet of the platen superheater of an oil-fired boiler. The tube metal temperature was above  $600^\circ\text{C}$ . Electron microprobe studies of the deposits revealed a layer of iron oxide and sulphide next to the steel with no vanadium. Next came a thinner layer containing sulphur, which must have consisted mainly of an iron-vanadium compound. Then came a sulphur-free and therefore sodium-sulphate-free layer of sodium vanadyl vanadate, about 80 nm from the steel boundary. These findings fully supported those of Brandel and Mousset (1975).

Kautz and Kirsch (1973) then conducted laboratory research to study the reactions of sodium vanadyl vanadate ( $\text{Na}_2\text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$ ) with  $\text{SO}_2$ ,  $\text{SO}_3 + \text{O}_2$ , and  $\text{SO}_3$  at temperatures from  $300^\circ\text{C}$  to  $600^\circ\text{C}$ . They concluded, in brief, that below outer tubewall temperatures of about  $600^\circ\text{C}$ , vanadium-containing deposits may affect a protective role by absorbing  $\text{SO}_3$  into the lattice structure. However, above  $600^\circ\text{C}$  the sodium vanadyl vanadate which forms can contribute to corrosion by catalyzing the formation of additional  $\text{SO}_3$  very near the tube metal surface. The dominant corrosion mechanism is concluded to be one of oxygen and sulphur from gaseous sulphur oxides reacting with the tube metal to form metal oxides and sulphides.

The body of literature addressing high-temperature corrosion phenomena is now so enormous that a comprehensive review would be a lifetime task. However, a review of 106 papers conducted by Al-Taie and Friedrich (1995) together with the foregoing summary, should provide sufficient background for the purposes of the present literature review.

## EMISSIONS

The combustion of oil can result in numerous emissions to the atmosphere, the nature and quality of which will depend upon characteristics of the fuel, combustion conditions and to some extent interactions among the emissions. Quantitatively the greatest emission is carbon dioxide, which, together with water vapour, is of concern with respect to global warming potential, but is outside the scope of this literature review. Of the others, usually those of greatest concern are sulphur oxides, nitrogen oxides and particulate matter. Additional emissions commonly are carbon monoxide, volatile organic compounds (VOC), polyaromatic hydrocarbons (PAH) and occasionally compounds involving chlorine such as HCl. Review of some recent papers will serve to clarify relationships among emissions, fuel type and combustion conditions.

### SO<sub>2</sub> and SO<sub>3</sub> Emissions

In oil-fired systems most but not all of the sulphur in the fuel can be expected to appear in the stack gas as SO<sub>2</sub>. As discussed in the section on corrosion under the firing conditions prevalent in industry 1 to 3% of the fuel sulphur may be oxidized to SO<sub>3</sub>. Some small portion may react with boiler metal, furnace and heat exchanger deposits and fuel ash constituents. Typical SO<sub>2</sub> emissions from fuel oils of various grades and sulphur content are recorded in Table 1. They show that for fuel oils in common usage, with sulphur content ranging up to 2% by wt, SO<sub>2</sub> emissions range from about 100 to 1000 ppmv on a dry flue gas basis normalized to 3 % O<sub>2</sub> in the flue gas. In the case of the bitumen-water emulsions, sulphur content was reported on a dry basis. Where SO<sub>2</sub> concentration is shown to vary widely, e.g., the data of Razbin et al. (1991) and Friedrich et al. (1992), the explanation is that SO<sub>2</sub> measurements were taken over several days of boiler operation while fuel sulphur was determined from only a few samples. Thus, fuel sulphur may have varied during the tests.

Stack emissions of SO<sub>3</sub> are typically two orders of magnitude below those of SO<sub>2</sub> but are sometimes of considerable local concern. They are likely to be in the form of H<sub>2</sub>SO<sub>4</sub> that has condensed on soot particles thus forming acid soot - greasy, corrosive and unsightly particulate matter released into the atmosphere (Razbin et al. 1991).

In laboratory tests with a blue-flame residential oil burner (Mohr et al. 2000) fired two distillate oils with sulphur contents of 0.164 and 0.042 wt %. It was found that particulate emissions were substantially lower with the low-sulphur oil.

Reduction of 90%+ in SO<sub>2</sub> emissions via fluidized bed combustion with limestone injection is now a well-established technology applied to high-sulphur coals. It is not often applied to fuel oil because the additional expense of particulate collection makes SO<sub>2</sub> scrubbers more attractive. However, in some situations where a modest, 10 to 40%, reduction in SO<sub>2</sub> emissions is required to meet environmental regulations, limestone injection into suspension flames is employed. In pilot-scale work with No. 6 fuel oil and emulsions of bitumen and water Whaley et al. (1995) also conducted limestone injection tests. The results are shown in Table 2.

**Table 1** Typical SO<sub>2</sub> emissions from various grades of fuel oil

Fuel type	S content wt %, dry fuel	SO <sub>2</sub> in flue gas ppmv at 3% O <sub>2</sub> , dry gas
Lee, 1997		
Ultra- low S No. 2, S increased step- wise with ditertiary butyl disulphide	0.0099	31
	0.1925	110
	0.4900	293
	0.6767	400
	1.1333	624
Miller et al. 1996		
No. 2	0.41	184
No. 5	1.42	793
No. 6 (low S)	0.49	226
No. 6 (high S)	1.66	740
Razbin et al. 1991		
No. 4	1.60	560-1000
Friedrich et al. 1992		
No. 4	1.41-1.46	812-893
No. 6	1.95-1.97	1170-1200
Gulyurtlu et al. 2001		
Waste oil	0.94	394-427
Whaley et al. 1995		
No. 6	1.36	779
Bitumen-water emulsion	5.12	2785
	5.00	2570
	5.27	3466

**Table 2** SO<sub>2</sub> reduction achieved via limestone injection

Fuel	Ca/S ratio	SO <sub>2</sub> reduction, %
No. 6 fuel oil S = 2.26%	0.89	8.4
	1.26	10.2
	1.89	13.4
Bitumen-water emulsion S = 5.13% (dry basis)	1.4	16.2
	2.8	26.4
	4.2	33.2

## NO<sub>x</sub> Emissions

The term NO<sub>x</sub> encompasses the gases nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). Of the two, NO is the dominant species formed in combustion processes, but upon emission to the atmosphere it oxidizes to NO<sub>2</sub>. The formation of NO<sub>x</sub> in flames and means for reducing it have been studied for some decades. A substantial array of reduction technology has reached commercial implementation. A convenient summary of the mechanisms of NO<sub>x</sub> formation is a CANMET technology assessment study (Federal Industrial Boiler Program 1994). The same publication provides data on typical NO<sub>x</sub> emissions from boilers firing natural gas and various grades of oil. It also reviews strategies and proprietary technologies for reducing NO<sub>x</sub> emissions.

For purposes of this study the following summary of NO<sub>x</sub> formation mechanisms may suffice.

Thermal NO<sub>x</sub> At the high temperatures encountered in flames some molecules of atmospheric oxygen and nitrogen dissociate to highly reactive atomic forms which may recombine to form NO. This mechanism occurs to some degree during combustion of any fuel and dominates in combustion of fuels such as natural gas that contain no organically-bound nitrogen. Thermal NO<sub>x</sub> can be minimized by reducing flame temperature and operating with a minimum of excess air.

Fuel NO<sub>x</sub> It results from the oxidation of organically combined nitrogen in the fuel in aromatic compounds such as amine and pyridine. The pathways are numerous and complex but radicals such as HCN and NH are important precursors. Fuel-rich firing conditions favours pathways that discourage NO formation and may break down some of the NO<sub>x</sub> that has formed. However, it has been found difficult to minimize NO<sub>x</sub> emissions from fuels with a high organic nitrogen content as is often found in heavy oil.

Prompt NO<sub>x</sub> So called because it forms early in the combustion process and results from the reaction of atmospheric nitrogen with hydrocarbon radicals formed during fuel cracking. The amounts produced are relatively small but difficult to reduce.

Table 3 presents typical NO<sub>x</sub> emission data obtained from the Federal Industrial Boiler Program (1994) for Canadian boilers with conventional burners. Table 4 presents similar data for boilers equipped with low-NO<sub>x</sub> burners employing flue gas recirculation. These data clearly show the impact of fuel NO<sub>x</sub> as fuel-bound nitrogen increases from nil in natural gas to about 0.3 to 0.5% in No. 6 oil.

Additional data for NO<sub>x</sub> emissions, in this case from combustion of ultra-low-sulphur No. 2 fuel oil is found in Lee (1997). In numerous tests, with the fuel oil doped to various levels of sulphur, in a pilot-scale apparatus with a firing rate of 7.00 L/h, NO<sub>x</sub> levels held at about 70 to 75 ppmv, corrected to 3% O<sub>2</sub> in the flue gas. The lower values were associated with high concentrations of sulphur in the fuel, a phenomenon that will be discussed later.

**Table 3** Typical NO<sub>x</sub> emissions from Canadian boilers with conventional burners

Boiler type	No. of boilers	NO <sub>x</sub> emissions, ppmv at 3% O <sub>2</sub>	
		Range	Average
<u>Natural gas</u>			
Firetube	9	34-126	88
Package watertube	5	35-104	55
Field-erected watertube	39	5-171	79
<u>No. 2 oil</u>			
Cast iron sectional	2	66-90	78
Firetube	10	57-156	111
Package watertube	3	81-148	122
Field-erected watertube	13	31-129	73
<u>No. 4 oil</u>			
Package watertube	5	143-356	221
Field-erected watertube	1	139-188	168
<u>No. 6 oil</u>			
Package watertube	7	162-389	296
Field-erected watertube	12	154-382	266

**Table 4** Typical NO<sub>x</sub> emissions from Canadian boilers with low-NO<sub>x</sub> burners

Boiler type	No. of boilers	NO <sub>x</sub> emissions, ppmv at 3% O <sub>2</sub>	
		Range	Average
<u>Natural gas</u>			
Firetube	1	15-23	18
Package watertube	4	16-37	30
Field-erected watertube	1	24-41	30
<u>No. 2 oil</u>			
Firetube	1	50-76	64
Package watertube	4	43-73	63
Field-erected watertube	1	63-90	78
<u>No. 4 oil</u>			
Package watertube	1	181-244	212
<u>No. 6 oil</u>			
Package watertube	1	249-304	268



Note:

- Firetube boiler refers to design configuration where the hot flue gas from combustion passes inside tubes and the heated water is on the outside.
- Watertube boiler refers to design configuration where the water is inside the tubes and hot combustion gases are on the outside.
- Package boilers are small, shop manufactured and assembled units.
- Field erected boilers are large with individual components put together in the field.

Miller et al. (1996) provided NO emissions shown in Table 5 from a range of fuel oils fired in a small firetube package boiler with an air-atomized oil burner. Two grades of No. 6 substantially different in sulphur content were used. A high-sulphur No. 5 oil was fired under four different conditions: baseline, low excess air, low oil temperature and low atomizing pressure. The low excess air condition reduced NO<sub>x</sub> by about 15%, in accord with general experience. The conditions of low oil temperature and low atomizing pressure, which could be expected to impair atomization, also produced reductions in NO<sub>x</sub>, albeit slight.

**Table 5** NO emissions from a range of fuel oils fired in a small firetube boiler (firing rate  $2 \times 10^6$  Btu/h)

Oil type	S content wt %	NO, ppmv at 3% O <sub>2</sub>	Stoichiometric ratio
No. 2	0.41	124	1.2
No. 5 (baseline)	1.42	242	1.2
No. 5 (low excess air)	1.42	207	1.05
No. 5 (low oil temp)	1.42	233	1.2
No. 5 (low atom. press.)	1.42	225	1.2
No. 6	0.42	254	1.2
No. 6	1.66	271	1.2

Herger et al. (1996) conducted emissions measurements in Austria on 299 small boilers firing a light residual oil. Boiler capacity ranged from 50 to 3000 kW but more than 50% lay between 150 and 500 kW capacity. All were firetube with watercooled furnaces fired by yellow-flame burners. The mathematical average of NO<sub>x</sub> emissions at full load was 116 mg/MJ for boiler capacities of 350 kW or less; 112 mg/MJ for the larger boilers. Standard deviation was about 12 mg/MJ. Differences due to boiler type were modest with three-pass boilers having somewhat lower emissions than reverse-flame designs.

A study aimed at improving combustion performance of Mexican heavy fuel oil containing 15 to 22% asphaltenes and 3 to 4% sulphur (Gallegos, et al, 2001) showed that swirler design could substantially influence NO<sub>x</sub> emissions. Burner configurations for a utility boiler were mathematically modeled to identify the influence of swirler geometry on recirculation zone. This work identified a swirler with curved blades as having substantial advantages over a bluff body or a swirler with straight blades. Subsequent

trials in a 300 MW power boiler produced NO<sub>x</sub> levels of 370 ppmv with the straight-blade swirler, compared with 250 ppmv with the curved-blade swirler. Results in both cases are for 1% O<sub>2</sub> in the flue gas at full load.

Combustion of waste oils such as used engine oil receives some interest partly as a low-cost fuel partly as a means of disposal. Concern is mostly focused on the impact of the high metals content on emissions but in a study of particulates Gulyurtlu et al. (2001) also measured NO<sub>x</sub> levels. The waste oil tested contained 0.37 % nitrogen by wt, presumably organically-bound. NO<sub>x</sub> emissions ranged from 122 to 131 ppmv at 3% oxygen in the flue gas. These are low values relative to the high nitrogen content of the fuel. A probable explanation is that the furnace of the test setup was small, 0.5 m square and watercooled. The consequent flame chilling would suppress formation of thermal NO<sub>x</sub>, leaving fuel NO<sub>x</sub> as the dominant mechanism.

To improve energy conservation the steel industry is shifting to reheat furnaces that employ very high combustion air preheat, up to 1300°C, by means of regenerative heat exchangers. One might accordingly expect high rates of thermal NO<sub>x</sub> production but it seems possible to mitigate this by a form of fuel staging. In pilot-scale work at the International Flame Research Station (IFRF) Weber et al. (2001) conducted experiments in a 2 m square refractory tunnel with a burner comprising a central air inlet on the axis of the tunnel and two oil nozzles spaced 280 mm to each side. Combustion air at a temperature of about 1300°C was provided from a direct-fired air preheater fuelled with natural gas. Oxygen was added to the preheater exhaust to bring the oxygen content back up to 21%. The combustion air, thus preheated, entered the furnace with a NO<sub>x</sub> content of about 70 ppmv. The oil nozzles employed nitrogen atomization.

In tests with a light fuel oil containing less than 0.05% nitrogen, furnace exit gases at 1130°C and 1.1% O<sub>2</sub> contained only 95 ppmv of NO<sub>x</sub>. There was no visible flame envelope. The entire furnace was full of glowing gas. With heavy oil containing 0.37 wt% nitrogen, NO<sub>x</sub> at the furnace exit was 215 ppmv while temperature was 1240°C and oxygen content was 1.1%. With heavy oil the flame envelope was clearly visible.

It seems likely that the location of the fuel nozzles away from the air stream results in both the air jets and the fuel jets entraining large quantities of flue gas before they mix. Much of the combustion therefore occurs in strongly sub-stoichiometric conditions which permit a so-called “reburning” mechanism, i.e., one in which NO decomposes to form molecular nitrogen. With the light oil this appears to destroy much of the NO<sub>x</sub> entering from the air heater and subsequent thermal NO<sub>x</sub> formation provides only a modest increase over the input condition. With the heavy oil the same NO breakdown mechanism is in play but is substantially overwhelmed by the contribution of fuel NO<sub>x</sub>.

The observations with high air preheat at the IFRF are somewhat reminiscent of CANMET’s experiences at the heating plant for Canadian Forces Base Halifax (Friedrich et al. 1992). At the time this plant fired No. 6 oil with uncontrolled nitrogen content. The newest boiler, a 55 000 lb/h watertube package installed in 1986, had been retrofitted with a low-NO<sub>x</sub> burner as a demonstration. This was a steam-atomized, dual-register

burner. The NO<sub>x</sub> reduction features consisted of a measure of air staging by means of secondary air nozzles projecting about 20 cm ahead of the oil nozzle and a flue gas recirculation system.

These features proved largely ineffective in reducing NO<sub>x</sub> from either a No. 6 oil with 0.45% nitrogen or a No. 4 oil with 0.33% nitrogen, as shown in Table 6. The narrow width and cold walls typical of a package boiler furnace seemed to be the major constraint. With the larger flame envelope generated by flue gas recirculation, intended to reduce thermal NO<sub>x</sub> by reducing peak flame temperatures, excess air levels had to be kept higher than desired to avoid flame impingement, high CO emissions and coke build up on the furnace walls.

The same oils were then fired in an older boiler in the same plant. This was a 30 000 lb/h field-erected boiler installed in 1942. It had originally been equipped with a coal stoker and subsequently converted to oil firing by means of a single, steam-atomized dual-register burner. The furnace had ample dimensions, i.e., a low furnace heat release rate and considerable refractory. This combination permitted steady-state operation with excess O<sub>2</sub> at about 2%, resulting in a furnace full of flame with no discernable envelope as experienced in the IFRF tests with No. 2 oil. NO<sub>x</sub> emissions were much lower than were achievable with the low-NO<sub>x</sub> burner in the package boiler.

**Table 6** NO<sub>x</sub> emissions data from CFB Halifax

Load, % MCR	Fuel	O <sub>2</sub> in flue gas %	NO <sub>x</sub> in flue gas ppmv at 3 % O <sub>2</sub>
Boiler A: package watertube installed 1986 MCR = 55 000 lb/h, single low-NO <sub>x</sub> burner, steam-atomized dual-register, air staging plus flue gas recirculation.			
97.8	No. 6 <sup>1</sup>	3.23	258
98.1	No. 4 <sup>2</sup>	3.83	244
Boiler B: field-erected watertube installed 1942 MCR = 30 000 lb/h, single steam-atomized dual-register burner.			
90.3	No. 6 <sup>1</sup>	1.90	190
91.2	No. 4 <sup>2</sup>	2.53	188

1: fuel nitrogen content = 0.45

2: fuel nitrogen content = 0.33

It should be noted that the conditions which produced the low NO<sub>x</sub> emissions from the smaller boiler could not be safely sustained under automatic control unless the control system was upgraded to ensure maintenance of adequate excess air levels during rapid changes in load.

Of the limited literature available on how sulphur/nitrogen interactions affect NO<sub>x</sub> formation in flames, an important study was conducted by Nimmo et al. (1998). In pilot-

scale studies employing a 0.8 m diam. refractory tunnel furnace, a light distillate oil was fired through a pressure jet burner which was supplied with combustion air in primary and secondary stages, and in some tests, with tertiary air as well. This permitted the stoichiometry of the primary combustion zone to be staged. The fuel was doped with quinoline to bring fuel nitrogen to 0.45 wt % and fuel sulphur content was varied at four levels from 0.2 to 0.45 wt % by adding either tetrahydrothiophene or SO<sub>2</sub>.

Varying fuel sulphur and primary zone stoichiometry had substantial and complex effects on the formation of thermal NO<sub>x</sub> and fuel NO<sub>x</sub> as shown in Figure 8. Increasing sulphur reduced thermal NO<sub>x</sub> in the case of a fuel-lean primary zone but had little effect when the primary zone was fuel-rich. On the other hand, fuel NO<sub>x</sub> increased slightly with increasing sulphur but dropped substantially as the primary zone was made progressively more fuel-rich. When sulphur was provided in the form of SO<sub>2</sub> rather than tetrahydrothiophene the trends were the same but the effects were smaller. The authors also measured ammonia and cyanide levels in the flame. By employing kinetic modeling they were able to postulate how sulphur affects the formation of those two important precursors of NO, to achieve the observed results.

## **Particulates**

The most obvious – and most frequently objected to – form of particulate emissions from oil-fired boilers is soot - large, black, greasy flakes most likely to be emitted from plants burning heavy oil during the daily routine of sootblowing or load-swing. With the levels of sulphur common in residual fuel oils the soot emissions are likely to contain condensed sulphuric acid making them corrosive as well as unsightly. Fortunately, this type of emission, sometimes called acid soot, is too heavy to travel far and can usually be greatly reduced by tuning or upgrading the burners and controls as proved to be the case at the Nova Scotia Hospital (Razbin et al. 1991).

However, there are numerous other particulate emissions from combustion of fuel oil that may pose greater health problems than acid soot. These may be very small particles combined with compounds of carbon, sulphur and the various metals that residual oils typically contain in trace quantities.

Important work in particulate emissions from combustion of heavy fuel oil has been conducted at Research Triangle Park, North Carolina, under the auspices of the U.S. Environmental Protection Agency. A small firetube package boiler has been used to fire a range of fuel oils, and emissions of hazardous air pollutants have been studied. The results for NO<sub>x</sub> and SO<sub>x</sub> have been discussed in previous sections. In one test program (Miller et al. 1996) four grades of fuel oil were fired at a rate of  $2 \times 10^6$  Btu/h using an air-atomized burner. Sulphur, chlorine and trace metals for these fuels are presented in Table 7. Emissions of total particulates and specific metals are presented in Table 8. The percentage of input metals recovered in the particulates are also presented. The

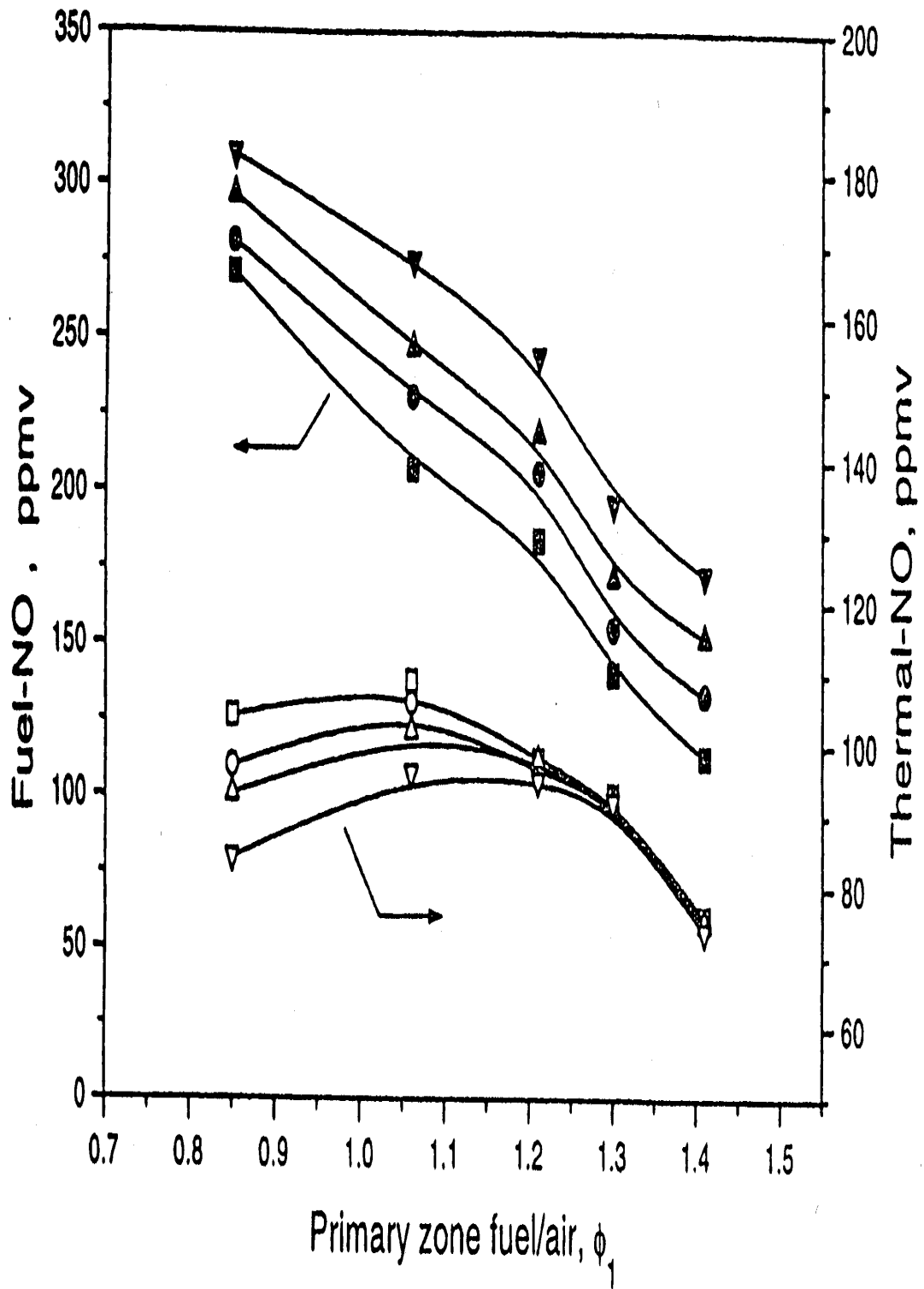


Fig. 9 - Influence of sulphur on thermal-NO and fuel-NO emissions for a range of primary zone stoichiometries

anomalous result for manganese from No. 2 oil is believed to relate to an abnormally low, perhaps erroneous, determination of manganese present in the oil.

**Table 7** Contaminants in fuels tested by Miller et al. (1996)

Element	Fuel oil grade			
	No. 2	No. 5	No. 6	No. 6
Ash, wt %	0.01	0.05	0.06	0.23
Sulphur, wt %	0.41	1.42	0.49	1.66
Chlorine, wt %	0.03	0.02	0.03	0.05
Arsenic, ppmw	<1	<1	<1	<1
Antimony, ppmw	<1	<1	<1	<1
Beryllium, ppmw	<0.5	<0.5	<0.5	<0.5
Cadmium, ppmw	0.01	0.08	0.09	0.26
Chromium, ppmw	0.05	0.41	0.43	1.06
Lead, ppmw	0.04	1.04	4	21
Manganese, ppmw	0.01	0.40	0.30	0.91
Mercury, ppmw	0.11	0.02	0.02	0.02
Nickel, ppmw	0.05	29.0	15.7	43.0
Selenium, ppmw	<1	<1	<1	<1
Vanadium, ppmw	0.06	132	7	146

**Table 8** Total particulates and metals emitted from fuels tested by Miller et al. (1996). (Values in brackets are percentage of input)

Emission	Fuel oil grade			
	No. 2 S = 0.41 %	No. 5 S = 1.42 %	No. 6 S = 0.49 %	No. 6 S = 1.66 %
Total particulates, g/m <sup>3</sup>	0.0061	0.0529	0.0148	0.1074
Antimony, lb/10 <sup>12</sup> Btu	0 (0)	4.96 (0)	17.6 (33)	15.5 (28)
Arsenic, lb/10 <sup>12</sup> Btu	0 (0)	8.48 (16)	2.84 (5)	3.61 (7)
Beryllium, lb/10 <sup>12</sup> Btu	0 (0)	0 (0)	0 (0)	0.066 (0)
Cadmium, lb/10 <sup>12</sup> Btu	0 (0)	0 (0)	0.934 (20)	7.22 (51)
Chromium, lb/10 <sup>12</sup> Btu	3.80 (148)	6.61 (31)	9.57 (42)	22.6 (39)
Lead, lb/10 <sup>12</sup> Btu	1.15 (56)	25.4 (45)	102 (48)	513 (45)
Manganese, lb/10 <sup>12</sup> Btu	6.11 (1110)	9.33 (43)	11.0 (70)	39.4 (80)
Nickel, lb/10 <sup>12</sup> Btu	2.96 (115)	896 (57)	508 (61)	1570 (67)
Selenium, lb/10 <sup>12</sup> Btu	0 (0)	3.46 (6)	0.687 (1)	2.68 (5)
Vanadium, lb/10 <sup>12</sup> Btu	2.72 (88)	5870 (82)	401 (108)	6020 (76)
Total metals, lb/10 <sup>12</sup> Btu	16.7	6820	1050	8190

The foregoing data essentially provide a snapshot of what contaminants may be found in fuel oil and at what input and output levels. It is perhaps noteworthy that while the No. 5

and low-sulphur No. 6 oils have about the same ash content the vanadium and sulphur contents of the No. 5 oil are similar to the high-sulphur No. 6 oil which has a higher ash content. Emissions of total metals correlate much better to input sulphur and vanadium than to ash content.

In a subsequent program employing the same equipment but a different series of fuel oils Miller et al. (1998) investigated particle size using an in-stack cascade impactor, a scanning mobility particle sizer, and an in-situ light-scattering system, as well as EPA Method 5 to obtain total particulates and EPA Method 60 to obtain metal analyses. Three No. 6 oils of different sulphur content were fired, and a high-sulphur No. 5 oil was fired under three conditions: baseline, low oil temperature, and low oil temperature plus low excess air. The last two conditions were intended to identify the effect of impaired atomization on carbon content of the particulates. Some data from these tests are presented in Table 9.

For the No. 5 oil the authors studied the effect of oil temperature on spray droplet size using optical light-scattering techniques. At 120°C the modal diameter, i.e., the most frequent size of the droplets was approximately 50 µm while at 65°C it was greater than 100 µm. The resulting effect on emissions is surprisingly modest. The loss on ignition of the collected material, largely reflecting carbon content, shows consistently higher carbon in the larger particles collected by the cyclone of a large dilution sampler, compared with the smaller particles collected by its downstream filter. It is also interesting that the No. 6 oil with the highest ash and sulphur contents (respectively 0.10 and 2.33 wt%) produced the lowest emissions. The authors attribute this to its high vanadium content, 220 µg/g, and the known effect of vanadium in catalyzing carbon oxidation.

**Table 9** Combustion conditions and particulate emissions for heavy oils tested by Miller et al. (1998)

Fuel type	No. 5			No. 6		
Sulphur content, %	1.73			0.53	0.93	2.33
Firing condition	Baseline	Low oil temp.	Low oil temp. , low O <sub>2</sub>	Baseline		
Boiler load, kW	590	598	596	606	622	619
Stack O <sub>2</sub> , % dry	3.40	3.56	2.46	3.60	3.45	3.45
Oil temp., °C	120	77	77	120	120	120
<u>Particulate matter</u>						
mg/m <sup>3</sup>	197.7	221.0	221.0	219.5	243.5	183.6
lb/10 <sup>6</sup> Btu	0.145	0.151	0.143	0.142	0.161	0.123
<u>Loss on ignition</u>						
Filter, wt %	64.1	78.5	75.3	65.8	79.0	86.6
Cyclone, wt %	88.3	87.7	93.5	90.3	95.8	96.9

Particle size distributions for particles 0.01 to 100  $\mu\text{m}$  in diameter were determined using the three methods mentioned earlier. The results were analyzed in considerable detail. Suffice to say that 30 to 50% of the particulate mass emissions are found in particles less than 1.8  $\mu\text{m}$  diameter. Data for the three conditions under which the No. 5 and No. 6 oils were fired shown in Figure 10 indicate a bimodal distribution. One mode at 0.07 to 0.08  $\mu\text{m}$  diameter, and a broader, coarser mode extending from 10 to 100  $\mu\text{m}$  and beyond. Similar data are shown in Figure 11 for the No. 6 oil.

Trace metals were measured in the fuel oils and in both the cyclone and filter samples obtained by the large dilution sampler. Concentrations follow patterns similar to those shown in Tables 7 and 8. The cyclone is claimed to have collection efficiencies of 50% at 1.8  $\mu\text{m}$  diameter and 95% at 2.5  $\mu\text{m}$  diameter. With very few exceptions the trace metals were found in higher concentrations in the finer particles collected on the filter rather than in the coarser particles trapped by the cyclone. Carbon, on the other hand, exhibited higher concentrations in the filter catch.

The cyclone and filter samples obtained by means of the large dilution sampler and comprising particles nominally  $>2.5 \mu\text{m}$  and  $<2.5 \mu\text{m}$  respectively were further analyzed by scanning electron microscopy, X-ray spectroscopy, X-ray diffraction and nuclear magnetic resonance (Huffman et al. 2000). This throws considerable light on the molecular structure of the carbon and metals, on the composition and morphology of the particles, and on the crystalline phases present. Part of the  $<2.5 \mu\text{m}$  fraction was found to consist of carbon particles cenospheric and vesicular, up to 10  $\mu\text{m}$  diameter. Presumably their low density prevented capture by the cyclone. Most of the metals were combined with sulphur in some form with sulphate predominating at 26 to 84% of total sulphur. It was more concentrated in the  $<2.5 \mu\text{m}$  particles than in the larger particles, by factors of about 3 to 6.

In the work with very high air preheat at the International Flame Research Foundation described previously in the section on  $\text{NO}_x$ , Weber et al. (2001) also examined concentrations of particulates and soot. In-furnace concentrations were high, 500 to 2000  $\text{mg}/\text{m}^3$ , and peaked near the centerlines of the oil injectors located 280 mm left and right of the furnace axis. Probe failure prevented particulate measurement at the furnace exit. The authors believed the concentration to be high because the fuel is injected into a zone of low oxygen concentration, permitting the formation of cenospheres which are slow to burn out in the oxygen-depleted atmosphere of these tests. Heavy fuel oil performs worse than light oil because it does not atomize as well and contains higher proportions of relatively unreactive asphaltenes.



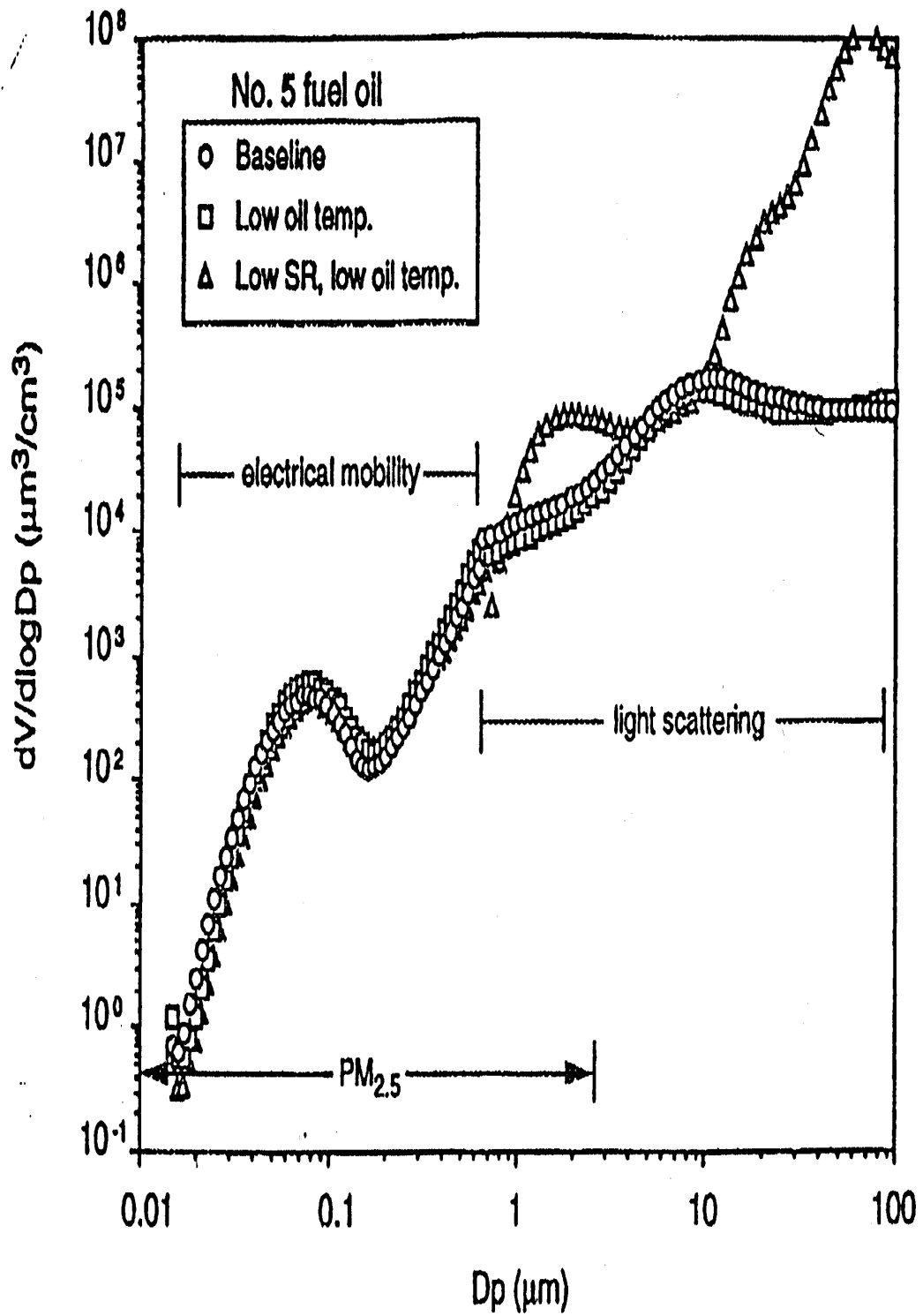


Fig. 10 - Particle volume distribution measured by electrical mobility and light scattering for No. 5 oil combustion

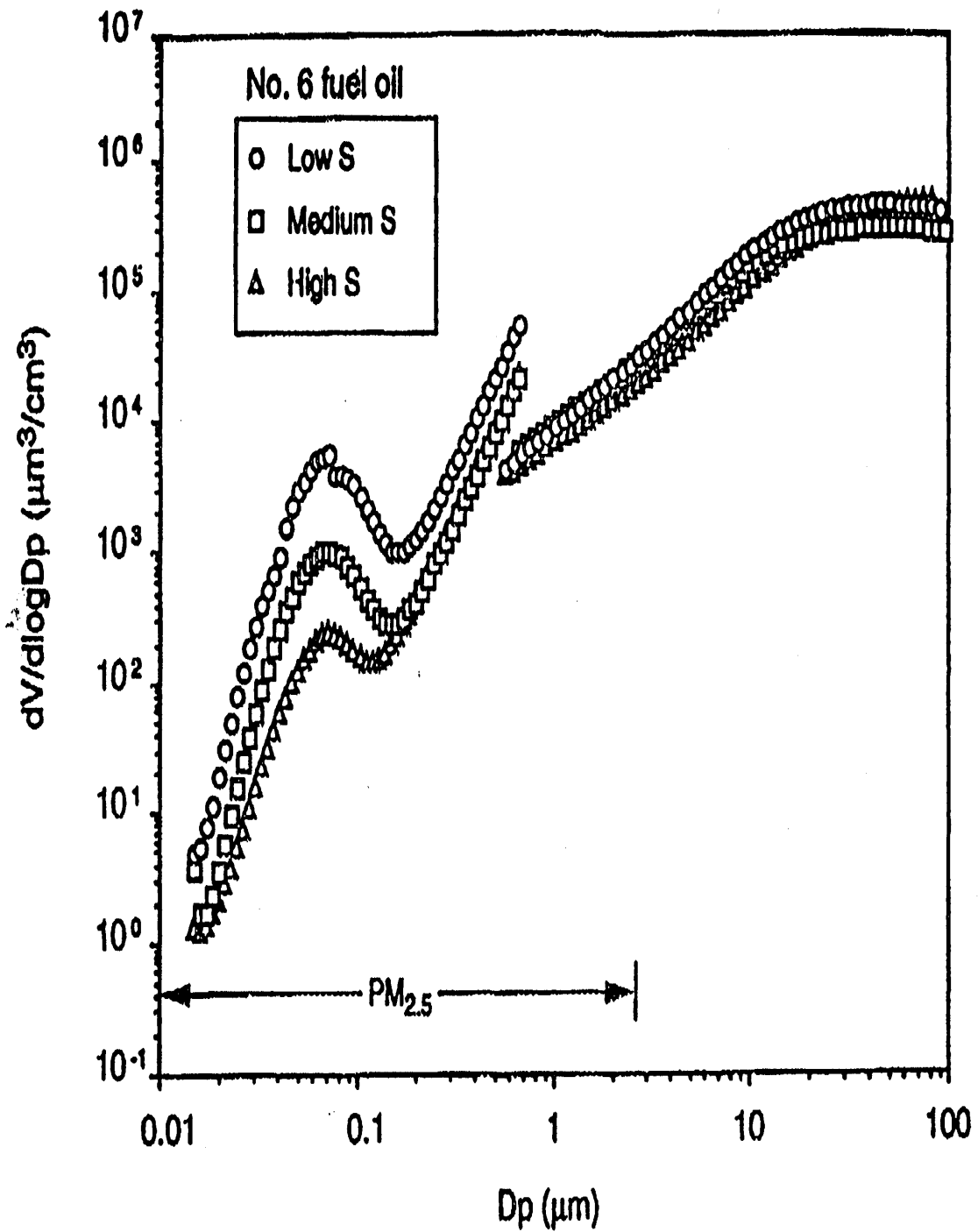


Fig. 11 - Particle volume distribution measured by electrical mobility and light scattering for No. 6 oil combustion

An excellent investigation of fine particle emissions from small oil burners is that of Mohr et al. (2000). Five residential oil burners with maximum heat output between 24 and 43 kW were tested in a laboratory setup equipped to determine particle number size distributions by means of a scanning mobility particle sizer. Two burners were of the yellow-flame type and three were of the blue-flame type. All were tested with a light fuel oil containing 0.164% sulphur. Two were tested with a very similar fuel oil containing only 0.042% sulphur. Additional variables were air/fuel ratio and the gap between nozzle and stabilization disk.

Figure 12 shows data for a yellow-flame burner with the standard fuel under several excess air conditions. With excess air between 1.5 and 5.77%, the mode of the distribution was 10 to 15 nm, with particle concentrations of about  $10^6/\text{cm}^3$ . Lower or higher excess air produced unacceptable levels of CO, shifted the mode to about 50 nm, and increased concentrations of particles tenfold or more. Figure 13 shows the effect of sulphur content on number particle size distribution. When operating with a blue-flame burner at acceptable CO levels, particle concentrations with the low-sulphur oil were about the same as when the higher-sulphur oil was fired in the yellow-flame burner, but the mode of distribution was somewhat smaller, perhaps 9 nm. The mode remained about the same but the concentrations increased sharply when the higher-sulphur oil was fired in the blue-flame burner.

It is interesting to compare the typical modal diameter of 10 nm found by Mohr et al. (2000) in his study with the typical modal diameter of 70 to 80 nm found by Miller et al. (1998). Probably the heavy oils fired by Miller et al. did not atomize to droplets as small as those achieved with the light oils fired by Mohr et al.. Indeed, with the blue-flame burners, particulates would be carbon resulting from cracking of vaporized fuel and could be expected to be very small. Also interesting is the comparison made by Mohr et al. of the particulates from their oil burner tests with those from engines burning gasoline and diesel fuel. As shown in Figure 14, the oil burners produce particles about an order of magnitude smaller than the engines but somewhere between gasoline and diesel fuel in terms of particle concentrations.

Gulyurtlu et al. (1996) in their study of waste oil combustion encountered high levels of particulates as would be expected from a fuel with about 1% ash. Particulate emissions at 3% O<sub>2</sub> in the flue gas ranged from 460 to 660 mg/m<sup>3</sup>. About 15% of this was metal, mostly lead. Distribution of particle sizes by weight, and concentrations of lead are shown in Table 10. The authors observe that about 80% of the lead in the oil was released to atmosphere and 70% of this was in particles of sub-micron size, probably formed by vaporization and subsequent condensation of the metal.

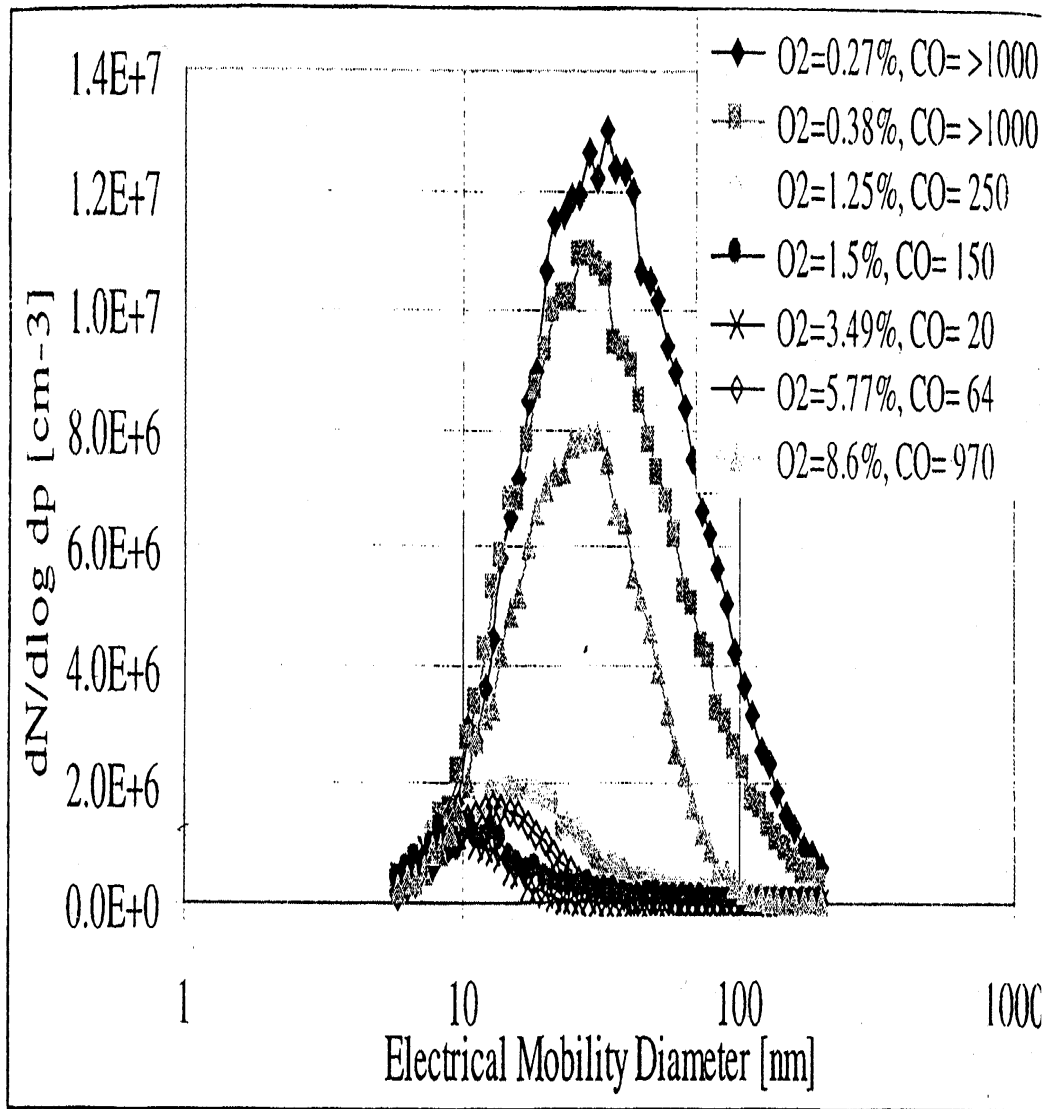


Fig. 12 - Effect of air fuel ratio on the number size distribution for burner Y-2

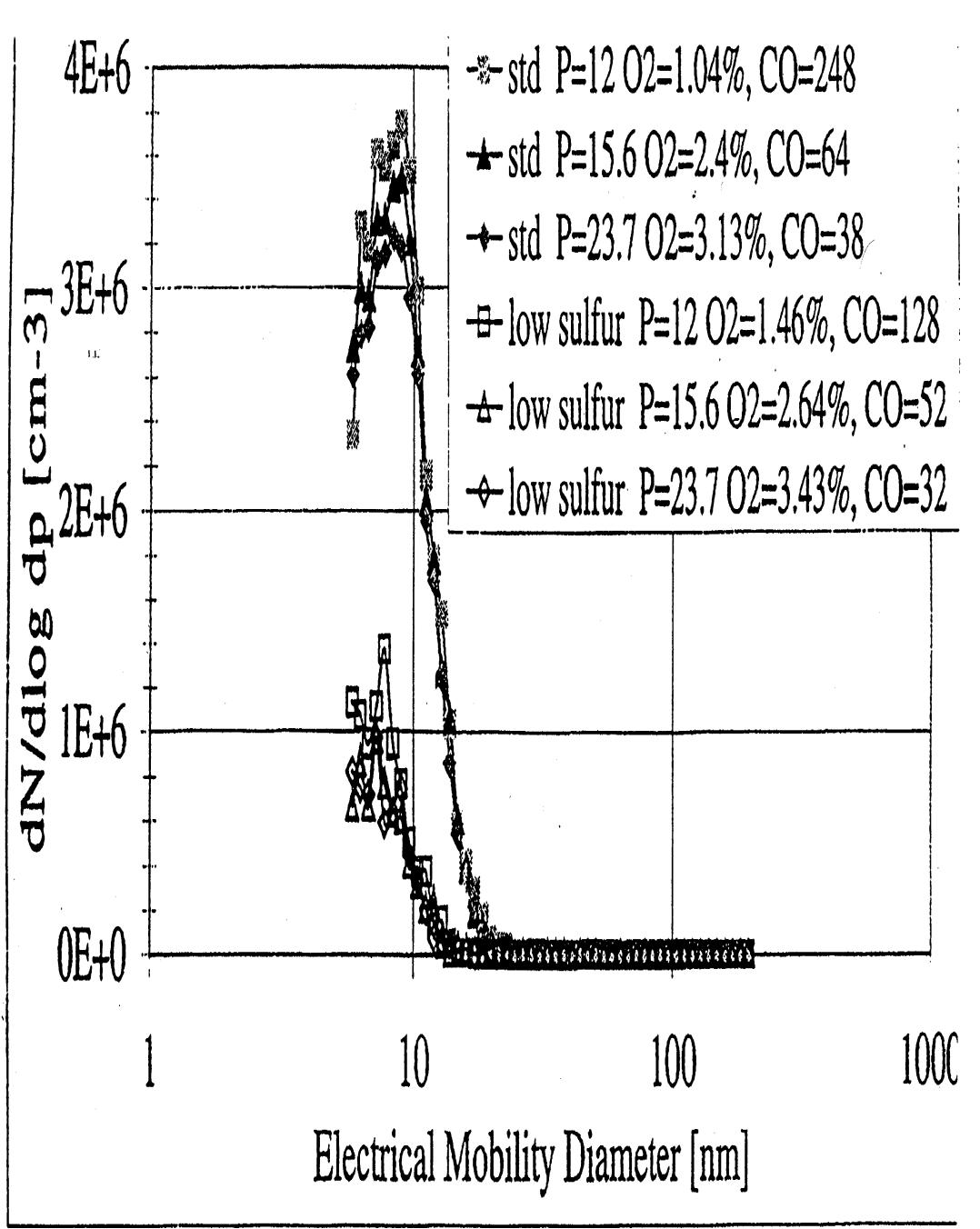


Fig. 13 - Effect of fuel sulphur content on the number size distribution for burner B-1 for different gap distances (P) between nozzle and stabilization disk

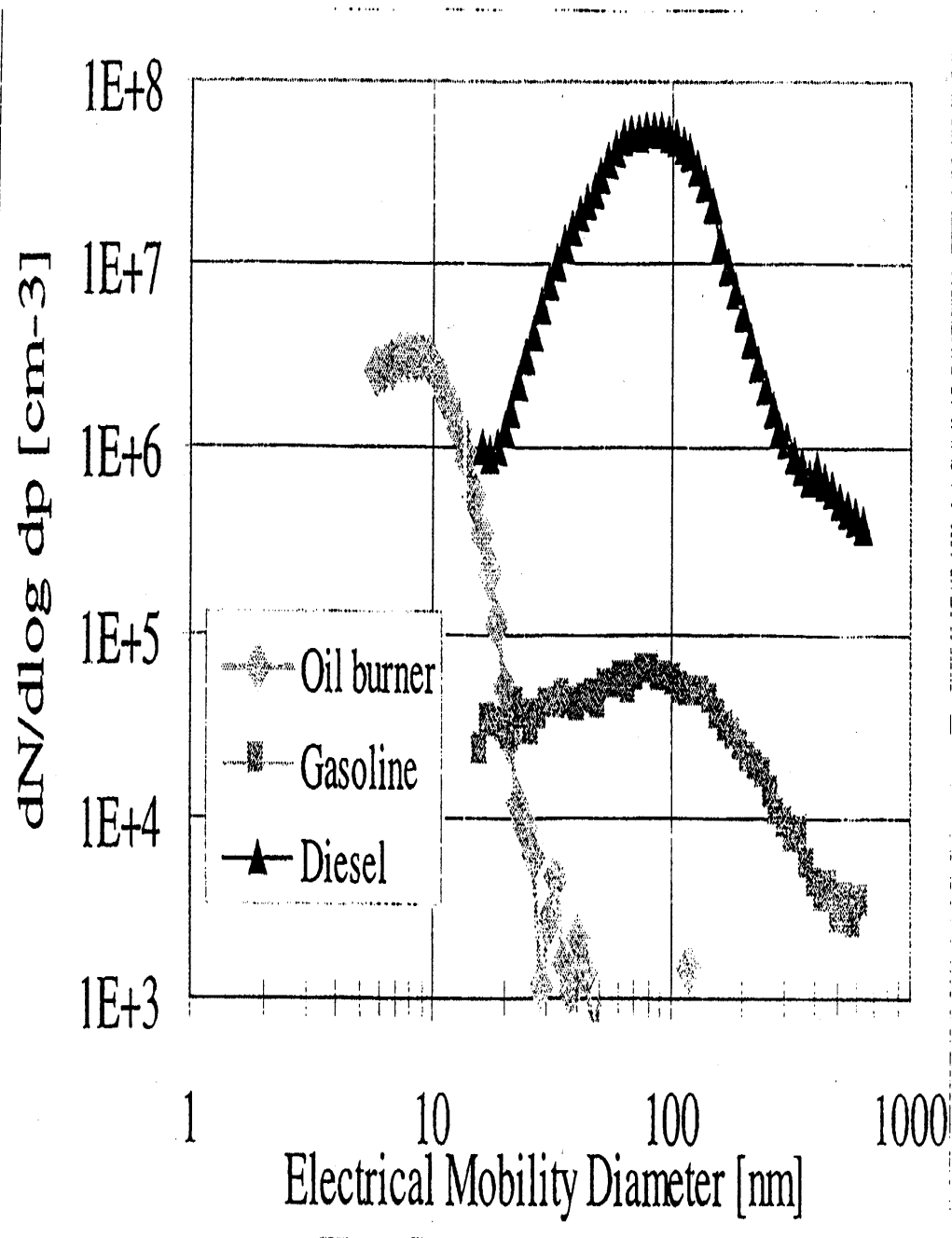


Fig. 14 - Comparison of fine particle emissions of oil burner and diesel and gasoline passenger car

**Table 10** Size distribution and lead concentrations in particulates from combustion of waste oil tested by Gulyurtlu et al. (1996)

Particle size, $\mu\text{m}$	Wt %	Pb, wt %
>15.14	15.72	<1.0
9.33-15.14	2.25	<6.0
6.31-9.33	5.24	<2.5
4.37-6.31	6.70	2.2
2.75-4.37	8.09	3.4
1.38-2.75	7.49	12.2
0.87-1.38	8.42	25.2
0.59-0.87	13.59	30.2
<0.59	32.49	30.2

### Carbon Monoxide

Emissions of carbon monoxide are of minor concern in well-operated combustion systems. Standards accepted by the Canadian Council of Ministers of the Environment allow 125 ng/J of CO from fossil-fuel-fired boilers in the industrial size range. For systems firing oil, 125 ng/J is equivalent to about 370 ppmv at 3% O<sub>2</sub> in the flue gas. Data from a variety of sources compiled in Table 11 show that CO emissions are commonly in the low double-digit range.

There is no apparent correlation between fuel sulphur and CO emissions. Obviously, low excess air levels can be expected to increase CO emissions but Table 11 shows that in some instances this can also result from high excess air levels, presumably by upsetting burner aerodynamics. Low excess air is used to reduce formation of both SO<sub>3</sub> and NO<sub>x</sub>. In the latter case CO can play a role in the mechanisms that inhibit NO formation.

Concentrations of CO in flue gas serve as a very useful diagnostic tool in assessing combustion system performance. At the threshold of poor performance, e.g., due to low excess air, poor fuel-air mixing or poor atomization, CO will rise very sharply from perhaps 30 ppm to several hundred or even several thousand ppm. This can identify flaws in burner tuning or control response. An example is shown in Figure 15, taken from Razbin et al. (1991). To pinpoint the cause of soot emission problems, CO was monitored while the boiler responded on automatic control to steam demand. It was found that when demand increased sharply the oil valve responded more quickly than the air damper resulting in brief periods of insufficient air, identified by the peaks in CO.

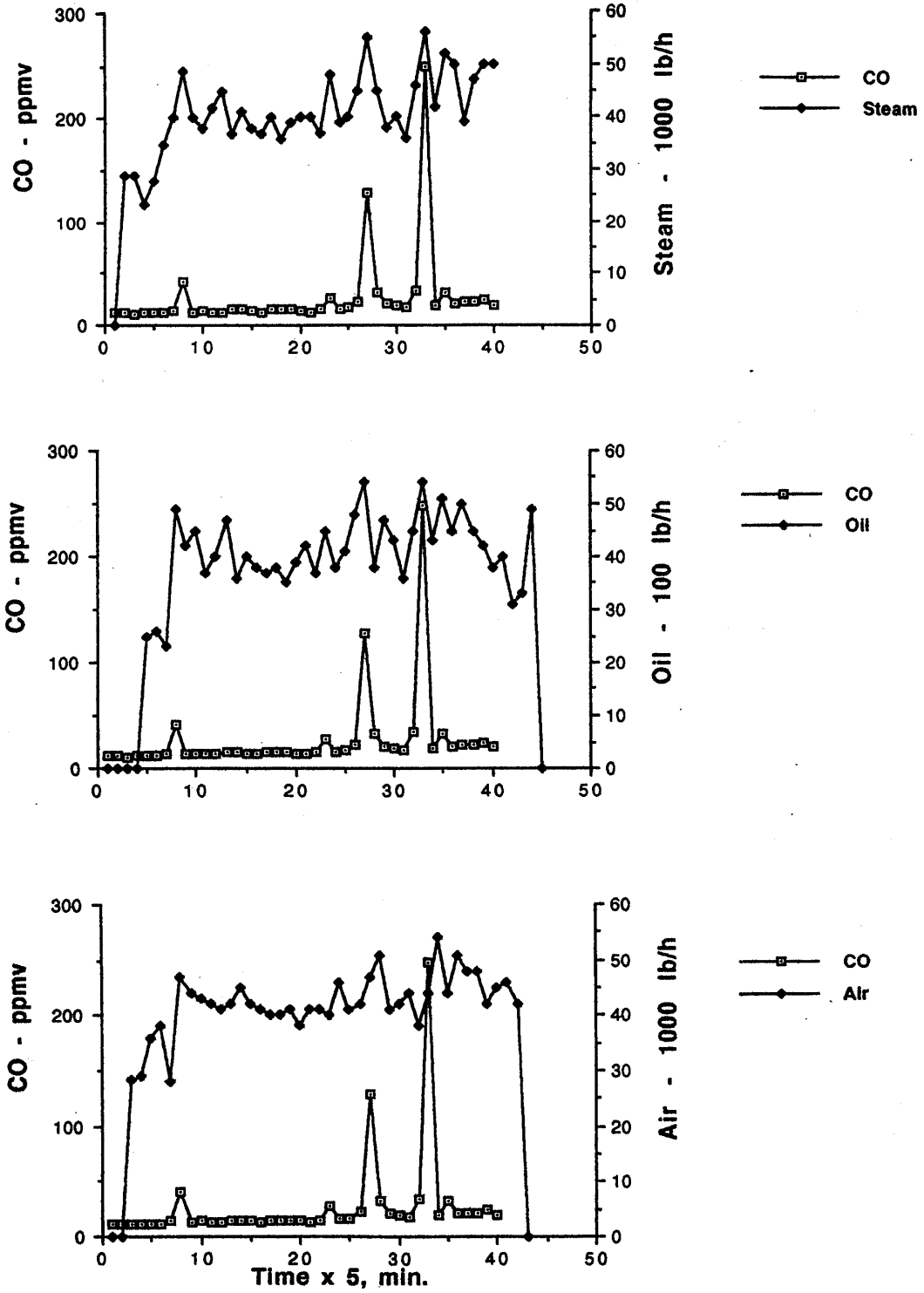


Fig. 15 - Correlation of CO emissions to steam, oil and air flow for Boiler 3



**Table 11** Typical CO emissions from oil-fired systems

Fuel type	Sulphur , wt %	O <sub>2</sub> in flue gas, %	CO in flue gas
<u>Herger et al. 1996</u> Small industrial boilers in Austria fired with yellow-flame burners			
Light residual oil	Not available	Not available	~8 mg/MJ
<u>Miller et al. 1996</u> Small package boiler, air-atomized burner, 2 x 10 <sup>6</sup> Btu/h input			
No. 2 oil	0.41	~4	1.24 ppmv @ 3 % O <sub>2</sub>
No. 5 oil	1.42	~4	3.55 ppmv @ 3 % O <sub>2</sub>
No. 6 oil	0.49	~4	1.30 ppmv @ 3 % O <sub>2</sub>
No. 6 oil	1.66	~4	5.34 ppmv @ 3 % O <sub>2</sub>
<u>Mohr et al. 2000</u> Domestic yellow-flame burner in a laboratory setup			
No. 2 oil	0.146	0.27	>1000 ppmv
		0.38	>1000 ppmv
		1.25	250 ppmv
		1.50	150 ppmv
		3.49	20 ppmv
		5.77	64 ppmv
		8.60	970 ppmv
Domestic blue-flame burner in a laboratory setup			
No. 2 oil	0.146	1.04	248 ppmv
		2.40	64 ppmv
		3.13	38 ppmv
No. 2 oil	0.042	1.46	128 ppmv
		2.64	52 ppmv
		3.43	32 ppmv
<u>Gulyurtlu et al. 2001</u> 240 kW pressure-atomized burner in a water-cooled laboratory furnace			
Waste oil	0.94	6.8	21 ppmv @ 3 % O <sub>2</sub>
		6.3	17 ppmv @ 3 % O <sub>2</sub>
		6.2	25 ppmv @ 3 % O <sub>2</sub>
		5.2	11 ppmv @ 3 % O <sub>2</sub>
		4.8	12 ppmv @ 3 % O <sub>2</sub>
<u>Whaley et al. 1995</u> Air-atomized burner of special design firing No. 6 fuel oil and oil-water emulsions in a research furnace at a rate of ~ 1600 MJ/h			
No. 6	1.36	3.2	47 ppmv
Emulsion fuel 2	5.12	2.9	69 ppmv
Emulsion fuel 3	5.00	3.2	28 ppmv
Emulsion fuel 5	5.72	3.0	135 ppmv

**Table 11 (cont'd)** Typical CO emissions from oil-fired systems

Fuel type	Sulphur, wt %	O <sub>2</sub> in flue gas, %	CO in flue gas
<u>Lee 1997</u> 100 kW laboratory rig, reverse-flow firetube design, pressure-atomized domestic burner, ultra-low sulphur No. 2 oil doped to various sulphur levels. CO was measured under cold-start (cs) and steady-state (ss) conditions.			
No. 2 oil	0.0099	5.3	93 ppmv (cs)
			19.2 ppmv (ss)
	0.0487	5.3	105 ppmv (cs)
			21 ppmv (ss)
	0.1925	5.4	88 ppmv (cs)
			12 ppmv (ss)
	0.49	5.3	111 ppmv (cs)
			24 ppmv (ss)
0.6767	5.5	111 ppmv (cs)	
		22 ppmv (ss)	
1.1333	5.7	85 ppmv (cs)	
		23 ppmv (ss)	
<u>Friedrich et al. 1992</u> 50 000 lb/h watertube package boiler with steam-atomized low-NO <sub>x</sub> burner Loads 40 to 100% of MCR			
No. 6 oil	1.95	2.2-3.5	30-400 ppmv @ 3% O <sub>2</sub>
Loads 50 to 100% of MCR			
No. 4 oil	1.45	1.8-5.3	60-135 ppmv @ 3% O <sub>2</sub>
burner 30 000 lb/h watertube field-erected boiler with steam-atomized Loads 41 to 90% of MCR			
No. 6 oil	1.95	1.9-8.4	42-216 ppmv @ 3% O <sub>2</sub>
Loads 37 to 91% of MCR			
No. 4 oil	1.45	2.5-3.4	49-74 ppmv @ 3% O <sub>2</sub>
<u>Razbin et al. 1991</u> 30 000 lb/h package boilers with steam-atomized burners Loads 25 to 88% of MCR			
No. 4 oil	1.60	2.0-6.6	25-50 ppmv @ 3% O <sub>2</sub>
55 000 lb/h package boilers with steam-atomized burners Loads 23 to 100% of MCR			
No. 4 oil	1.60	1.65-6.53	18-48 ppmv @ 3% O <sub>2</sub>

## Organic Emissions

The literature is sparse on organic emissions from combustion of fuel oils, doubtless because of the expense involved in sampling and analysis. Fortunately, Miller et al. (1996) conducted extensive measurements involving 195 organic compounds, finding emission rates for No. 2 oil, No. 5 oil, low-sulphur No. 6 oil and high-sulphur No. 6 oil of 187, 272, 326 and 250 lb/10<sup>12</sup> Btu, respectively. Of the emissions, carbonyls comprised 69 to 87%, followed in order of magnitude by volatile organics, semi-volatile organics and polyaromatic hydrocarbons. Figures 15 and 16 and Table 12 give more detailed results.

**Table 12** Emission rates of polyaromatic hydrocarbons from four grades of fuel oil, as reported by Miller et al. (1996)

Grade of oil	No. 2	No. 5	No. 6	No. 6
Sulphur content	0.41	1.42	0.49	1.66
<b>PAH</b>	<b>Emission rate, lb/ 10<sup>12</sup> Btu</b>			
Acenaphthene	0.019	0	0	0.036
Acenaphthylene	0.018	0.078	0	0.062
Anthracene	0	0.043	0.031	0
Benzo(a)anthracene	0.348	0.037	0.095	0.044
Benzo(a)pyrene	0.695	0	0	0
Benzo(b)fluoranthene	0.859	0	0	0
Benzo(g,h,i)perylene	0.042	0.0287	0.027	0.066
Benzo(k)fluoranthene	0.745	0	0	0
Chrysene	0	0	0	0.029
Dibenz(a,h)anthracene	0.430	0.093	0.038	0
Fluoranthene	0.882	0	0.052	0.049
Fluorene	0.098	0.042	0.041	0.072
Indemo(1,2,3-cd)pyrene	0.129	0.033	0.028	0
Naphthalene	0.042	0.640	0.218	2.36
Phenanthrene	1.10	0.056	0.118	0.132
Pyrene	0.148	0	0.022	0.052
<b>Total PAH</b>	5.93	1.05	0.669	2.90

These results are comparable to the measured PAH emissions cited in a comprehensive EPA review of HAP emissions data from oil and coal combustion by Brooks (1989). Although the data cited in Brooks' review are taken from a 30 year old report, they lend support to the findings by Miller et al. (1996) that PAH emissions from the No. 2 oil can be higher than those from the combustion of heavier oils, as reported by Hanksbrack et al. (1964). PAH emissions are in part a function of burner firing system design and temperatures in the flame zone. Arrangement of the radiative heat adsorption surfaces and residence time of the flue gases in the high temperature zone, which are functions of the boiler type and design, would also influence the levels of PAH emissions.

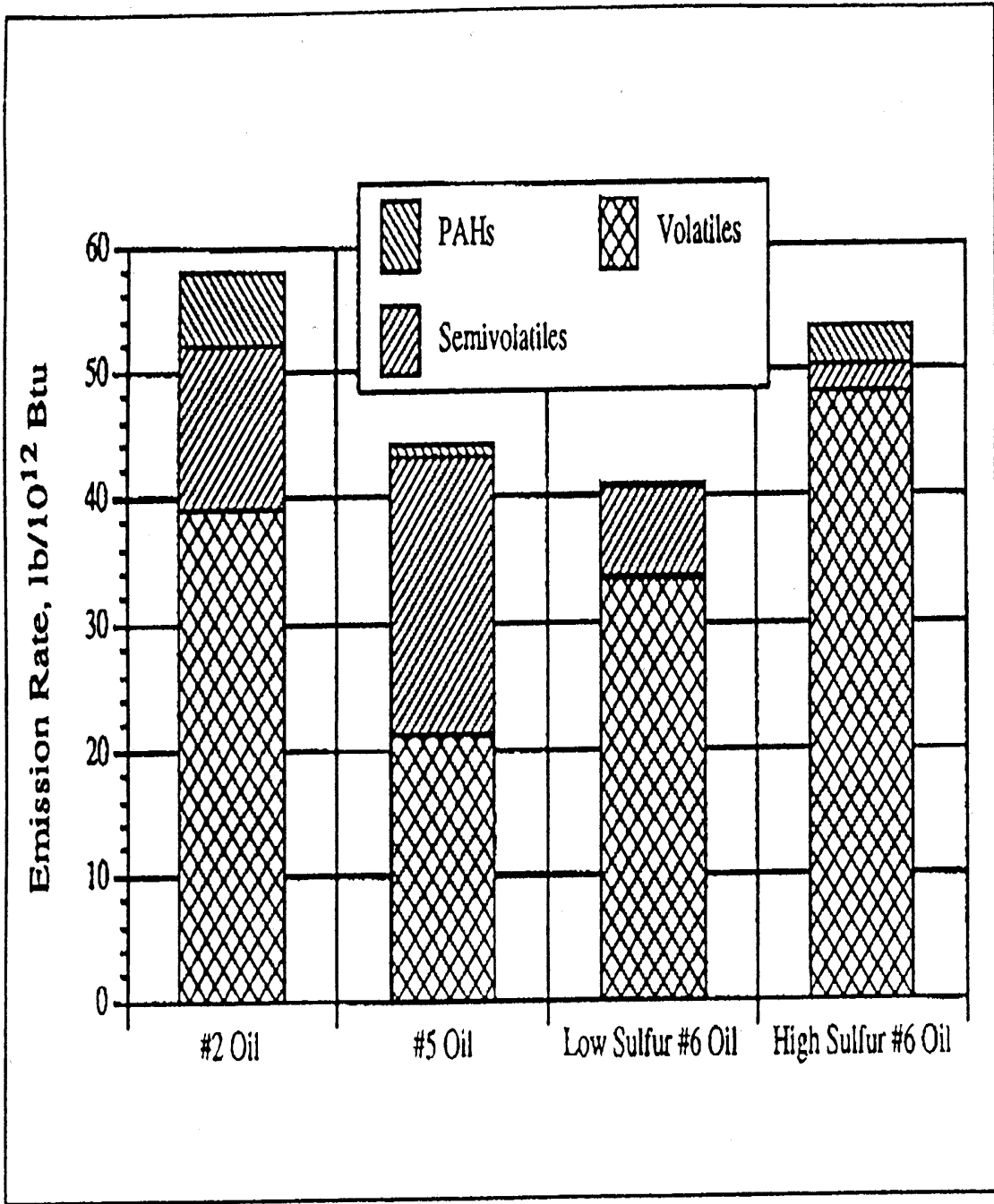


Fig. 16 - Total noncarbonyl volatile and semivolatile organic emission rates for four oils

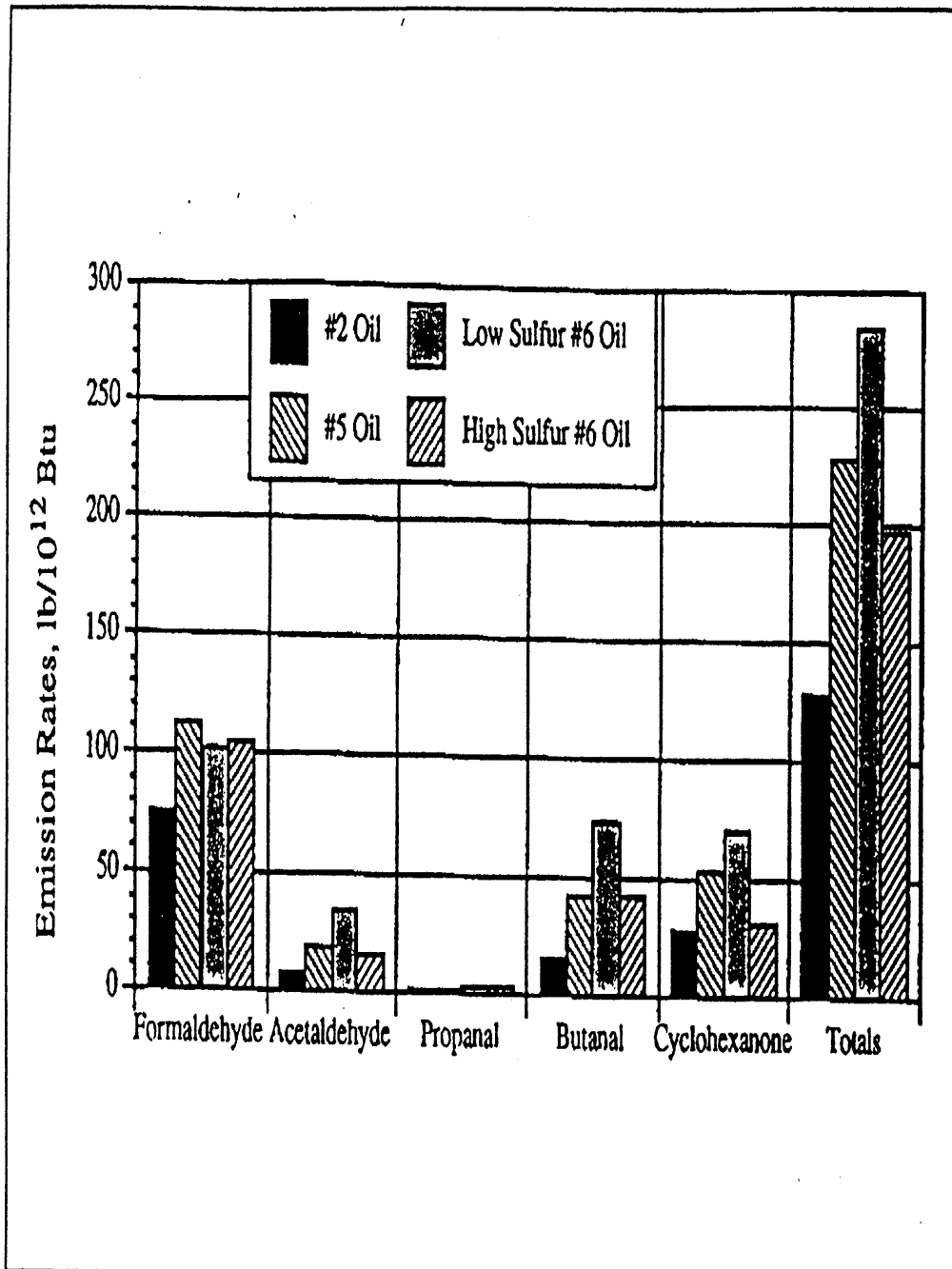


Fig. 17 - Measured emission rates of carbonyl (aldehydes and ketones) for the four oils

# FUEL UPGRADING

## Basic Refining Processes

The refining processes by which crude oil are turned into gasoline, diesel fuel, light and heavy fuel oil and numerous other products are many and complex. The raw feedstock – crude oil or, as is common in Canada, bitumen – may vary in the proportions of carbon and hydrogen, the main fuel components. Also variable are the concentrations of contaminants such as sulphur, metals, and organically-bound nitrogen. The nature of the hydrocarbons themselves may vary according to the source of the crude oil e.g., straight-chain hydrocarbons vs. polyaromatics and polycyclics, compounds of low molecular weight and high volatility vs. heavy, semi-solid asphaltenes.

Over the past century refiners have developed a range of techniques to obtain the desired products from whatever feedstock is available. The hypothetical refinery flowsheet in Figure 18, presented by Stacey (1971) indicates some of the means available to the refiner. As a first step the crude oil is distilled at atmospheric pressure and the more volatile fractions such as gasoline and light fuel oil are separated according to range of boiling point. The remaining fraction from the atmospheric tower may be subjected to “visbreaking” which cracks much of the high-molecular-weight material into lighter molecules producing more of the high-value light fractions. This may be followed by vacuum distillation to achieve a further separation of light products. Finally, the heavy residues may be subjected to hydrogenation, i.e., hydrogen is added under conditions of high temperature and pressure, in the presence of catalysts, to convert heavy compounds of high carbon/hydrogen ratio to lighter, more valuable compounds of higher hydrogen content. In the process contaminants such as sulphur, nitrogen, halogens and metals may be displaced at least in part. The extent to which hydrogenation is carried out is determined by economics. Usually some residue remains, perhaps as much as 50% of the input if the refining process is fairly simple. In that case it is a tar-like fuel oil, pumpable when heated. More severe refining may reduce the residue to a petroleum coke. In any case, the residue will contain most, but not all, of the contaminants.

## Sulphur Removal

A report published by CONCAWE (de Vecchi et al. 1996) gives a helpful picture of the quantities of sulphur dealt with by the oil refineries of Western Europe and how it is distributed in the resulting products. Table 13 presents some of the data. The average sulphur content of the crude oil, at 1.05%, is about half what one might expect in other parts of the world, reflecting the influence of low-sulphur crude oil from the North Sea. Of the approximately  $6 \times 10^6$  te/y of intake sulphur, about 31% is removed by the refineries, primarily to meet legislated limits on sulphur content of gasoline and fuel oils. The sulphur thus removed is usually reduced to elemental form, marketable for industrial purposes such as sulphuric acid production. On the other hand, the refineries usually meet their process energy requirements by burning the least marketable product streams, thereby emitting substantial quantities of SO<sub>2</sub> to atmosphere, about 9% of sulphur intake.

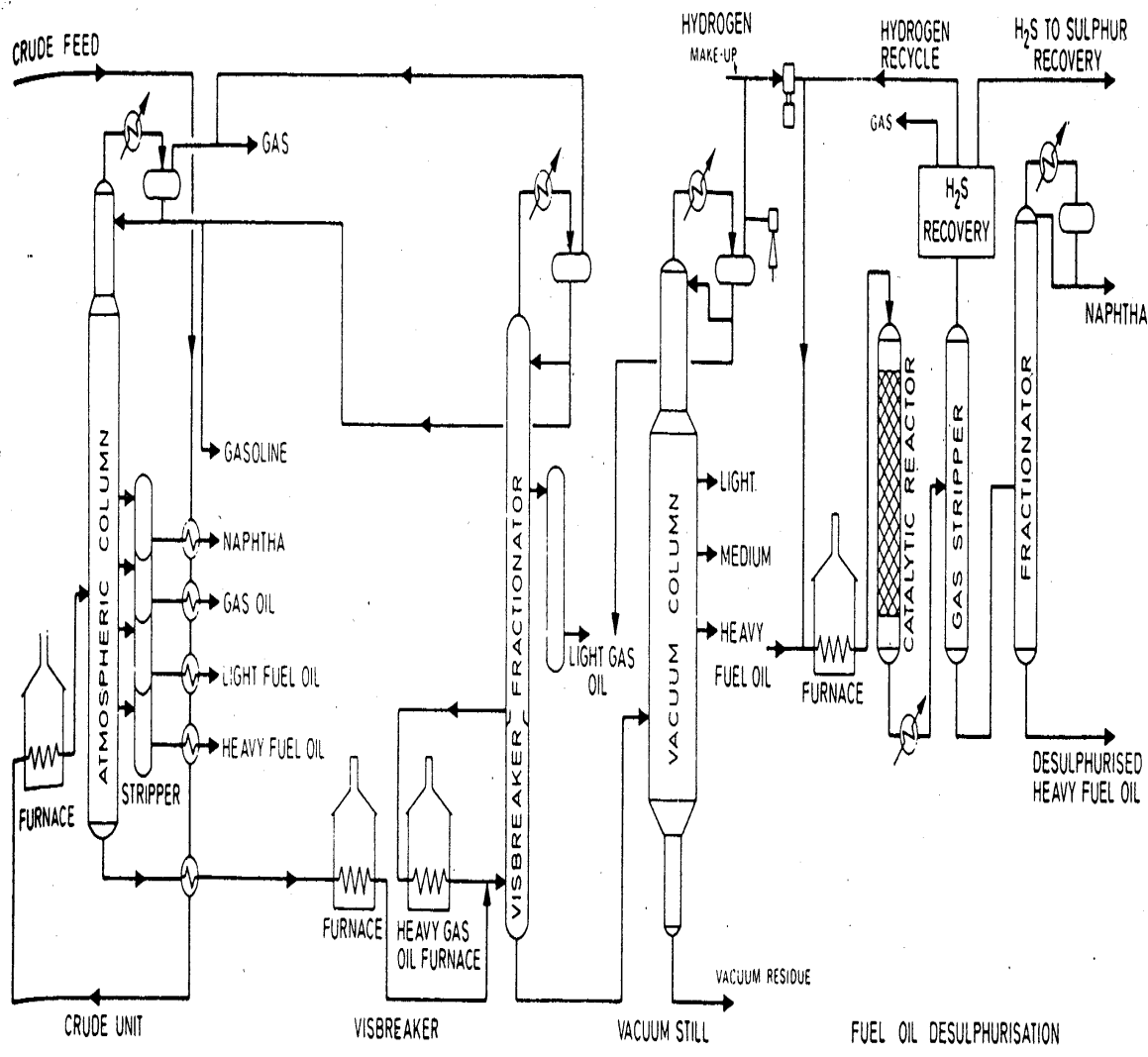


Fig. 18 - Hypothetical refinery flowsheet including atmospheric distillation, visbreaking, vacuum distillation and catalytic hydrodesulphurization units

**Table 13** CONCAWE data for sulphur in crude oil and products for Western Europe in 1992 (De Vecchi et al. 1996)

Crude oil throughput, 10 <sup>6</sup> te/y	582
Sulphur content, average, wt %	1.05
Sulphur intake with crude oil, 10 <sup>3</sup> te/y	6122
Sulphur recovered at refinery, 10 <sup>3</sup> te/y	1889
Sulphur recovered, % of intake	30.9
Sulphur in SO <sub>2</sub> emitted by refineries, % of intake	9.06
Sulphur in oil products, 10 <sup>3</sup> te/y	3565
Sulphur in oil products, % of intake	58.2
Sulphur in LPG & naphtha, weighted avg. %	0.02
Sulphur in intermediates & blendstock, weighted avg. %	1.26
Sulphur in gasoline, weighted avg. %	0.035
Sulphur in jet fuel & kerosene, weighted avg. %	0.09
Sulphur in diesel fuel, weighted avg. %	0.21
Sulphur in distillate heating oil, weighted avg. %	0.21
Sulphur in bunker fuel oil, weighted avg. %	3.1
Sulphur in heavy fuel oil, weighted avg. %	2.2

In the end about 58% of the sulphur intake appears in the marketable products in concentrations ranging from 0.035 wt % in gasoline to 2 or 3% in residual fuel oils.

The concept of desulphurizing crude or fuel oils is not new. In 1963 Voorhies et al. (1963A) recognizing a demand for fuel oils with reduced sulphur content, undertook pilot-plant investigations to establish feasibility. Working with three feedstocks, an Arabian crude oil with 1.75% S, a Kuwait crude oil with 2.65% S, and a 3.75% S residuum from atmospheric distillation of the Kuwait crude oil, a relatively low-severity process was applied to achieve fuel oils with sulphur contents of 2.5 and 1.0%. Because the resulting fuel oil represents a fraction in which is concentrated much of the sulphur in the crude oil, the latter had to be desulphurized to some level below the targets of 2.5 and 1.0%. The results of the tests are shown in Table 14, expressed in terms of relative feed rate; e.g., for the same conditions of temperature, pressure and catalyst age, to achieve a fuel oil with 1.0% sulphur, the Arabian crude oil can be processed at 1.4 times the feed rate of the higher-sulphur Kuwait crude oil.



**Table 14** Relative feed rates for desulphurization of oil (Voorhies et al. 1963A)

<b>Sulphur content of product fuel oil, %</b>	<b>2.5</b>	<b>1.0</b>
<b>Feedstock</b>	<b><u>Relative feed rate</u></b>	
Kuwait crude oil, 2.65% S	3.4	1.0
Arabian crude oil, 1.75% S	-	1.4
Kuwait atmospheric residuum, 3.76% S	2.0	0.6

The authors observe that for a given sulphur level in the fuel oil product the Kuwait crude oil can be processed at nearly double the rate of the atmospheric residuum from it. Therefore only a 33% larger reactor is required to produce the same volume of the low-sulphur fuel oil when processing the whole crude stream than when processing the residuum only. Sulphur content of the light fractions distilled from the desulphurized crude oil was also much reduced.

Costs for desulphurization, based on a 60 000 bbl/day plant processing Kuwait crude oil were estimated at 27.7 ¢/bbl of crude oil for the fuel oil with 2.5% sulphur, 37.4 ¢/bbl of crude oil for the fuel oil with 1.0% sulphur, presumably in 1963 U.S. dollars. Finally, the authors believe that a greater degree of desulphurization is technically feasible, but at greatly increased cost.

The foregoing work by Voorhies et al. was carried out at the Esso Research Laboratories at Baton Rouge, Louisiana. About the same time Bechtel Corp. investigated the costs of desulphurization for the American Petroleum Institute. Taking as the base case a Caribbean refinery having a capacity of 300 000 bbl/stream.day and producing 57.4 vol% of No. 6 oil (172 000 bbl/stream.day) containing 2.6% sulphur, capital and operating costs for desulphurization were estimated. The resulting incremental costs of reducing the sulphur content of No. 6 oil to values as low as 0.2% are shown in Fig. 19. The cost estimates were based on a four-year payout. Remarkably, the relation of cost increase to degree of sulphur reduction is fairly linear, at least down to 0.5% sulphur in the No. 6 oil. An incremental cost of 12 ¢/10<sup>6</sup> Btu to reduce the sulphur content of No. 6 fuel oil from 2.6 to 1.0% seems rather modest, but it must be kept in mind that this study was conducted about 1964.

A more recent study by Halkos (1995) compares pre-combustion, during-combustion and post-combustion technologies for desulphurization for both coal and oil. For oil, two types of pre-combustion desulphurization, direct and indirect, are discussed. In the direct method the residue from initial distillation is reacted with hydrogen in the presence of a catalyst to form H<sub>2</sub>S, which is removed and converted to elemental sulphur. The desulphurized product is then reblended with the distillates and perhaps processed further.

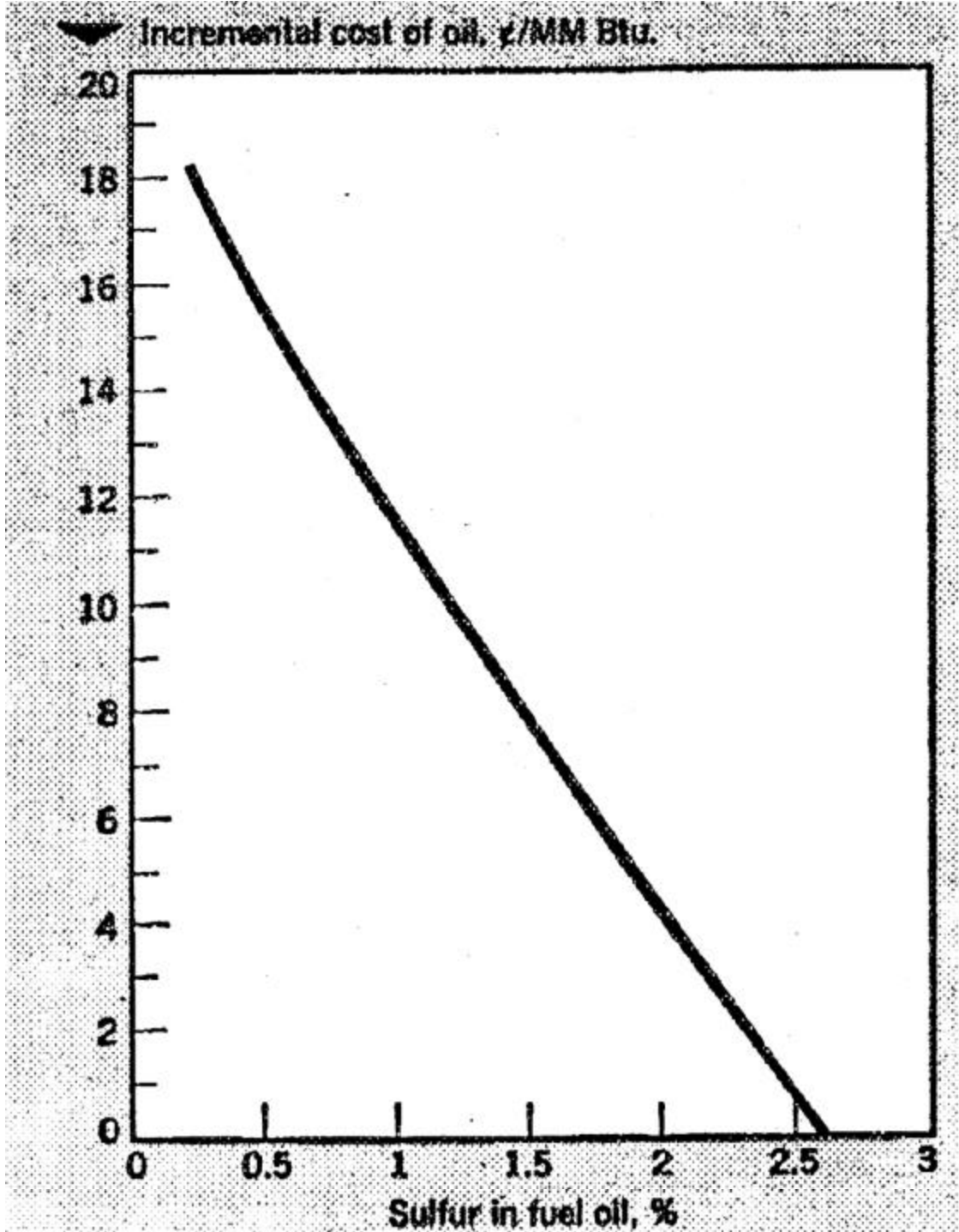


Fig. 19 - Incremental cost for low-sulphur residual oils

This method can remove up to 90% of the input sulphur with an associated fuel loss of about 8%. In the indirect method the light oils produced from atmospheric distillation of crude oil are re-distilled under vacuum, hydrotreated to remove the sulphur, then blended with the heavy oil to produce a lighter, lower-sulphur fuel oil. This method can achieve a sulphur reduction of about 40%, with an associated fuel loss of about 5%.

Halkos observes that costs of desulphurization can vary widely, depending on the size of the refinery, the degree of desulphurization, the nature of the crude oil, and its cost. He cites one study which estimates as follows in \$U.S., 1985:

Reducing heavy fuel oil from 2.15 to 1.0% S; \$333./te of SO<sub>2</sub> removed.

Reducing heavy fuel oil from 1.0 to 0.7% S; \$722/te of SO<sub>2</sub> removed.

Processes for removing sulphur during combustion such as fluidized-bed combustion or limestone injection require high-efficiency particulate cleanup systems and so are not usually applied to oil-fired boilers. Post-combustion desulphurization by means of flue gas scrubbers is estimated to add 15 to 20% to the total cost of a power plant, and operating costs for oil-fired plants are between 610 and 720 \$U.S./te of sulphur removed (Halkos, 1995).

Conventional refining processes of the mid-twentieth century converted perhaps 40 to 60% of the crude oil to refined products. The remainder was marketed as heavy fuel oil containing most of the feedstock contaminants. For example, the Bechtel study cited earlier assumed 57.4 vol % of the feedstock crude appearing in the stream of No. 6 oil. Subsequent trends have been toward increased demand for motor fuels and lower sulphur content in all fuels.

How this might best be accomplished in Russia was addressed by Koslov et al. (1993). They considered five different schemes for producing 10<sup>6</sup> te/y of boiler fuel with S = 0.3% from a medium-sulphur west Siberian crude oil. The processes for each scheme are given in Table 15. Dashes indicate steps not taken in that scheme.

Table 15 presents the quantities processed per year by each step in each scheme. Table 16 presents the quantities of each product as a percentage of input. Table 17 presents the annual quantities of input and product by weight, as well as some cost figures, calculated as a percentage of the costs for Scheme 3, which is the simplest. The cost of crude oil was taken as 20 000 rubles/tonne.

In Schemes 1, 2 and 3 straight-run atmospheric residuals are separated by vacuum distillation into vacuum gasoil (at temperatures between 350°C and 500°C) and vacuum residual (at temperatures > 500°C). The vacuum gasoil, alone in Scheme 3, or mixed with heavy coker gasoil in Schemes 1 and 2, is hydrotreated to produce diesel oil and low-sulphur (= 0.3%) boiler fuel.

**Table 15** Five crude oil processing schemes and quantities processed by each (Koslov et al. 1993)

Scheme	1	2	3	4	5
<b>Process</b>	<b>Feedstock processed, 10<sup>3</sup> te/y</b>				
Vacuum distill. of atmos. residuals	1817	1817	1955	-	-
Hydrotreating 350-500 °C cut	1245	1518	1112	-	-
Delayed coking of vacuum residuals	783	783	-	-	-
Hydrodesulph. of atmos. residuals	-	-	-	1253	-
Adsorption-catalytic treatment of atmos. residuals	-	-	-	-	2167
Hydrotreating fractions distilling above 180°C from adsorption-catalytic treat.	-	-	-	-	1760
Asphalt production	-	-	843	-	-
Catalytic reforming	110	114	-	28	136
Hydrogen production	10	15	10	15	18
Sulphur production	19	26	18	25	28

**Table 16** Outputs for five crude oil processing schemes, as percentage of medium-sulphur atmospheric residuals input (Koslov et al. 1993)

Scheme	1	2	3	4	5
<b>Feedstocks in</b>	<b>Wt %</b>				
Med. S atmos. residual	100.0	100.0	100.0	100.0	100.0
Hydrogen	0.6	0.9	0.5	1.2	0.8
<b>Products out</b>					
AI-92 automotive gasoline	5.3	5.5	0.7	1.95	5.4
L-0.2 summer diesel fuel	5.8	19.2	4.2	13.0	31.0
Furnace oil, 1.1 % S	15.1	-	-	-	-
Low-S boiler fuel (=0.3% S)	55.0	56.0	51.2	79.8	45.7
Asphalt	-	-	41.2	-	-
Coke	11.1	11.1	-	-	-
Sulphur	1.0	1.3	0.8	1.8	1.2
Gas and oil for refinery use	6.0	6.3	0.7	3.3	8.4
Loss	0.9	1.0	1.7	1.2	1.1
<b>Total</b>	<b>100.6</b>	<b>100.9</b>	<b>100.5</b>	<b>101.2</b>	<b>100.8</b>

**Table 17** Tonnage outputs for five crude oil processing schemes, and relative costs (Koslov et al. 1993)

Scheme	1	2	3	4	5
	Quantities 10 <sup>3</sup> te/y				
Atmos. resid. processed	1817	1817	1955	1253	2187
Products					
AI-92 unleaded gasoline	97	100	13	24	119
L-0.2 diesel fuel	106	350	82	163	678
Furnace oil	273	-	-	-	-
Low-sulphur boiler fuel	1000	1017	1000	1000	1000
Coke	202	202	-	-	-
Asphalt	-	-	806	-	-
Sulphur	18	24	17	23	26
<b>Total*</b>	<b>1695 (93)</b>	<b>1692 (93)</b>	<b>1918 (98)</b>	<b>1210 (97)</b>	<b>1822 (83)</b>
<b>Cost breakdown</b>	<b>Percentage of Scheme 3</b>				
Capital, with allowance for general refinery facilities	138	160	100	209	183
Incl. purchased technology	139	164	100	220	192
Cost of commercial products	95	96	100	70	112
Including value of feedstock	93	93	100	64	112
processing costs	118	135	100	148	110
Invest. payback period, years	3.0	3.4	2.0	6.0	3.4

- Values in parentheses denote percentage relative to feed.

In Schemes 1 and 2 the vacuum residuals are subjected to delayed coking to obtain gasoil fractions and commercial coke. In Scheme 3 the vacuum residuals are used to produce asphalt. In Scheme 4 the straight-run atmospheric residuals are hydrotreated at high pressure to remove sulphur. In Scheme 5 these residuals are subjected to adsorption-catalytic treatment followed by hydrotreating and segregation of a diesel fuel cut and a +350°C residue. Schemes 1, 2 and 3 would be classified as indirect; Schemes 4 and 5 as direct desulphurization processes.

The authors conclude that from the viewpoint of producing 10<sup>6</sup> te/y of low-sulphur boiler fuel, Scheme 4 provides the lowest total cost of the products, reflecting the greatly reduced input requirement, which more than offsets the high capital cost. However, demand for a different product mix may make other schemes more attractive. All the schemes can increase the yield of high-quality engine fuels by 40 to 70%, through catalytic and hydrogenative processing of vacuum gasoil.

Recent book by Speight (2000) provides an extensive and detailed overview of current technologies for desulphurization of heavy oils and residua, including the refinery distillation, visbreaking and coking process. It covers process and flow sheets of modern refinery concepts for both distillate fractions and residues, including the chemistry of the sulphur species in distillates and petroleum fractions. Thermal and catalytic cracking, coke formation and hydro-treating reactions of sulphur compounds are included in section on desulphurization chemistry. Various uses of the latest industry-standard catalysts, such as Ni/Mo and Co/Mo sulfides, are presented together with practical operational problems, such as plugging of packed-bed hydrogenation reactors and coke and vanadium sulphide deposition within the catalyst porous structure. Variability in feedstock properties and how they would influence the refinery processes and catalyst performance is extensively discussed. Various processes involved in the production of hydrogen, which is an essential part of the hydrodesulphurization process, are also covered. The hydrogen production methods include the technologies of partial oxidation, gasification and steam reforming.

Speight (2000) describes various hydrodesulphurization process options that are common and commercially proven in modern day refineries. Hydrotreating processes have two defined roles: (1) desulphurization to supply low-sulphur fuel oils and (2) pretreatment of feed residua for residuum fluid catalytic cracking. The main goal is removal of sulphur, metals and asphaltene content from residua and other heavy feedstock. Speight (2000) gives an outline, with sufficient technical details, of 20 different process for hydroconversion of heavy feedstocks that have evolved during the last three decades. They are: Asphaltenic Bottom Cracking Process, Aquasconversion, CANMET Hydrocracking Process, Chevron RDS Isomax and VRDS Process, Chevron Deasphalted Oil Hydrotreating Process, Gulf Resid Hydrodesulphurization Process, H-Oil Process, HYCAR Process, Hyvahl F Process, IFR Hydrocracking Process, Isocracking Process, LC-Fining Process, Microcat-RC Process, MRH Process, RCD Unibon Process, Residfining Process, RHC Process, Shell Residual Oil Desulphurization, Unicracking Hydrodesulphurization Process and Veba Combi-Cracking (VCC) Process

## **Metals Removal**

Crude oils typically contain trace amounts of metals with vanadium and nickel being the most common. Usually they are in an oil-soluble form, not removable by water-washing or filtration, and in conventional refining processes they become concentrated in the residual fuel oil fractions as shown in Table 17. Vanadium may occur in crude oil at concentrations up to 400 ppmv, and often causes severe corrosion problems with high-temperature metal surfaces in steam generators. The metals also tend to form particulate emissions in the sub-micron range as discussed earlier in “Emissions” section.

Demetallization is practical, as was demonstrated in pilot-scale work by Voorhies et al. (1963B). A Venezuelan crude oil, high in metals, was subjected to treatments of varying severity. The results shown in Table 18. Even low-severity treatment reduced vanadium by 75%, while high-severity treatment removed 95 % of the vanadium and 60 % of the nickel.

**Table 18** Results of demetallization of Venezuela crude oil (Voorhies et al. 1963B)

<b>Treatment severity</b>	<b>None</b>	<b>Low</b>	<b>Medium</b>	<b>High</b>
Yield, %	100	99.5+	99.5+	99.5+
Vanadium, ppmw	400	100	42	18
Nickel, ppmw	57	35	30	22
Gravity, °API	15.2	14.8	14.5	15.2
Viscosity, SSF at 122°F	159	187	180	350
Naphtha insolubles, wt %	9.0	9.0	8.5	9.0
Sulphur, wt %	2.4	2.4	2.4	2.4
Nitrogen, wt %	0.4	0.4	0.4	0.4

Loss of oil yield and consumption of treating agent were below the limits of accurate measurement. Oil viscosity was increased. Sulphur and nitrogen were unaffected.

The same demetallization process was then applied to other feedstocks both high and low in metals with equally good results as shown in Table 19. Based on a 30 000 bbl/day stream removing 90% of metals, costs were estimated at about 15 ¢/bbl, 1963 \$U.S.

Aside from reducing corrosion and air pollution, demetallization of petroleum feedstocks can be beneficial to the refinery processes as well, because the trace metals can negatively affect catalyst activity. Koslov et al. (1993) include a preliminary stage of feedstock demetallization in Scheme 4, presumably to prevent poisoning of the catalyst required for hydrodesulphurization.

### **Nitrogen Removal**

Fuel NO<sub>x</sub> resulting from fuel-bound nitrogen is difficult to minimize in the combustion process as discussed under “Emissions”. Unfortunately, this literature review revealed nothing on the removal of organic nitrogen components from petroleum products during the refining process.

**Table 19** Results of demetallization of various petroleum feedstocks  
(Voorhies et al. 1963B)

<b>Treatment severity</b>	<b>None</b>	<b>Low</b>	<b>High</b>
<b>Bachaquero (Venezuela) visbreaker tar</b>			
Yield, %	100	99.5+	-
Vanadium, ppmw	585	143	-
Nickel, ppmw	79	59	-
Gravity, °API	8.8	8.2	-
<b>West Texas vacuum residuum</b>			
Yield, %	100	99.5+	99.5+
Vanadium, ppmw	47	6.7	0.6
Nickel, ppmw	27	13	4.0
Gravity, °API	9.4	9.0	8.7
<b>Kuwait vacuum residuum</b>			
Yield, %	100	-	99.5+
Vanadium, ppmw	76	-	3
Nickel, ppmw	26	-	17
Gravity, °API	7.3	-	6.1
<b>West Texas deasphalted vacuum residuum</b>			
Yield, %	100	99.5+	-
Vanadium, ppmw	3.0	0.0	-
Nickel, ppmw	3.0	0.2	-
Gravity, °API	18.1	18.9	-



## SUMMARY AND CONCLUSIONS

The chief contaminants in fuel oil are sulphur, organically-bound nitrogen and metals. Within refinery and combustion processes they can cause problems such as catalyst poisoning and corrosion. Upon emission to the atmosphere as  $\text{SO}_2$ ,  $\text{NO}_x$  and particulates, likely supplemented by VOC, PAH and carbon particulates, they contribute to acid rain, smog and numerous negative health effects. With respect to the foregoing, it is instructive to compare petroleum fuels with the clean fuel of choice, natural gas, taking due account of the fact that they are not fully interchangeable, especially as fuels for transport.

Natural gas contains essentially no sulphur. Therefore when combusted it emits neither  $\text{SO}_2$  nor  $\text{SO}_3$ , has no sulphur-related high-temperature corrosion problems, and having no problems with acid dewpoint, is amenable to high-efficiency condensing heat recovery. Only highly-desulphurized fuel oils enjoy these advantages. The data of Lee (1997) obtained from firing furnace oil of varied sulphur level into a heat exchanger with surfaces below dewpoint, show a linear, approximately forty fold increase in soluble iron deposits, that is, corrosion product, as fuel sulphur content was increased from 99 to 12 000 ppmw. Because of low-temperature corrosion, condensing heat exchange is not usually employed with oil-fired systems unless acid-resistant heat exchangers are in place. Also, sulphur is a major factor in wastage of steam generator metals operating at high temperature.

Natural gas contains no organic nitrogen but during combustion some forms via the thermal  $\text{NO}_x$  process. However, with adroit combustion systems thermal  $\text{NO}_x$  can be limited to perhaps 30 ppmv as shown in Table 4. It has therefore been possible to set lower  $\text{NO}_x$  emission limits for equipment fired with natural gas than can be achieved with petroleum fuels. Fuel oils contain organically-bound nitrogen in concentrations ranging from 0.1 to 0.5 wt %, the higher concentrations being associated with heavy residual oil. Organic nitrogen forms  $\text{NO}_x$  via mechanisms that are not easily counteracted. As a result light fuel oils typically have double, and heavy fuel oils have eight or ten times, the  $\text{NO}_x$  emissions of natural gas.

With respect to particulates, natural gas, having no ash and being a very simple hydrocarbon, only emits particulates, as carbon, under very extraordinary combustion conditions. Heavy fuel oils contain ash, perhaps 0.25% or higher, much of which are compounds of metals such as vanadium and nickel. In combustion these are emitted as particulates in the micron or sub-micron range. Also, fuel oils are commonly atomized for combustion, that is, broken up into droplets with a modal diameter of about 50 nm. Poor atomization of poor fuel/air mixing can result in the volatile components of some droplets being driven off, leaving carbon which is emitted as particulates, again in the micron or sub-micron range. It is common for particulates from oil firing to comprise about 80 or 90% carbon, as shown in Table 9. When firing heavy oil, 30 to 50% of the particulates is likely to be less than 1.8 nm in diameter, and this fraction will contain most of the metals, usually in combination with sulphur. Refined oils, properly fired, produce low concentrations of particulates, almost entirely carbon, but they may be small, e.g., a

modal diameter of 10 to 15 nm. Metals such as vanadium, and in complex combinations with sulphur, present serious corrosion problems in utility steam generators.

Figure 20, taken from Squires (1969), relates significant health effects to concentration and length of exposure to SO<sub>2</sub>. Information gained since 1967 doubtless shifts the threshold limit of significant health effects down and to the left. Likewise, the more that is learned about particulates the more danger there seems to be in small particulates of any composition. Thus, from the viewpoints of (1) human health, (2) reducing SO<sub>x</sub> and NO<sub>x</sub>, precursors to acid rain, (3) reducing equipment maintenance costs due to corrosion and (4) improving process efficiencies by enabling operation at both higher and lower temperatures, there seems to be much merit in removing sulphur and all other contaminants possible from petroleum products used for fuel.

Nearly forty years ago Voorhies et al. (1963B) demonstrated the feasibility of metals removal from crude oil and concluded that 90% removal could be accomplished at a cost of about 15 ¢/bbl, 1963 \$U.S.

About the same time, the same research team (Voorhies et al. 1963A) concluded that a crude oil containing 2.65% S could be desulphurized at a cost of 27.7 ¢/bbl to produce a residual fuel with 2.5% S, or at a cost of 37.4 ¢/bbl, to produce a residual fuel with 1.0% S. Costs presumably are again in 1963 \$U.S. A study by Bechtel Corp. in 1964 produced the graph shown in Figure 14, which indicates that 90% desulphurization of fuel oil can be accomplished at a cost of about 18 ¢/10<sup>6</sup> Btu. (\$U.S., about 1964.) The more recent study by Koslov et al. (1994) identifies several ways in which crude oil can be processed to a range of desired products, nearly all with sulphur contents less than 0.3 %.

In all the above cases, sulphur removal is accomplished by treating the crude oil or a sulphur-enriched portion of the refinery stream with hydrogen at high pressure in the presence of a catalyst. The process is admittedly sensitive to peculiarities of the feedstock, and may require prior demetallization, of itself desirable. But the technology exists, is widely used, and doubtless can be improved, in terms of effectiveness and economy, through research.

Estimates of the cost of reducing emissions tend to suffer from a too-narrow frame of reference. Table 20 from Halkos (1995) serves as an illustration. For the case of a 500 MW, coal-fired power plant, costs of desulphurization are presented in terms of dollars per tonne of sulphur removed, with some information about applicability and sulphur removal efficiency. Fuel oil desulphurization is shown as the highest-cost option, but flue gas desulphurization, supposedly more cost-effective, takes no account of boiler wastage and downtime due to corrosion. Yet corrosion is claimed to add more than 10% to the cost of electricity from, and be responsible for 50% of forced outages of thermal power plants (Syrett, 1994).

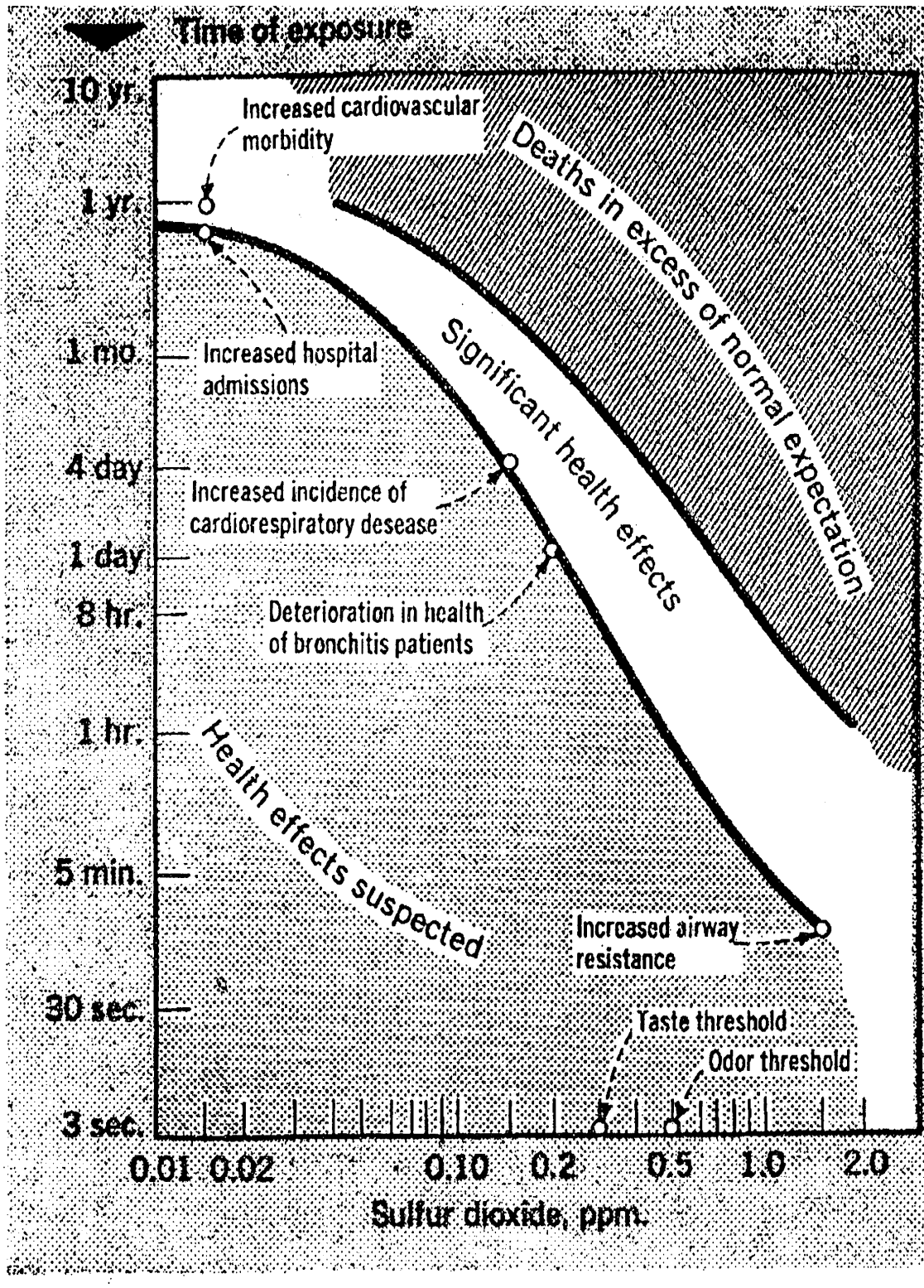


Fig. 20 - Hazards to health from sulphur dioxide pollution

Likewise, legislators may place a stringent limit on sulphur in automotive fuels and refiners may comply by shifting the sulphur to residential fuel oil, which, like the engine fuels, results in emissions close to ground level.

**Table 20** Sulphur emission abatement options and costs (Halkos, 1995)

Abatement method	Applicability	S removal efficiency %	Capital cost 10 <sup>6</sup> \$ US	Op. & maint. cost 10 <sup>6</sup> \$ US (1985)		Cost effectiveness \$/tonne of S reduction
				Fixed	Variable	
Fuel switching (e.g., coal to gas)	All users	<99	-	-	-	*
Physical coal cleaning	All users	25	-	-	-	635-1625
Heavy fuel oil desulphurization	All users	80	7.775	6.32	12.28	2100-2930
Sorbent injection		50	0.344	0.22	2.59	485-750
Atmospheric fluidized bed combustion	New power plants and industrial boilers	80	3.259	0.16	2.71	238-446
Circulating fluidized bed combustion	New plants only	85	7.061	0.35	4.77	529-835
Flue gas desulphurization	Power plants, industr. boilers and process emissions	90	29.462	1.67	4.02	650-1200
Gas oil desulphurization	All users	90	1.918	1.93	2.2	2900-3740

Costs are based on a new, 500 MW power plant using hard coal of 2% sulphur content, 70% load factor, and 5 % retention factor.

Dash indicates there is no corresponding cost.

\* Depends on relative price and sulphur content.

In the case of petroleum-based fuels, if an accurate, broadly-based cost/benefit study could be accomplished, one that encompassed effects on health, environment, equipment performance and maintenance, as well as costs of minimizing one emission or another, it might well conclude that high-severity measures to remove contaminants from crude oil at the refinery is the most cost-effective approach. Government support of the necessary research and capital investment might be justified, and essentially pure-hydrocarbon fuel oils could enjoy much of the benefit of cleanliness that is now held by natural gas.

## REFERENCES

Al-Taie and Friedrich, 1995 I. M. Al-Taie and F. D. Friedrich. "Materials for Low-NO<sub>x</sub> Boilers" CANMET review for the Canadian Electrical Association. November 1995.

Balajka, 1973 J. Balajka, "Verhütung Rauchgasseitiger Korrosionen bei der Verbrennung von Rückstandsölen" VGB Kraftwerkstechnik Vol. 53, No. 10, October 1973.

Barkley et al. 1947 J. F. Barkley, L. R. Burdick and A. A. Berk. Modern Power and Engineering, 41, 68, 1947.

Baumann, 1975 K. Baumann. "Korrosionen und Korrosionenschutz auf der Rauchgasseitige von Dampferzeugern" VGB Kraftwerkstechnik Vol. 55, No. 3, March 1975.

Brandel and Mousset, 1973 A. Brandel and P. Mousset. "Bemerkungen über die Hochtemperaturkorrosionen der mit Schweröl-Gefeuerten Dampferzeuger" VGB Kraftwerkstechnik Vol. 53, No. 4, April 1973.

Brooks, 1989 G. Brooks "Estimating Air Toxic Emissions from Coal and Oil Combustion sources" EPA-450/2-89-001 (NTIS PB 89-194229), U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, N.C., April 1989.

Coats, 1969 A. W. Coats. "The Chemistry of Deposits in Oil-fired Boilers: The Na<sub>2</sub>SO<sub>4</sub>-V<sub>2</sub>O<sub>5</sub>-SO<sub>3</sub> System" J. Inst. Fuel, Vol. 42, pp 72-85, 1969.

Crossley, 1946 H. F. Crossley. "Fuel and Future" Conference, Boiler Availability Session, Paper 4, London, Oct. 1946.

Cutler et al. 1974 A. J. B. Cutler, A. B. Hart, J. W. Laxton and C.G. Stevens. "Die Derzeitige Probleme durch Rauchgasseitige Korrosionen bei der CEGB und Neuere Forschungen zu deren Lösung" VGB Kraftwerkstechnik Vol. 54, No. 9, September 1974.

De Vecchi et al. 1996 G. De Vecchi, M. Joutsimo, R. Lecok, G. F. Munters and J. McKay. "Sulphur Dioxide Emissions from Oil Refineries and Combustion of Oil Products in Western Europe (1992)." CONCAWE Report (ISSN 0253-8644) N.6/94, April 1996.

## REFERENCES (cont'd)

- Dooley and Whittingham, 1946      A. Dooley and G. Whittingham. Trans. Faraday Society, 42, 354, 1946.
- Dooley and McNaughton, 1994      R. B. Dooley and W. P. McNaughton. "The Analysis and Mitigation of Boiler Tube Failures: Theory and Practice" Vol. 2 Water-Touched Tubes Draft Report, December 1994.
- Faller et al. 2001      M. Faller, M. Schicker and P. Richner. "Corrosion Protection of Condensing Boilers with Organic Coatings" 2000 EU Conference on Industrial Furnace And Boilers, pp 447 – 456, August 2000.
- Federal Industrial Boiler Program, 1994      "Low NO<sub>x</sub> Technology Assessment and Cost/Benefit Analysis" Prepared by Federal Industrial Boiler Program, CANMET, Natural Resources Canada, 1994.
- Friedrich et al. 1992      F. D. Friedrich, V. V. Razbin and F. L. Wigglesworth. NO<sub>x</sub> and SO<sub>2</sub> Emissions with No. 6 and No. 4 Fuel Oils at Canadian Forces Base Halifax" Energy Research Laboratories Division Report ERL 92-27, CANMET, Energy, Mines and Resources Canada, March 1992.
- Gallegos et al. 2001      M. A. Gallegos, C. A. Romo, H. M. Espino, E. J. Garza and A. M. Gonzalez. "Influence of Burner Design on Formation of Pollutant Emissions in Oil Combustion" Technologies and Combustion for a Clean Environment Vol. II 20.3, pp 653 – 658, 2001
- Glaubitx, 1963A      F. Glaubitx. "The Economic Combustion of Sulphur-Containing Heating Oil, Part I" Combustion, Vol 34, No. 7, pp 31-35, January 1963.
- Glaubitx, 1963B      F. Glaubitx. "The Economic Combustion of Sulphur-Containing Heating Oil, Part II" Combustion Vol. 34, No. 9, pp 25-27, March 1963.
- Goksøyr and Ross, 1963      H. Goksøyr and K. Ross. "The Relationship Between Acid Dewpoint and Sulphur Trioxide Content of Flue Gases." Thornton Research Center, Shell Research Ltd., 1962.
- Gulyurtlu et al. 1996      I. Gulyurtlu, H. Lopes and I. Carbita. "The Determination of Emissions of Pollutants from Burning Waste Oils" Fuel Vol.75 No. 8 pp 940-944, 1996
- Halkos, 1995      G. Halkos. "Evaluation of the Direct Cost of Sulphur Abatement Under the Main Desulphurization Technologies" Energy Sources, Vol. 17, pp 391-412, 1995.

## REFERENCES (cont'd)

- Hangebrauck et al. 1964 R. P. Hangbrauck, D. J. Von Lehmden, J. E. Meeker. "Emissions of Polynuclear Hydrocarbons and Other Pollutants from Heat-Generation and Incineration Processes" J. Air Pollution Control Assoc., 14, 267 – 278, 1964.
- Hedley, 1962 A. B. Hedley. "Sulphur Trioxide in Combustion Gases" Fuel Society Journal, 43, pp 45-54, 1962.
- Herger et al. 1996 M. Herger, C. Hubner, F. Hegler, P. Zobl and A. Hackl. "Emissionen aus Ölheizungen in Stationären Betriebszustand." Erdöl, Erdgas Kohle, 112 Jahrgang, Hieft 10, October 1996.
- Huffman et al. 2000 G. P. Huffman, F. E. Huggins, N. Shah, C. A. Miller, W. P. Linak, et al. "Characterization of Fine Particulate Matter Produced by Combustion of Residual Oil." JA&WMA Vol. 50, pp 1106–1114, July 2000.
- Illinois State Geological Survey, 1992 "Behavior of Sulphur and Chlorine During Combustion and Boiler Corrosion." The Center for Research on Sulphur in Coal, Quarterly Report for the Period Ending 2/29/92, Illinois State Geological Survey.
- Johnstone, 1929 H. F. Johnstone. "An Electrical Method for the Determination of the Dew Point of Flue Gases." Univ. Ill. Engineering Experimentation Station Circular 20, 1929
- Johnson et al. 1994 D. W. Johnson, K. H. Schulze and J. F. Carrigan. "Integrated Flue Gas Treatment and Heat Recovery Using a Condensing Heat Exchanger." Babcock and Wilcox RDTPA 94-54, presented at the Institute of Clean Air Companies Forum '94, Arlington, Virginia, November 1-2, 1994.
- Kautz and Kirsch, 1973 K. Kautz and H. Kirsch. "Zur Einfluß des Vanadiums auf die Hochtemperaturkorrosionen in lgefeuerten Kesseln." VGB Kraftwerkstechnik Vol. 53, No. 9, September 1973.
- Kirsch and Reichel, 1977 H. Kirsch and H. Reichel. "Role of Oxide Layers in Gas-side High Temperature Corrosion." VGB Kraftwerkstechnik (English edition) Vol. 57, No. 8, August 1977.
- Koslov et al. 1993 I. T. Koslov, S. G. Ashitko, M. B. Kostyukovskaya and N. M. Karpova. "Comparative Evaluation of Prospective Technologies for the Production of Low-Sulphur Boiler Fuel" Chemistry and Technology of Fuels and Oils. Vol. 29, No. 11-12, 1993.

## REFERENCES (cont'd)

Krause, et al, 1975 H. H. Krause, D. A. Vaughan and W. K. Boyd. "Corrosion and Deposits from Combustion of Solid Wastes. Part III – Effects of Sulfur on Boiler Tube Metals" Transactions of the ASME, Journal of Engineering for Power, 97(3) Series A, pp 448-452, July 1975.

Kung and Eckhart, 1993 S. C. Kung and C. F. Eckhart. "Corrosion of Iron-base Alloys in Reducing Combustion Gases." Paper No. 242, NACE Corrosion Conference, 1993.

Lee et al. 1966 G. K. Lee, E. R. Mitchell, R. G. Grimsby and D. H. Benn. "Formation of Oil Ash Deposits on Boiler Surfaces and Control by an Additive." Proceedings of the American Power Conference, Vol 28, pp 613- 631, 1966.

Lee et al. 1967 G. K. Lee, Friedrich, F. D. and E. R. Mitchell. "Effect of Fuel Characteristics and Excess Combustion Air on Sulphuric Acid Formation in a Pulverized-Coal-Fired Boiler" J. Inst. Fuel, 1967 (Sept.), 40, pp 397 – 405.

Lee et al. 1969 G. K. Lee, G.K. Lee, F.D. Friedrich and E.R. Mitchell. "Control of SO<sub>3</sub> in Low Pressure Heating Boilers by and Additive" J. Inst. Fuel, Vol. 67, February 1969

Lee, 1997 W. Lee. "The Performance of Oil-fired Boilers: The Influence of Fuel Sulphur on Emissions and Appliance Integrity." ASHRAE Transactions Vol 103, part 1, 1997.

Levy and Merryman, 1965 A. Levy and E. L. Merryman. "SO<sub>3</sub> Formation in H<sub>2</sub>S Flames." Transactions of the ASME, Journal of Engineering for Power, 87 Series A, pp 116-123, January 1965.

Levy and Merryman, 1966 A. Levy and E. L. Merryman. "Interactions in Sulphur Oxide-Iron Oxide Systems." ASME Paper No. 66-WA/CD-3. Journal of Engineering for Power, pp 297-303, April 1967.

Lin and Hsieh, 1995 Cheung-Yuan Lin and Ming-Ju Hsieh. "Emissions of Oil-Fired Furnaces Burning with Sodium Chloride-contained Air" J. Environ. Sci. Health, A30(7), pp 1473-1487, 1995.

Lisle and Sensenbaugh, 1965 E. S. Lisle and J. D. Sensenbaugh. "The Determination of Sulphur Trioxide and Acid Dewpoint in Flue Gases" Combustion 36, 7, pp 12-16, January 1965.



## REFERENCES (cont'd)

- Miller et al. 1996 C. A. Miller, J. V. Ryan and T. Lombardo. "Characterization of Air Toxics from an Oil-fired Firetube Boiler" JA&WMA, Vol. 46, pp 742–748, August 1996.
- Miller et al. 1998 C. A. Miller, W. P. Linak, C. King and J. O. L. Wendt. "Fine Particle Emissions from Heavy Fuel Oil Combustion in a Firetube Package Boiler" Combustion Science and Technology Vol. 134, pp 477-502, 1998.
- Mohr et al. 2000 M. Mohr, V. Schmatloch and H. P. Zaugg. "Investigation of Fine Emissions of Small Oil-Fired Boilers." Second European Conference on Small Burner and Heating Technology Vol. I, pp 179–186, 2000.
- Nimmo et al. 1998 W. Nimmo, E. Hampartsoumian, K. J. Hughes and A. S. Tomlin. "Experimental and Kinetic Studies on the Effect of Sulphur-Nitrogen Interaction on NO Formation in Flames" Twenty-Seventh International Symposium on Combustion, pp 1419–1426, 1998.
- Pollman, 1965 S. Pollman. "Mineralogisch-kristallographische Untersuchungen an Schlacken und Rohrbelägen aus dem Hochtemperaturbereich Ölgefeuerter Gro-kessel." Mitteilungen der VGB, Vol. 94, 1965.
- Razbin et al. 1991 V. V. Razbin, F. D. Friedrich and S. W. Lee. "Heating Plant Performance and Emissions, Nova Scotia Hospital, Dartmouth, N. S." Energy Research Laboratories Division Report ERL 91-86 CANMET, Energy, Mines and Resources Canada, 1991.
- Reese et al. 1965 J. T. Reese, J. Jonakin and V. Z. Caracristi. "Prevention of Residual Oil Combustion Problems by Use of Low Excess Air and Magnesium Additive" Transactions of the ASME, Journal of Engineering for Power, pp 229-236, April 1965.
- Schneider et al. 2000 D. R. Schnieder, N. Duic and Z. Bogdan. "SO<sub>3</sub> Reduction in the 210 MWe Oil-fired Power Plant Sisak." 2000 EU Conference on Industrial Furnace and Boilers, pp 301–309, August 2000.
- Singer, 1981 J. G. Singer, editor. "Combustion – Fossil Power Systems" Third Edition, 1981. Combustion Engineering Inc.
- Squires, 1967 A. M. Squires. "Air Pollution: The Control of SO<sub>2</sub> from Power Stacks – Part I - The Removal of Sulphur from Fuels" Chemical Engineering, pp 260–268, November 6, 1967.

## REFERENCES (cont'd)

- Speight, 2000 J. G. Speight "The Desulphurization of Heavy Oils and Residua", 2<sup>nd</sup> Edition, Marcel Dekker, New York; 2000, ISBN 0-8247-8921
- Stacey, 1971 M. J. Stacey. "Oil Refineries Prepare for Anti-Pollution Controls" Chemical and Process Engineering, pp 63–70, March 1971.
- Stelliga and Burnett, 1970 D. J. Stelliga and D. J. Burnett. "The Design and Development of Low Excess Air Burners for Oil and Gas" Babcock and Wilcox Canada Ltd. Bulletin 70-4, 1970.
- Syrett, 1994 B. C. Syrett. "Impact of Corrosion in Electric Power Plants" Materials and Components in Fossil Energy Applications, No 110, June 1994.
- Taylor, 1942 A. Alan Taylor. J Inst. Fuel 16, 25, 1942.
- Tolley, 1948 G. Tolley. J. Soc. Chem. Ind. 67, pp 369-401, 1948.
- Voorhies et al. 1963A A. Voorhies, W. J. Metrailler, C. N. Kinberlin, Jr. and C. E. Jahnig. "Improvement of Fuel Oil Quality Part II – Desulphurization of Residual Fuels." Mechanism of Corrosion by Fuel Impurities, Proceedings of the International Conference held at Marchwood Engineering Laboratories, Marchwood, Hampshire, May 20–24, 1963.
- Voorhies et al. 1963B A. Voorhies, C. E. Adams, C. N. Kinberlin, Jr. and C. E. Jahnig. "Improvement of Fuel Oil Quality Part I – Demetallization of Residual Fuels." Mechanism of Corrosion by Fuel Impurities, Proceedings of the International Conference held at Marchwood Engineering Laboratories, Marchwood, Hampshire, May 20–24, 1963.
- Wahnschaffe, 1971 E. Wahnschaffe. "Ein Beitrag zur Umwandlung von SO<sub>2</sub> zu SO<sub>3</sub>" Mitteilungen der VGB Vol. 51, No. 5, October 1971.
- Whaley et al. 1995 H. Whaley, J. Wong, G. Banks and W. Lee. "The Composition and Handling Properties of Several Heavy Bitumen Emulsions" ASME International Joint Power Conference, Minneapolis MN, 1995.
- Whaley et al. 1996 H. Whaley, J. Wong, S. Win Lee and G. Banks. "Combustion, Heat Transfer and Handling Characterization of a Biomass-Derived Fast Pyrolysis Liquid Fuel Product" Finnish-Swedish Flame Days 1996, September 3–4, 1996.

## REFERENCES (cont'd)

Weber et al. 2001 R. Weber, S. Orsino, A. L. Verlaan and N. Lallemand.  
“Combustion of Light and Heavy Fuel Oils in High-Temperature Air” Journal of the  
Institute of Energy Vol. 74, pp 38-47, June 2001.

Whittingham, 1948 G. Whittingham. Trans. Faraday Society, 44, 141, 1948.

Whittingham, 1949 G. Whittingham. “The Oxidation of Sulphur Dioxide in  
Combustion Processes” Third Symposium on Combustion, Flame and Explosion  
Phenomena, University of Wisconsin, pp 453-459 1949.