

**SULFUR DIOXIDE REMOVAL
FROM
WASTE GASES**

SECOND EDITION

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**A.V. Slack
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NOYES DATA CORPORATION

Park Ridge, New Jersey

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PREFACE TO SECOND EDITION

Almost all of that which was said nearly four years ago in the preface to the first edition of this book applies equally well today. Sulfur oxide removal from waste gases is still a problem of major concern, and the technology is still changing very rapidly.

There have been several major changes and developments in the field. Some of the methods described in the first edition are omitted from the present one because they have been casualties of the competitive situation. Others that were mentioned only sketchily or not at all have come to the fore and now occupy significant positions.

Probably the main development is the rapid increase in the number of full-scale scrubber installations, of which there were very few in 1971. This is particularly true in Japan where regulations are fast becoming more stringent.

A better understanding of the basic chemical and physical factors in SO_2 absorption has also been developed over the past few years, but there is still some distance to go.

The authors appreciate the many indirect contributions by development, engineering, and operating people in the field. Since most of the work is not yet published, a book like the present one could not be written without such contributions.

A.V. Slack

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March 30, 1975

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March 30, 1975

PREFACE TO FIRST EDITION

This book is not a reference work, but rather a status report on a technology that is being developed under forced draft. Sulfur oxide removal from waste gases is not a new problem. Smelter operators for more than a century have coped with the unwanted fumes produced by oxidation of the sulfur in the ore during roasting. Power plants, refineries, sulfuric acid plants, and Claus sulfur plants have perhaps a more recent history, but even for these industries the problem goes back for half a century or more. It is only in the last few years, however, that sulfur oxide removal has become a major research and development effort. Pressures to improve the environment have made it necessary to greatly expand activity in the field, in somewhat of a crash program.

Presently there are hundreds of organizations around the world giving attention to the problem, in a general way or in developing removal methods and evaluating them for use. Processes are in all stages of development, from the idea stage to plant trials. Numerous and widely differing chemical paths are being explored, and process flowsheets ranging from very simple to very complicated are being developed.

In this context, a reference book does not seem appropriate because the technology is changing too fast. There is no basic body of information that could be presented, because the various processes under study not only cut across much of the entire field of sulfur chemistry but also involve many of the chemical engineering unit operations. Moreover, the nitrogen oxide and particulate matter problems cannot be dissociated from that of removing sulfur oxides.

Because of this, the book is intended to serve only as an overview of the current development situation, written from the viewpoint of one who is involved both in process development and in the selection of processes for use by a major utility. An effort has been made to list all the major processes (and as many of the minor ones as feasible), summarize the basic chemistry of each, analyze the engineering problems, identify advantages and disadvantages, evaluate the effect of major economic factors, and make a guess as to how each process compares with the others.

This is obviously an ambitious undertaking and one that cannot be wholly accurate and well-documented; it is, however, the type of analysis that must be carried out by those responsible for fitting plants around the world with sulfur oxide removal facilities. No process yet proposed is a completely satisfactory solution to the problem but many have promise; at some point it is necessary to set them all side by side and see which looks best, even though in a preliminary and incomplete way. This book represents such a beginning.

The information on which the analyses presented herein are based comes from many sources. Some of it is readily available as published material, but the bulk is from two sources: unpublished reports and published documents not widely distributed or publicized, and discussions with other workers in the field. There is a large amount of such information that is nonproprietary but not widely known. Of particular benefit have been visits to research organizations in all the countries of Europe and Asia (with the exception of the USSR) that have active programs in the field.

It should be emphasized that the analysis presented is for the current situation only. With the fast moving pace in the field, such an overview made a year from now may be quite different. New processes will be announced, older ones will change in status, and commercial units now being constructed will add the final proof to some processes. If this book has any value, it is in getting everything together to serve as a starting point in analyzing sulfur oxide removal technology with adjustments to be expected as the technology matures. In spite of best efforts, errors no doubt have crept into the descriptions and evaluations of some of the processes. Hopefully, these will be few.

The list of acknowledgements due is too long to include. The main contribution have come from the large number of research and development people with whom I have discussed the problems in developing an effective and economical sulfur oxide removal technology (and whose indulgence I invite where my evaluations differ from theirs). Several of my coworkers have reviewed and corrected the text, and my secretary, Mrs. Juanita Hargett, carried out the mechanics of the project quite efficiently. Finally, without the patience and forbearance of my wife, this project would have failed in the early stages.

A.V. Slack

Muscle Shoals, Alabama

June 17, 1971

CONTENTS AND SUBJECT INDEX

1. THE PROBLEM	1
Sources	1
Power Production from Coal	2
Power Production from Oil	12
Other Uses of Coal and Oil	13
Metal Ore Smelting	13
Petroleum Refining	14
Sulfuric Acid Production	14
Alternatives for Control	15
High Stacks	15
Low Sulfur Fuel	16
Operational Control	17
Major Considerations in Removal from Stack Gas	17
Process Type	18
Throwaway Versus Recovery	18
Wet Versus Dry	19
Degree of Removal Needed	19
New Plant Versus Retrofit	20
Scope of Present Effort	20
Current Status of Process Development	23
2. THROWAWAY OPERATION—DRY PROCESSES	26
History of the Process	27
Thermochemistry	30
Calcination	30
Sulfation and Oxidation	31
Disproportionation of Sulfite	31
Decomposition of Sulfite and Sulfate	31
Kinetics	31
Chemical Considerations	32
Mass Transfer and Overall Reaction Models	36
Process Considerations	40
Fluidized Bed Combustion	40

Limestone Availability	43
Fuel Type	44
Solids Disposal and Water Pollution	44
Economics	45
Investment	45
Operating Costs	45
3. THROWAWAY OPERATION—DIRECT LIME/LIMESTONE SCRUBBING	47
History of the Process	49
Chemistry	52
Kinetics	61
Rate Factors	62
Transfer Rates	68
Process and Design Considerations	68
Choice of Absorbent	68
Dust Removal	70
Gas Recooling	71
Deposition of Soft Solids	72
Scaling	73
Scrubber Design and Performance	77
Absorption Efficiency	81
Mist Separation	84
Stack Gas Reheat	86
Sludge Disposal	91
Water Balance	95
Materials of Construction	97
New Developments	98
Use of Weak Acids	99
Calcium Chloride Addition	99
Rotary Drum Scrubber	100
Economics	101
Investment	101
Operating Cost	102
4. THROWAWAY OPERATION—INDIRECT LIME/LIMESTONE SCRUBBING	103
Current Status	106
Sodium-Based Processes	106
ADL-CEA	106
General Motors	112
FMC	112
Envirotech	116
Kureha-Kawasaki	116
Showa Denko	118
Ammbnia-Based Processes	119
Nippon Kokan	119
Kuhlmann	119
Smelter Control Research Association (SCRA)	120
Other Absorbents	120
Monsanto	120
Kurabo	120
Dowa Mining	123

Water Scrubbing	124
Carbon Adsorption	126
5. ECONOMIC FACTORS IN RECOVERY	127
General Considerations	127
Investment and Operating Cost Factors	128
Physical Form of Sorbent	129
Fuel Type	131
Sulfur Content of Fuel or Ore	132
New Versus Existing Plant	134
Plant Size	134
Plant Complexity	135
SO ₂ Removal	137
Dust Removal	137
Capacity Factor	137
Product Type	139
Basis of Financing	141
Product Marketing	145
Plant Location	145
Product Quality	146
Market Potential	147
6. RECOVERY PROCESSES—GENERAL PROBLEMS	149
Dust Removal	152
High Temperature Processes	152
Liquid Absorbents	153
Types of Dust Removal Equipment	154
Sorption by Solids	155
Contactor Design	155
Granule Resistance to Cycling	158
Absorption by Liquids	159
Gas Humidification and Cooling	159
Scrubber System Design	160
Conversion of Intermediates	161
Sulfur Dioxide	161
Hydrogen Sulfide	165
Other Intermediates	166
Nitrogen Oxides	166
7. ALKALI ABSORBENTS	169
Sulfite-Bisulfite Equilibrium	170
Ammonia Scrubbing	172
Absorption Chemistry and Kinetics	173
Scrubber Design	174
Fume	176
Regeneration Process	179
Sodium Compounds	204
Absorption by Solids	204
Scrubbing Processes	207
Potassium Compounds	222
Thermal Regeneration	222
Reduction	224
Mixed Carbonates	224

8. ALKALINE EARTH ABSORBENTS	227
Magnesium	227
Analogy to Magnesium-Based Wood Pulping	227
Scrubber Design and Performance	229
Drying and Calcination	230
Process Variations	233
Calcium	238
Chemistry of Absorption Product Regeneration	238
Analogy to Gypsum Reduction	240
Process Variations in Regeneration	243
Nonregenerative Methods	248
9. METAL OXIDES	249
Chemistry of Metal Oxide Sorption	249
Process Variations	251
Manganese Oxides	251
Copper Oxide	254
Zinc Oxide	260
Iron Oxides	262
Other	262
10. ADSORPTION	264
Chemical and Physical Factors	264
Process Variations	266
Regeneration by Heating	266
Regeneration by Washing	271
Regeneration by Reduction	277
11. CATALYTIC OXIDATION AND REDUCTION	280
Oxidation in Dry Systems	280
High Temperature	282
Low Temperature	289
Oxidation in Aqueous Systems	291
Reduction	292
Reduction with H_2S	293
Reduction with CO	293
Reduction with Carbon	294

THE PROBLEM

Of the several air pollutants that plague the world, sulfur oxides (SO_2 , sulfur dioxide, and SO_3 , sulfur trioxide) have received special attention—more so than any other polluting material except perhaps particulate matter (dust). The severity of the problem—effects on people, animals, and vegetation—is a matter on which there are varying opinions and will not be debated here. A more important consideration for the present discussion is that control of sulfur oxide emission has come to be regarded as a matter of great importance both by governmental regulatory agencies and the general public.

A major concern is the very large amount of sulfur oxides emitted. Various estimates have been made; the general consensus is that the U.S. emission in 1970 was over 35,000,000 tons. Similar data for other parts of the world are not readily available but it is known that emission is heavy in all highly industrialized countries, particularly in areas such as the Ruhr Valley in Germany and the Tokyo area in Japan. Emission is also increasing at a rapid rate. The potential emission for the year 2000 has been estimated to be over three times that for 1970.

SOURCES

Practically all SO_2 (and SO_3) comes from combustion of naturally occurring sulfur compounds, either as elemental sulfur or as a constituent of an ore or a fossil carbonaceous material. Examples are organic sulfur compounds in coal and petroleum, pyrites (FeS_2), both as such and as a constituent of coal, hydrogen sulfide (H_2S) in sour natural gas, and metal sulfide ores. The reasons for oxidizing these materials are varied; elemental sulfur and pyrites are burned to make SO_2 in the process of producing sulfuric acid, metal ores are roasted to burn away the sulfur in recovering the elemental metal (e.g., zinc, copper, and lead), the H_2S is separated from natural gas and part of it burned to SO_2 as one step in conversion to elemental sulfur, and coal and oil are burned for heating and for power production.

In most cases the overall process includes a unit for recovering SO_2 from the gas stream emitted, either because sulfur or sulfuric acid is the primary product or because the SO_2 concentration in the gas is high enough to make recovery as a by-product economical. (However, there is still a pollution problem because recovery is never complete.) The burning of carbonaceous fuel is a major exception; the exit gases from heat recovery units are so dilute in SO_2 that no effort normally is made to remove the pollutant from the stack gas. The relative contributions of the various sources to the SO_2 emission problem are given in Table 1.1.

TABLE 1.1: WORLD-WIDE SO_2 EMISSION

<u>Sources</u>	<u>Emissions, 10^6 tons per yr</u>
Coal	102
Petroleum	28
Nonferrous smelting	16
Industrial	6
Total man-generated SO_2 :	152
Marine	60
Land H_2S (SO_2 equivalent)	140
Total natural sources oxidized to SO_2 :	200
Sulfur in SO_4 from sea salt (SO_2 equivalent)	88
Total world-wide:	440

It is clear from these data that coal is the main culprit, contributing almost 70% of the total man-made emission. Moreover, other data show that production of power from coal and oil accounts for almost half the man-made total.

Power Production from Coal

Since the problem thus is centered in power plants and mainly in coal-burning power plants, the future of coal-based power becomes a major consideration. With the exception of oil, the other major competitors to coal as an energy source, hydroelectric and nuclear, do not produce SO_2 and therefore one way of reducing the problem is to adopt such alternate sources to a greater degree. The potential for hydroelectric is well nigh exhausted and further significant growth is not expected.

Nuclear, however, is increasing rapidly (Figure 1.1). It is estimated that by 2000 over half of the electrical power will be generated by the nuclear method, with coal (plus other fossil fuel) declining to about 30%. Nevertheless, overall power production is expected to increase so much by 2000 that fossil fuels, while losing percentagewise, will increase in total usage by almost twofold over current consumption. Hence the severity of the SO_2 problem will continue to grow.

FIGURE 1.1: PROJECTED SOURCES OF POWER IN THE U.S.

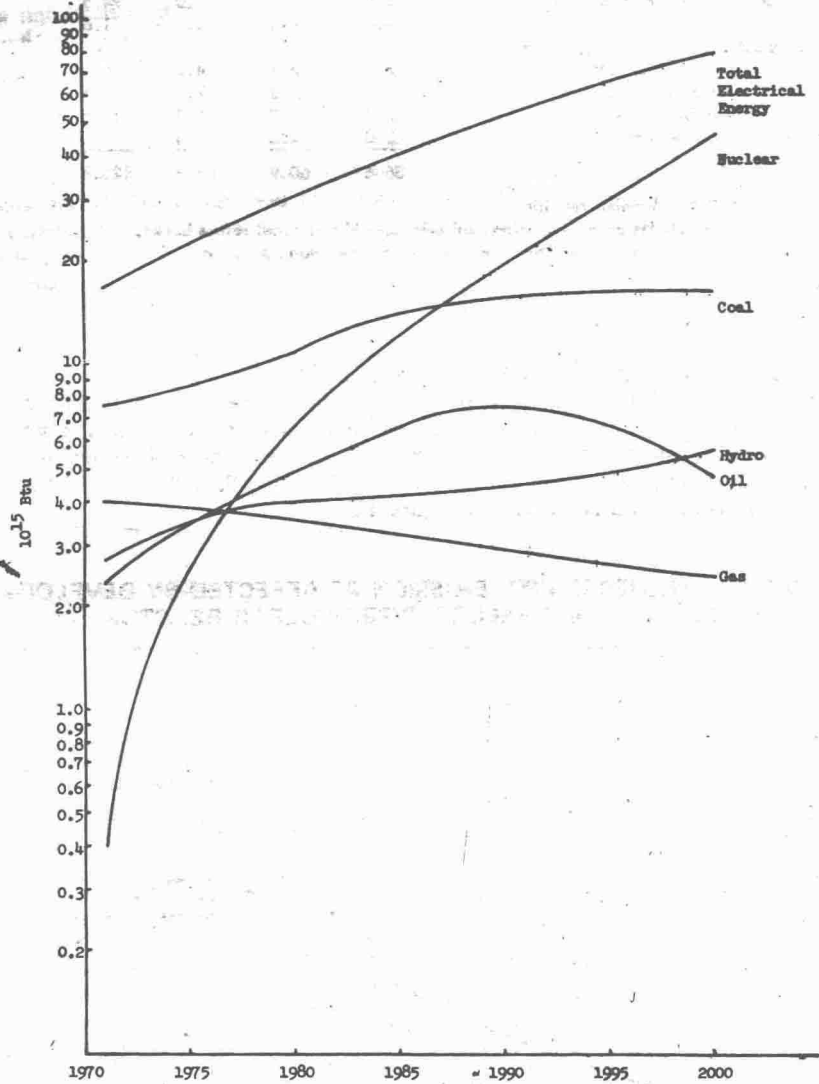


TABLE 1.2: ESTIMATED SULFUR DIOXIDE EMISSION IN U.S. WITHOUT ABATEMENT

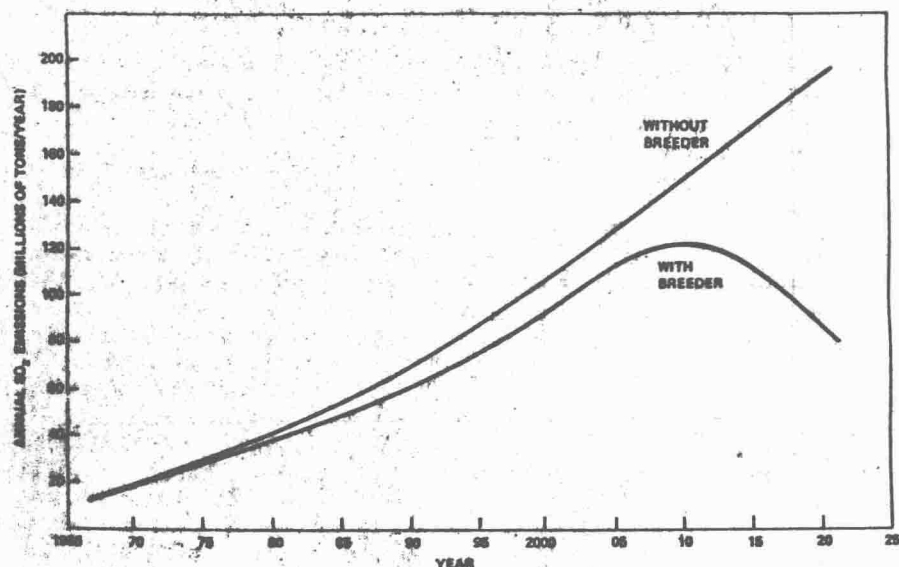
	Annual Emission of Sulfur Dioxide (millions of tons)			
	1970	1980	1990	2000
Power plant operation (coal and oil)*	20.0	41.1	62.0	94.5
Other combustion of coal	4.8	4.0	3.1	1.6
Combustion of petroleum products (excluding power plant oil)	3.4	3.9	4.3	5.1
Smelting of metallic ores	4.0	5.3	7.1	9.6
Petroleum refinery operation	2.4	4.0	6.5	10.5
Miscellaneous sources**	2.0	2.6	3.4	4.5
Total	36.6	60.9	86.4	125.8

* With breeder reactor.

** Includes coke processing, sulfuric acid plants, coal refuse banks, refuse incineration, and pulp and paper manufacturing.

February 1970 estimates by National Air Pollution Control Administration, excluding transportation.

The changing distribution between sources is given in Table 1.2 above. It should be noted that even the major increase in this estimate may be conservative as it assumes development and wide adoption of the breeder reactor, which is generally considered essential for major conversion to nuclear power as an energy source. Potential power plant emission of SO_2 in the U.S. with and without the breeder reactor are compared in Figure 1.2.

FIGURE 1.2: PROJECTED SO_2 EMISSION AS AFFECTED BY DEVELOPMENT OF THE BREEDER-TYPE NUCLEAR REACTOR

Source: NAPCA, February 1970

Another factor will also aggravate the situation. In the interest of economy, the evolutionary trend has been to larger and larger power production units and to greater production (by multiple units) at individual sites. Boiler size has reached the 1100 to 1300 Mw (megawatt; equals 1000 kilowatts or 1,000,000 watts) range and central stations producing over 2500 Mw are in operation; for a typical coal of the high-sulfur type, such stations emit over 1,500 tons of SO_2 per day. The significance of this is that damage from a pollutant such as SO_2 depends mainly on its concentration at ground level, and this depends much more on the amount emitted at a particular site than on the total amount over the entire country.

Increase in overall amount mainly produces more sites at which emission becomes a problem; larger central stations, however, make the individual problem more severe and intensify the need for remedial action. The amount of SO_2 emitted at a particular site depends, of course, on the sulfur content of the coal burned. Coals vary widely in this respect; the bituminous type generally used in power plants is highest in sulfur, although there is much bituminous coal of low sulfur content. Subbituminous, lignite, and anthracite generally contain less than 1% sulfur. The situation in regard to coal type and geographical location of reserves (in the U.S.) is summarized in Table 1.3. The totals given are for the total coal in the United States of the type listed. States with small amounts are not listed and for some of the states listed, the amount is insignificant as indicated by a dash.

TABLE 1.3: SULFUR CONTENT OF U.S. COAL RESERVES*

Coal Type and Location		Billion Tons of Coal with Indicated Sulfur Content		
		<1%	1 to 3%	>3%
Bituminous				
Alaska		21	—	—
Colorado		62	—	—
Illinois		—	21	119
Indiana		—	16	19
Kentucky (West)		—	5	32
Kentucky (East)		22	7	—
Missouri		—	—	79
New Mexico		11	—	—
Ohio		—	13	38
Pennsylvania		1	50	7
Utah		22	—	4
West Virginia		47	45	9
Wyoming		13	—	—
Total		215	191	322
Subbituminous				
Alaska		71	—	—
Colorado		17	—	—
Montana		131	—	—
New Mexico		51	—	—
Wyoming		108	—	—
Total		387	—	—

(continued)

TABLE 1.3: (continued)

Coal Type and Location	Billion Tons of Coal with Indicated Sulfur Content		
	<1%	1 to 3%	>3%
<u>Lignite</u>			
Montana	84	--	--
North Dakota	319	--	--
Total	406	41	--
<u>Anthracite</u>			
Pennsylvania	12	--	--
Total	15	--	--
Grand Total	1,023	234	322
Per cent	65	15	20

* Only major reserves are included.

From this it is evident that there is plenty of low sulfur coal (defined as coal of less than 1% sulfur content) in the ground. Unfortunately, most of it is of the type not usually burned in power plants. Moreover, by far the greatest tonnage is in the western states where population density is low; in the eastern areas, where power consumption is high and where most of the power is produced, only a relatively small area (West Virginia and eastern Kentucky) has significant low sulfur coal reserves.

The nonbituminous, low sulfur types can be burned in power plants, of course, but normally are not because of factors such as low heating value, difficulty in getting good combustion, and location. Recent advancements have reduced the boiler design problem, but the other drawbacks still remain.

The composition of the combustion gases evolved in the burning of coal is an important factor in pollution abatement, not only because of pollutant concentrations but also because nonpollutants in the gas stream can have major effects on processes or techniques for pollutant removal. Only nitrogen (from the combustion air) passes through the removal system without effect.

Coal is such a complex and variable raw material (Table 1.4) that the combustion gas contains many compounds, both gaseous and solid. Moreover, the variability in coal composition is so great that a generally applicable analysis of the stack gas cannot be given.

The composition given in Table 1.5 is fairly typical of stack gases evolved in burning western Kentucky coal. Variations from this occur for various reasons, including composition of the coal, type of boiler, and the way in which the boiler is operated; typical effects of such factors are shown in Table 1.6.

TABLE 1.4: EXAMPLE OF COAL COMPOSITION*

Constituent	Percent by Weight
Volatile matter	32.9
Fixed carbon	46.4
Sulfur	3.3
Moisture	5.4
Ash	12.0
	100.0
H	4.5
N	1.3
C	66.0
O	7.5
S	3.3
Ash	12.0
Moisture	5.4
	100.0

* Coal from western Kentucky. Coals vary so widely in composition that this example should not be regarded as typical.

TABLE 1.5: COMPOSITION OF STACK GAS EVOLVED IN BURNING COAL FROM WESTERN KENTUCKY*

Constituent	Percent by Volume**
Nitrogen (N ₂)	74.56
Carbon dioxide (CO ₂)	12.55
Oxygen (O ₂)	4.87
Water vapor (H ₂ O)	7.76
Sulfur oxides (SO _x)	
Sulfur dioxide (SO ₂)	0.22
Sulfur trioxide (SO ₃)	0.001
Nitrogen oxides (NO _x)	0.04
Particulate matter,	
Percent by weight	0.66
Grains per standard cu. ft. (scf)	3.59

* Composition, percent: C, 66.0; S, 3.3; ash, 12.0; N, 1.3.

** Except as indicated.

TABLE 1.6: EFFECT OF BOILER TYPE AND SULFUR CONTENT OF COAL ON STACK GAS COMPOSITION

Boiler type	Pulverized coal (horizontal, frontal-fired)			Cyclone-fired		
	2.0	3.5	5.0	2.0	3.5	5.0
Sulfur content of coal, % by wt						
Flue gas composition, % by volume						
Nitrogen	74.62	74.55	74.49	74.59	74.52	74.46
Carbon dioxide	12.57	12.55	12.54	12.57	12.55	12.54
Oxygen	4.85	4.86	4.85	4.85	4.85	4.82

(continued)