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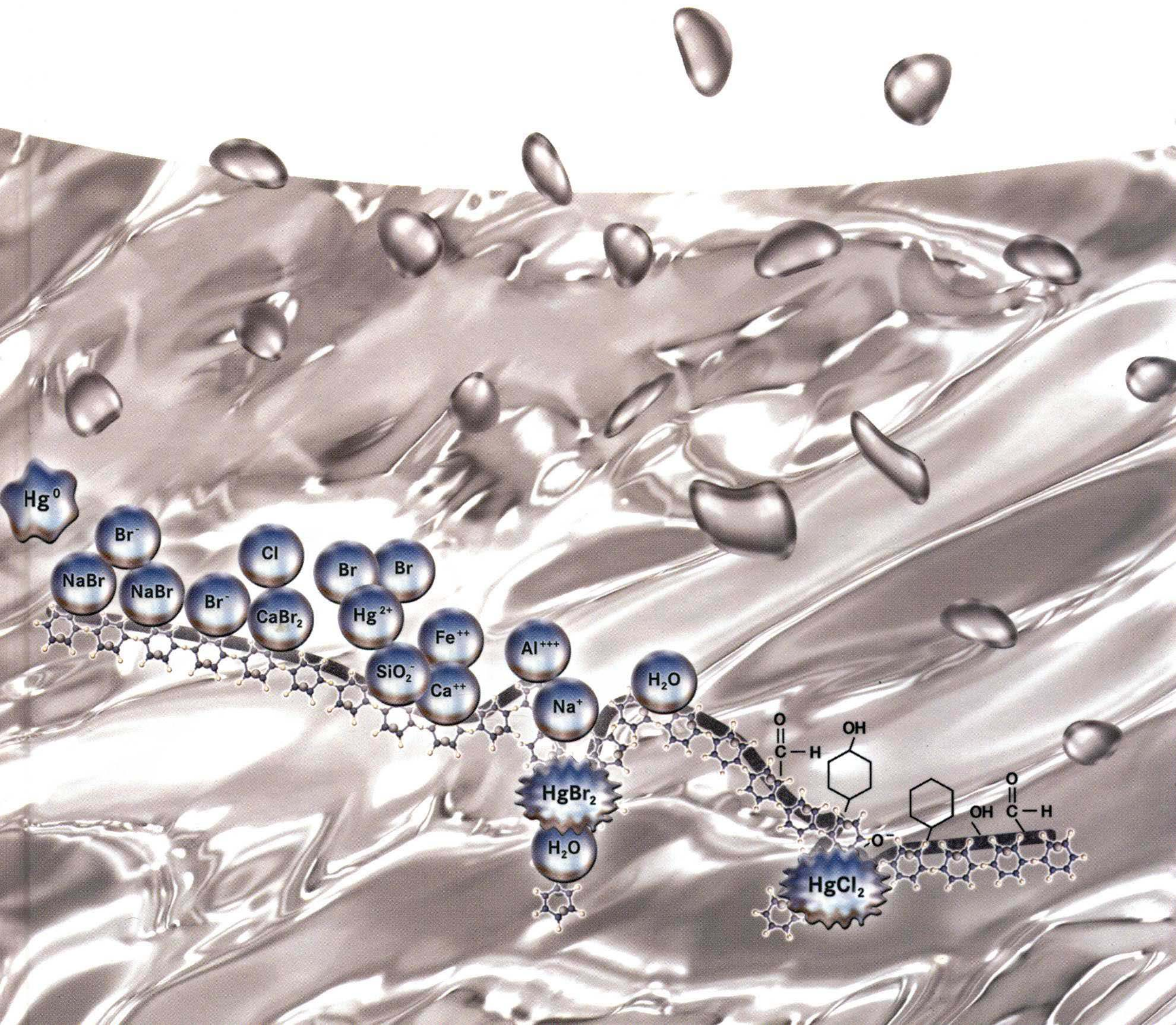
Edited by Evan J. Granite, Henry W. Pennline,
and Constance Senior

Mercury Control

for Coal-Derived Gas Streams



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Mercury R&D Book Foreword

This book is very timely and important, because as I write this foreword, the U.S. Environmental Protection Agency (EPA) is finalizing the first mercury emission limitations on coal-fired power plants, known as the *Mercury and Air Toxics Standards* (*MATS*) rule. This regulation will require significant reductions of the amount of mercury (and other chemicals) contained in the coal fuel before the flue gas is released into the atmosphere.

The information in this volume has mostly been developed over the past decade, where I was engaged as a front line research manager for one of the largest power companies in the United States, Southern Company, which has many coal-fired power plants in its fleet. I have testified before the U.S. Senate on mercury chemistry and behavior in coal-fired boilers (*http://epw.senate.gov/108th/Monroe_060503.htm*), and have been in a leadership position for the utility industry in several organizations, namely, the Electric Power Research Institute (EPRI), the Coal Utilization Research Council (CURC), and the Utility Air Regulatory Group (UARG). I was the project manager for one of the first full-scale power plant tests of dedicated mercury control, at Alabama Power's Plant Gaston – which won an *R&D Magazine* "R&D 100" award in 2003. The Gaston project involved many of the authors included in this volume, especially Tom Feeley, Ramsay Chang, and Sharon Sjostrom. This is a subject that I know well.

In addition, several authors and I have collaborated on other related mercury studies. One of the most intriguing was the innovative research of the fate of mercury in coal power plant plumes, using first a fixed wing airplane and then an airship for plume sampling. This effort was led by Leonard Levin of EPRI, and included Dennis Laudal (University of North Dakota) and Jeff Ryan (U.S. EPA). Another cooperative effort through EPRI has been the computer modeling of mercury in power plants in two different efforts, led by Constance Senior and Steve Niksa.

The utility industry was taken by surprise with the announcement by the outgoing Clinton administration that it would be subject to a Maximum Achievable Control Technology (MACT) rule for mercury on 14 December 2000. That action kicked the industry into a frantic search for any data or information that could help us develop reliable control technology choices. Notably, EPRI, through the efforts of Ramsay Chang, and the U.S. Department of Energy (DOE)'s National

Energy Technology Laboratory (NETL), had already started working on mercury chemistry and control for coal-fired power plants. The subsequent efforts have largely been successful as an example of a public – private R&D partnership; where the utility industry and the suppliers of technology and materials to the industry worked with the DOE NETL to quickly advance the state of knowledge.

As the R&D progressed, an informal steering group of utility researchers, vendors of hardware and materials, and the U.S. DOE NETL was able to leverage the NETL funding to explore different options for controlling mercury from almost all power plant and coal-type combinations. In the early years of R&D, we found that we knew less and less about mercury chemistry with every new test and discovery, as contradictory results were more the rule.

The editors have assembled an experienced group of authors to make this volume, a "Who's Who's" of mercury research from the United States over the past decade. I feel lucky to have worked with virtually every one of the assembled group, and call most of them close friends. There is no better group of technical professionals to guide you in understanding the issues of mercury in coal-derived gas streams.

The volume is arranged in a logical sequence, beginning with the fate of mercury in the environment, written by Leonard Levin of EPRI. The applicable regulations, both for the United States and the international context, follow along with descriptions of trace elements in coal and the means to measure mercury in gas streams. The heart of the work is presented in the following sections on mercury chemistry, research programs, and the different technology systems that can be used and adapted for mercury control. The important topic of the stability of mercury in the solid coal combustion residues is also addressed next. Finally, the state-of-the-art in mercury modeling, both at the fundamental and process levels, is presented.

This is the manuscript that I – and the whole industry – needed back in 2000, as we contemplated what we would have do to reduce mercury emissions to meet upcoming regulations. It will serve as both a reference for those already engaged in the research and control efforts, and as an invaluable introduction for those just now becoming interested in the subject. I highly recommend it to the technical reader.

October 2014

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Preface

This book has its genesis in a Department of Energy (DOE) Topical Report on "Sorbents for Mercury Removal from Flue Gas" that Henry Pennline asked me to write in 1996. As a new post-doc hired to study sorbents for the capture of mercury, Henry suggested that a thorough literature review and survey would be an excellent way to start. As the topical report progressed and was nearly complete in 1997, I suggested to Henry that we write a book about mercury in flue gas. Henry shot this idea down at the time, correctly stating that we had much more to learn. Henry Pennline has turned out to be the best supervisor, researcher, colleague, and friend I could ever have. He was a little skeptical of my abilities at first, having observed my unusual photographic memory for foods; my suit and tie attire in the laboratory (unusual at DOE); and my dropping a large $25 quartz tube for the micro-balance on my first day on the job. I hope I end up doing something good in my research career to justify Henry's faith in me.

Mercury is a semi-noble metal, with both a fascinating chemistry and numerous applications throughout human history. Coal-derived flue gas and coal-derived syngas are both complex stews containing numerous species and exist over a wide temperature range at pulverized combustion and integrated gasification combined cycle (IGCC) plants, respectively. Having completed a MS thesis on coal gasification, I already knew going into the DOE that one could happily study coal flue gas and syngas for many lifetimes. Being introduced to mercury at DOE, I quickly found a terrific subject, with many wonderful colleagues.

In 1998 I met Dr Constance Senior at DOE in Pittsburgh. Constance was leading a large DOE-funded study on the behavior of the trace elements in coal-fired power plants. She impressed me immediately as a tenacious leader and terrific researcher. Constance exhibited extraordinary leadership – her efforts in corralling a large and diverse group of researchers from industry, academia, and the government resulted in a nearly 800-page report for DOE; a special issue of Fuel Processing Technology on the trace elements in coal-fired power plants in 2000; and a great expansion of our understanding of mercury in flue gas. I had the pleasure of meeting Constance again at the Workshop on Source Emission and Ambient Air Monitoring in Minneapolis in 1999. Despite the fact that I was an unknown post-doc at DOE, she introduced me to many of the researchers at dinner (a large pot of minestrone soup and a gigantic pizza that covered the entire table) in the Mall of America. I learned a lesson that day from Constance; always be nice to your colleagues. Hopefully I have done this. Dr Senior made Herculean efforts to help this book get completed; she is one-in-a-million.

Our work at DOE has allowed us to meet many wonderful colleagues at venues such as the Annual Mercury Control Technology Meetings that were held in Pittsburgh; the AIChE and ACS National Meetings; the Air Quality Conferences, and the Mega Symposiums. At the joint ACS-AIChE National Meeting held in the spring of 2008 in New Orleans, I recruited Tom Feeley, Ramsay Chang, and Constance Senior to be my keynote speakers on mercury. They did an outstanding job, highlighting a program that had 29 speakers on the various aspects of mercury in coal-derived gases. The idea for the book on mercury, having never left my mind, was revived. In 2009 I came up with a draft outline for this book, and happily in 2010, Dr Julia Stuthe from John Wiley recruited me to organize a book on mercury in coal-derived gases. Having already planned a book, I bent her ears with a 40-page PowerPoint presentation, abstract, and outline over a burrito and spicy chicken tortilla soup dinner in San Antonio during the 2010 AIChE National Meeting. Julia – forgive me. Dr Stuthe has recently left John Wiley, and I wish her great success. Lesley Belfit from John Wiley has done an outstanding job in helping us complete this book.

Coal contains a trace level of mercury of approximately 0.1 ppm. Mercury is a neurotoxin, and can travel long distances once emitted through the stacks of coal-burning power plants. Approximately 30–40% of the electricity in the United States is generated through the combustion of coal. Coal is an abundant resource in the United States – the country has a supply for at least 200 years. The challenge is to utilize the abundant domestic coal for energy independence in environmentally friendly ways.

With the US EPA issuing a national regulation on 21 December, 2011, requiring 91% removal of mercury, and many states already with their own regulations, the need exists for low-cost mercury removal techniques that can be applied to coal-burning power plants. The injection of powdered activated carbon into the ductwork upstream of the particulate control device is the most developed technology for mercury capture. Alternative techniques for mercury capture will also play a role in the near future because of the numerous configurations of air pollution control devices present within the power plants, as well as the many different coals being burned. These methods employ sorbents, catalysts, scrubber liquors, flue gas or coal additives, combustion modification, flue gas cooling, barrier discharges, and ultraviolet radiation for the removal of mercury from flue gas streams. The DOE Mercury Program has been a huge success, spurring development, demonstration, and commercialization of many technologies for the capture of mercury.

The future research needs for mercury control include improved sorbent-flue gas contact, development of poison-resistant sorbents and catalysts, new scrubber additives for retention of mercury within wet flue gas desulfurization

(WFGD) systems, concrete-friendly activated carbons, new continuous measurement methods, by-products research, and development of an ASTM standard laboratory test for sorbent activity for mercury capture.

This book aims to cover the technologies for mercury capture and measurement from coal-derived flue gas. The fate of mercury in the environment, a great motivation for the regulations, research, development, and commercialization of capture and measurement methods, is covered in Chapter 1. The trace elements in coal are detailed in Chapter 2. In addition, the regulatory issues, both in the United States and internationally, are discussed in Chapters 3 and 4. Methods for the detection of mercury in flue gas are covered in Chapters 5 and 6. Later chapters discuss the many methods for mercury control, the various research programs, activated carbon technologies, the cement industry, gasification, mercury carbon surface chemistry, and modeling.

I thank Constance and Henry for their outstanding efforts in making this book become a reality. Constance and Henry took my crude initial outline for the book and greatly improved it. Tom Feeley deserves many thanks for the great success of the DOE Mercury Program, and for supporting our in-house research on flue gas. Gary Stiegel and Jenny Tennant from DOE have been terrific in supporting our efforts in understanding the trace elements in gasification systems. Our authors and colleagues Constance Senior, Henry Pennline, Larry Monroe, Leonard Levin, Allan Kolker, Jeff Quick, Leslie Sloss, Nick Hutson, Denny Laudal, Carrie Yonley, Tom Feeley, Ramsay Chang, Tom Gale, Brian Higgins, April Sibley, Gary Blythe, Joe Wong, Nick Lentz, Sharon Sjostrom, Rob Nebergall, Behrooz Ghorshi, Ed Olson, Karen Uffalussy, Jennifer Wilcox, and Steve Niksa did an outstanding job. They are the leading figures in the mercury capture research, development, demonstration-commercialization communities; and are also terrific colleagues and friends. Some of our authors have been working on the mercury issue for over 20 years.

Finally, I thank Phil and Rita Granite, for interest in mercury, suggestions over the years for techniques for mercury control, and for being terrific parents. The same thanks also go to my brother Larry Granite at Environmental Protection Agency (EPA). Linda Granite has humored me, feigning interest in mercury while we were dating (I bent her ears with papers on sorbents and photochemical removal of mercury on our first date – a steak dinner; despite this she went out with me again!), and has been an angel through the years as my mind is sometimes elsewhere on the topic of mercury. Linda and our daughters Ana and Marissa Granite always provide inspiration.

October 2014

Evan Granite
Pittsburgh, PA

List of Abbreviations

ACI	Activated carbon injection
APCD	Air pollution control device
APH	Air preheater
BAT	Best available technique or technology
BEP	Best environmental practice
CAMR	Clean air mercury rule
CEMS	Continuous emission monitoring system
CFBC	Circulating fluidized bed combustor
CSAPR	Cross-states air pollution rule
CS-ESP	Cold-side ESP
DOE	Department of Energy
DSI	Dry sorbent injection
EC	European Commission
ECN	Economizer
EGU	Electricity generating unit
ELV	Emission limit value
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	Electrostatic precipitator
ESPc	Cold-side electrostatic precipitator
ESPh	Hot-side electrostatic precipitator
EU	European Union
FBC	Fluidized bed combustor
FF	Fabric (or baghouse) filter
FGD	Flue gas desulfurization
GHSV	Gas hourly space velocity
HAP	Hazardous air pollutant
HELCOM	Helsinki Commission
ICI	Industrial, commercial, and institutional
ICR	Information collection request
IED	Industrial Emissions Directive
IPPC	Integrated pollution prevention and control
L/G	Ratio of volumetric flowrates of liquid to gas in WFGD

LCPD	Large Combustion Plant Directive
LNB	Low NOx burner
LOI	Loss on ignition
LRTAP	Long-range transboundary air pollution
MATS	Mercury and air toxics standards
MEPOP	Mercury and persistent organic pollutants
MW	Megawatt
NARAP	North American regional action plan
NEPM	National Environmental Protection Measures (Australia)
NERP	National Emission Reduction Plan
NETL	National Energy Technology Laboratory
NHMRC	National Health and Medical Research Council (Australia)
NPI	National Pollutants Inventory
OFA	Overfire air
OSPAR	Oslo and Paris Commission
PAC	Powdered activated carbon
PCD	Particulate control device
PM	Particulate matter
SCEM	Semi-continuous emissions monitor
SCR	Selective catalytic reduction
SDA	Spray dry absorber for flue gas desulfurization
SED	Solvent Emissions Directive
SNCR	Selective non-catalytic reduction
SO_2	Sulfur dioxide
TOXECON	Advanced sorbent injection configuration licensed by EPRI
UBC	Unburned carbon
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
WFGD	Wet flue gas desulfurization
WID	Waste Incineration Directive
XAFS	X-ray absorption fine structure
XPS	X-ray photoemission spectroscopy

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