Coal Combustion Byproducts and Environmental Issues

Kenneth S. Sajwan Irena Twardowska Tracy Punshon Ashok K. Alva Editors

Coal Combustion Byproducts and Environmental Issues



Kenneth S. Sajwan Department of Natural Sciences and Mathematics Savannah State University Savannah, GA 31404 USA

Irena Twardowska Institute of Environmental Engineering Polish Academy of Sciences 41-819 Zabrze Poland

Tracy Punshon Savannah River Ecology Laboratory University of Georgia Aiken, SC 29802 USA

and

Environmental and Occupational Health Sciences Institute Rutgers University Piscataway, NJ 08854 USA

Ashok K. Alva Vegetable and Forage Crops Research Unit USDA-ARS, Pacific West Area Prosser, WA 99350 USA

Library of Congress Control Number: 2005930800

ISBN-10: 0-387-25865-5 ISBN-13: 978-0387-25865-2

Printed on acid-free paper.

© 2006 Springer Science+Business Media, Inc.

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, Inc., 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden.

The use in this publication of trade names, trademarks, service marks and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed in the United States of America. (TB/IBT)

9 8 7 6 5 4 3 2 1 SPIN 11423706

springeronline.com

IN GRATITUDE TO

My family, Maria, Mia, and Joseph Sajwan Who've been through it all before

and

Dr. George Gobran

Swedish University of Agricultural Sciences, Uppsala, Sweden For his major contribution in organizing the Seventh International Conference on the Biogeochemistry of Trace Elements, of which the present work is a part.

Preface

The massive accumulation of coal fly ash generated by electric power plants during fossil fuel combustion has become a major environmental health concern in the United States. Even though, stringent environmental regulations have been mandated by the Environmental Protection Agency through the Clean Air Act, Clean Water Act, and the Resource Conservation and Recovery Act, coal combustion products continue to pose serious environmental concerns due to our major reliance upon fossil fuels to meet ever increasing demands for energy production within the United States. The concentrations of trace elements in coal residues are extremely variable and depend upon the composition of the original coal, conditions experienced during combustion, the efficiency of emission control devices, storage and handling procedures, and overall climatic conditions.

The research papers carefully selected for publication within this book were originally presented as a part of the Seventh International Conference on the Biogeochemistry of Trace Elements held at the Swedish University of Agricultural Sciences, Uppsala, Sweden, from June 15–19, 2003. This conference offered the unique opportunity for international scientists and scholars to share the most current knowledge concerning the source, pathways, behavior, interactions, and effects of trace elements in soils, water, plants, and animals. Notably, this book also contains the invited research papers from leading scientists who have conducted significant research within the area of coal and coal combustion products. All of the research papers presented herein have been subjected to a peer review process. The editors have arranged the articles systematically by topic, beginning with introductory chapter entitled "Production of Coal Combustion Products and Their Potential Uses" followed by the sections on Environmental Impact of Coal Combustion Residues, Trace Elements in Fly Ashes, Transport and Leachability of Metals from Coal and Ash Piles, and the Use of Coal Ash as an Agricultural Soil Amendment.

This book addresses the major implications and critical issues surrounding coal combustion products and their impact upon the environment. It provides invaluable information particularly to scientists specializing and conducting research in coal and coal combustion products. Even so, it will certainly appeal beyond this initial target audience to serve a wide variety of scientists, scholars, academicians, and professionals within the fields of public health, engineering, energy industry, and a wide realm of environmental science related disciplines. It is our sincere endeavor that this volume of work will serve as a valuable resource tool for those engaged in fossil fuel energy research to benefit both our economy and environment to assure quality of life for future generations. The editors wish to generously express their genuine appreciation and gratitude to all of the contributing authors for their professional insight and scientific contributions to this body of knowledge, along with their diligence and patience throughout the publication process.

> Kenneth S. Sajwan Irena Twardowska Tracy Punshon Ashok K. Alva

Contributors

S. A. Aburime

Department of Engineering, Clark Atlanta University, 233 James P. Brawley Drive, Atlanta, GA 30314, USA.

Domy C. Adriano The University of Georgia, Savannah River Ecology Laboratory, Aiken, SC 29802, USA.

J. Afolabi

Department of Natural Sciences and Mathematics, Savannah State University, Savannah, GA 31404, USA.

A. K. Alva USDA-ARS, Pacific West Area, Vegetable and Forage Crops Research Unit, 24106 N. Bunn Rd., Prosser, WA 99350, USA.

Christopher Barton Department of Forestry, University of Kentucky, Thomas Poe Cooper Bldg., Lexington, KY 40546-0073, USA.

Nanthi Bolan Institute of Natural Resources, Massy University, Palmerston North, New Zealand.

Joanna Burger The University of Georgia, Savannah River Ecology Laboratory, Aiken, SC 29802, USA.

D. Chaudhuri Department of Applied Science, College of Engineering, University of California, Davis, Livermore, CA 94550, USA.

Jianjun Chen

Mid-Florida Research and Education Center, IFAS, University of Florida, Apopka, FL 32703, USA.

E. M. D'Angelo Department of Agronomy, University of Kentucky, N-122K Ag. Science-North, Lexington, KY 40546-0091, USA.

Holger Ecke

Division of Waste Science & Technology, Lulea University of Technology, SE-97187, Lulea, Sweden.

X. Feng Ferro Corporation, Cleveland, OH 44114, USA.

G. E. Fryxell Pacific Northwest National Laboratory, Richland, WA 99352, USA.

G. S. Ghuman

Department of Natural Sciences and Mathematics, Savannah State University, Savannah, GA 31404, USA.

B. R. Hart Department of Earth Sciences, University of Western Ontario, London, N6A 5B7, Canada.

Mike Hedley Institute of Natural Resources, Massy University, Palmerston North, New Zealand.

Dave Horne Institute of Natural Resources, Massey University, Palmerston North, New Zealand.

J. M. Hutchison

Advanced Analytical Center for Environmental Sciences, Savannah River Ecology Laboratory, The University of Georgia, Aiken, SC 29802, USA.

Brian P. Jackson The University of Georgia, Savannah River Ecology Laboratory, Aiken, SC 29802, USA.

A. D. Karathanasis Department of Agronomy, University of Kentucky, N-122K Ag. Science-North, Lexington, KY 40546-0091, USA.

U. M. Khodke College of Agricultural Engineering, Marathwada Agricultural University, Parbhani, Maharashtra, 431 402, India.

Ryunosuke Kikuchi Department of Basic Science and Environment, CERNAS; ESAC—Polytechnic Institute of Coimbra, Bencanta, 3040-316, Coimbra, Portugal.

Waldemar Klassen

Tropical Plant Research and Education Center, Institute of Food and Agricultural Sciences, University of Florida, Homestead, FL 33031, USA.

Anna S. Knox

Savannah River National Laboratory, Westinghouse Savannah River Company, 773-42A, Savannah River Site, Aiken, SC 29802. USA.

John D. Knox

Columbia County Board of Education, Appling, GA 30802, USA.

Bon-Jun Koo

Department of Forestry, University of Kentucky, Thomas Poe Cooper Bldg., Lexington, KY 40546-0073, USA.

Jurate Kumpiene

Division of Waste Science & Technology, Lulea University of Technology, SE-97187, Lulea, Sweden.

Yuncong Li Tropical Plant Research and Education Center, IFAS, University of Florida, Homestead, FL 33031, USA.

Sally Maharaj Department of Forestry, University of Kentucky, Thomas Poe Cooper Bldg., Lexington, KY 40546-0073, USA.

S. V. Mattigod Pacific Northwest National Laboratory, Richland, WA 99352, USA.

Christian Maurice

Division of Water Science & Technology, Lulea University of Technology, SE-97187, Lulea, Sweden.

William P. Miller Department of Crop and Soil Sciences, University of Georgia, Athens, GA 30602-7272, USA.

Lee Newman University of South Carolina, Arnold School of Public Health, 800 Sumpter St., Columbia, SC 29208, USA.

R. K. Panda Department of Agricultural and Food Engineering, Indian Institute of Technology, Kharagpur, 721 302, West Bengal, India.

S. Paramasivam Department of Natural Sciences and Mathematics, Savannah State University, Savannah, GA 31404, USA.

K. E. Parker Pacific Northwest National Laboratory, Richland, WA 99352, USA.

E. M. Piers Pacific Northwest National Laboratory, Richland, WA 99352, USA.

M.C. Potts Department of Natural Sciences and Mathematics, Savannah State University, Savannah, GA 31404, USA.

M. A. Powell Department of Earth Sciences, University of Western Ontario, London, N6A 5B7, Canada.

T. Prahraj

Department of Earth Sciences, University of Ottawa, 140, Louis Pasteur, Ottawa, KIN 6N5, Canada.

Tracy Punshon

Savannah River Ecology Laboratory, The University of Georgia, Aiken, SC 29802, USA. /Consortium for Risk Evaluation with Stakeholder Participation, Environmental and Occupational Health Sciences Institute, Division of Life Sciences, Rutgers University, 604 Allison Road, Piscataway, NJ 08854, USA.

J. E. Robinson

Department of Agronomy, University of Kentucky, N-122K Ag. Science-North, Lexington, KY 40546-0091, USA.

Kenneth S. Sajwan

Department of Natural Sciences and Mathematics, Savannah State University, Savannah, GA 31404, USA.

Maxim Schlossberg

Department of Crop and Soil Sciences, University of Georgia, Athens, GA 30602-7272, USA.

John C. Seaman

The University of Georgia, Savannah River Ecology Laboratory, Aiken SC 29802, USA.

Sebastian Stefaniak

Polish Academy of Sciences, Institute of Environmental Engineering, 34 M. Sklodowska-Curie St., 41-819 Zabrze, Poland.

S. Tripathy

Department of Geology & Geophysics, Indian Institute of Technology, Kharagpur, 721 302, West Bengal, India.

Irena Twardowska

Polish Academy of Sciences, Institute of Environmental Engineering, 34 M. Sklodowska-Curie St., 41-819 Zabrze, Poland.

H. Veeresh

Department of Soil Science and Agricultural Chemistry, U.A.S., G.K.V.K., Banglore, Karnataka, 560 065, India.

F. Clint Waltz, Jr.

Department of Crop and Soil Sciences, Georgia Agricultural Experiment Station, 119 Redding Building, Experiment, GA 30212, USA.

Hailong Wang

Forest Research, Private Bag 3020, Rotorua, New Zealand.

Qingren Wang

Tropical Plant Research and Education Center, Institute of Food and Agricultural Sciences, Homestead, FL 33031, USA.

Paul F. Ziemkiewicz

West Virginia Water Research Institute, West Virginia University, Morgantown, WV 26506, USA.

Contents

Preface	. vii
Contributors	. ix
 Part I Introduction 1 Production of Coal Combustion Products and Their Potential Uses	. 3
Part II Environmental Impact of Coal Combustion Residues	
2 Coal and Coal Combustion Products: Prospects for Future and Environmental Issues Irena Twardowska and Sebastian Stefaniak	. 13
3 Alternative By-Products of Coal Combustion and Simultaneous SO ₂ /SO ₃ /NO _x Treatment of Coal-Fired Flue Gas: Approach to Environmentally Friendly Use of Low-Rank Coal	. 21
4 Fly Ash as a Sealing Material for Spontaneous Combustion and Acid Rock Drainage Prevention and Control <i>Irena Twardowska and Sebastian Stefaniak</i>	. 33
5 Delineation of Water and Sediment Contamination in River Near a Coal Ash Pond in Orissa, India S. Tripathy, and T. Praharaj	. 41
6 Prediction of Coal Ash Leaching Behavior in Acid Mine Water: Comparison of Laboratory and Field Studies Paul F. Ziemkiewicz and Anna S. Knox	. 50

Part III Trace Elements in Flyashes

7	Occurrence and Sorption of Radionuclides Onto Coal-Fired Power Plant Combustion Waste Irena Twardowska and Sebastian Stefaniak	61
8	Heavy Metals Adsorption and Their Distribution in Three Soil Types of India: Effect of Coal Fly Ash and Sewage Sludge Amendment S. Tripathy, H. Veeresh, D. Chaudhuri, M.A. Powell, and B.R. Hart	66
Part	t IV Transport and Leachability of Metals from Coal and Ash Piles	
9	Impact of Grassed Swales on the Fate of Metals Leached from Roads Built with Municipal Solid Waste Incineration Bottom Ashes Jurate Kumpiene, Holger Ecke, and Christian Maurice	87
10	Removal of Mercury from Aqueous Streams of Fossil Fuel Power Plants Using Novel Functionalized Nonoporous Sorbents S.V. Mattigod, G.E. Fryxell, X. Feng, K.E. Parker, and E.M. Piers	99
11	Leachability of Trace Metals from Sandy or Rocky Soils Amended with Coal Fly Ash Yuncong Li and Jianjun Chen	105
12	Arsenic and Selenium Speciation in Aged Flue Gas Desulfurization Amended Soil Tracy Punshon, Brian P. Jackson, John C. Seaman, Domy C. Adriano, and Joanna Burger	114
13	Trace Element Transport in Putting Green Root Mixes Amended by Coal Combustion Products (CCP) Maxim J. Schlossberg and William P. Miller	124
14	Solute Leaching from Fly Ash Amended Soil Under Varying Degrees of Saturation J.M. Hutchison, J.C. Seaman, B.P. Jackson, and S.A. Aburime	134
15	Solution Geochemistry Gradients in an Acid Mine Drainage Wetland Substrate A.D. Karathanasis, and J.E. Robinson, and E.M. D'Angelo	142
16	Removal of Trace Elements from Aqueous System: Comparison of Two Fly Ash Materials	150
Part	t V Use of Coal Ash as Agriculture Soil Amendment	

17	Transport and Plant Uptake of Zn in an Oxyaquic Haplustalf Amended	
	with Coal Ash and Sewage Sludge: A Field Study	159
	U.M. Khodke, S. Tripathy, R.K. Panda, H. Veeresh, and K.S. Sajwan	

19	Amendment of Fly Ash to Container Substrates for Ornamental Plant Production Jianjun Chen and Yuncong Li	177
20	Influence and Coal Combustion Flue Gas Desulfurization Waste on Element Uptake by Maize (<i>Zea Mays L.</i>) <i>Anna S. Knox, John D. Knox, Domy C. Adriano, and Kenneth S. Sajwan</i>	184
21	Amelioration of Soil Acidity with a Class-C Fly Ash: A Field Study Maxim J. Schlossberg, F. Clint Waltz Jr., and William P. Miller	190
22	Phytoavailability of Trace Elements from a Landfill Containing Coal Combustion Waste Sally Maharaj, Christopher Barton, Bon-Jun Koo, and Lee Newman	195
23	Potential Uses of Fluidised Bed Boiler Ash (FBA) as a Liming Material, Soil Conditioner and Sulphur Fertilizer Hailong Wang, Nanthi Bolan, Mike Hedley, and Dave Horne	202
24	Potential of Fly Ash and Organic Wastes for Uses as Amendments to Agricultural Soils: A Review G.S. Ghuman, K.S. Sajwan, and S. Paramasivam	216
25	Evaluation of Bahiagrass (<i>Paspalum notatum</i>) as a Vegetative Cover for a Landfill Containing Coal Combustion Waste <i>Bob-Jun Koo, Christopher Barton, and Domy Adriano</i>	225
Abo	but the Editors	232
Inde	ех	235

I Introduction

1 Production of Coal Combustion Products and Their Potential Uses

K.S. Sajwan¹, T. Punshon², and J.C. Seaman²

¹Department of Natural Sciennces and Mathematics, Savannah State University, Savannah, GA 31404, USA ²Savannah River Ecology Laboratory, The University of Georgia, Aiken SC 29802, USA

Abstract

Coal Combustion Products (CCPs) arise from the combustion of coal for energy, with fly ash (FA), bottom ash (BA) and flue-gas desulfurization residues (FGD) the most abundant. Our reliance on fossil fuel for energy is set to continue into the 21st century, and research into the environmental safety of beneficial re-use options, as well as novel re-use options, must continue. Since previous editions of collected CCP research¹, significant changes have been made to both the New Source Review and the Clean Air Act that directly impact CCP production figures. New techniques such as x-ray absorption spectroscopy are increasingly being used to reveal micron-scale elemental characteristics of CCPs, and aid our understanding of the distribution and chemical form of the metallic constituents. This chapter summarizes production and use covering the period 2001–2003, new trends in reuse applications and discusses new research on the environmental safety of CCP re-use.

Introduction

Coal Combustion Products (CCPs) predominantly consist of fly ash (FA), bottom ash (BA), boiler slag (BS) and flue gas desulfurization residue (FGD or synthetic gypsum). In 2003, approximately 110.4 million metric tons (Mt) of CCPs were produced², an increase of about 8% on the previous year. Continued disposal of material on this scale is no longer considered feasible, and beneficial re-use is essential. Re-use in various construction applications, by far the most common avenue, now stands at 38.1% of the total CCP produced, although clearly the scope of CCP re-use can be expanded in the future. The focus of this volume is to collate information that will promote environmentally safe CCP re-use and foster this expansion.

The environmental hazards associated with CCPs are posed by the content of potentially toxic trace metals and metalloids which readily leach out when they enter $soils^{3-5}$. While the metal (loid) content of CCPs reflects that of the parent coal, the most commonly found elements of concern are boron (B)⁶, molybdenum (Mo)^{7.8}, arsenic (As)^{9–11} and Selenium (Se)^{12,13}. A variety of other metals have also been reported in CCPs, such as nickel (Ni), cadmium (Cd), mercury (Hg) and lead (Pb)¹². The waste from coal and lignite burning power stations can also be enriched with radionuclides, such as uranium (²³⁸U), radon (²²⁶Ra), lead (²¹⁰Pb), thorium (²³²Th) and potassium (⁴⁰K)¹⁴. Lasting environmental damage has been attributed, at least in part, to Se from CCP release in to settling lagoons, because this metalloid has a tendency to be transferred through the food chain^{15,16}. For instance, developmental abnormalities in the mouthparts of amphibians living in FA disposal ponds are thought to be due to elevated Se¹⁷, and there is also evidence of direct toxicity^{6,18,19}.

It is the major elemental properties of FA and FGD residues, such as the presence of calcium (Ca), potassium (K), sodium (Na), and sulfur (S), that has led to their application to soil in the hope that they can be safely used as amendments for various soil problems. Adding FA and FGD to nutrient poor soils has been reported to increase short term crop yield²⁰, correct nutrient deficiencies²¹, and change the physical structure to alleviate compaction²². Nonetheless, the presence of metals and metalloids in CCPs is a significant impediment to their agronomic use and it is now believed that CCP application to soil should only occur after rigorous elemental analysis of the CCP, the soil and the crop requirement²¹.

In addition, the input of mercury (Hg) into the atmosphere and aquatic ecosystems from coal combustion is currently receiving attention. Coal combustion is one of the most significant sources of Hg input into the biosphere^{12,23–26}, and Hg is currently unregulated in the U.S. The recent fish consumption advisory by the U.S. Environmental Protection Agency²⁷ has raised the profile of atmospheric Hg, and has prompted the formulation of a regulatory framework to address monitoring and safe limits²⁸.

Current CCP re-use rates are at their highest ever, although there is much research needed to address the safe exploitation of CCPs. Our understanding of metal(loid) bioavailability is still developing, and is directly applicable to CCP disposal and re-use issues. This volume brings together key biogeochemical studies, using novel techniques to directly address long-term toxicity and bioavailability. They include analysis of varying types of vegetation cover on the physical mobility of potentially toxic metals and metalloids leaching from CCPs, novel sorbents for Hg removal from aqueous CCPs, soil sorption characteristics when CCPs are combined with organic waste materials such as sewage sludge, the influence of CCPs on plant growth and elemental composition and the long term bioavailability and speciation of elements of concern in the soil following CCP application.

Coal Combustion Products

Fly Ash

Fly ash is a fine powder made up of hollow ferroaluminosilicate particles enriched with Ca, K and Na²⁹⁻³¹, and is collected by mechanical filters or electrostatic precipitators from the flue gas during coal combustion. Typical FA particle sizes are within 0.1–1.0 µm, and electron microscopy has revealed particles with rough surfaces covered with smaller adhering spherical particles³¹. Composite FA³² comprises several types of particles, including true hollow particles, smaller aggregations known as microspheres, and opaque magnetite spheres³³. Trace elements, including potentially toxic metals and metalloids, condense upon the surface of FA particles during combustion^{29,33,34}. Fly ash is pozzolanic in nature; a siliceous (or combination siliceous and aluminous) material that forms cementitious compounds when in the presence of moisture³⁵. Using x-ray absorption fine structure spectroscopy (XAFS), Shoji et al.¹¹ showed S to be present predominantly as sulfate, with some thiophene and sulfite in larger particle size fractions (>2.5 μ m in diameter). X-ray absorption near-edge structure spectroscopy (XANES) showed Cr to be present as the toxic Cr^{6+} valence state in 10–30% of western U.S. coal fly ashes, but only Cr^{3+} was detected within the eastern U.S. bituminous coal FA. They identified As in all FA as As^{5+} , although there were small spectral differences in As speciation between eastern and western coals, which were not clarified. Significant variation in Zn speciation was observed between different FA phases of eastern and western coals, with ZnFe₂O₄ the principal form in eastern coal fly ashes. Struis et al.36 found that 60% of the Zn in raw FA was hydrozincite $(Zn_5(CO_3)_2(OH)_6)$ and the remaining 40% was inert forms such as willemite (Zn₂SiO₄) and gahnite (ZnAl₂O₄). Pires and Querol³⁷ investigated the composition of Brazilian fly ashes using ICP-MS, ICP-AES, x-ray diffraction (XRD) and scanning electron microscopy, finding that in the leachable fraction the metal classification was B (40-50%)>Mo>Cu>Ge= lithium (Li) =Zn=As>, Ni, tin (Sb), thallium (Tl), U > barium (Ba), Cd, strontium (Sr), vanadium (V)(0.3-2%). Utilization of micron-scale spatial metal analysis techniques to determine metal(loid) species within coal and resultant combustion products^{38–40} is a significant development within CCP

research; it will allow engineers to adjust the combustion conditions for parent coal type so that toxic species of metal(loid)s do not predominate in the resultant FA, and will allow the potential environmental hazards as a result of FA use to be more fully understood, by understanding the bioavailability and distribution of metal(loid) species within the soil and biota.

Bottom Ash

Bottom ash is uncombusted material that settles to the bottom of the boiler; boiler slag is formed when operating temperatures exceed ash fusion temperature and the slag remains molten until drained from the bottom of the combustion chamber⁴¹. Bottom ash is granular and is similar to concrete sand⁴². Boiler slag is a shiny, black granular material that has abrasive properties, and is used as grit for snow and ice control, structural embankments, aggregate and as road base material (Table 1). The re-use potential of BA is influenced by its physical characteristics, such as grain-size distribution, staining potential and color⁴³, which are typically variable properties⁴⁴. In the scientific literature, the BA derived from coal and municipal solid waste (MSW) are frequently confused; and some workers suggest that these materials have considerable similarities²⁶, or are similar in nature to FA. However, in the present volume, which focuses on the chemical properties of the CCPs, distinctions are made between those arising from coal, and those from the combustion of other solid materials.

Flue Gas Desulfurization Residues

The Clean Air Act Amendments of 1990 (CAAA '90 Public Law 101-549) placed stringent restrictions on the release of sulfur oxide (SO_x) from coal-fired power plants, with a two phase implementation plan, requiring electric utility companies to reduce SO₂ emissions, in an effort to reduce atmospheric pollution and acid rain⁴⁵. The majority of utility companies previously used high-sulfur bituminous coal, which was thought to have significantly contributed to incidences of acid rain in North America. Following the instatement of the act, many companies switched to low-sulfur coal or fuel oil for partial and rapid compliance with regulations, although retrofitting power plants with flue-gas scrubbing systems was ultimately necessary to fully comply. This change effectively resulted in the creation of a new waste stream, termed flue-gas desulfurization residue (FGD).

Flue gas desulfurization residue is the alkaline material produced when SO_x is extracted from coal-fired power plant fluegases^{46,47}. There are several technologies currently in use, differentiated by the type of sorbent (e.g. lime or dolomitic lime) used and the method of SO_x extraction⁴⁸, however, FGD typically consists of calcium sulfite (CaSO₃), calcium sulfate (CaSO₄), unreacted sorbent, and FA particles. Other types of FGD can include magnesium, ammonium or sodium sulfites and sulfates.

TABLE 1. Production and use of ca	ttegory I (dry) an	d II (ponded) co.	al combustion pr	oducts (CCPs) in 1	the United State	s during the peri	od of 2001–2003	(metric tons).	
		2001			2002			2003	
	FA	BA	FGD	FA	BA	FGD	FA	BA	FGD
PRODUCED	61,841,517	17,044,190 TOTAI	25,839,153 104 774 860	69,399,630	17,962,257 Tota	10,341,906 07 703 703	63,639,007	16,420,043 Tota I	10,795,498 00 824 548
USED			000-17/101						01
Cement/Concrete/Grout	11,213,022	707,170	443,170	11,411,600	368,548	54,981	11,126,774	270,505	59,505
Raw Feed for Clinker	937,470	147,408	27,946	1,739,699	531,138	275,609	2,744,170	447,936	381,057
Flowable Fill Material	729,107	6,749	0	412,785	0	0	123,938	18,440	0
Structural Fill/Embankments	2,911,617	1,052,572	172,330	3,811,067	1,856,594	0	4,986,747	2,216,439	0
Road Base etc.	931,516	553,257	35,474	695,976	1,335,640	0	447,684	1,032,468	0
Soil Modification/Stabilization	668,582	103,022	0	820,771	89,366	0	467,674	61,687	0
Mineral Filler in Ashphalt	96,651	7,423	1,181	93,597	87,287	0	47,725	0	0
Snow/Ice Control	0	774,212	0	2,400	696,223	0	1,749	620,112	0
Blasting Grit/Roofing Granules	0	36,368	0	56,213	124,697	0	0	38,650	0
Mining Applications	743,518	107,452	127,215	1,713,540	728,089	0	620,446	1,074,948	0
Wallboard	0	0	5,647,109	0	0	6,575,144	0	0	7,058,719
Waste Stabilization/Solidification	1,305,808	62,532	42,872	2,891,899	17,319	0	3,556,071	27,676	0
Agriculture	18,603	20,057	103,949	0	6,235	70,488	11,013	3,206	29,500
Aggregate	ш	иа	ш	0	615,170	5,639	124,439	465,176	0
Miscellaneous	406,665	1,603,978	278,387	507767.6059	519,569	66,964	359381.2189	1204557.123	0
TOTAL	19,962,559	5,182,200	6,879,631	24,157,313	6,975,877	7,048,825	24,617,812	7,481,800	7,528,780
% USE	32.3	30.4	26.6	34.8	38.8	68.2	38.7	45.6	69.7

FGD residues are a rapidly changing group of CCPs; research is continually underway to increase scrubbing efficiency⁴⁹ resulting in a higher sulfur content of the final product. In common with other CCPs, the quality of the product also depends on the characteristics of the parent coal, the type of scrubbing system used (i.e., wet or dry⁴⁷) and the handling and stabilization procedures. Stabilization usually takes the form of mixing the FGD with FA²⁰, and this often changes the re-use options of the stabilized material. Fly ash and additional quicklime are usually added to stabilize FGD filter cake prior to landfilling⁵⁰.

Production of Coal Combustion Byproducts

The American Coal Ash Association (ACAA) reports the production of 107 million metric tons (Mt) of CCPs in 2001⁵¹; an increase of 8.4% from the previous year. However, in 2003, CCP production was seven million Mt less than the previous year (Table 1)^{2,52}. In February 2002, the U.S. Administration proposed significant changes to the New Source Review (NSR), and the Clean Air Act⁵³, known as the 'Clear Skies' initiative. The NSR is the section of the Clean Air Act which requires industrial organizations and factories to install modern pollution control devices (such as the flue-gas scrubbers which produce FGD) whenever they make changes in their activities or output that result in an increase in pollution. These changes have been perceived by environmental groups as a weakening of the NSR; widening pre-existing loopholes and allowing some facilities to bypass pollution control installment or upgrade, and in effect increase atmospheric pollution, rather than decrease it. These changes can be clearly seen in the figures reported by the ACAA in Table 1, which shows production and re-use of all classes (wet and dry) of FA, BA and FGD (million Mt)^{2,51,52}. The production of FGD in particular has shown a dramatic fall; down by 60% in 2002 and 58% in 2003, despite the previous trend of increasing production concurrent with the total production of CCPs⁴⁸ and the increasing consumption of coal which has steadily increased from 961 million Mt in 2001 to 992 million Mt in 200354,55.

Potential Uses of Coal Combustion Products

The percentage of FA re-used in the United States has steadily increased from 7% in 1966 to 38.7% in 2003; an average increase of approximately 0.5 million Mt per year. On average the production of FA has increased approximately 4.5% per year between 1966 and the present, or approximately 1.3 million Mt a year⁴⁸. Although re-use rates of FGD residues appear to have increased dramatically (Table 1), this is due to the changes in FGD production.

Fly Ash

Application of FA alone to agricultural land does not meet all crop requirements for essential nutrients such as N and P, but can enhance K, Ca, S, B, Mo levels, as well as other essential micronutrients such as Zn in the short term. Alkaline FA can be effective in neutralizing soil acidity⁵⁶, and when mixed with other coal refuse, has effectively controlled acid mine drainage⁴. The presence of potentially toxic metal(loids) in FA limit its potential use for land application²¹. Historically, the use of FA in agriculture has been based on its liming potential and supply of essential elements such as Ca, B, S, and Mo⁵⁷, although the metal(loid) enrichment has diverted FA research toward determining leaching potential and minimizing environmental risks of the materials. Many agricultural studies conclude that FA may only be of use in situations where the plants are tolerant to the salinity⁵⁸, metal contamination⁵⁹ and are nitrogen fixers⁵⁹.

The advantages and disadvantages of FA application to agricultural land are well documented, and includes metal(loid) enrichment and toxicity, plant nutrient imbalance such as P deficiency from soils treated with alkaline FA⁶⁰, and antagonistic interactions among elements due to of excessive Ca, K, and S^{57,61,62}. Research into the agronomic use of CCPs continues, however, although many now focus on using CCPs in a specifically formulated mix with organic matter. For example, Schumann and Sumner²¹ used nutrient availability data and linear programming to formulate mixtures of FA and biosolid (sewage sludge and animal manure) to successfully avoid FArelated issues such as B toxicity, excessive As levels and overliming, and derive environmentally safe FA formulations. In addition, Schlossberg et al.63 adopted a similar technique of mixing FA with an organic waste product to successfully establish and manage bermudagrass sod production.

Successful, and perhaps more appropriate use of FA however, has been in the remediation of severely eroded lands^{64,65}, where FA is mixed with an organic waste material such as poultry litter, to supply nitrogen and phosphorus to plants. In terms of restoration, the combination of FA with other industrial by-products such as sewage sludge, can result in a high quality restoration material ^{22,66}, and applied to eroding soils that require physical stabilization in addition to chemical improvement. Sajwan *et al.*⁶⁵ combined FA with sewage sludge (SS) and applied various mixture (ratios of SS:FA mixtures of 4:1, 4:2, 4:3, and 4:4) to *Sorghum vulgaris* var. Sudanese Hitche ("sorgrass") and found stimulating in biomass at rates of 50–100 tons acre-1 of all ratios of SS:FA mixtures.

Flue-Gas Desulfurization Residues

Flue-gas desulfurization residue is increasingly being used in the production of wallboard material, with over 7 million Mt re-used in 2003, amounting to 93% of the FGD re-used for that year. Due to their alkaline nature, FGD residues have potential value as neutralizing agents^{50,67} for agricultural soils which suffer from excessive acidity⁶⁸, or for the alleviation of excessive sodicity ^{69,70}. In comparison with FA, considerably more FGD residue is used in agricultural applications; in 2001, 103,949 Mt of FGD was used in agricultural applications compared to 18,603 Mt FA. The use of FGD in agriculture, however, has steadily decreased during the 2001–2003 period; from 0.1 to 0.03 million Mt.

New research into the agronomic application of FGD has similarly applied the material in a mixture with an organic waste material, such as dairy, swine or broiler litter manures; Zhang *et al.*⁷¹ found that co-application of FGD with organic waste reduced the availability of P, from the water-soluble to the bicarbonate extractable, which retained its availability for plant uptake, while reducing the likelihood of environmental losses through leaching. Stout *et al.*^{72,73} also used FGD to reduce the bioavailability of P in high-P soils, reducing surface P runoff effectively for a period of several years. This reduction can be attributed to the amount of Ca supplied from both the FGD and organic amendment. High-P soils pose environmental problems from P run-off, which damages water quality by causing algal blooms through eutrophication.

Using an FGD residue without co-application of an organic waste product, Clark and Baligar^{74,75} compared its effect on growth⁷⁵ and mineral composition⁷⁴ of plants grown on an acidic soils (pH 4) to that CaCO₃, CaSO₄ and CaSO₃. They reported growth enhancement of *Medicago sativa*, *Trifolium repens* and *Festuca arundinacea* as a result of FGD addition, and in particular when magnesium (Mg) was co-applied. In this study, only FGD materials high in B and lower in CaSO₃ were found to be detrimental to plant growth, and overall increased the growth responses of plants in an otherwise infertile acidic soil. Sakai *et al.*⁷⁶ used FGD residues to restore pH balance, without a detectable increase in the metal(loid) concentration (in comparison with FGD-free controls) of the plant material grown on amended soil. In this case, their product was a combination of wet and semi-dry desulfurization.

Conclusion

Although the beneficial re-use of CCPs such as FA and FGD have been impeded in the past by the presence of potentially toxic metal(loids), research is now moving ahead to better understand the distribution and chemical speciation of metal(loids) in parent coals, combustion products and environmental matrices using analytical techniques which have a high resolution, and capabilities for micron-scale spatial analysis. The future of CCP research into finding new and safer re-use applications depends on the information these techniques can provide. Agronomic use of these materials has been advanced a great deal in recent years by incorporation with organic wastes, and by using these more balanced mixtures to fertilize non-food source crops. Acknowledgments. This work was supported by the Environmental Remediation Science Division of the Office of Biological and Environmental Research, U.S. DOE, through the financial assistance award number DE-FC09-96SR18546 to the University of Georgia Research Foundation.

References

- Sajwan, K.S., Alva, A.K. and Keefer, R.F. eds. ed. Chemistry of Trace Elements in Fly Ash. 2003. Kluwer Academic/Plenum Publishers: New York. 346.
- ACAA 2003. 2003 Coal Combustion Product (CCP) Production and Use Survey. <u>http://www.acaa-usa.org/CCPSurvey</u> <u>Short.htm</u>,
- Choi, S.-K., Lee, S., Song, Y.-K. and Moon, H.-S. 2002. Leaching characteristics of selected Korean fly ashes and its implications for the groundwater composition near the ash disposal mound. *Fuel* 81: 1083–1090.
- Stewart, B.R., Daniels, W.L. and Jackson, M.L. 1997. Evaluation of leachate quality from codisposed coal fly ash and coal refuse. *J. Environ Qual.* 26: 1417–1424.
- Ugurlu, A. 2004. Leaching characteristics of fly ash. *Environmental Geology* 46(6–7): 890–895.
- Pavlovic, P., Mitrovic, M. and Djurdjevic, L. 2004. An ecophysiological study of plants growing on the fly ash deposits from the "Nikola tesla-A" thermal power station in Serbia. *Environmental Management* 33(5): 654–663.
- Furr, A.K., Parkinson, T.F., Gutenmann, W.H., Pakkala, I.S. and Lisk, D.I. 1978. Elemental content of Vegetables, Grains and Forages Field-Grown on Fly-Ash Amended Soil. *J. Agric. Food Chem.* 26(2): 357–359.
- Elseewi, A.A. and Page, A.L. 1984. Molybdenum enrichment of plants grown on fly-ash amended soils. *J. Environ Qual.* 13: 394–398.
- 9. Jackson, B.P. and Miller, W.P. 1998. Arsenic and selenium speciation in coal fly ash extracts by ion chromatographyinductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry* 13(10): 1107–1112.
- Jackson, B.P. and Miller, W.P. 1999. Soluble arsenic and selenium species in fly ash organic waste-amended soils using ion chromatography inductively coupled plasma mass spectrometry. *Environmental Science & Technology* 33(2): 270–275.
- Shoji, T., Huggins, F.E., Huffman, G.P., Linak, W.P. and Miller, C.A. 2002. XAFS spectroscopy analysis of selected elements in fine particulate matter derived from coal combustion. *Energy & Fuels* 16(2): 325–329.
- Huang, Y.J., Jin, B.S., Zhong, Z.P., Xiao, R., Tang, Z.Y. and Ren, H.F. 2004. Trace elements (Mn, Cr, Pb, Se, Zn, Cd and Hg) in emissions from a pulverized coal boiler. *Fuel Processing Technology* 86(1): 23–32.
- Moscoso-Perez, C., Moreda-Pineiro, J., Lopez-Mahia, P., Muniategui-Lorenzo, S., Fernandez-Fernandez, E. and Prada-Rodriguez, D. 2004. As, Bi, Se(IV), and Te(IV) determination in acid extracts of raw materials and by-products from coalfired power plants by hydride generation-atomic fluorescence spectrometry. *Atomic Spectroscopy* 25(5): 211–216.
- Karangelos, D.J., Petropoulos, N.P., Anagnostakis, M.J., Hinis, E.P. and Simopoulos, S.E. 2004. Radiological characteristics and investigation of the radioactive equilibrium in the ashes

produced in lignite-fired power plants. *Journal of Environmental Radioactivity* 77(3): 233–246.

- Jackson, B.P., Allen, P.L.S., Hopkins, W.A. and Bertsch, P.M. 2002. Trace element speciation in largemouth bass (*Micropterus salmoides*) from a fly ash settling basin by liquid chromatography-ICP-MS. *Analytical and Bioanalytical Chemistry* 374(2): 203–211.
- Wallschlager, D. and Carlton, R.G. Selenium speciation and cycling in fly ash ponds. Proceedings of 6th International Conference on the biogeochemistry of Trace Elements. 2001. Guelph, Canada.
- Jackson, B.P., Hopkins, W.A., Unrine, J., Bainonno, J. and Punshon, T. Selenium speciation in amphibian larvae developing in a coal fly ash settling basin. Proceedings of 9th International Conference on Plasma Source Mass Spectrometry. 2004. Durham, UK: University of Durham.
- Hopkins, W.A., Staub, B.P., Snodgrass, J.W., DeBiase, A., Taylor, B., Roe, J.H. and Jackson, B.P. 2004. Responses of benthic fish exposed to contaminants in outdoor mesocosms: Examining the ecological relevance of previous laboratory toxicity tests. *Aquatic Toxicology* 68(1): 1–12.
- Staub, B.P., Hopkins, W.A., Novak, J. and Congdon, J.D. 2004. Respiratory and reproductive characteristics of eastern mosquitofish (Gambusia holbrooki) inhabiting a coal ash settling basin. *Archives of Environmental Contamination and Toxicology* 46(1): 96–101.
- Punshon, T., Adriano, D.C. and Weber, J.T. 2001. Effect of Flue Gas Desulfurization Residue on Plant Establishment and Soil and Leachate Quality. *Journal of Environmental Quality* 30(3): 1071–1080.
- 21. Schumann, A.W. and Sumner, M.E. 2004. Formulation of environmentally sound waste mixtures for land application. *Water Air and Soil Pollution* 152(1–4): 195–217.
- Chang, A.C., Lund, L.J., Page, A.L. and Warneke, J.E. 1977. Physical properties of fly-ash amended soils. *Journal of Environmental Quality* 6: 267–270.
- 23. Billings, C.E. and Matson, W.R. 1972. Mercury Emissions from Coal Combustion. *Science* 176(4040): 1232–&.
- Fthenakis, V.M., Lipfert, F.W., Moskowitz, P.D. and Saroff, L. 1995. An Assessment of Mercury Emissions and Health Risks from a Coal-Fired Power-Plant. *Journal of Hazardous Materials* 44(2–3): 267–283.
- Huang, H.S., Wu, J.A.M. and Livengood, C.D. 1996. Development of dry control technology for emissions of mercury in flue gas. *Hazardous Waste & Hazardous Materials* 13(1): 107–119.
- 26. Goodwin, R.W. and Schuetzenduebel, W.G. Residues from mass burn systems: testing, disposal and Utilization issues. Proceedings of *New York State Legislative Commission of Solid Waste Management and Materials Policy Conference*. 1988. New York.
- US-FDA and US-EPA, 2004. What you need to know about mercury in fish and shellfish. United States Food and Drug Administration and United States Environmental Protection Agency, Washington, DC., EPA-823-F-04-009 2.
- Mason, R.P., Abbott, M.L., Bodaly, R.A., Bullock Jr, O.R., Driscoll, C.T., Evers, D., Lindberg, S.E., Murray, M. and Swain, E.B. 2004. Monitoring the response to changing mercury deposition. *Environmental Science and Technology* 39(1): 15A– 22A.

- Page, A.L., Elseewi, A.A. and Straughan, I. 1979. Physical and chemical properties of fly ash from coal-fired power plants with references to environmental impacts. *Residue Rev.* 71: 83–120.
- 30. El-Mogazi, D.D., Lisk, D.J. and Weinstein, L.H. 1988. A review of physical, chemical and biological properties of fly ash and effects on environmental ecosystems. *Science of the Total Environment* 74: 1–37.
- Peng, M., Ruan, X.G., Chen, X.M., Xu, J.W. and Jiang, Z.C. 2004. Study on both shape and chemical composition at the surface of fly ash by scanning electron microscope, focused ion beam, and field emission-scanning electron microscope. *Chinese Journal of Analytical Chemistry* 32(9): 1196–1198.
- Fisher, G.L. and Natusch, D.F.S. 1979. Size dependence of the physical and chemical properties of coal fly ash. in *Analytical methods for coal and coal products.*, C. Karr Jr., Editor. Academic Press: New York. 489–541.
- Mattigod, S.V., Rai, D., Eary, L.E. and Ainsworth, C.C. 1990. Geochemical Factors Controlling the Mobilization of Inorganic Constituents from Fossil Fuel Combustion Residues: I. Review of the major elements. *J. Environ Qual.* 19: 188–201.
- US-EPA, 1988. Wastes from the combustion of coal by electricity power plants. U.S. Environmental Protection Agency, Washington DC.
- 35. Manz, O.E. 1999. Coal fly ash: a retrospective and future look. *Fuel* 78: 133–136.
- Struis, R.P.W.J., Ludwig, C., Lutz, H. and Scheidegger, A.M. 2004. Speciation of zinc in municipal solid waste incineration fly ash after heat treatment: An X-ray absorption spectroscopy study. *Environmental Science & Technology* 38(13): 3760–3767.
- Pires, M. and Querol, X. 2004. Characterization of Candiota (South Brazil) coal and combustion by-product. *International Journal of Coal Geology* 60(1): 57–72.
- Camerani, M.C., Golosio, B., Somogyi, A., Simionovici, A.S., Steenari, B.M. and Panas, I. 2004. X-ray fluorescence tomography of individual municipal solid waste and biomass fly ash particles. *Analytical Chemistry* 76(6): 1586–1595.
- Huggins, F.E., Huffman, G.P., Linak, W.P. and Miller, C.A. 2004. Quantifying hazardous species in particulate matter derived from fossil-fuel combustion. *Environmental Science & Technology* 38(6): 1836–1842.
- Galbreath, K.C. and Zygarlicke, C.J. 2004. Formation and chemical speciation of arsenic-, chromium-, and nickel-bearing coal combustion PM2.5. *Fuel Processing Technology* 85(6-7): 701– 726.
- 41. Bluedorn II, D.C. Recent environmental regulation of coal combustion wastes—revised. Proceedings of 2001 Conference on Unburned Carbon (UBC) on Utility Fly Ash. 2001: National Energy Technology Laboratory.
- Keefer, R.F. 1993. Coal ashes—Industrial wastes or beneficial byproducts? in *Trace Elements in Coal and Coal Combustion Residues.*, R.F. Keefer and K.S. Sajwan, Editors. Lewis Publishers: Ann Arbor. 3–9.
- 43. Kula, I., Olgun, A., Sevine, V. and Erdogan, Y. 2002. An investigation on the use of tincal ore waste, fly ash and coal bottom ash as Portland cement replacement materials. *Cement and Concrete Research* 32: 227–232.
- 44. Bethanis, S., Cheeseman, C.R. and Sollars, C.J. 2004. Effect of sintering temperature on the properties and leaching of

incinerator bottom ash. *Waste Management & Research* 22(4): 255–264.

- Kalyoncu, R. 1998.Coal Combustion Products. <u>http://minerals.usgs.gov/minerals/pubs/commodity/coal/874498.pdf</u>
- Punshon, T., Knox, A.S., Adriano, D.C., Seaman, J.C. and Weber, T.J. 1999. Flue Gas Desulfurization residue (FGD): Potential Applications and Environmental Issues. in *Biochemistry of Trace Elements in Coal and Coal Combustion Byproducts.*, K.S. Sajwan and R.F. Keefer, Editors. Lewis Publishers: Boca Raton, FL. 7–28.
- 47. Punshon, T., Seaman, J.C. and Adriano, D.C. 2002. The effect of flue gas desulfurization residue on corn (*Zea mays* L.) growth and leachate salinity: Multiple season data from amended mesocosms. in *Chemistry of Trace Elements in Fly Ash*, K.S. Sajwan, A.K. Alva, and R.F. Keefer, Editors. Kluwer Academic/Plenum Press: New York, NY. In press.
- Punshon, T., Seaman, J.C. and Sajwan, K.S. 2003. The production and use of coal combustion products. in *Chemistry of Trace Elements in Fly Ash*, K.S. Sajwan, A.K. Alva, and R.F. Keefer, Editors. KluwerAcademic/Plenum Publishers: New York. 1–11.
- Baege, R. and Sauer, H. 2000. Recent developments in CFB-FGD technology. VGB Powertech 80(2): 57–60.
- Chen, L., Dick, W.A. and Nelson, S. 2001. Flue gas desulfurization addition to acid soil: alfalfa productivity and environmental quality. *Environmental Pollution* 114(2): 161–168.
- ACAA 2001. 2001 Coal Combustion Product (CCP) Production and Use (Short Tons). <u>http://www.acaa-usa.org/CCP</u> <u>SurveyShort.htm</u>,
- ACAA 2002. 2002 Coal Combustion Product (CCP) Production and Use Survey. <u>http://www.acaa-usa.org/CCPSurvey</u> <u>Short.htm</u>,
- Cooney, C.M. 2002. 'Clear skies' may be ahead for electric power plants. *Environmental Science and Technology* 136(9): 181A–182A.
- EIA, 2001. Annual Coal Report. Energy Information Agency, Washington, DC, DOE/EIA-0584 (2001) 73.
- EIA, 2003. Annual Coal Report. Energy Information Administration, Washington, DC, DOE/EIA-0584 (2003) 78.
- Matsi, T. and Keramidas, V.Z. 1999. Fly ash application on two acid soils and its effect on soil salinity, pH, B, P and on ryegrass growth and composition. *Environmental Pollution*. 104: 107–112.
- Adriano, D.C., Page, A.L., Elseewi, A.A., Chang, A.C. and Straughan, I. 1980. Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems. A review. *Journal of Environmental Quality* 9: 333–334.
- Adriano, D.C., Webber, J., Bolan, N.S., Paramasivam, S., Koo, B.-J. and Sajwan, K.S. 2002. Effects of high rates of coal fly ash on soil, turfgrass and groundwater quality. *Water Air and Soil Pollution* 139: 365–385.
- Gupta, D.K., Rai, U.N., Tripathi, R.D. and Inouhe, M. 2002. Impacts of fly-ash on soil and plant responses. *Journal of Plant Research* 115(1122): 401–409.
- Kukier, U. and Sumner, M.E. 1996. Boron availability to plants from coal combustion by-products. *Water, Air & Soil Pollution* 87(1–4): 93–110.
- 61. Carlson, C.L. and Adriano, D.C. 1993. Environmental impacts of coal combustion residues. *Journal of Environmental Quality* 22(2): 227–247.

- Gary, C.A. and Schwab, P. 1993. Phosphorus fixing ability of high pH, high calcium, coal combustion waste material. *Water Air and Soil Pollution* 69: 309–320.
- Schlossberg, M.J., Vanags, C.P. and Miller, W.P. 2004. Bermudagrass sod growth and metal uptake in coal combustion by-product-amended media. *Journal of Environmental Quality* 33(2): 740–748.
- Punshon, T., Adriano, D.C. and Weber, J.T., 1999. Restoration of Eroded Land Using Coal Fly Ash and Biosolids. Electrical Power Research Institute, Pal Alto, CA., TR-113940.
- 65. Sajwan, K.S., Ornes, W.H. and Youngblood, T. 1995. The effect of fly ash/sewage sludge mixtures and application rates on biomass production. *Journal of Environmental Science and Health* A30(6): 1327–1337.
- Sloan, J.J. and Cawthorn, D. 2003. Mine soil remediation using coal ash and compost mixtures. in *Chemistry of Trace Elements in Fly Ash*, K.S. Sajwan, A.K. Alva, and R.F. Keefer, Editors. Kluwer Academic/Plenum Publishers: New York. 309– 318.
- 67. Schlossberg, M.J., Sumner, M., Miller, W.P. and Dudka, S. Utilization of coal combustion by-products (CBP) in horticulture and turfgrass industries: technical and environmental feasibility studies. Proceedings of 6th International Conference on the Biogeochemistry of Trace Elements. 2001. Guelph, Canada.
- Stehouwer, R.C., Sutton, P. and Dick, W.A. 1996. Transport and plant uptake of soil-applied dry flue gas desulfurization by products. *Soil Science* 161(9): 562–574.
- Clark, R.B., Ritchey, K.D. and Baligar, V.C. 2001. Benefits and constraints for use of FGD products on agricultural land. *Fuel* 80(6): 821–828.
- Chun, S., Nishiyama, M. and Matsumoto, S. 2001. Sodic soils reclaimed with by-product from flue-gas desulfurization: corn production and soil quality. *Environmental Pollution* 114(3): 453–459.
- Zhang, G.Y., Dou, Z., Toth, J.D. and Ferguson, J. 2004. Use of flyash as environmental and agronomic amendments. *Environmental Geochemistry and Health* 26(2): 129– 134.
- Stout, W.L., Sharpley, A.N. and Pionke, H.B. 1998. Reducing soil phosphorus solubility with coal combustion by products. *J. Environ Qual.* 27: 111–118.
- Stout, W.L., Sharpley, A.N. and Weaver, S.R. 2003. Effect of amending high phosphorus soils with flue-gas desulfurization gypsum on plant uptake and soil fractions of phosphorus. *Nutrient Cycling in Agroecosystems* 67(1): 21–29.
- Clark, R.B. and Baligar, V.C. 2003. Mineral concentrations of forage legumes and grasses grown in acidic soil amended with flue gas desulfurization products. *Communications in Soil Science and Plant Analysis* 34(11–12): 1681– 1707.
- Clark, R.B. and Baligar, V.C. 2003. Growth of forage legumes and grasses in acidic soil amended with flue gas desulfurization products. *Communications in Soil Science and Plant Analysis* 34(1–2): 157–180.
- Sakai, Y., Matsumoto, S. and Sadakata, M. 2004. Alkali soil reclamation with flue gas desulfurization gypsum in China and assessment of metal content in corn grains. *Soil & Sediment Contamination* 13(1): 65–80.

II Environmental Impact of Coal Combustion Residues

2 Coal and Coal Combustion Products: Prospects for Future and Environmental Issues

Irena Twardowska and Sebastian Stefaniak

Polish Academy of Sciences, Institute of Environmental Engineering, 34, M. Sklodowska-Curie St., 41-819 Zabrze, Poland

Abstract

At the background of the overview of prospects for coal-based electricity production, the present and projected status and trends of coal combustion products (CCP) management was discussed. According to the latest projections, coal-based electricity share will remain the largest in world's energy balance and is set to double in the first three decades of 21st century. The majority of this growth is forecasted for developing Asian economies, but also for some developed countries not bound by the Kyoto Protocol (USA, Australia). Coal combustion products (CCP) are one of the most abundant high-volume waste materials worldwide that are partially being reused in a number of commercially and environmentally proven applicationsboth traditional and advancing, some are in the stage of extensive studies. Despite of numerous beneficial properties, their reuse rates are still far from being satisfactory; also statistics on CCP generation is fragmentary. There is also different approach to CCP in terms of its legal definition: ACAA (American Coal Ash Association) considers CCP as a "product" and a mineral commodity equivalent to natural materials; also some other countries-large coal producers and CCP generators adopted this approach (e.g. India). European legislation treats CCP as a waste, though it does not mean that the material is a waste in all circumstances, but only where the definition of waste is met. In view of anticipated CCP generation and growth in the future, a crucial task is to identify and remove obstacles and barriers in the way of increasing CCP utilization, along with developing new application fields. Based on the analysis of regulatory instruments and enforcement procedures compared to the utilization effects, it has been stated that the pro-environmental and pro-recovery CCP recycling policy must be based on the term "waste" and the "polluter pays" principle. The rationale of this statement is that the legal definition in no case should absolve the producer or the holder from the responsibility for the generated waste until it is transformed into an environmentally safe product. The exemplified practice confirms that the efficient regulatory and enforcement mechanisms should comprise a well-balanced system of precepts, prohibitions and charges for CCP disposal (fees, penalties) that would encourage power plants as waste generators to support financially the environmentally safe utilization of CCP by the waste reuse industry on a cost-benefit basis, in order to reduce charges for the disposal and to assure competitiveness of these products in the market.

1. Introduction

At the beginning of the third Millennium coal remains the primary fuel used in generation electricity worldwide—in 2002 coal generated 39.0% of the world's electricity. Total global hard coal production in 2003 has been estimated for 4037.5 Mt and increased 3.3% over the previous year (in 2002 it accounted for 3909.9 Mt). In the past 25 years it showed over 46% growth.

Coal domination in electricity generation is based on coal abundant and widely dispersed resources compared with oil and gas that is also a matter of energy security and minimizes the risk of energy supply disruption. Coal deposits occur in about 70 countries. At present extraction level, the proven coal reserves are estimated to last over 190 years. In contrast, oil and gas reserves are estimated to last for 41 and 67 years, respectively; besides, over 69% of oil and 67% of gas reserves are concentrated in the Middle East and Russia, which makes these resources highly insecure and endangered by supply disruption¹. This strongly justify use coal incineration in power plants for electricity generation. This process causes formation of large amounts of coal combustion residues that are environmentally problematic, but at the same time display a number of beneficial properties, that might make these materials recyclable in a wide number of efficient and cost-effective applications. Up to now, though, not all the beneficial properties of these materials are well recognized and adequately utilized. At the same time, it should be taken into consideration that these materials are not environmentally safe and might adversely affect the ambient environment, if improperly handled. This chapter is focused on discussion of beneficial and adverse properties of fly ash (FA) that is the most abundant coal incineration residue in a context of potential applications, as well as on regulatory aspects that might optimize its management.

2. Coal as A Source of Electricity

The countries that are major producers are also major consumers of hard coal for electricity generation (Table 1). A number of countries use imported coal as a significant component in a balanced energy mix (Japan, Republic of Korea, Chinese Taipei, Germany and UK). The major steam coal exporters are Australia, PR China, Indonesia, S. Africa, and in lesser amounts (<50 Mt) Russia and Colombia; USA and Poland exported below 20 Mt.

Data presented in Table 1 reflect both temporary fluctuations in coal generation, but also permanent trends connected with growth of electrification rate, particularly strong in Asian/Pacific region. A dynamic increase of coal generation is observed in China, Indonesia and India; The EU and OECD countries show stagnation or even decreasing trend, which greatly depends on the implementation of the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCC) that sets mandatory targets on greenhouse gas (GHG) emissions for the parties that ratified the Protocol. The Protocol was first negotiated at COP3 in Japan in 1997 and will finally enter into force on 16 February 2005, when it will be legally binding on its 128 parties, 30 of whom are industrialized EU and OECD countries with emissions targets. Refusal to ratify Protocol by the USA that is the world's largest emitter and Australia, as well as the absence of targets for developing countries reduces Kyoto Protocol implementation to countries responsible for only 32% of global emissions³. It should be though noted that the US declared the alternative "voluntary targets" program that rely on recommendations outlined by the Council of Economic Advisors.⁴

According to the latest edition of the IEA—International Energy Agency's World Energy Outlook 2004^{5,6}, coal-based electricity share will remain the largest in world's energy balance. Between 2002 and 2030, coal demand is projected to grow annually by 1.4% and by 2030 will reach the amount of over 7 billion tons that is almost 50% higher than at present. In 2030 coal will meet 22% of energy needs, similarly to the present level (23%). Asian countries will show continuous increase in demand for coal; China and India are estimated to participate for 68% in this growth.

Coal-based electricity is set to double in the first three decades of 21st century, from 16,074 TWh in 2002 to 31,657 TWh in 2030 and will continue to play a key role in world electricity generation. Despite high nominal growth of coal-based electricity generation, its share in total electricity generation (in %) will remain in 2003 close to the current level showing only slight decrease from 39 to 38%. The strongest increase of coal-based electricity gross generation is projected in developing countries, in particular in China, where a quarter of the total growth will occur^{5,6}. By 2030 developing countries will reach almost half of total energy demand. Though the majority of this growth is forecasted for developing Asian economies (China, ASEAN, India), also in some developed countries not bound by the Kyoto Protocol (USA, Australia), increasing competition will favour low cost coal-based electricity generation⁷. The EU and OECD countries with emission targets that ratified Kyoto protocol are tending to reduce share of this kind of energy, mainly by increasing gas use and developing alternative renewable electricity sources (Table 2). Nevertheless, having in mind almost double increase of electricity generation, similar or even reduced share of coal as a source of electricity, means significant nominal increase of incinerated coal.

In the cited outlook, IEA for the first time has used an Energy Development Index that is a composite measure reflecting commercial energy consumption per capita, share of commercial energy in total energy use and share of population with

TABLE 1. Coal production ar	d major producers in	001 (after WCI—	World Coal Institute, 2004 ^{1,2}).
-----------------------------	----------------------	-----------------	-------------------------------------------	----

		Production					
	М	lt	% of Total		Coal-based electricity % of total		
Hard coal	2002	2003e	2002	2003e	2002p	2003p	
World	3837.0*	4037.5	100	100	38.7	39.0	
China	1326.0	1502.4	34.5	37.2	76.2 (2001 data)	77.5	
USA	916.7	891.9	23.9	22.1	49.9	52.2	
India	333.7	340.4	8.7	8.4	78.3 (2001 data)	70.1	
Australia	276.0	274.1	7.2	6.8	76.9	76.9	
S. Africa	223.0	239.3	5.8	5.9	93.0	92.2 (2002 data)	
Russia	163.6	188.4	3.5	4.7			
Indonesia	101.2	120.1	2.6	3.0		39.7	
Poland	102.6	100.4	2.7	2.5	94.8	94.7	
Kazakhstan	70.6	74.8	1.8	1.9		69.9 (2002 data)	
Ukraine	82.9	56.8	2.2	1.4			

*Data from 2003 edition of Coal Facts; after 2004 edition the world coal production in 2002 was 3909.9 Mt; e-estimated; p-preliminary;

	Share in electricity generation (%)						
	OECD		Transition economics		Developing countries		
Electricity source	2002	2030	2002	2030	2002	2030	
Coal	38	33	22	16	45	47	
Oil	6	2	4	2	12	5	
Gas	18	29	37	54	17	26	
Nuclear	23	15	18	11	2	3	
Hydro	13	11	19	15	23	16	
Other renewables*	3	10	0	2	1	3	

TABLE 2. Projections of world's electricity generation trends over the period of 2002–2030^{6,7}

*Solar, wind, biomass, waste incineration etc

access to electricity. According to IEA projection, electrification rates in developed countries will increase from 66% in 2002 to 78% in 2030; the total number of people without electricity will account for 1.4 billions in 2030, while electrification rates in developing countries vary significantly—from over 98% in China to an average 23% in Sub-Saharan Africa, where there is a number of countries with electrification rate <5% (Figure 1).

This shows that in the future (after 2030) further increase of coal use as a source of energy can be anticipated unless novel energy sources are developed by that time.

3. Coal Combustion Products (CCP) Generation, Use and Disposal

Coal combustion products (CCP) are one of the most abundant high-volume waste materials worldwide. Their proportion in the total waste stream highly depends upon the role of coal in power production, and is as a rule the highest in coal producing countries. Despite the omnipresence of CCP, the statistical data concerning its generation and managing in the different countries of the world are fragmentary⁹.

American Coal Ash Association (ACAA) regularly publishes in its web site CCP generation and use annual surveys based on a representative sampling of several hundreds of coalfueled power plants in the U.S.^{10,11,12} (e.g. 2002 data are estimates based on a sampling survey of nearly 600 utilities)¹⁰. These data show distinct increase of CCP generation and use in the last eight years covered by ACAA reports (1996–2003) (Table 3). The last available data for 2003 estimate total CCB amount for 110.44 Mt. that means an extrapolated increase of about 19.5% compared to 1996. It should be noted that total CCP generation can vary distinctly from tear to year depending on the amount and ash content of coal burned, though the general trend is distinctly increasing since 1996^{10,11,12}. Its category structure in the last reported years 1996-2003 remains practically stable and consists predominantly of fly ash (ca. 58%), bottom ash (ca.15%), boiler slag (1.5–2.5%), FGD solids (23-25%) and FBC Ash (<1%, 0.7% in 2003), fly as being invariably the largest by mass component of CCP. Though in 1966–1996, along with growth of CCP generation, also its use was growing, an overall CCP utilization for this period remained at almost unchanged level at around 25%. An observed significant and regular upward trend of overall CCP utilization rate at 13.4% in 1996–2003 in parallel with an increase of CCP generation evidences an unquestionable success of utilization industry in the field of coal combustion products usage.

The growth of CCP use under the conditions of a slow economy and a relatively flat construction industry ACAA tentatively explains by possible local material/mineral



FIGURE 1. Electrification rates for selected developing world countries (after World Energy Outlook, IEA)⁸.