



## ENVIRONMENTAL SEPARATION of HEAVY METALS

ENGINEERED PROCESSES



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Edited by

## Arup K. SenGupta

Professor of Environmental Engineering Lehigh University



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## Preface

We all know that an unmixed blessing is non-existent in the real world. Since the advent of the industrial revolution, the beneficial use of metals has seen a tremendous growth around the world and essentially has reshaped our civilization. For a long time, a number of these metals, many of them toxic, were indiscriminately released into the environment. It required decades for the fate, transport, and deleterious effects of these metals to be comprehended. Gradually their impact on the quality of life on our planet surfaced as a matter of grave concern, ushering in a series of environmental regulations during the last thirty years. Metals that are potential carcinogens warranted closer scrutiny and were later included in the United States Environmental Protection Agency's (U.S.EPA's) list of priority pollutants. It would, however, be wrong to isolate industrial emissions and discharges as the sole source of environmental problems pertaining to toxic metals. In some instances, nature plays an unfriendly role in deteriorating environmental quality. Worldwide contamination of groundwater by arsenic, chromium, and selenium through geochemical soil leaching represents one example to this effect.

In order to be in regulatory compliance, industries and organizations in both the private and public sectors have sought new technologies for efficient heavy metals removal. Over the course of time, the emphasis has shifted from mere removal to recovery and reuse. Attaining "zero discharge" is today a common slogan in almost every industrial sector. Such cultural changes, along with new technologies, have warranted judicious use of efficient heavy-metal-separation technologies. This book seeks to provide comprehensive coverage of advanced technologies for heavy metals separation from groundwater, wastewater, contaminated soils, flue gases, industrial sludges and other contaminated sources. Separation of heavy metals is carried out to meet stringent environmental regulation with respect to priority pollutants, especially arsenic, mercury and lead, which are discussed in depth. Altogether the book contains ten chapters. The first chapter sets the stage by introducing heavy metals chemistry and the underlying principles for heavy metals separation. The remaining nine chapters pertain to technologies such as specialty sorption, magnetic separation, chelating ion exchange, polyelectrolyte-aided membrane separation, and advanced precipitation, among others. The book is designed to enable engineers and non-engineers alike to learn, select and adapt the best means to remove and, in certain instances recover, heavy metals through the use of appropriate technologies. The book is also intended to be of use to graduate students and professionals undertaking research and development work in heavy metals, remediation and related areas.

Before closing, I would like to sincerely thank the lead authors of the chapters and their co-authors for their time, effort and active cooperation during the last eighteen months. Ping Li's assistance in preparing several illustrations included in the book is gratefully acknowledged. Eleanor Nothelfer's editing of several manuscripts helped improve the final quality. Thanks are also due to Joe Eckenrode and Teresa Wiegand of Technomic Publishing Co., Inc. for their prompt help and quick turnaround time during the production stage of the book. Last but not the least, I would like to thank my wife, Susmita, for her encouragement and forbearance throughout this endeavor, which made working on it a pleasure.

ARUP K. SENGUPTA

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### **Contributing Authors**

Kashi Banerjee, USFilter Corporation, USA Amjad Fataftah, ARCTECH, Inc., USA Matthias Franzreb, Forschugzzentrum Karlsruhe GmbH, Germany John E. Greenleaf, Lehigh University, USA Roberto Passino, Instituto di Ricerca Sulle Acque, Italy Domenico Petruzzelli, The Polytechnic University of Bari, Italy Brian Reed, University of Missouri at Columbia, USA Thomas W. Robinsson, Los Alamos National Laboratory, USA H. G. Sanjay, ARCTECH, Inc., USA Nancy N. Sauer, Los Alamos National Laboratory, USA Arup K. SenGupta, Lehigh University, USA Sukalyan Sengupta, University of Massachusetts at Dartmouth, USA Barbara F. Smith, Los Alamos National Laboratory, USA Giovanni Tiravanti, Instituto di Ricerca Sulle Acque, Italy Radisav D. Vidic, University of Pittsburgh, USA Daman Walia, ARCTECH, Inc., USA James H. P. Watson, University of Southampton, UK



### **Principles of Heavy Metals Separation: An Introduction**

ARUP K. SENGUPTA<sup>1</sup>

#### **HEAVY METALS: WHAT ARE THEY?**

THE term "heavy metal," in spite of its widespread usage among professionals and lay-L men, does not have a rigorous scientific basis or a chemical definition. Although many of the elements listed under "heavy metals" have specific gravities greater than five, major exceptions to this rule remain. In hindsight, this group should preferably have been referred to as "toxic elements," for they are all included in the United States Environmental Protection Agency's (USEPA's) list of priority pollutants. Figure 1.1 shows the periodic table containing the heavy metals that are of significant environmental concern. For comparison, commonly occurring light alkali and alkali-earth metals have also been included in the same figure. Strictly from a chemical viewpoint, heavy metals constitute transition and post-transition elements along with metalloids, namely, arsenic and selenium. They are indeed significantly heavier (i.e., higher specific gravities) than sodium, calcium and other light metals. These heavy metal elements often exist in different oxidation states in soil, water and air. The reactivities, ionic charges and solubilities of these metals in water vary widely. For their short- and long-term toxic effects, the maximum permissible concentrations of these heavy metals in drinking water as well as in municipal and industrial discharges are closely regulated through legislation. Nevertheless, barring the exceptions of cadmium, mercury and lead, heavy metals are also required micronutrients, i.e., essential ingredients for living cells. Toxicity effects of these elements are, thus, largely a function of concentration. These elements are beneficial and have nutritional values lower than some critical dosages but become inhibitory to toxic with an increase in concentration, as shown in Figure 1.2. The threshold toxic concentrations differ for each heavy metal and are governed primarily by the chemistry of each heavy metal in question and associated physiological effects. On the contrary, nonessential heavy metal elements are inhibitory at all concentrations.

Metal cycles on a regional and global basis have been profoundly modified by human ac-

<sup>1</sup>Department of Civil and Environmental Engineering, Lehigh University, 13 E. Packer Avenue, Bethlehem, PA 18015, U.S.A., aks0@lehigh.edu



Figure 1.1 A modified periodic table showing commonly encountered regulated heavy metals, metalloids and unregulated light metals.

tivity and industrial development during the last fifty years. While mining, metallurgical, electroplating industries, etc., have greatly boosted the production and usage of heavy metals in our life cycles, the lowering of pH in rain and surface waters and the increased use of surfactants, which have greatly enhanced the mobility of heavy metals in the environment. Understandably, the presence of heavy metals in aquatic, terrestrial and atmospheric environment is of concern. In the aqueous phase, such heavy metals may exist as cations, anions, nonionized species and complex macromolecules. As most of the heavy metals and their compounds have extremely high boiling points, they are practically absent in the atmo-



Figure 1.2 Nutritional and inhibitory effects of heavy metal concentration on living cells/microorganisms.

sphere under ambient conditions, with the glaring exception of elemental mercury. Flue gases from fossil fuel-fired steam generators and waste incinerators are major industrial sources of mercury emission into the atmosphere. Higher volatility and relative inertness compared to other heavy metals allow elemental mercury to persist in the environment for a prolonged period of time. Following the phaseout of leaded gasoline in industrial countries, the short- and long-term presence of lead in the atmosphere has greatly subsided. In the soil phase, heavy metals exist primarily as insoluble precipitates or as bound solutes on the surface sorption sites of microparticles. Mobility and fate of the heavy metals in the soil phase are often influenced by the chemical composition of the contacting liquid phase.

#### HEAVY METALS SEPARATION: UNDERLYING CHEMISTRY

#### **Lewis Acid-Base Interaction**

The speciation and fate of metals in the natural environment as well as their separation and/or control by engineered processes are ultimately governed by the electronic structures of the heavy metals. Such electronic structures also dictate the biochemical actions of metals as nutrients or toxicants. In order to develop an insight, let us consider the electronic configurations of a light metal cation (say  $Ca^{2+}$ ) and a heavy metal cation (say  $Cu^{2+}$ ) as shown below:

$$Ca^{2+}: 1s^2 2s^2 2p^6 3s^2 3p^6 \tag{1}$$

$$Cu^{2+}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$$
(2)

Note that  $Ca^{2+}$  has the noble gas configuration of Krypton, i.e., its outermost electron shell is completely filled, and the octet formation is satisfied. Thus,  $Ca^{2+}$  is not a good electron acceptor and, hence, a poor Lewis acid. Ions like  $Ca^{2+}$  are not readily deformed by electric fields and have low polarizabilities. They are referred to as "hard" cations, and they form only outer sphere complexes with aqueous-phase ligands containing primarily oxygen donor atoms.

In contrast, the transition metal cation,  $Cu^{2+}$  or Cu(II), has an incomplete d-orbital and contains electron clouds more readily deformable by electric fields of other species. In general, these ions are fairly strong Lewis acids and tend to form inner sphere complexes with ligands in the aqueous phase. Electrostatically,  $Ca^{2+}$  and  $Cu^{2+}$  are identical, i.e., both  $Ca^{2+}$ and  $Cu^{2+}$  have two charges. However, Cu(II) is a stronger Lewis acid or electron acceptor and a relatively "soft" cation. Table 1.1 classifies several metal cations in three categories, namely, hard, borderline and soft [1,2]. Note that most of the heavy metals of interest fall under "borderline" and "soft." In general, the toxicity of metals increases as one moves from hard cations to borderline and then to soft. Relative affinities of these metal ions to form complexes with O-, N- and S-containing ligands, vary widely. While hard cations prefer oxygen-donating ligands (Lewis bases), borderline and soft cations exhibit higher affinities toward nitrogenous and sulfurous species. The soft cations thus bind strongly with sulfhydryl groups in proteins of the cells. Because sulfhydryl groups form active sites on proteins, their blockages through heavy metal binding result in severe toxic effects [3].

The foregoing phenomenon prompted Nierboer and Richardson to recommend that toxic metals be classified by their relative complex forming abilities with O-, N- and S-containing ligands, for such affinities are the primary determinants of physiological toxicity

Туре	Name of Cations	Salient Properties
1. Hard cations	Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Al <sup>3+</sup> , Be <sup>2+</sup> , etc.	Spherically symmetric and electronic configurations conform to inert gases; form only outer-sphere complexes with hard ligands containing oxygen donor atoms; weak affinity toward ligands with nitrogen and sulfur donor atoms; besides beryllium, most are non-toxic at low concentrations.
2. Borderline cations	Fe <sup>3+</sup> , Cu <sup>2+</sup> , Pb <sup>2+</sup> , Fe <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup> , Co <sup>2+</sup> , Mn <sup>2+</sup>	Spherically not symmetric, and electronic configurations do not conform to inert gases; form inner-sphere complexes with O- and N-atom-containing ligands; excepting iron and manganese, all are toxic.
3. Soft cations	Hg+, Cu+, Hg <sup>2+</sup> , Ag+, Cd <sup>2+</sup>	Spherically not symmetric, and electronic configurations do not conform to inert gases; except high affinity toward S-atom-containing ligands; they are most toxic from a physiological viewpoint.

TABLE 1.1. Classification of Selected Metal Cation	IS.
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caused by the metals [4]. The fact that many heavy metals bind strongly onto proteins also suggests that these functional groups in proteins, when immobilized onto a solid phase, may selectively capture dissolved heavy metals from the aqueous phase. Widely used chelating exchangers essentially conform to this principle of separation. Tens of polymeric chelating exchangers have been synthesized to date, and are commercially available with various types of covalently attached functional groups. Physically, they are all the same, i.e., spherical beads with high mechanical strength and durability. Figure 1.3 illustrates several commercially available chelating exchangers with linear polymer chains, cross-linkings and a variety of covalently attached functional groups. Understandably, it is the Lewis acid-base interaction that governs the binding affinity of a heavy metal cation to a chelating exchanger. Such binding affinities (often expressed as separation factor values) are correlated to corresponding aqueous-phase stability constant values between the heavy metal ions and the representative ligands, and they can be modeled by the Linear Free Energy Relationship (LFER) [5]. Figure 1.4 shows the relationship between copper/calcium separation factor values for three commercial chelating exchangers and the corresponding aqueous-phase stability constant values for representative ligands [6]. Noteworthy is the fact that as the composition of the functional groups in Figure 1.4 changes from hard oxygen donor atoms (i.e., carboxylate) to relatively soft nitrogen donor atoms (bispicolylamine), the affinity of Cu(II), a borderline Lewis acid, is greatly enhanced over the hard cation, Ca<sup>2+</sup>. Understandably, the composition of the functional groups in chelating exchangers can be judiciously tailored to improve specific affinities toward target metal ions. Chelating exchangers with S-containing thiol functional groups offer significantly higher selectivity for soft Hg(II) over Cu(II) and Zn(II). Along the same vein, Figure 1.5 shows the separation factor values of five different heavy metal cations for a weak-acid cation exchange resin with carboxylate functional groups (IRC DP-1, Rohm and Haas Co., Philadelphia, PA, USA). Note that the sequence and relative affinity of dissolved heavy metals are strongly correlated to their aqueous phase metal-acetate stability constant values [7].

Metals' sorption onto polymeric chelating exchangers is, however, kinetically slow, and



(Aminophosphonate)

Figure 1.3 An illustration depicting a chelating polymer bead with different covalently attached functional groups.



Figure 1.4 Relationship between copper/calcium separation factors for commercial chelating exchangers and corresponding aqueous-phase stability constant values with representative ligands.

intraparticle diffusion is often, if not always, the rate-limiting step. Due to the rigid structure and tortuous pathways, the effective intraparticle diffusivities for metals within chelating ion exchangers are several orders of magnitude lower than they are in the solvent phase. Solvent Impregnated Resins (SIRs) can greatly overcome this shortcoming. Even more important, SIRs do not require covalent attachment of organic functional groups onto the parent polymer beads and thus conveniently avoid major steps in chemical synthesis for their preparation. In SIR, an organophilic complexant is sorbed within macroporous copolymer beads, and the combined material serves as the metal-selective sorbent [8,9]. One critical disadvantage of SIRs is the gradual loss of complexant through aqueous-phase dissolution, which is a significant problem and precludes adaptation of SIRs in environmental application.

In order to eliminate the loss of complexant, a new SIR has been prepared wherein a thin coating is formed around each bead [10]. This coating is hydrophilic, thus preventing transport of the hydrophobic complexant out of the bead while permitting transport of the hydrophilic metal ion into the bead. Figure 1.6 illustrates the characteristic features of the modified SIR. Conceptually similar techniques have also evolved in membrane processes where hollow-fiber contained liquid membranes are used to selectively remove dissolved heavy metals from the aqueous phase with a minimum loss of the organic extractant in the aqueous phase [11,12].

Equipment configurations and physical arrangement of the processes for heavy metals removal often vary widely. Nevertheless, barring a few minor exceptions, Lewis acid-base interaction aided by precipitation, sorption, sieving, etc., constitutes the primary mechanism for heavy metals separation. Many biorenewable materials such as naturally occurring humus, dead bacterial and fungal cells and seaweeds, contain surface functional groups (carboxylate, carbonyl, phenolic) with moderate to high affinity toward heavy metals. Significant progress has been made in the recent past in modifying such materials into chemically stable, mechanically strong, durable sorbents [13,14]. As we lay an increased empha-



Figure 1.5 Relationship between experimentally determined metal/calcium separation factors for IRC DP-1 and aqueous-phase metal-acetate stability constant values.



Figure 1.6 An illustration of the characteristic features of the modified solvent-impregnated resin (SIR).

sis on sustainable development, these sorbent materials are likely to be economically competitive, and large-scale commercial production will follow.

#### **Redox Chemistry**

Cycling of heavy metals in the environment as well as their removal by engineered processes are influenced by redox reactions. The following four examples to this effect cover a broad spectrum and provide an engineering perspective regarding how redox chemistry can be manipulated to achieve efficient separation of heavy metals.

$$CrO_4^{2-} + 5H^+ + 3e^- \xrightarrow{Reduction} Cr(OH)_{3(s)} \downarrow +H_2O$$
(3)

$$\begin{array}{c} Oxidation \\ H_2AsO_4^- + 3H^+ + 2e^- & H_3AsO_3 + H_2O \\ (Strongly Adsorbable) & (Poorly Adsorbable) \end{array}$$
(4)

$$Cd^{2+} + SO_4^{2-} + 8H^+ + 8e^- \xrightarrow{Reduction} CdS_{(s)} \downarrow + 4H_2O$$
(5)  
(Mobile)

$$\frac{\text{Hg}^{\circ} \quad \text{Oxidation}}{\text{S}^{\circ} \quad \text{Reduction}} \longrightarrow \text{HgS}_{(s)} \downarrow$$
(6)

Each of the four foregoing reactions deserve some discussion to elucidate possible application of redox chemistry in achieving heavy metals separation.

- (1) Toxicity, accompanied by widespread industrial applications and high mobility, has earned Cr(VI) an unusual notoriety in the area of environmental pollution. Contrary to Cr(VI) species or chromates, Cr(III) is less toxic and very insoluble at neutral to alkaline pH. As a result, chemical reduction of Cr(VI) to Cr(III), followed by precipitation as chromic hydroxide, Cr(OH)<sub>3(s)</sub>, has been the traditional approach for treating Cr(VI)-laden wastewater [15,16]. For relatively low concentrations of Cr(VI) using polymeric anion exchangers [17,18]. Subsequently, Cr(VI) can be concentrated through regeneration, and Cr(VI) in the spent regenerant can efficiently be reduced to relatively innocuous Cr(III) hydroxide.
- (2) In many naturally contaminated groundwaters, dissolved As(III) compounds are significantly present along with As(V) species [19,20]. Sorption affinity of As(III) oxyacid (i.e., HAsO<sub>2</sub>) onto aluminum oxide particles is poor [21]. That is why removal of As(III) through use of activated alumina adsorbent or alum coagulant is very inefficient [22]. Arsenic(V) oxyanions, on the contrary, are well adsorbable onto alumina particles. Thus, oxidation of As(III) to As(V) by chlorination or through use of manganese dioxide solids significantly improves overall arsenic [23,24].
- (3) Changes in the oxidation states of accompanying species may also be utilized to remove heavy metals from the aqueous phase. Under anoxic or anaerobic conditions, sulfate in water is reduced by sulfate-reducing bacteria to sulfide, thus facilitating heavy metals precipitation due to very low solubility products of metal sulfides. Microbially mediated sulfate reduction is thus a viable mechanism for heavy metals separation. Many engineered biological processes and wetland systems judiciously utilize sulfate reduction as a means to reduce heavy metals concentrations from industrial wastewaters [25,26].
- (4) Of all the heavy metals present in the environment, mercury is conspicuous due to its volatility in the elemental state; its ability to exist in all three phases, namely, air, soil and water, in different oxidation states; and its susceptibility to undergo biomethylation and concentrate in the food chain. Flue gases from industrial furnaces and incinerators are the primary contributors of mercury into the atmosphere. One viable process for removal of elemental mercury involves use of novel sulfur-impregnated porous adsorbents [27,28]. Selective mercury separation within this adsorbent is primarily a redox chemisorption process as shown in Equation (6), where elemental mercury is essentially immobilized within the porous adsorbent as highly insoluble mercuric sulfide, HgS<sub>(s)</sub>, in +II oxidation state.

It is well recognized that in many hazardous waste sites, the chemical state and mobility of toxic metals are closely linked to biogeochemical redox reactions that occur as a result of organic carbon being degraded by different microorganisms using a series of terminal electron acceptors [29,30]. In such environments, trace heavy metals can be mobilized/immobilized via processes such as reduction/oxidation, sorption/desorption, precipitation/dissolution, and/or the formation of complex compounds. Figure 1.7 illustrates how the arsenic or chromium speciation changes with the changes in electron acceptors responsible for biological reactions. It is important to note that in the reduced state, chromium or Cr(III) becomes insoluble and, hence, immobile. In contrast, arsenic in the reduced state, i.e., As(III), is nonionized and, hence, more mobile. The underlying scientific principles governing adsorbability and solubility of heavy metals in the natural environment are often the same as those applied in engineered processes for achieving efficient metals separation.



Figure 1.7 Change in arsenic and chromium speciation with the change in biogeochemistry of the subsurface environment (adapted from Bouwer and Zehnder, 1993, *Trends in Biotechnology*, 11, 360–367).

#### SEPARATION STRATEGIES AND CHAPTERS IN THE BOOK

Ionic charges, Lewis acidity/basicity, sorption affinity onto particulates containing surface functional groups, aqueous-phase solubility, physical sizes of the metal-ligand complexes, redox state, etc., can be manipulated to achieve efficient separation of heavy metals from the aqueous phase and other complex systems. Speciation of heavy metals in the dissolved states varies, and so do the sizes of these species. Table 1.2 provides the estimated sizes of divalent heavy metal cations, Me(II), in different physicochemical forms. Fate and transport behaviors of these heavy metals in a natural environment are also influenced by their relative sizes. Figure 1.8 shows a schematic illustrating a wide variety of strategies for heavy metals separation. Understandably, each of them has the potential to be a viable metal separation process under a specific set of conditions. In certain instances, combination of

State Dissolved	Speciation	Approximate Diameter (Nanometer)
Water	H <sub>2</sub> O	0.2
Hydrated free metal ion	$[Me(H_2O)_n]^{2+}$	Around 0.5
Inorganic complexes	[Me(NH <sub>3</sub> ) <sub>n</sub> ] <sup>2+</sup> [MeOH] <sup>+</sup> [Me(OH) <sub>2</sub> ] <sup>0</sup> [MeCO <sub>3</sub> ] <sub>2</sub> <sup>2-</sup>	Less than 1.5
Organic complexes	[Me(COO) <sub>2</sub> ] <sup>0</sup> [Me(NH <sub>3</sub> ) <sub>7</sub> ] <sup>2+</sup> [Me(EDTA)] <sup>2-</sup>	1–5
Macromolecules/colloids	Me—Humate Complex Me—Fulvate Complex Me—NOM-coated silica	10500
Surface binding onto microparticles	FeO <sup>-</sup> (Me <sup>2+</sup> ) FeO <sup>-</sup>	100-10,000
Precipitates	Me(OH) <sub>2(s)</sub> MeCO <sub>3(s)</sub>	>500

TABLE 1.2. Size of a Heavy Metal Cation (Me<sup>2+</sup>) in Water in Different Physicochemical States.

more than one, i.e., a hybrid process, may be the most suitable. All such applications, however, tend to have one major drawback—they are unable to recover individual heavy metals with a high degree of purity and reuse it. With pollution prevention guidelines and the concept of industrial ecology in place, research and development works are under way to separate individual heavy metals and enhance their purities in recovered materials.

In addition to this concise introduction, the book contains nine chapters—all geared toward environmental separation of heavy metals. In choosing topics for inclusion in the book, the primary intent has been to provide comprehensive coverage to those recent developments that have potentials for applications in the near future. It is true that most of the chapters have very specific titles. However, their contents go well beyond the targeted goals. Underlying fundamentals and approaches elaborated in each chapter can be extended to understand and investigate other problems. The following provides a brief summary delineating the contents of each chapter.

The presence of elemental mercury in the flue gases of coal-fired utilities and waste incinerators has emerged as a major environmental concern. Chapter 2 provides a detailed account of equilibrium and kinetic properties of mercury removal using well-characterized carbon-based materials.

Underlying principles of chelating ion exchange and recent advances toward tailoring highly selective polymeric exchangers are elaborated in Chapter 3. Also included in this chapter are two challenging issues confronting heavy metals separation: first, selective removal of trace amounts of heavy metal precipitates from the background of innocuous sludge or residual solids; and second, separation of individual heavy metals.

Chapter 4 is dedicated toward the growing field of magnetic separation of heavy metals. In general, heavy metal precipitates have poor magnetic properties, i.e., they are dia- or weak paramagnetic particles. Co-precipitation with magnetically active iron oxide particles greatly enhances their specific magnetic susceptibilities. Subsequently, the resulting precipitates can be effectively removed using high gradient magnetic separation





technique or other magnetic processes. The chapter also highlights how microbially mediated biological reactions can be integrated into magnetic separation of heavy metals.

Sizes of dissolved heavy metal ions are often less than 10 Angstroms (or one nanometer) and, hence, they are not amenable to separation by low pressure ultrafiltration processes. Heavy metal ions can, however, form macromolecules with tailored polyelectrolytes through formation of metal-ligand complexes. These soluble macromolecules are often two to three orders of magnitude greater in size than pure metal ions and are removable by low-pressure membrane processes. Chapter 5 provides a detailed account of polyelectrolyte-mediated membrane processes for metals removal from contaminated soils or sludges.

Precipitation alone is often inadequate to satisfy the stringent regulations in regard to residual dissolved metal concentrations in the liquid phase. Co-precipitation in concert with specific surface adsorption may greatly overcome such shortcomings in many real-life situations. Two detailed case histories to this effect are summarized in Chapter 6.

Activated carbon is an inexpensive and widely used adsorbent, but its application to date is limited to removing dissolved hydrophobic organic compounds. Through controlled oxidation, concentration of carboxylate and phenolic groups in activated carbon particles can be greatly enhanced, leading to high metal removal capacity. Chapter 7 discusses metals sorption by surface complexation, regenerability and possible reuse of activated carbons for a multiple number of cycles.

In January 2001, under a federal rule signed by the United States Environmental Protection Agency (USEPA) and the former US president, a revised arsenic Maximum Contaminant Level (MCL) to 10  $\mu$ g/L was made effective five years from its promulgation; however, this ruling was later reversed in March 2001, by the current USEPA administration. Currently, the 60-year old arsenic MCL of 50  $\mu$ g/L is the highest among all the developed countries in the world but a revised standard is scheduled to come into effect by January 2002. A world away, over seventy million people in Bangladesh and the Indian subcontinent are routinely exposed to arsenic poisoning through drinking water. Chapter 8 discusses salient aspects of geochemical contamination of groundwater by arsenic and underlying principles of various arsenic removal technologies.

Use of trivalent chromium or Cr(III) reagent has been widely practiced in leather or tanning industries around the world for centuries. It is well recognized that once discharged into the environment, Cr(III) is amenable to oxidation into more toxic and mobile Cr(VI). Chapter 9 provides information pertaining to recovery and reuse of Cr(III) in tanning industries.

Naturally occurring humus is a biorenewable material with an ability to complex heavy metals through its carboxylate, phenolate and similar other oxygen-containing functional groups. Chapter 10 discusses techniques used to chemically modify humus materials into viable heavy metal sorbents and presents experimental data to this effect.

As the editor of this treatise, I am quite optimistic about its value and usefulness to the professional community. The practicing engineers, scientists, and researchers who are directly involved in the application and research pertaining to heavy metals would very likely welcome this book as a ready reference for its thoroughness and up-to-date information on areas of current interest. Also, the book would serve the needs of those trying to explore and identify new technologies in the areas of heavy metals control and pollution prevention.

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### Adsorption of Elemental Mercury by Virgin and Impregnated Activated Carbon

RADISAV D. VIDIC1

#### INTRODUCTION

#### **Mercury in the Environment**

**E**WIRONMENTAL control agencies and researchers have become increasingly concerned with the mobilization of trace elements to the environment from fossil fuel burning and solid waste incineration. Mercury is the trace element of particular concern, because during combustion, most of the mercury present in the feed stream is transferred into the vapor phase due to its high volatility. There is considerable evidence in the literature that currently used pollution abatement technologies (flue gas desulfurization, control of NO<sub>x</sub> and SO<sub>x</sub> emissions and particulate control devices) are not capable of controlling gas-phase mercury emissions [7–11,56].

Mercury is emitted into the atmosphere from various anthropogenic and natural sources. Natural sources of mercury include volatilization from soils, vegetation and the ocean. The global marine emissions of vapor-phase mercury are estimated to be about 2,000 ton/year [1]. Nriagu and Pacyna [2] estimated that the global anthropogenic emissions of vapor-phase mercury produced from human activities are about 1,000–6,000 ton/year, while Porcella [1] reported that about 2,000–3,400 ton/year of mercury emitted from anthropogenic sources accounts for about 30–55% of global atmospheric mercury emissions.

Physical forms of mercury in ambient air can be divided into two categories: vapor phase, which is dominant in the atmosphere, and particulate phase (associated with aerosols), which only comprises a few percent of total airborne mercury emissions [3]. Chemical forms determine the transport between different environmental media (air, water and soil) [1,4], and the mercuric compounds can be classified into elemental and divalent forms. The elemental form of mercury (Hg<sup>o</sup>) is the dominant form (>98%) of vapor-phase mercury

<sup>&</sup>lt;sup>1</sup>Department of Civil and Environmental Engineering, 943 Benedum Hall, University of Pittsburgh, PA 15261, U.S.A., vidic@civeng1.civ.pitt.edu

in the atmosphere [1,3,5], and, following dissolution in cloud water or rainwater, is readily converted (oxidized) to more soluble mercury species [3]. Elemental mercury possesses relatively high vapor pressure and low solubility [6]. The former property leads to considerable mercury evaporation into the ambient air, while the latter makes it difficult for the existing air pollution control devices to remove mercury from the emission sources. Divalent mercury forms include inorganic (Hg<sup>2+</sup>, HgO, HgCl<sub>2</sub>) and organic oxidized forms (CH<sub>3</sub>Hg, CH<sub>3</sub>HgCl, CH<sub>3</sub>HgCH<sub>3</sub>)[1,3,6]. Divalent forms possess higher solubilities and readily combine with a variety of reactants, such as sulfite, chloride and hydroxide ions, in the aqueous phase [6].

Once discharged to the atmosphere, mercury persists in the environment and creates a long-term contamination problem. Furthermore, well-documented food chain transport and bioaccumulation of mercury, together with high toxicity to mammalians and severe health problems caused by the ingestion of mercury even at low levels, require strict control of mercury emissions from coal-fired power plants. Subsequently, the Clean Air Act Amendments of 1990 (Title III, Section 112[b][1]) require major sources to use maximum available control technology (MACT) to reduce mercury emissions.

#### **Current State of Mercury Control Technologies**

Many existing air pollution control technologies and several innovative methods have been evaluated for the control of vapor-phase mercury emissions from combustion processes. Sodium sulfide (Na<sub>2</sub>S) has been used for vapor-phase mercury control in municipal solid waste combustors in Canada, Sweden, Germany and British Columbia. Sodium sulfide injection is usually combined with dry sorbent injection (DSI) and fabric filters (FFs) for acid gas and particulate matter (PM) control [7,8]. It has been reported that mercuric sulfide (HgS) is generated as a fine particulate in the process, which may prove difficult to capture in less efficient electrostatic precipitators (ESPs). Other potential problems for this process include corrosion, hydrogen sulfide formation and chemical storage and handling [9]. These problems, compounded by the lack of test data on full-scale coal-fired power plants [7,8], cloud the utility of sodium sulfide injection for the control of mercury emissions.

Wet scrubbers have been routinely used to remove hydrochloric acid and sulfur dioxide from the flue gases of industrial factories, coal-fired power plants and municipal waste combustors. Considerable interest in the use of wet scrubber systems to simultaneously remove sulfur dioxide and mercury has recently been expressed [7,9–11]. The removal of vapor-phase mercury in the wet scrubber system would also occur by absorption in the scrubbing slurry, whereby the mechanism of mercury removal depends on the solubility of mercury in the scrubbing slurry, contact time and solution chemistry. Elemental mercury is essentially insoluble in the wet scrubbing slurry, while some of the oxidized species, such as mercuric chloride, are highly soluble. Therefore, oxidized mercury can be easily absorbed with sufficient gas-liquid contact, while the removal of elemental mercury would remain limited [7–10]. Chang and Owens [12] reported that the treatment of a coal-fired power plant flue gas using only a wet scrubber allowed 70–75% of elemental mercury to be discharged into the atmosphere, while other studies reported 30–70% removal of elemental mercury by wet scrubbers [11].

In the past decade, spray dryer adsorption (SDA) systems have been applied to more than 17,000 MW of coal-fired boilers and several hundred municipal waste and hazardous waste

incinerators [13,14]. The SDA process has been specified as one of the best available control technologies (BACT) to treat gas contaminants. The essence of the contaminant removal in the SDA process is the reaction with the alkali adsorbents. The alkali adsorbent can be lime (CaO), soda ash ( $Na_2CO_3$ ), NaOH or NaHCO<sub>3</sub>. Because of the nature of the waste product and its capability of meeting emission requirements, lime is the best choice for the adsorbent in most applications. Total mercury removal in the range of 3–50% can be achieved by the SDA process because only the oxidized forms of mercury can be captured, which elemental mercury will pass through the system [13,14]. For the effective control of vapor-phase mercury emission, the SDA system can be augmented with an activated carbon injection system that can increase the removal of mercury to more than 90% [13,14].

#### Adsorption-Based Technologies for Mercury Control

Activated carbon adsorption is the technology that offers great potential for the control of mercury concentrations in gas-phase emission. Otani et al. [15] studied the adsorption of mercury vapor on particles at room temperature using soot particles generated by incineration of sewage sludge and activated carbon particles. They observed that ash adsorbed very little mercury so that most mercury behaves as a vapor even in the presence of soot particles. Activated carbon, on the other hand, had an order of magnitude higher capacity that was accurately described by the Freundlich isotherm equation. Sinha and Walker [16] reported that sulfur-impregnated carbon due to the reduction in the surface area induced by the impregnation process. However, at higher temperatures (150°C), the adsorptive capacity of sulfur-impregnated carbon greatly surpassed the capacity of virgin-activated carbon due to chemisorption of mercury and formation of mercuric sulfide. Furthermore, they reported that water vapor reduces adsorption of mercury for sulfur-impregnated carbon.

Matsumura [17] used steam-activated carbon from coconut shell in his studies of the effects of oxidation and iodization of activated carbon surface on the removal efficiency for mercury vapor. He concluded that oxidized or iodized activated carbon adsorbed mercury vapor 20–160 times more than untreated activated carbon when mercury vapor in concentrations of up to 40 mg/m<sup>3</sup> in a nitrogen stream at 30°C was brought into contact with these adsorbents. Oxidized carbons were successfully regenerated with hydrochloric acid. Iodized activated carbons were shown to be suitable adsorbents for mercury vapor though adsorbed mercury was not proportional to the amount of iodine adsorbed on the carbon.

Teller and Quimby [18] evaluated the performance of activated carbons impregnated with copper chloride or sulfur for the removal of mercury under the conditions representative of solid waste incinerators. They concluded that moisture content of the carrier gas and temperatures tested in their study had no effect on copper chloride-impregnated carbon capacity for mercury vapor. They also concluded that as the impregnate concentration increases (for copper chloride), mercury removal increases, but they were not able to correlate these two parameters. They observed that copper chloride-impregnated carbon exhibits as much as 300 times higher capacity for mercury removal as compared to untreated activated carbon. Sulfur-impregnated carbon exhibited only a 60% improvement in the breakthrough time. On the other hand, Henning et al. [19] examined the influence of potassium iodide and sulfur as impregnates for improving the ability of activated carbon to adsorb mercury. Their results indicated that 11 wt% sulfur addition increased the adsorption capacity by a factor of 400. Direct injection of activated carbon into the flue gas stream has been proposed as a relatively simple approach for controlling mercury emissions [12]. Injected activated carbon binds the vapor-phase mercury through physical adsorption and/or chemisorption and is collected in downstream particulate collection devices, such as FFs or ESPs. Results from several tests indicated that effectiveness of activated carbon injection in removing mercury vapor depends on the type and composition of burned materials, flue gas composition and temperature, mercury speciation, activated carbon properties and injection rate, and operating conditions [5]. Lowering the flue gas temperature from 345 to 250°F with direct injection of virgin activated carbon improved mercury removal efficiency from 0% to 37%. Further tests showed that virgin activated carbon injection at 200°F resulted in greater than 90% mercury removal [13]. Because activated carbon can be collected effectively in the existing particulate control devices, direct activated carbon injection has several potential advantages over SDA and wet scrubbing processes: (1) simpler operation, (2) lower operational cost, (3) lower capital cost, (4) no wastewater problems, (5) simpler waste-disposal, (6) easier maintenance and repair and (7) greater efficiency for mercury removal.

Based on the success of field-scale trials conducted on a number of municipal solid waste (MSW) incinerators, it was anticipated that powdered activated carbon injection into the flue gas with subsequent collection at the fabric filters can also be used for the control of mercury emissions from coal-fired power plants. However, due to the fact that mercury concentrations in MSW incinerator flue gas (200–1,000  $\mu$ g/m<sup>3</sup>) are one to two orders of magnitude higher than for coal-fired power plants (2–20  $\mu$ g/m<sup>3</sup>), as well as other differences in process conditions (e.g., HCl content, flow rate, SO<sub>2</sub> and NO<sub>x</sub> concentration), carbon to mercury ratios required for effective control of mercury in MSW flue gas are an order of magnitude lower than those necessary to achieve similar mercury emissions from coal-fired power estimates for the control of mercury emissions from s14,400 to \$38,200 per pound of mercury removed [12]. Clearly, the use of virgin activated carbon is too costly and too low in efficiency to be practical. Therefore, further sorbent improvements must be made in order to facilitate commercial success of this promising technology.

#### MERCURY UPTAKE BY VIRGIN ACTIVATED CARBON

#### **Experimental Approach**

Detailed description of the experimental system and analytical methods used to evaluate the rate of mercury uptake by commercially available activated carbon (BPL, Calgon Carbon Corporation, Pittsburgh, PA, USA) is provided by Vidic et al. [20] and is briefly described here. Schematic representation of the experimental setup is shown in Figure 2.1. Differential-bed reactor was charged with 100 mg of activated carbon, placed in a laboratory oven and operated in a downflow mode. Six feet of Teflon tubing was placed in the oven upstream of the column to facilitate heating of the influent gas to a desired temperature. In order to prevent damage of the system components due to high effluent temperature in the recirculation loop, the recirculation loop was first passed through a condenser to cool the effluent gas coming out of the oven. Mercury laden gas was recirculated in the system at a flow rate of 75 L/min, which provided a gas turnaround time of 10 seconds. Mercury concentration in this closed system was continuously monitored using the atomic adsorption spectrophotometer equipped with a quartz cell and a hollow cathode lamp adjusted to a wavelength of 253.6 nm.



#### **Modeling Adsorption Kinetics**

The homogeneous surface diffusion model (HSDM) was used to describe the kinetics of adsorption of compounds from the carbon surface into the particle. Because numerous articles have extensively described the theory behind the HSDM [21–23], only the primary assumptions are presented here. The HSDM was coupled to a model for a batch system to describe the uptake of Hg from the bulk phase onto the activated carbon. The key assumptions for the batch model and HSDM include the following: (a) removal of Hg from the bulk is due solely to adsorption by activated carbon; (b) the activated carbon particles are all spherical, uniform in size and well-dispersed in the gas phase; (c) a mass transfer boundary layer causes resistance to mass transfer from the bulk to the activated carbon surface; (d) adsorption equilibrium between the activated carbon surface and the gas phase is described by the Langmuir isotherm; (e) mass transfer within the activated carbon particle is controlled by surface diffusion; and (f) the activated carbon particle is isothermal.

A mass balance on Hg in the activated carbon particle and the bulk can be written as

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} q \tag{1}$$

$$V\frac{dc_b}{dt} = -m_c \frac{dq_{ave}}{dt}$$
(2)

where

$$q_{ave} = \frac{3}{r_p^3} \int_0^{r_p} q(r,t) r^2 dr$$
(3)

Equations (1) and (2) are subject to the following initial and boundary conditions:

$$q(r,t=0) = 0$$
 (4)

$$c_b(t=0) = c_o \tag{5}$$

$$\frac{\partial q(r=0,t>0)}{\partial r} = 0 \tag{6}$$

$$\rho_p D_s \frac{\partial q(r=r_p, t>0)}{\partial r} = k_f (c_b - c_s) \tag{7}$$

$$q(r = r_p, t > 0) = \frac{q_{\max}bc_s}{1 + bc_s}$$
(8)

Using the following dimensionless variables,

$$C = \frac{c}{c_o} \qquad Q = \frac{q}{q_o} \qquad T = \frac{D_s t}{r^2} \qquad R = \frac{r}{r_p} \qquad Bi = \frac{k_f r_p c_o}{D_s \rho_p q_o} \qquad \lambda_b = \frac{m_c q_o}{V c_o} \tag{9}$$

where

$$q_o = \frac{q_{\max} b c_o}{1 + b c_o} \tag{10}$$

Equations (1) to (8) can be rewritten in the following dimensionless format:

$$\frac{\partial Q}{\partial T} = \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} Q$$
(11)

$$\frac{dC_b}{dT} = -\lambda \frac{dQ_{\text{ave}}}{dT} \tag{12}$$

$$Q_{\rm ave} = 3 \int_0^1 Q(R, T) R^2 dR$$
 (13)

$$Q(R, T = 0) = 0 \tag{14}$$

$$C_b(T=0) = 1$$
 (15)

$$\frac{\partial Q(R=0,T>0)}{\partial R} = 0 \tag{16}$$

$$\frac{\partial Q(R=1,T>0)}{\partial R} = Bi(C_b - C_s) \tag{17}$$

$$Q(R = 1, T > 0) = \frac{1 + bc_o}{1 + bc_o C_s}$$
(18)

Equations (11) and (12) were reduced to ordinary differential equations using orthogonal collocation methods with 11 collocation points in the activated carbon particle [24]. The resulting system of equations was solved using DDASSL, a subroutine capable of simultaneously solving algebraic and ordinary differential equations [24].

The Langmuir isotherm constants  $(q_{\max} \text{ and } b)$ , the film mass transfer coefficient  $(k_f)$ , and the surface diffusion coefficient  $(D_s)$  were obtained by fitting the mathematical model simultaneously to several data sets obtained from batch experiments conducted at the same temperature using different initial mercury concentrations. The sum of the squares of the differences between the model output and the data sets (i.e., sum of squares of errors or SSE) was minimized by varying the four parameters using simulated annealing as a global minimization algorithm [24].

Table 2.1 shows the parameter values obtained at the two temperatures, and Figures 2.2(a) and 2.2(b) show the model fit and experimental data at 25°C and 140°C, respectively [24].

An increase in temperature results in a lower capacity of the carbon for Hg, which is characteristic of an exothermic adsorption process and is consistent with other studies [2,12,13]. The Langmuir coefficient, b, which can be conceptualized as the ratio of the kinetic coefficient for adsorption to the kinetic coefficient for desorption, increased with tem-

	Tempe	erature	
Parameter	25°C	140°C	
q <sub>max</sub> (μg/g) b (m <sup>3</sup> /μg) k <sub>i</sub> (cm/s) D <sub>s</sub> (cm <sup>2</sup> /s)	123 9.15 × 10 <sup>-3</sup> 12.0 2.29 × 10 <sup>-7</sup>	27.5 2.06 × 10 <sup>-2</sup> 19.4 1.21 × 10 <sup>-6</sup>	2

TABLE 2.1. Parameter Values Obtained from Model Fit (from Flora, Vidic, Liu and Thurnau, *J. AWMA*, 48:1051, 1998. With Permission from Air and Waste Management Association).

perature. If the effect of temperature on both kinetic coefficients can be described using an Arrhenius relationship, then b should not change with temperature. It is possible that with an increase in temperature, the kinetic coefficient for adsorption increased, but the kinetic coefficient for desorption did not increase with the same magnitude. A shift in the adsorption mechanism from physical to chemical at a higher temperature could result in a proportionately lower increase in the desorption kinetic coefficient [12].

#### **Model Predictions**

Because this research focuses on the removal of Hg under conditions that may be encountered in the flue gases of coal-fired power plants, the isotherm parameters and  $D_s$  obtained from the batch experiments at 140°C were used for the simulations. Because the process configuration for the laboratory tests was different from what would be encountered in a flue gas stream,  $k_f$  was estimated using an empirical correlation for forced convection around a solid sphere as described by Flora et al. [24].

The model developed for a batch system was adapted to estimate the performance of virgin activated carbon in a flue gas stream, where steady-state, plug-flow conditions were assumed. Figure 2.3 shows the impact of particle radius on the fractional removal of Hg from the influent of flue gases as a function of retention time in the flue gas stack for a C/Hg ratio of 10<sup>6</sup>. An initial mercury concentration of 20  $\mu$ g/m<sup>3</sup> was used in all calculations. The fractional removal of Hg increases with longer retention times, with the fractional removal asymptotically reaching a maximum value. At this maximum value, the carbon particles are at equilibrium with the bulk Hg concentration, and further Hg removal cannot be realized. Longer residence time is required for particles with larger radii to reach equilibrium because of the longer distance that the Hg has to diffuse into the carbon. Assuming the average residence time of activated carbon injected into the flue gas of 2 seconds, it can be seen from Figure 2.3 that the equilibrium is reached for particles with radius below 30  $\mu$ m, with larger particles having lower mercury removal.

One strategy to increase mercury removal from flue gases is to use carbon particles with a higher adsorptive capacity. To analyze the impact of carbon capacity, simulations were performed with varying  $q_{max}$  for various particle radii, while keeping other parameters constant. Figure 2.4 shows the required C/Hg ratio to achieve 90% removal of Hg for various carbon capacities. Because equilibrium is achieved for small particle radii, the required C/Hg ratio decreases linearly with an increase in capacity. This linear relationship holds for a fixed removal efficiency if all other parameters remain constant. For large particle radii, the required C/Hg ratio is less sensitive to the carbon capacity because the system is mass-transfer limited. This is particularly evident for particles with a radius greater than  $3 \times 10^{-3}$  cm (30 m) and for  $q_{max}$  greater than 200 µg/g. Under these circumstances, Hg removal



Figure 2.2 Rate of mercury uptake by virgin activated carbon at: (a) 25°C and (b) 140°C (from Flora, Vidic, Liu and Thurnau, J. AWMA, 48:1051, 1998. With permission from Air and Waste Management Association).



Figure 2.3 Fractional mercury removal for a carbon/mercury injection ratio of  $10^6$  and an influent mercury concentration of 20 mg/m<sup>3</sup> (from Flora, Vidic, Liu and Thurnau, *J. AWMA*, 48:1051, 1998. With permission from Air and Waste Management Association).



Figure 2.4 Impact of adsorptive capacity on carbon/mercury injection ratio required for 90% mercury removal.

is primarily dependent on the amount of Hg that can diffuse from the bulk into the carbon particle. Using a smaller particle size would provide more efficient use of the carbon for Hg removal.

#### MERCURY UPTAKE BY IMPREGNATED ACTIVATED CARBONS

#### Sulfur-Impregnated Activated Carbons

Initial studies on the effectiveness of sulfur impregnation on mercury uptake were performed using a commercially available sulfur-impregnated activated carbon (HGR, Calgon Carbon Co., Pittsburgh, PA, USA) and activated carbon produced by the reaction with elemental sulfur at 600°C and denoted as BPL-S [25]. This temperature was selected based on an earlier report that the chemisorption of sulfur onto activated carbon is maximized at 600°C [24]. Although the two different impregnation methods used in the production of these sorbents yielded similar sulfur contents (Table 2.2), the BET specific surface area of BPL carbon that was used as a starting material for both sorbents was reduced by 53 and 20% for HGR and BPL-S, respectively (Table 2.2). Due to the higher impregnation temperature, the sulfur in BPL-S carbon is suspected to be more evenly distributed in the pore structure, occupying the deeper, narrower pores. The sulfur in HGR carbon, on the other hand, is most likely condensed at the external surface of the carbon particle, blocking the access to the narrower high-energy pores [25].

Thermogravimetric analysis (TGA) was conducted by heating samples of BPL, HGR and BPL-S carbons up to 400°C in an argon atmosphere. Both BPL and BPL-S carbons underwent negligible decreases in weight, while the weight of the HGR carbon sample decreased by 8.5%. Because both HGR and BPL-S carbons are manufactured by impregnating BPL carbon with sulfur, this outcome implies that BPL-S carbon lost a negligible amount of its impregnated sulfur, while HGR carbon lost 88% of its sulfur content.

Sulfur exists in several allotropes, including  $S_{\lambda}$  (S8 rings),  $S_{\pi}$  (S8 chains) and  $S_{\mu}$  (chains of variable length), with S8 rings as the only form at room temperature [27–29]. Because the sulfur vapor at 200°C is in the form of  $S_8$  (76.5%) and  $S_6$  (23.5%) rings [27,29], it is reasonable to assume that HGR carbon contains sulfur predominantly in the form of voluminous S8 rings. At 600°C, sulfur vapor possesses a significant fraction of  $S_6$  (58.8%) and  $S_2$ (16.4%) molecules [29], which are less voluminous and more reactive because they possess a greater fraction of sulfur terminal atoms [30]. Therefore, the smaller  $S_2$  and  $S_6$  chains can more easily migrate into the narrower pores of the carbon matrix and, as the carbon cools to room temperature at the completion of the impregnation process, steric hindrance impedes reformation of the more voluminous  $S_8$  rings from the other two allotropes [30–33].

Based on the discussion presented above, it is believed that the sulfur in HGR carbon is predominantly in the form of  $S_8$  rings and is weakly bonded to the carbon surface in the macroporous region of the carbon particle. On the other hand, the sulfur in BPL-S carbon is

GAC Type	Sulfur Content (wt%)	BET A <sub>sp</sub> (m <sup>2</sup> /g)
BPL	0.7	1026
HGR	9.7	482
BPL-S	10.0	824

TABLE 2.2. Comparison of GAC Types (from Korpiel and Vidic, *Environ. Sci. Technol.*, 31(8):2319, 1997. With Permission from American Chemical Society).