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CONTROL OF TOXIC METALLIC EMISSIONS FORMED DURING THE COMBUSTION OF OHIO COALS

FINAL REPORT

Project Duration: September 1994 to March 1996
(Second Year Report)

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

The objective of the project "Control of toxic metallic emissions formed during the combustion of Ohio coals" was to characterize metallic emissions from representative coals and develop strategies for their control. Though metallic emissions from coal combustors have been extensively studied, more studies need to be performed to better characterize the interaction of various species which is required for the selection and design of sorbents for effective control of these emissions. Furthermore, this characterization is important as the 1990 Clean Air Act Amendments (CAAA) have targeted a list of air toxics for further regulation under Title III. Eleven metallic species and their compounds - antimony, arsenic, beryllium, cadmium, chromium, cobalt, lead, manganese, mercury, nickel and selenium are in this list, and most of them are prevalent in coal. Major sources (industries emitting 10 tons per year of any single air toxic or 25 tons per year of any combination) will be initially targeted, and many utilities and industrial facilities using coal fall in this category. The other feature of the 1990 CAAA is that USEPA has been instructed to set stringent technology based standards, and therefore control techniques have to be developed. Some coals are rich in sulfur, and utilities using these coals will have to use some form of Flue Gas Desulfurization (FGD). A technique for FGD is the use of calcium based sorbents, and the degree of metals capture of these sorbents under different conditions will be researched.

The objective of the first year of the study was to understand the evolution of metallic aerosol size distributions and the capture characteristics of various sorbents. Also, the metallic emissions resulting from the combustion of two seams of Ohio coals were to be characterized. Studies on the evolution of the metallic aerosol size distributions have been completed and the use of silicon and calcium based sorbents for capture of lead species has been examined. Co-injection of metallic compounds along with organometallic silicon indicated a high degree of capture of lead in a certain temperature regime. Preliminary results with Calcium based sorbents also indicate capture of metallic species. To gain a further understanding of the capture processes, in situ optical diagnostic studies were performed in collaboration with researchers at the National Institute of Standards and Technology. Spectroscopic studies (laser induced fluorescence coupled with particle scattering) were performed to help understand the mechanisms of metallic species capture. Characterization of metallic emissions from the combustion of Ohio coals is in progress. Several modeling efforts have also been initiated. A detailed thermodynamic equilibrium model to predict metallic species capture rates has been developed and a number of simulations have been carried out to establish conditions for optimal removal of metallic species. As several competing mechanisms determine metallic species behavior in combustion systems, a detailed model accounting for competing effects of chemical reaction, nucleation, condensation and coagulation is being developed for comparisons with controlled experiments and to help develop design criteria. The results of some of the studies described above are discussed in some detail later.

In the second year, the work was extended to examine three different aspects:

(I) understanding the mechanisms of capture of metals by vapor phase sorbents,
(ii) role of chlorine in speciation of metals and its importance in metals capture, and
(iii) capture of mercury by aerosol transformation.

It was established that aerosol formation rates for Hg species is rather slow under typical combustion conditions, and hence would not be an effective way of capture of mercury. However, the use of titania based sorbents have provided exciting results. This is being developed further for effective capture of Hg species in combustion environments.

Several theoretical investigations were also carried out to better understand and predict trace metal behavior in combustion environments. Publications and conference presentations resulting from work this year is also listed.

Due to the novelty of the approach, the use of vapor phase sorbent materials, a patent was filed for the control of metallic emissions. This was done after a review of the existing patents. Several industries contacted us for further development and commericialization of this approach for metal control.

The results of the proposed study will enable characterization of metallic species during the combustion of Ohio coals. The results of the controlled tests will provide information and data to determine the impact of these emissions from Ohio coals and allow a comparison to results of previous studies on coals from other locations in the United States. The results of the metals capture studies will demonstrate the use of potential technologies for reducing metallic emissions. Operating conditions wherein sorbents for FGD can be potentially used for metals control will be established, providing for cost effective solutions.

INTRODUCTION

A. Background

A brief overview is presented here, a detailed scientific discussion was provided in the Year 1 and 2 proposals. Coal used for combustion purposes in the United States typically contains between 3 to 20% mineral matter by weight (Bailie, 1978), this ranging from 8 to 13% for Ohio coals (Knapp, 1977). The ash particles that are in the flue gases of coal combustion are controlled with particulate control devices, primarily electrostatic precipitators. As most of these particles are removed by such devices, ash received little attention as an air pollutant. However, a number of researchers such as Davison et al. (1974) have clearly shown that many of the toxic species such as lead, mercury, arsenic, selenium and cadmium are enriched in the smaller submicrometer sized particles. The particulate control devices have a minima in collection efficiencies in these size ranges. Therefore, even though most of the particles may be captured in control devices such as electrostatic precipitators, the particles that escape collection contain disproportionately high concentrations of toxic species. Though currently arsenic and mercury are the only metals regulated under the National Emission Standards for Hazardous Air Pollutants (NESHAPS), metals emissions from coal combustion facilities will come under further regulation under Title III of the 1990 Clean Air Act Amendments (CAAA). Antimony (Sb), Arsenic (As), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni) and Selenium (Se) from major sources have been targeted for regulation under Title III of the Clean Air Act (Quarles and Lewis, 1990). Major sources have been classified as industries that emit 10 tons per year of any single air toxic or 25 tons per year of any combination of the air toxics. Many coal combustion facilities fall in this category. There is therefore a renewed interest in examining emissions of these species from coal combustion sources. It must be noted that Congress under the 1990 CAAA instructed the USEPA that stringent *technology-based* *emission standards* be developed for the hazardous air pollutants (HAPs), that include the metals listed above. The Title III provisions of the CAAA establish for the first time that technology based criteria, the maximum achievable control technology (MACT), be used to set standards. This has led to renewed interest and research in control technology. To effectively control the emissions of the metallic species, it is imperative to understand the formation mechanisms and then develop control strategies.

A number of studies (Davison et al., 1974; Kaakkinen et al., 1975; Quann et al., 1982; Kang et al., 1990) have examined ash formation in coal combustion systems, a detailed review being provided by Flagan and Friedlander (1978). Two major mechanisms are considered to be important in the formation of particles. The first is due to the residual ash particles that remain when the coal particle burns out. The coal particle breaks up into fragments in the combustor due to thermal stresses. Volatile fractions originally present in the coal or formed during pyrolysis, result in the break up of the particle. Each fragment so formed may contain a portion of the original mineral matter that was present in the original coal particle. Many large ash particles are formed along with a large number of smaller particles which are comparable in size to the mineral intrusions in coal. Particles range in size from a few tenths of a micrometer to several micrometers. The second mechanism involves a smaller fraction of the ash that vaporizes at the high temperatures and nucleates to form very fine particles (angstrom size) which grow by condensation and coagulation to form larger particles in the submicrometer range.

Most of the metals targeted in the 1990 Clean Air Act Amendments are present in coal and are enriched in the emissions. Coles et al. (1979) have reported that Sb, As, Be, Cd, Co, Ni, Pb and Se are enriched in the finer particle size ranges in stack fly ash from a coal fired power plant. Mn was the only metal (in the Air Toxics list) that was not found to be enriched, no data was reported for mercury. Similar results have been reported by Smith et al. (1979) for fly ash from a coal combustor. Davison et al.(1974) have reported that enrichment in the ambient aerosol of these metals are of the order of 100 to 1000 fold over their natural crustal abundance. Billings and Matson (1972) indicate that 90% of the mercury in coal burned in a pulverized coal furnace is in the flue gas in the stack.

The findings of all these studies can be summarized as (i) the above listed metallic species are enriched in the stack flue gas, (ii) the particles are in the submicrometer size ranges, (iii) particles in these size ranges are readily inhaled and deposit in the lungs, and (iv) these metallic species are toxic and pose a significant health hazard. It is therefore essential to effectively control the emissions of these metallic species. The 1990 Clean Air Act Amendments therefore aim at developing regulations for these metals, and there is a renewed interest in effectively controlling their emissions. The proposed study aims to

- determine the metallic emissions during combustion of representative coals; better understand the chemistry of formation and growth dynamics of these species by comparison to emissions using specific metallic compounds;

- evaluate the degree of capture of these metallic species on sorbents potentially targeted for SO_2 control (such as Calcium based sorbents), and compare the degree of removal by the above sorbents to that by fly ash particles and other metals complexing agents;

- evaluate potential system modifications for capture of metallic species.

B. Work Accomplished to Date

The project involved both experimental and theoretical aspects. The progress made in each of these areas is summarized briefly here and discussed in detail later. A list of publications and conference presentations resulting from the second year study is appended.

Experimental

The flow reactor with real time measurement of particle size distribution constructed in Year 1 was used to perform bench scale tests of metallic emissions characterization from coal combustion. Three sets of experiments were performed: (i) control of vapor phase lead compounds by the use of in situ generated silica particles, (ii) effects of chlorine content on the resultant particle size distribution of lead compounds, and (iii) capture of elemental mercury vapor by aerosol transformation. The system was also used to determine metal speciation during combustion of Ohio coal provided by CG&E.

The primary parameters varied in the first set of experiments were temperature and silicon to lead (Si/Pb) ratio. The silicon compound (decomposes to silica in the reactor) is a very good sorbent for lead species above 750 °C. The absence of lead oxide in the presence of silica (the primary product being lead silicate) was confirmed by X-ray diffraction, infrared spectroscopy and Raman spectroscopy. In addition, the silicon compound is shown to be very efficient because the complete removal of lead oxide can be achieved for Si/Pb ratio as low as 12.

In the second set of experiments, chlorine to lead (Cl/Pb) ratio was varied to study its effect. Lead chloride particles are found to be larger than lead oxide paritcles of the same lead feed rate. Intermediate lead species were identified by X-ray diffraction with higher particle concentrations for intermediate Cl/Pb ratios. The oxidation mechanism revealed by the existence of intermediate lead species explains the effectiveness of sorbent materials under the presence of chlorine.

In the third set of experiments, the oxidation of mercury in the air with subsequent particle formation was studied by varying temperature and residence time. Although minor particle formation was detected, the oxidation was found to be too slow to be practical in real systems. On the other hand, prelimanry studies for titania sorbent show promising results.

Theoretical

Nucleation of metallic vapors typically results in particle size in the submicron regime which the minimum collection efficiency of typical particulate control devices is located. Hence the nucleation characteristics of a metallic system is very important in determining the ultimate emissions. Multicomponent nucleation was investigated by applying classical theory. It was shown that nucleation was initiated earlier in a multicomponent system than in a single component system indicating a higher emission possibility in a multicomponent system.

It is well known that the actual processes taking place in a combustion environment have to be described by kinetic mechanisms. A rigorous model was developed to address these issues. The different mechanisms considered were: chemical reaction (kinetic description) of metallic species, nucleation of various vapors, condensation onto particles and coagulation of particles. These mechanisms result in the ultimate evolution of the metallic species size distribution, and it is this size distribution that determines what is captured in control devices. The comparisons of the simulation results have been made to controlled experiments of lead species and the dominant mechanisms of particle formation and growth have been identified.

List of Publications and Conference Presentations

Journal Publications

Owens T.M., Wu C.Y. and Biswas P., "An Equilibrium Analysis for Reactions of Metal Compounds with Sorbents in High Temperature Systems", *Chemical Engineering Communications*, **133**, 31-52, 1995.

Owens, T. M. and Biswas, P., "Vapor Phase Sorbent Precursors for Toxic Metal Emissions Control from Combustors", *Ind. Eng. Chem. Res.*, **35(3)**, 1996, 792-798.

Biswas P. and Zachariah M.I. "Planar Imaging of PbO Concentration Profiles , I. Experimental", in preparation for *Env. Sci. Technol.*, 1996.

Wu, C. Y., Biswas P. and Zachariah, M.I., "Discrete-Sectional Modeling of PbO-Sorbent Reaction", in preparation for *A.I.Ch.E. J., 1996.*

Biswas, P., Owens, T. M. and Wu, C. Y., "Control of Toxic Metal Emissions from Combustors Using Vapor Phase Sorbent Materials", *Journal of Aerosol Science*, **26(suppl. 1.)**, 1995, S217-218.

Owens, T. M. and Biswas, P., "Characteristization of Products of Reaction between Vapor Phase Lead Compounds and *In Situ* Generated Silica Particles at various Pb:Si Feed Ratios", to appear in *J. Air Waste Manage. Assoc.*, 1996.

Wu, C. Y. and Biswas, P., "Lead Species Aerosol Formation and Growth in Multicomponent High Temperature Environments", submitted to *Journal of Aerosol Science*, November, 1995.

Conference Presentations

Ferg, J. and Biswas, P., "Kinetic Parameters of Metals Oxidation", *Poster Presentation at the 12th Annual Meeting of the American Association for Aerosol Research*, Paper 7P.4, Oak Brook, IL, October, 1993.

Owens, T., Wu, C. Y. and Biswas, P., "An Equilibrium Analysis for Reactions of Metal Compounds with Sorbents", *Poster Presentation at the 12th Annual Meeting of the American Association for Aerosol Research*, Oak Brook, IL, October, 1993.

Owens T. M., Wu C. Y., Ferg, J. A. and Biswas, P., "Evolution of Metallic Aerosol Size Distribution in High Temperature Environments: Applications in Waste Incineration", *Proc. 1993 Technical Meeting of the Eastern States Section of the Combustion Institute*, pp. 49-52, Princeton, NJ, October 25-27, 1993.

Wu C.Y. and Biswas P., "Competing Effects of Chemical reaction, Nucleation and Condensation on Metallic Aerosol Formation in Combustion Systems", *Proc. 1994 Technical Meeting of the Central States Section of the Combustion Insititute*, Madison, Wisconsin, June, 1994.

Owens T.M. and Biswas P., "An Equilibrium Analysis for Reaction of Cadmium with Sorbent Materials in High Temperature Systems", Paper 94-RP 114B.04, *87th Annual Meeting of the Air & Waste Management Association*, Cincinnati, OH, June 19-24, 1994.

Wu, C. Y., Biswas, P. and Fendinger, N. J., "Determination of Entrainment Factors of Metals during Municipal Solid Waste Incineration", *Presentation at the 87th Annual Meeting of the Air & Waste Management Association,* Paper 94-MP17.03, Cincinnati, OH, June 19-24, 1994.

Wu, C. Y., "Thermodynamic Equilibrium Analyses of the Behaviors of the Eleven Regulated Toxic Metals in Municipal Solid Waste Incineration", *Poster Presentation at the 87th Annual Meeting of the Air & Waste Management Association, student paper,* Cincinnati, OH, June 19-24, 1994.

Owens, T.M., Wu C.Y., Biswas, P. and Zachariah, M.R. (1994) "Experimental Study of Metal Sorbent Reactions in High Temperature Environments", Pg. 394, *Fourth International Aerosol Conference,* Los Angeles, California, 1994.

Biswas, P., Wu, C. Y., Owens, T. M., McMillin, B., Aquino, M. and Zachariah, M. R., "Evolution of Toxic Metal Aerosol Size Distributions and their Reaction with Sorbents in Combustion Systems", *1994 Annual Meeting of the American Institute of Chemical Engineering*, Paper 215a, San Francisco, November 13-18, 1994.

Wu, C. Y., Owens, T. M. and Biswas, P., "Aerosol Formation of Lead Species in Multicomponent High Temperature Environments", *Presentation at the Joint Meeting of Central States/Western States/Mexican National Sections, The Combustion Institute,* San Antonio, TX, April 23-26, 1995.

Wu, C. Y. and Biswas, P., "Modeling of Toxic Metallic Aerosol Formation in a Multicomponent System at High Temperatures Using a Discrete-Sectional Model", *Proceedings of the 50th Purdue Industrial Waste Conference*, West Lafayette, IN, May 8-10, 1995.

Owens, T. M. and Biswas, P., "Experimental Study of Toxic metal-Sorbent Reactions in a Bench Scale Combustor", *Presentation at the 50th Purdue Industrial Waste Conference,* West Lafayette, IN, May 8-10, 1995.

Biswas, P, Owens, T. M., Wu, C. Y. and Zachariah, M., "Study of Lead and Sorbent Reaction in High Temperature Environments: Characterization by Real-Time Aerosol

Instruments and Planar Laser-Induced Fluorescence Imaging, *4th International Congress on Toxic Combustion Byproducts*, Berkeley, CA, June 5-7, 1995,

Wu, C. Y. and Biswas, P., "Study of Chlorine Effects on the Aerosol Formation of Lead Species in Multicomponent High Temperature Environments", *Poster Presentation at the 1995 International Conference on Aerosol Science and Technology*, Taipei, Taiwan, August 31 - September 2, 1995.

Wu, C. Y. and Biswas, P., "Role of Speciation of Lead on Aerosol Formation in High Temperature Environments", *Presentation at the 14th Annual Meeting of the American Association for Aerosol Research*, Pittsburgh, PA, October 9-13, 1995.

Wu, C. Y., Arar, E. and Biswas, P., "Mercury Capture in Combustion Environments by Aerosol Transformation", to be presented at *the Spring Meeting of the Central States Section, The Combustion Institute,* St. Louis, MO, May 5-7, 1996.

Wu, C. Y. and Biswas, P., "Mercury Capture by Aerosol Transformation in Combustion Environments", to be presented at *the 89th Annual Meeting of the Air & Waste Management Association,* Nashville, TN, June 23-28, 1996.

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Coles D.G., Ragaini R.C., Ondov J.M. Fisher G.L., Silberman D. and Prentice B.A. (1979) "Chemical Studies of Fly Ash from a Coal Fired Power Plant", Environ. Sci. Tech., 13, 455-459.

Davison R.L., Natusch D.F.S., Wallace J.R. and Evans C.A. (1974) "Trace Elements in Fly Ash", Environ. Sci. Tech., 8, 1107-1113.

Flagan R.C. and Friedlander S.K. (1978) "Particle Formation in Pulverized Coal Combustion: A Review", in Recent Developments in Aerosol Science, D.T. Shaw, Ed., 25-.

Kaakkinen J.W., Jorden R.M., Lawasani M.H. and West R.E. (1975) "Trace Element Behaior in Coal-Fired Power Plant", Environ. Sci. Tech., 9, 862-869.

Kang S.G., Kerstein A.R. Helble J.J. and Sarofim A. R. (1990) "Simulation of Residual Ash Formation During Pulverized Coal Combustion: Bimodal Ash Particle Size Distribution", Aerosol Sci. Tech., 13, 401-412.

Knapp N.F. (1977) "Trace Elements in Ohio Coals", Ohio Division of Geological Survey, Report No. 103.

Quann R.J., Neville M., Janghorbani M., Mims C.A. and Sarofim A.F. (1982) "Mineral Matter and Trace Element Vaporization in a Laboratory Pulverized Coal Combustion System", Environ. Sci. Tech., 16, 776-781.

Smith R.D., Campbell J.A. and Nielson K.K. (1979) "Concentration Dependence upon Particle Size of Volatilized Elements in Fly Ash", Environ. Sci. Tech., 13, 553-558.

II. TECHNICAL DISCUSSION

The technical discussion portion of this report is presented as seven separate sections and listed in the appendices:

A. Equilibrium analyses for reactions of metal compounds with sorbents in high temperature systems. The results are presented as part of a papers in *Chem. Eng. Comm.*, **133**, 31-52, 1995. Removed for separate cycling

B. Vapor phase sorbent precursors for toxic metal emissions control from combustors. The results are presented as part of a papers in *Ind. Eng. Chem. Res.*, **35(3)**, 792-798, 1996. Reprint removed for separate cycling

C. Characterization of products of reaction between vapor phase lead compounds and in situ generated silica particles at various Pb:Si feed ratios. The results are presented as part of a paper to appear in *J. Air Waste Manage. Assoc.*, 1996. Preprint removed

D. Lead species aerosol formation and growth in multicomponent high temperature environments. The results are presented as part of a papers submitted to *Journal of Aerosol Science*, November, 1995. Preprint removed

E. Mercury capture by aerosol transformation in combustion environments. The results are presented in the form of a paper that will be given at *the 89th Annual Meeting of the Air & Waste Management Association,* Nashville, TN, June 23-28, 1996. Conf. paper removed for separate cycling

F. Nucleation in single-component, binary and ternary metallic systems at high temperatures.

G. Modeling of Toxic Metallic Aerosol Formation in a Multicomponent System at High Temperatures Using a Discrete-Sectional Model. The results are presented as part of a paper in *Proceedings of the 50th Purdue Industrial Waste Conference.* Removed for separate cycling

III. MARKETING/COMMERCIALIZATION

During the course of this work, a process has been discovered which may greatly reduce toxic metal emissions from combustors. A process patent has been filed by the University of Cincinnati on behalf of inventors Dr. Pratim Biswas and Timothy Owens. The invented process involves the use of vapor phase sorbent materials that are injected into the high temperature region of the combustor where physical/chemical reaction with the metal vapors takes place. The result is an increase in the resulting metal aerosol mean size which allows easier capture by conventional control equipment, and a chemical transformation to a metal species that might be considered non-toxic. Other avantages of vapor phase sorbents for metals capture include: mass transfer resistances are the lowest, and result in better mixing; depending on the temperature history in the system, kinetically favorable regimes can be chosen for faster reaction; costs are reduced due to cheaper and safer handling requirement, and usage of sorbent material is lower. In summary, in the proposed system, the toxic metal will chemically react with the sorbent material to form a benign compound, and also be in a size range that its release and emission to the atmopsphere is prevented. The process has potential application in coal combustors, waste incinerators and smelter.

Project Cost Summary – removed

APPENDIX I

An Equilibriun Analysis for Reactions of Metal Compounds with Sorbents in High Temperature Systems

Chemical Engineering Communications, **133**, 31-52, 1995.

Removed for separate cycling

APPENDIX II

Vapor Phase Sorbent Precursors for Toxic Metal Emissions Control from Combustors

Industrial and Engineering Chemistry Research, **13(3)**, 792-798, 1996

removed

APPENDIX III

Characterization of Products of Reaction between Vapor Phase Lead Compounds and *In Situ* Generated Silica Particles at Various Pb:Si Feed Ratios

removed

Journal of Air & Waste Management Association, **46**, 530-538, 1996

APPENDIX IV

Lead Species Aerosol Formation and Growth in Multicomponent High Temperature Environments

Removed

submitted to *Journal of Aerosol Science*, 1995

APPENDIX V

Mercury Capture by Aerosol Transformation in Combustion Environments

to be presented at *the 89th Annual Meeting of the Air & Waste Management Association*,
Nashville, TN, 1996, Paper 96-MP2.02.

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APPENDIX VI

Study of Nucleation in Single-Component, Binary and Ternary Metallic Systems at High Temperatures

INTRODUCTION

Toxic metallic particulate emissions from coal combustion are of great public concerns. According to the research conducted on coal combustion, metal compounds in the coal matrix first evaporate or are entrained as particles into the gas stream where they undergo chemical reactions to form vapor phase species. These metallic vapors thereafter are either depleted by condensing on the surface of existing seed particles or by nucleation to form tiny particles when the system temperature decreases. If these particles are not effectively collected in the particulate pollution control devices, a portion of the particles will then be emitted through the stack, disperse in the atmosphere and pose health risks to human beings (Kelly, 1986; Wu et al., 1994). Hence, to prevent the emissions of these particulate pollutants, it is necessary to understand the formation mechanisms of these metallic aerosols and the controlling parameters of these particulate pollutants.

Particle size distribution is one of the most important parameters that affect the collection efficiency of the particulate pollution control devices (Flagan and Seinfeld, 1987). Several studies (Bennett and Knapp, 1982; Ondov et al., 1979; Linak and Peterson, 1984) have shown that the particle size distributions from coal combustion systems are bimodal - one in the supermicron regime and the other in the submicron regime. Unfortunately, several metals (V, Cu, Zn, Cd, Sn and Pb) are reported (Bennett and Knapp, 1982) highly enriched in the fine mode of the fly ash. The enrichment of the metals in the fine mode indicates that the condensation mechanism is not effective enough to deplete the metallic vapors and tiny particles of high concentration are possibly produced by homogeneous nucleation from vapor phase directly.

Homogeneous nucleation is the formation of particles directly from vapor phase. Although there are several theories proposed for nucleation, the classical theory is the one that is most commonly applied. The central assumption of the classical theory is the capillarity approximation which applies the macroscopic properties (bulk density, thermodynamic properties and surface tension of a planar interface) to the microstructure, and saturation ratio is the key factor that affects the nucleation rate. In recent years, classical theory has also been developed for multicomponent systems such as those developed by Laaksonen et al., (1993), Wilemski (1987) for binary systems and Lin and Biswas (1993) for a ternary system. In the work by Lin and Biswas, it was found that the nucleation barrier was lowered if the compounds were miscible. They concluded that the onset of nucleation was earlier and more small particles would probably be formed in a ternary system.

In this work, the nucleation in single-component, binary and ternary systems are studied and compared. Highly nonlinear equations are solved to obtain the critical saturation ratios, and graphics are used to help visualize the critical point for particle formation. The effects of saturation ratios are studied, and the impact of an additional species is discussed.

THEORY

According to the classical theory (Seinfeld, 1986), the energy of a cluster is defined by the competition of its body force and surface. Following are the theories developed for the single-component, binary and ternary nucleation, respectively. To compare the speciation effects in multicomponent systems, it is good to start from a simple single-component system then to expand it to a more complicated multicomponent system.

Single-Component System

The free energy of formation of a single-component cluster is defined as (Friedlander, 1977; Seinfeld, 1986)

$$\Delta G = -nkT\ln S + 4\pi r^2\sigma \tag{1}$$

where *n* is the number of molecules in the cluster, *k* is the Boltzman constant, *T* is the temperature, *S* is the saturation ratio (vapor partial pressure/vapor saturation pressure), *r* is the cluster radius and σ is the surface tension.

Particles will be formed when the critical point is reached, which is determined by

$$\frac{\partial \Delta G}{\partial n} = 0 \tag{2}$$

and the energy at this point is the critical energy, *G** with the number of molecules in the cluster to be *n**. Adding a molecule to clusters containing molecules less than *n** will result in the increase of the cluster's free energy. However, adding a molecule to clusters containing molecules more than *n** will result in the decrease of the cluster's free energy, and stable particles are then formed. Hence, at the critical point, the system is a metastable condition and the free energy is maximum.

The nucleation rate is defined as the rate of addition of a single molecule to the cluster, which can be expressed as

$$I = -\beta N\, 4\pi \mathrm{r}^{*2} Exp(-\frac{\Delta G^*}{kT})\sqrt{-\frac{1}{2\pi kT}\frac{\partial^2 \Delta G^*}{\partial n^{*2}}} \tag{3}$$

where β is the molecule impinging rate ($P/\sqrt{2\pi mkT}$), N is the molecular number concentration, P is the vapor partial pressure, m is the molecular mass. Traditionally, the critical saturation ratio is defined as the saturation ratio when the nucleation rate is 1 #/cc/s because the nucleation rate under 1 #/cc/s is not observable.

Binary System

The classical theory can be similarly applied to the binary system (Lin, 1993). The free energy is defined as

$$\Delta G = -n_1 kT \ln S_1 - n_2 kT \ln S_2 + 4\pi r^2 \sigma \tag{4}$$

where the subscript represent the different species.

In a binary system, the critical point is not a maximum. Here it's a saddle point, and can be defined as

$$\left(\frac{\partial \Delta G}{\partial n_i}\right)_{n_j} = 0, \quad \forall\, i \;=\; 1,2 \text{ and } i \neq j \tag{5}$$

The nucleation rate is

$$I = -\frac{\beta_1 \beta_2 (N_1 + N_2)}{\beta_1 \sin^2 \theta + \beta_2 \cos^2 \theta} 4\pi r^{*2} Exp\left(-\frac{\Delta G^*}{kT}\right)\sqrt{-\frac{X'}{Y}} \tag{6}$$

where

$$X' = \frac{1}{2}\left(\frac{\partial^2 \Delta G^*}{\partial n_1^{*2}}\cos^2\theta + \frac{\partial^2 \Delta G^*}{\partial n_2^{*2}}\sin^2\theta + \frac{\partial^2 \Delta G^*}{\partial n_1^* \partial n_2^*}\cos\theta \sin\theta\right) \tag{7}$$

$$Y = \frac{1}{2}\left(\frac{\partial^2 \Delta G^*}{\partial n_1^{*2}}\sin^2\theta + \frac{\partial^2 \Delta G^*}{\partial n_2^{*2}}\cos^2\theta - 2\frac{\partial^2 \Delta G^*}{\partial n_1^* \partial n_2^*}\cos\theta \sin\theta\right) \tag{8}$$

and

$$\theta = \tan^{-1}(n_2^* / n_1^*) \tag{9}$$

Ternary System

The free energy of the cluster in a ternary system is defined similarly as (Lin, 1993)

$$\Delta G = -n_1 kT \ln S_1 - n_2 kT \ln S_2 - n_3 kT \ln S_3 + 4\pi r^2 \sigma \tag{10}$$

The critical point is also defined by the saddle point as

$$(\frac{\partial\Delta G}{\partial n_i})_{n_j,n_k}=0,\quad \forall\ i\ =\ 1,2,3 \text{ and } i\neq j\neq k \tag{11}$$

The ternary nucleation rate (Lin, 1993) is

$$I=-\frac{\beta_1\,\beta_2\,\beta_3\,(N_1+N_2+N_3)}{\beta_1\,\beta_2\cos^2\phi+\beta_3\sin^2\phi(\beta_1\sin^2\theta+\beta_2\cos^2\theta)}4\pi r^{*2}Exp(-\frac{\Delta G^*}{kT})\sqrt{-\frac{X\pi kT}{YZ}} \tag{12}$$

where

$$\begin{aligned}X=\frac{1}{2}(&\frac{\partial^2\Delta G^*}{\partial n_1^{*2}}\cos^2\theta\sin^2\phi+\frac{\partial^2\Delta G^*}{\partial n_2^{*2}}\sin^2\theta\sin^2\phi+\frac{\partial^2\Delta G^*}{\partial n_1^*\partial n_2^*}\cos\theta\sin\theta\sin^2\phi\\&+\frac{\partial^2\Delta G^*}{\partial n_3^{*2}}\cos^2\phi+\frac{\partial^2\Delta G^*}{\partial n_2^*\partial n_3^*}\sin\theta\cos\phi\sin\phi+\frac{\partial^2\Delta G^*}{\partial n_3^*\partial n_1^*}\cos\theta\cos\phi\sin\phi)\end{aligned} \tag{13}$$

$$\begin{aligned}Z=\frac{1}{2}(&\frac{\partial^2\Delta G^*}{\partial n_1^{*2}}\cos^2\theta\cos^2\phi+\frac{\partial^2\Delta G^*}{\partial n_2^{*2}}\sin^2\theta\cos^2\phi+\frac{\partial^2\Delta G^*}{\partial n_1^*\partial n_2^*}\cos\theta\sin\theta\cos^2\phi\\&+\frac{\partial^2\Delta G^*}{\partial n_3^{*2}}\sin^2\phi-\frac{\partial^2\Delta G^*}{\partial n_2^*\partial n_3^*}\sin\theta\cos\phi\sin\phi-\frac{\partial^2\Delta G^*}{\partial n_3^*\partial n_1^*}\cos\theta\cos\phi\sin\phi)\end{aligned} \tag{14}$$

$$\phi=\cot^{-1}(\sqrt{n_1^{*2}+n_2^{*2}}\,/\,n_3^*) \tag{15}$$

RESULTS AND DISCUSSIONS

Lead is chosen as an example metal studied in this work because it is one of the 11 toxic metals regulated in 1990 Clean Air Act Amendments, and its relatively higher concentration than the other metals in coal matrix has already made it the target and a lot of research has focused on it. In a typical combustion system, oxide is the predominant form for most metals. On the other hand, chlorine is usually present in coal and waste system. Since most metals have strong affinities to bond with chlorine, chloride is also often observed as well. Therefore, Pb, PbO and $PbCl_2$ are considered in this work. The temperature is chosen to be 1000 K as it is typically encountered in waste incineration. Table 1 lists the physical properties of these 3 lead species. MATHEMATICA is used to implement the calculation and graphics work. Below is the discussion for the 3 systems respectively.

Table 1

Physical Properties of Pb, PbO and $PbCl_2$ at 1000 K

	Pb	PbO	$PbCl_2$
Molecular Weight (g/mol)	207.19	223.19	278.1
Surface Tension (dyne/cm)	500	250	130
Saturation Pressure (atm)	1.26×10^{-5}	3.0×10^{-3}	4.66×10^{-2}
Solid Density (g/cm^3)	11.3437	9.53	5.85

Single-Component System

Figure 1 shows the free energy of a PbO cluster as a function of the number of molecules in the cluster for different saturation ratios. The critical point can be explained clearly by using the graph. Take Figure 1b ($S = 5$) for example. If $n < 64$, adding one more molecule will increase the cluster's free energy which is not favored. Therefore, clusters with molecules less than 64 under this saturation ratio are not stable and will not form particles. On the other hand, if $n \geq 64$, adding one more molecule will reduce the cluster's free energy which is favored. Hence, clusters greater than this size ($n=64$) will form stable particles. Figure 1c-1e are the results for increasing saturation ratios (10, 25 and 50). The results show that the critical number decreases as the saturation ratio increases, and the free energy decreases. Figure 1f shows the comparisons of these results by placing all the figures together.

The result for $S=2$ is different from the others. It indicates that when the saturation ratio is small, a very large number of molecules is required to generate a stable particle. Actually, it has be pointed out (Friedlander, 1977) that no stable particles can be formed if $S < 1$.

In the single-component system, the number of molecules in the critical cluster, n^*, can be obtained as an explicit function of the saturation ratio, S, by solving the energy maximization equation, Eq. (2). At 1000 K, the result is $n^* = 301.231/LnS^3$. Using this expression, the nucleation rate can then be determined as a function of S only, the results of which are shown in Figure 2. As we can see, the nucleation rate, I, is very sensitive to S. It increases very fast with respect to S. Increasing S by one will change the rate by even one order. As stated in the theory, the critical saturation ratio has been defined as the one when the nucleation rate is 1 #/cc/s, and it is customarily accepted that the onset of nucleation is when the nucleation rate reaches 1 #/cc/s (or S exceeding the critical value). From the graph, the critical saturation ratio is shown to be 6.67.

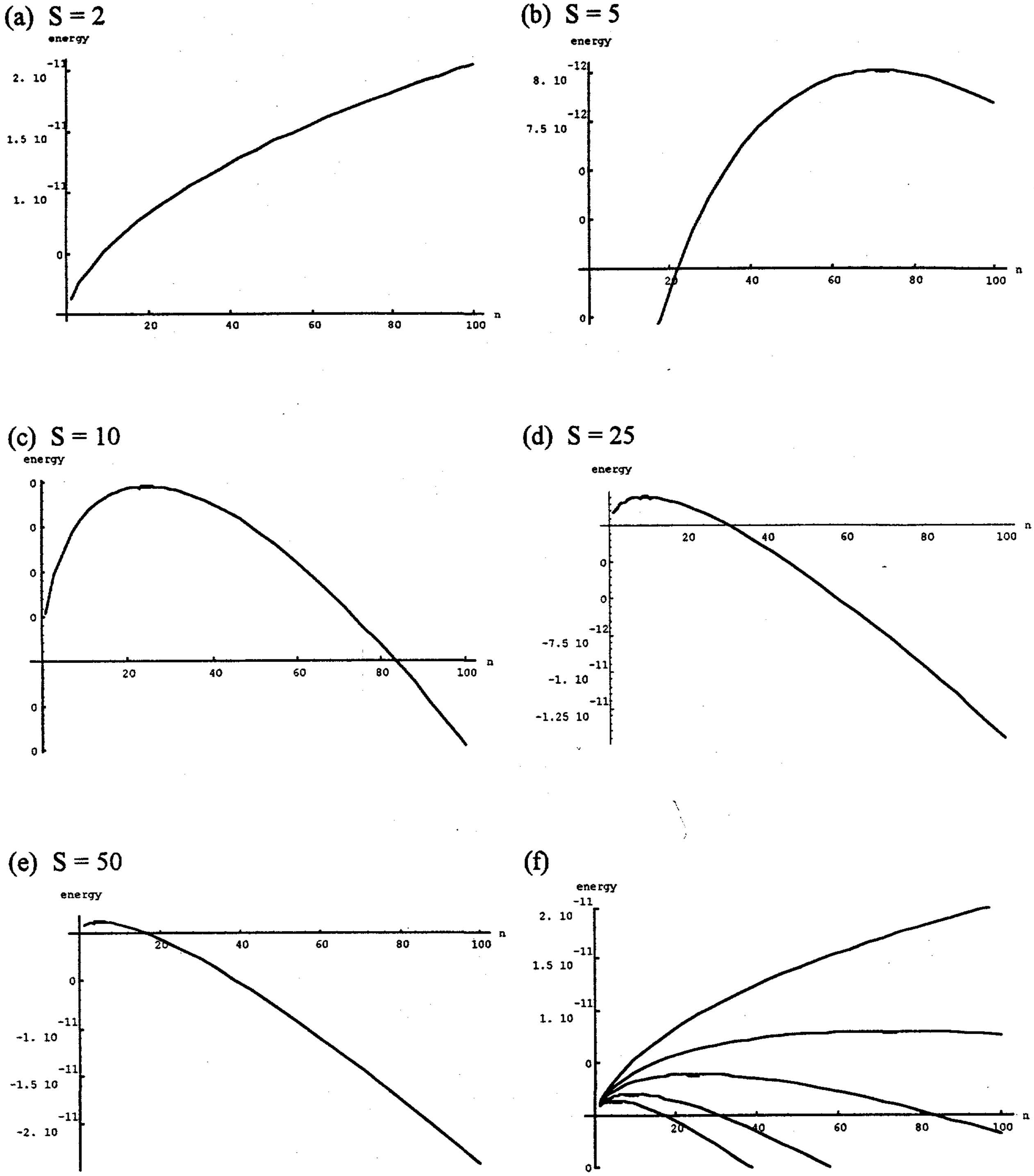

Figure 1. Free energy of the PbO cluster at 1000 K as a function of the number of molecules in the cluster for different saturation rations: (a) S = 2; (b) S = 5; (c) S = 10; (d) S = 25; (e) S = 50; (f) all S.

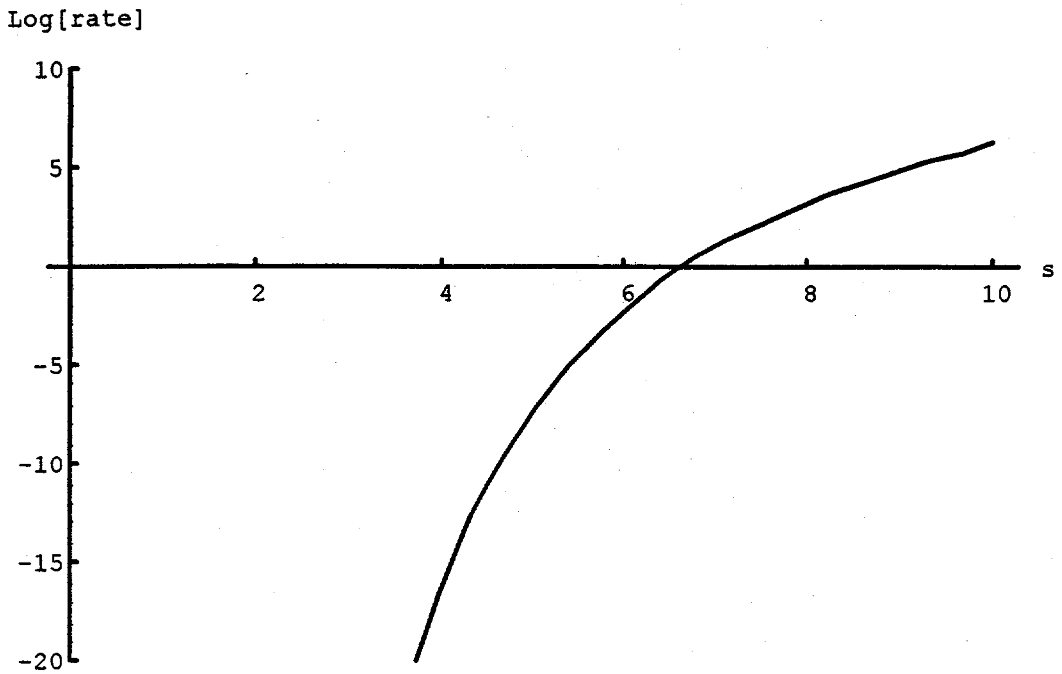

Figure 2. The nucleation rate of PbO particles at 1000 K as a function of the saturation ratio.

Binary System

As stated in the introduction, one of the objective it to see whether adding other species would reduce the required saturation to initiate nucleation. The first step is to compare the binary system. Here PbO and $PbCl_2$ (species 1 and species 2, respectively) are chosen.

Figure 3 shows the free energy of the PbO-$PbCl_2$ cluster as a function of the numbers of molecules (species 1 and species 2) in the clusters for different saturation ratios. In a binary system, the critical point is not defined as the maximum energy in the single-component system, but it is the saddle point which can be seen from the graph. Although the system tends to remain in the lower energy state, the cluster has to pass the saddle point to be in the lower energy state. Therefore, for n1 and n2 smaller than the saddle point, adding either molecule will result in the increase of free energy of the cluster which is not preferred. Only for points beyond the saddle point can then the stable particles be formed. Hence, the saddle point is the critical point to initiate nucleation. Figure 3b shows the results by increasing the saturation ratios to observe the effects. As shown, the free energy is lowered and the saddle point moves closer to the origin (smaller n1 and n2). Consequently, nucleation is initiated earlier because the required number of molecules decreased as well as lower cluster free energy is achieved.

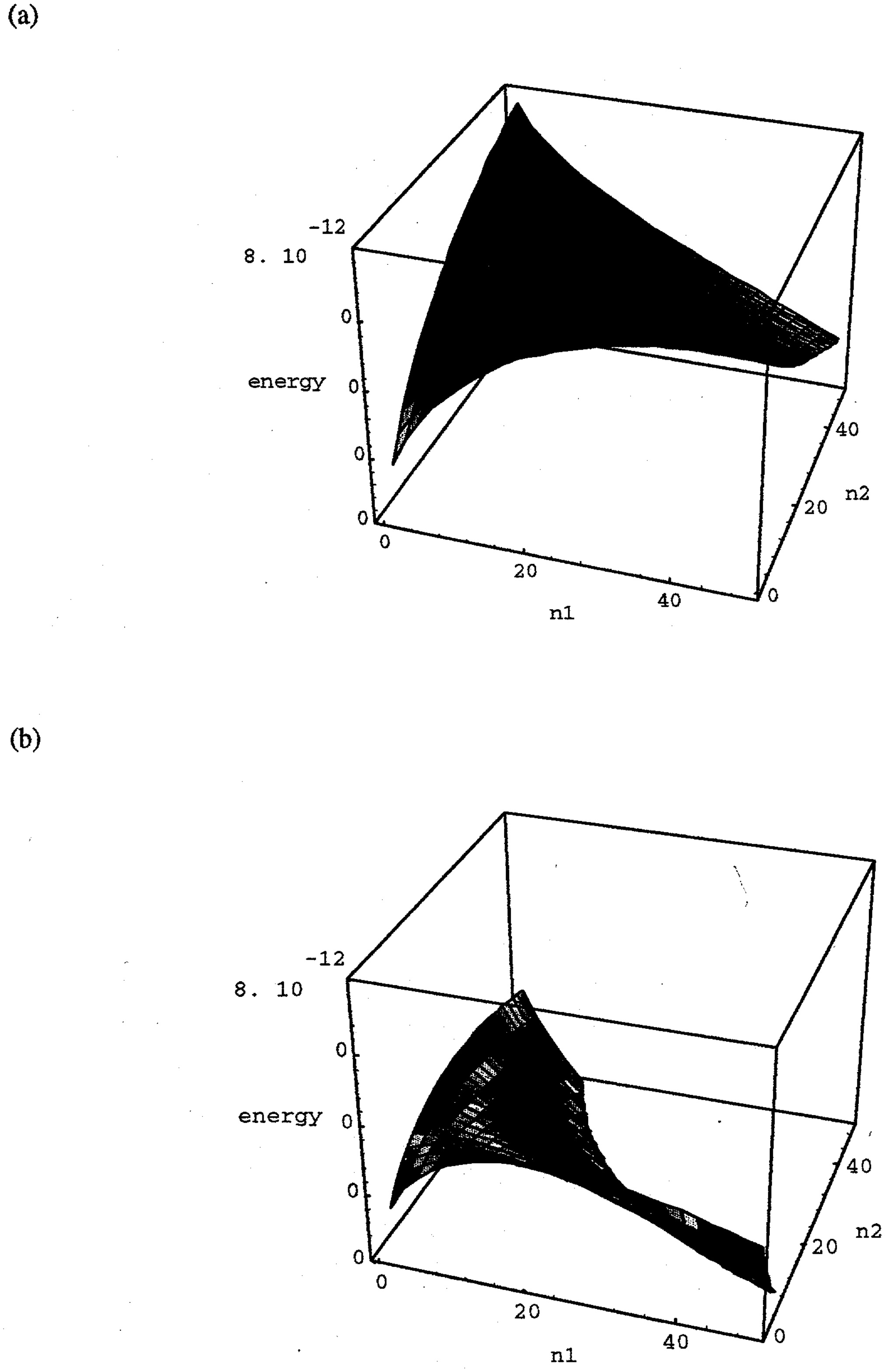

Figure 3. The cluster free energy as a function of the number of PbO and $PbCl_2$ molecules for different saturation ratios: (a) $S_{PbO} = 5$, $S_{PbCl_2} = 3$; (b) $S_{PbO} = 10$, $S_{PbCl_2} = 6$.

The next step is to determine the nucleation rate as a function of different sets of saturation ratios. The rate expression is a function of n1, n2, S1 and S2. In a single-component system, the relationship between the critical number and the saturation can be expressed explicitly. However, in a binary system, this can not be achieved, and the relationship can only be obtained by solving the two energy maximization equations (Eq. (5) for both species) simultaneously with specified S1 and S2. The determined n1 and n2 are then substituted to the rate equation (Eq. (6)) to calculate the rate, and the results are shown in Figure 4. As in the single-component system, the nucleation rate is very sensitive to the saturation ratios.

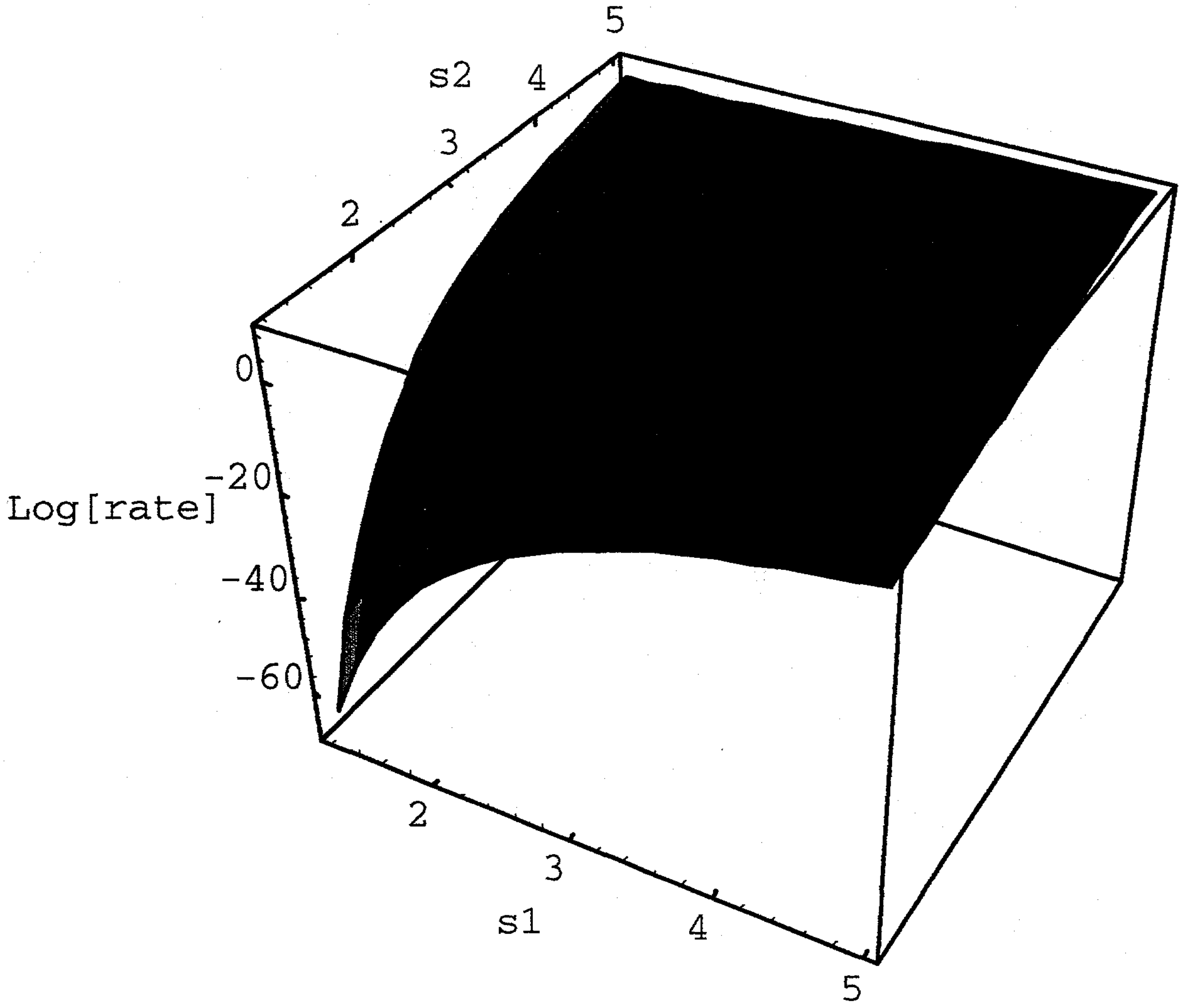

Figure 4. The nucleation rate of PbO-$PbCl_2$ cluster as a function of different sets of saturation ratios.

As in the single-component system, the critical saturation ratios, which are defined as the saturation ratios for the nucleation rate to be 1 #/cc/s, are the key interested parameters and need to be determined. The results are obtained by solving the two energy maximization equations with the rate equation (Eq. (6)) simultaneously, and are plotted in Figure 5. These results also form a line in Figure 4 corresponding to the rate of 1 #/cc/s. This information can also be used for the comparison to the single-component system. In the PbO only system, the critical saturation ratio is 6.67. In the binary system, the required saturation ratio for PbO is only 5 if S_{PbCl_2} is 1.6, and only 2 if S_{PbCl_2} is 3.2. This shows that the required saturation ratio is lowered if an additionally species is present. The information can also be obtained by looking at Figure 3. By comparing the n1 of maximum energy point for different n2, it is clear that n1 decreases as n2 increases.

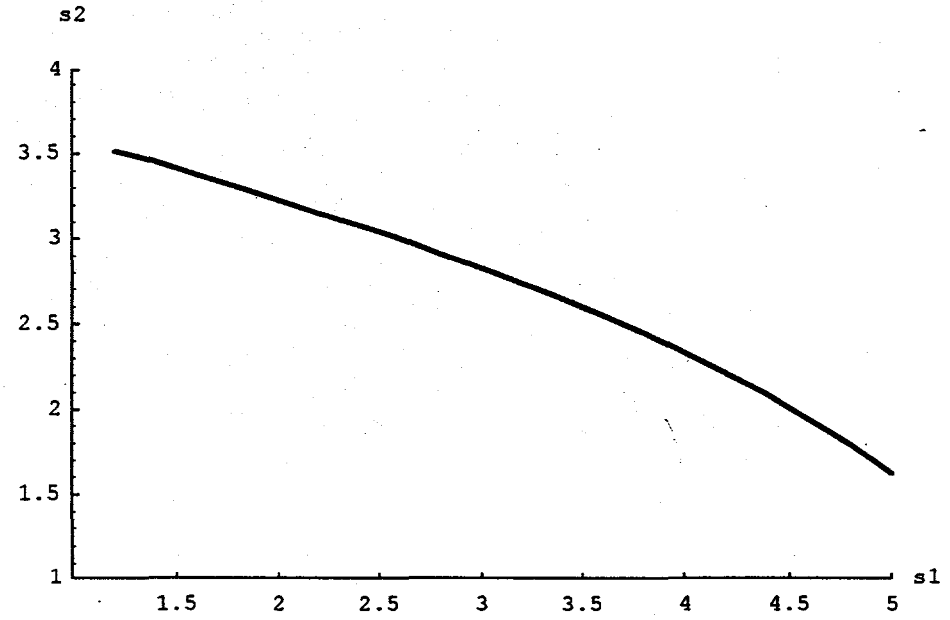

Figure 5. Critical saturation ration of $PbCl_2$ as a function of the PbO saturation ratio.

Ternary System

The next system to be explored is the Pb, PbO and $PbCl_2$ (species 1, 2 and 3 respectively) system. The first thing is to locate the saddle point. However, it is impossible to show the energy with respect to the 3 numbers of molecules in the cluster in a 3-D diagram. Hence, the system is studied by varying only n2 and n3 with a constant n1 in one figure and then changing n1 in another figure. The results are shown in Figure 6.

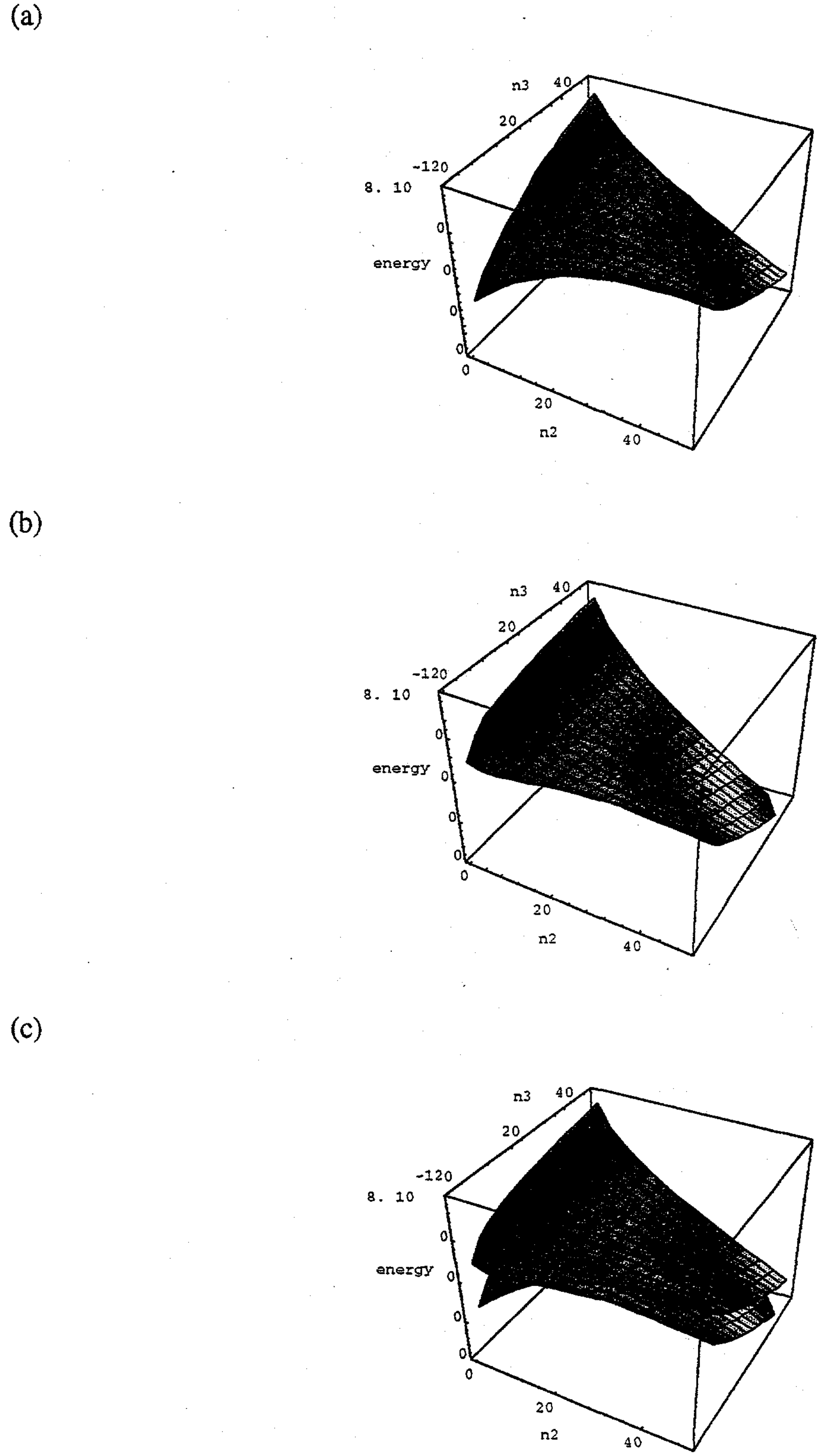

Figure 6. The cluster free energy as a function of the number of PbO and $PbCl_2$ molecules with varied number of Pb molecules: (a) $n_{Pb} = 15$; (b) $n_{Pb} = 30$; (c) both.

The diagram is similar to that of a binary system since only 2 variables are shown. Thus, the saddle point can be located in the same way used in the binary system. Notice that the saddle point in the binary system diagram may not be the saddle point for the ternary system. However, the saddle point of the ternary system can be located by the observation of the saddle points of the binary systems with different n1. As too many plots are required to construct the graph, in this work, the ternary saddle point is only determined numerically by solving the 3 energy maximization equations simultaneously. The results for different sets of saturation ratios are listed in Table 2.

Table 2
Critical Points in the Ternary System for Various Sets of Saturation Ratios

Case #	S1	S2	S3	n1	n2	n3
1	30	5	3	2.36	15.30	9.62
2	15	5	3	1.11	16.03	14.19
3	60	10	6	0.15	5.37	9.10

If the saturation ratio of one species is reduced, e.g. S1 in case 1 compared with case 2, n1 is reduced although n2 and n3 increase. This indicates that more other species are necessary to compensate the energy increase. On the other hand, if the saturation ratios are increased, e.g. case 3 compared with case 1, the required numbers are greatly reduced for all the species. This, again shows that the presence of the additional species initiates nucleation earlier.

Next, the critical saturation ratios are to be determined. Due to the stiffness of the ternary system around the saddle point, the nonlinear equation solver provided by MATHEMATICA is not capable of solving this problem without good initial guesses. Therefore, the 3-D graph for the n1, n2 and n3 relationship can not be constructed though the results for certain sets of combinations are solved and are shown in Table 3. By comparing the results in the ternary system to those in the binary system, again it shows the presence of additional species will initiate the nucleation earlier and the particles are smaller. For example, if S_{Pb} is 1.6, the required S_{PbCl_2} is only 1 in the ternary system rather than 1.6 in the binary system with S_{PbO} to be 5. In a real coal combustion system, as the metal speciation in the combustion system is usually complicated and the knowledge is rarely known, typically the nucleation is predicted assuming the single-component. However, the above results indicate that the nucleation will be initiated earlier than the single-component prediction as there exist many species in a real system.

Table 3
Critical Saturation Ratios of the Ternary System

Case #	S1	S2	S3	n1	n2	n3
1	1.6	5	1	1.2	44.7	6.5
2	6.4	4	2	2.3	29.5	15.9
3	12.1	4	1	8.6	32.5	3.6
4	23.2	3	1	15.3	19.6	1.3
5	32.6	2	1	20.1	10.3	0.47
6	31.1	2	2	18.9	11.4	1.4
7	40.7	1	1	23.2	4.0	0.18
8	38.8	1	2	23.3	4.4	0.45
9	38.0	1	3	23.0	4.7	0.8
10	37.9	2	2	22.1	4.9	1.3

CONCLUSIONS

The simulations performed show that the cluster's free energy is lowered in a multicomponent system than in the single-component system. The required critical saturation ratio to initiate nucleation is also reduced if an additional species is added into the system. Nucleation rate is shown to be very sensitive to the saturation ratio. Increasing the saturation ratio by one will result in the increase of nucleation rate by an order. In a real coal combustion system, as the metal speciation is usually complicated, nucleation will be predicted to be initiated slowlier if only single-component system is accounted for.

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APPENDIX VII

Modeling of Metallic Aerosol Formation in a Multicomponent System at High Temperatures Using a Discrete-Sectional Model

Proceedings of the 50th Purdue Industrial Waste Conference

Removed for separate cycling