## Identification and Significance of the Problem

Metalorganic chemical vapor deposition (MOCVD) is a key materials technology for the production of many of the epitaxial structures required for high frequency optical and microwave devices such as lasers, field effect transistors, solar cells, and photocathodes. Conventional MOCVD growth of gallium arsenide, GaAs, employs the pyrolytic decomposition of trimethyl gallium (TMG) and arsine in a hydrogen atmosphere within a cold wall silica reaction chamber. This reaction is described by the equation below:

$$(CH_3)_3Ga + AsH_3 \;||||||> GaAs + 3\; CH_4$$

TMG is pyrophoric but far worse is arsine, which is typically used at concentrations of 10% in hydrogen; it is lethal at levels as low as 6 ppm.[1] $AsH_3$ is perhaps the most acutely toxic form of arsenic and one of the major industrial causes of sudden extensive hemolysis. The American College of Government Industrial Hygienists has set 50 ppb as the maximum safe concentration for prolonged arsine exposure. Other hydride gases used in MOCVD include phosphine and silane. Phosphine, $PH_3$ is a severe pulmonary irritant and an acute systemic poison. The effect of exposure to $AsH_3$ and $PH_3$ are summarized below in Table I.[2,3,4] No specific antidote to poisoning by either $AsH_3$ or $PH_3$ is known.

### Table 1
### Effects of Various Degrees of Exposure to Arsine and Phosphine

| Human Effects | Exposure (min) | $AsH_3$ conc. (ppm) | $PH_3$ conc. (ppm) |
|---|---|---|---|
| Lethal | 1-2 | 500 | 2000 |
| Life threatening | 30-60 | 6-15 | 400-600 |
| No serious symptoms | 60-120 | 3 | 7 |
| Odor threshold | - | 0.5 | 1-3 |
| Maximum permissible exposure limit (PEL) | Threshold limit value | 0.05 | 0.3 |

The potential safety risk is significant in MOCVD production and considerable attention has been paid to the design of MOCVD reactors and facilities. Recent articles describe safety issues[5,6,7] and approaches to safe handling, detection, measurement, and removal of arsine and phosphine. There is no clear strategy for detoxifying these poisonous gases and it is apparent that a clearer methodology is needed for their general application and use. Commercial production of III-V epitaxial layers may require the processing of multipound quantities of pure arsine. One of the critical steps in the sequence of safety related operations is the capture and containment of arsine from the reaction chamber exhaust. A number of arsine containment methods have evolved including high temperature incineration and adsorption on activated carbon. At this point, it appears that adsorption on activated carbon will be widely used in research scale operations due to its overall convenience.[8] Shown below are two schemes used to handle the effluent from a MOCVD reactor system with a carbon adsorbent bed on the left and an oxygen incinerator on the right.
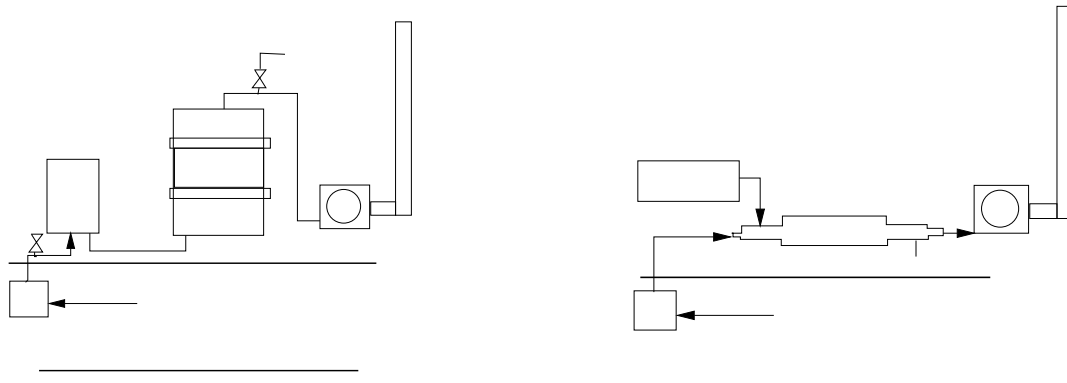
The interest in a safe and effective way to contain arsine by activated carbon adsorption has stimulated studies on understanding the underlying adsorption mechanisms[9,10] on commercially available granular carbons such as Calgon Type FCA (impregnated with copper and chromium oxides). Haacke et al[9] noted that there are two processes responsible for the adsorption of arsine on FCA carbon, chemisorption and physical adsorption.  They indicated that both processes take place in parallel with 60% $AsH_3$ being chemisorbed so that it will not readily come back off while the remaining 40% is physically adsorbed and will desorb off the carbon when a purge gas is passed through the carbon bed at room temperature. This desorption behavior is rather worrisome in that it indicates a safety risk unless certain precautions are taken to anchor the adsorbed arsine to the support. A common technique is to oxidize the adsorbed $AsH_3$ by periodically flowing oxygen or air diluted with nitrogen through the carbon bed to convert the arsine to $AsO_3$ which is a relatively safe form.

Then the carbon bed can continue to be used until the entire bed is spent. Typical arsine loadings for Calgon FCA carbon are 13 lbs $AsH_3$ per 150 lbs carbon(8.7%). Values reported by Haacke[7] were in the range of 13-14 % for chemisorbed arsine while Colabella et al [8] observed arsine saturation adsorption capacity of 7-9% before oxidation/regeneration was required; once regenerated, additional arsine can be adsorbed on the carbon bed.

Impregnated activated carbon is highly effective for removing toxic contaminant from breathable air. For example activated carbon impregnated with ammoniacal salts of copper, chromium, and silver has been widely used since World War I in military gas masks for protection from toxic gases , such as cyanogen chloride (CNCl) and hydrogen cyanide (HCN). ASC Whetlerite is one such version and contains 6-8 % copper, 2-3% chromium, and about 0.2% silver.  These charcoals react irreversibly and rapidly with gases to produce ammonia and ammonium chlorides through a variety of intermediates. Calgon presently supplies Type ASC with the principal users being the US Government and manufacturers of industrial respirators. Krishnan et al[11] the role of chromium and concluded that a stoichiometric oxidation rather than catalysis was responsible for the removal of HCN. On the other hand McIntyre et al[12] studied the role of copper via X-ray photon spectroscopy (XPS) and how aging, specifically moisture exposure, would change the oxidation state of the copper.  The literature suggests that there is uncertainty about how the impregnated carbons function for toxic gas containment. New ideas have emerged on the use of copper-chromium oxidation catalysts for emission control of auto exhaust; doping with small amounts of platinum or palladium have shown extraordinary enhancement in performance and by analogy may also apply to toxic gas adsorption. There appears to many areas for improvement of the existing carbon adsorption technology. The important observation is that the same carbons that are being applied today to contain arsine and phosphine in the semiconductor industry are essentially the same types developed many years ago for chemical warfare. Furthermore, they have not been improved on significantly since then.

A new superactivated carbon shows strong potential for achieving a significant improvement in removing arsine from the effluent of MOCVD reactors. It has been demonstrated by the Natick Laboratories to be extraordinarily superior to any commercially available carbon that has been evaluated in chemical protective fabrics[13].  This carbon has a BET surface area in excess of 3000 $m^2$/g and is a high performance adsorbent with exceptional capabilities.  The high surface area is derived from a propensity

of very small pores, typically 7 Å in diameter, and it is most aptly described as a gas adsorbing carbon (bimodal distribution of micro pores <20 diameter and macro feeder pores >600 Å diam) versus the liquid phase carbons, which have a trimodal pore distribution and are used to decolorize or purify liquids. The superactivated carbon may be produced from coal or petroleum coke and is chemically activated at high temperature with potassium hydroxide. Amoco researchers[14,15] patented the process in 1978 and several large batches of the PX-21 powder were made before the research program was suspended. The basic process is to mix KOH and petroleum coke in a 2.7/1 ratio, initially heating in a precalciner at 400-50$0^O$ C and then calcine at 800 - 90$0^O$C to form the ultra high surface area carbon.

Although the superactivated carbon is produced as a powder, Robinson[16] has developed granulation technology which allows it to be extended to applications calling for a granular form such as toxic gas adsorption. Furthermore, Mega-Carbon is continuing to develop more granulation technologies in our Phase I SBIR contract granted by the EPA to develop high performance carbons for drinking water treatment. A number of binders have been identified which will produce carbon granules with little degradation in the surface area or adsorption properties as measured by the Iodine and Methylene Blue tests.

## Technical Objectives - Phase I

Although MOCVD processing with arsine gas continues to increase, detoxification methods seem to be closely tied to charcoal adsorbents developed for chemical warfare in World War I. There is a critical need to advance this detoxification technology and improve it so that the current semiconductor industry can operate safely and reliably. A fundamental understanding of the chemistry of detoxification is a first step to be taken and set the basis for improvements. Current adsorbents are typified by Calgon FCA carbon consisting of a gas adsorbing carbon impregnated with copper and chromium. More efficient metal dispersion, different metals, and higher surface area carbons may lead the way to significant improvements in carbon adsorbents. This leads to the following questions to consider:

* How can activated charcoal be treated to increase to increase its chemisorption properties for arsine gas?

* What other adsorbing materials can be used for arsine (eg molecular sieves, glasses, etc)?

* How will the adsorbed gases be removed and detoxified?

* Are mass transport process (ie film diffusion and pore diffusion) or mixing important in the overall arsine adsorption process?

* How can carbon bed exhaustion be accurately monitored or predicted so that arsine breakthrough does not occur unexpectedly?

### Objectives

The following objectives for Phase I will address the questions listed above:

1. Develop a fundamental understanding of arsine adsorption on activated carbons and identify strategies to increase adsorption capacity.

2. Explore alternate carbons and adsorbent materials and identify which will have strong potential as an arsine adsorbent.

3. Develop a reliable and convenient procedure to anchor the chemisorbed arsine to the adsorbent and ways to transform it to a non-toxic state via oxidation, etc.

4. Investigate the role of mass transport processes on arsine adsorption and gas flow regime(mixing, contacting, laminar versus turbulent flow) using analogies to heterogeneous catalysis.

5. Develop methodology to define movement of the arsine mass transfer zone in a carbon adsorbent bed and how to anticipate breakthrough so that 100% removal efficiency is routinely achieved.

# Work Plan - Phase I

The work plan, below, is structured to accomplish the five objectives in the previous section. Most importantly, we believe that the application of the superactivated carbon will lead to significant improvements in arsine containment based on its demonstrated superior performance for chemical warfare applications as reported by Natick laboratories[13].The Phase I work plan is primarily directed at surveying and identifying possible approaches to arsine detoxification with a small amount of supporting laboratory work to establish or confirm key assumptions. No toxic gases will be used in these confirmatory tests with that aspect reserved for Phase II when a hazardous gas test unit has been designed and constructed with comprehensive safeguards.

Organization of Work Plan

**Task 1.** Chemical/Physical Processes of Arsine Adsorption
    Subtask 1.1:     Chemisorption of arsine on carbon.
    Subtask 1.2:     Physisorption of arsine on carbon.
    Subtask 1.3:     Mass transfer influences of arsine adsorption.

**Task 2.** Treatment of Active Carbon for Enhanced Arsine Adsorption
    Subtask 2.1:     Improved dispersion of Cu/Cr oxides on carbon.
    Subtask 2.2:     Promoters to enhance/assist Cu/Cr oxides (Ag, Pt, Pd).
    Subtask 2.3:     Alternative supported metal oxides.

**Task 3.** Alternative Adsorbents for Arsine Adsorption
    Subtask 3.1:     High surface area superactivated carbon.
    Subtask 3.2:     Molecular sieve adsorbents.
    Subtask 3.3:     Alumina and silica adsorbents.

**Task 4.** Methods for Removal/Detoxification of Adsorbed Arsine
    Subtask 4.1:     Controlled oxidation and passivation.
    Subtask 4.2:     Monitoring/Prediction of arsine mass transfer zone.

Details of the above work plan are listed below with the methodology for accomplishing each task.

Details of the Work Plan

**Task 1: Chemical/Physical Processes of Arsine Adsorption**

Most, if not all, of the existing literature for arsine adsorption on activated carbon is unclear on how it exactly takes place. Without performing any experiments, one can still draw on the field of heterogeneous catalysis to draw a consistent and rational hypothesis to be tested. The adsorption process is most likely a combination of weak physisorption( $H_{ad}$ = 2-6 kcal/mole) and stronger chemisorption ( $H_{ad}$ > 20 kcal/mole). The literature suggests that arsine physisorbs initially and then slowly chemisorbs on the impregnated metal oxides( Cu, Cr). Similar to a porous catalyst, there are mass transport processes involved for the adsorbate to go from the bulk fluid phase to the carbon surface plus diffusion into the pores. Thus it is necessary to develop a comprehensive picture of the overall adsorption process. We have broken down Task 1 into three subtasks for 1. chemisorption, 2. physisorption, and 3. mass transport effects.

**Subtask 1.1** Chemisorption of Arsine on Carbon

There have been some recent attempts to understand arsine adsorption by Haacke et al[10]. Haacke used XPS to monitor the oxidation state of copper and chromium. Arsine reduce the metal oxides when it absorbed with $C^{2+}$ -->$Cu^0$ and $Cr^{6+}$-->$Cr^{3+}$. Colabella et al[9] focused on the oxidation stat of arsenic _after_ it was air oxidized and concluded it was consistent with

$$2 \, AsH_3 + 3O_2 \longrightarrow As_2O_3 + 3 \, H_2O$$

Brown et al[17] thought that the hexavalent Cr was a catalytic agent for converting HCN to oxamide but Krishnan et al[11] studied ASC Whetlerite charcoals and showed that the Cr was stoichiometric agent that is consumed in the HCN oxidation. Thus the role of the impregnated metals is unclear and needs to be better defined.

Articles on the chemistry of arsine adsorption are located in diverse journals, one group related to semiconductor manufacturing, and the other on chemical warfare. Furthermore there are a series of patents by Phillips researchers[18,19,20,21] on techniques or removing trialkyl arsines from hydrocarbon streams. We will conduct a computerized information search accessing databases in these areas to identify pertinent articles. Professional literature searchers have long known that a critical element to any search is knowing which databases to access. Mega-Carbon has access to a limited number of database systems already (DIALOG), but will make arrangements to set up access to others which have access to some of the less familiar journals. Also it is clear from an initial pass of the literature, that there is a significant body of information in Japanese journals on arsine containment. Consequently it will be necessary to access these foreign journals and have articles translated into English. The key issues we will try to address are:

   * What is the role of the supported copper?
   * What is the role of supported chromium?
   * What other metals would be good or better candidates for arsine      adsorption?

**Subtask 1.2**    Physisorption of Arsine on Carbon

The general field of gas-adsorbing carbons holds much of the information needed to better understand physisorption of arsine. We propose to focus on the general phenomenon of gas adsorption and what are the interaction between adsorbate molecules and the adsorbent. The literature on natural gas adsorption on carbon already contains many of the key ideas on the relation of the molecular dimensions of the adsorbate and pore size.

All activated carbons contain a distribution of micropores, transitional (meso) pores and macropores. Pore size distribution is critical in how an activated carbon behaves. For example, the main distinction between gas-adsorbing and decolorizing carbons likes in the pore volume distribution, areas being similar[22]. A comparison of the PSD's for a gas carbon is shown on the right. Technical journals and patent literature will be critically surveyed to develop information on gas adsorbing carbons and other sorbents(zinc oxide, alumina, silica) as suggested by Nowack et al[20] at Phillips Petroleum.
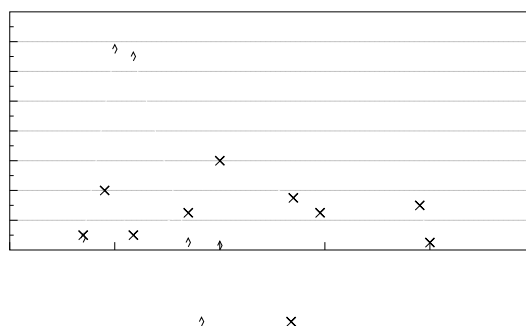
**Subtask 1.3** Mass Transfer Influences of Arsine Adsorption

Mass transport processes can play an important role in arsine adsorption on a solid adsorbent. If we trace the path of an arsine molecule, it must first move from the bulk gas phase through a gas film surrounding the adsorbent particle. Then it will subsequently diffuse into the particle through the network of pores and ultimately adsorb on the surface. These mass transport resistance have been thoroughly analyzed by Satterfield[23]. The diagram on the right shows the concentration profile for arsine during the adsorption process. If the chemisorption step is relatively fast, it is possible for the overall rate of adsorption to be controlled by either external mass transfer through the film or pore diffusion within the particle. We think that a comprehensive analysis of arsine adsorption should include understanding and estimating the influence of mass transport effects.
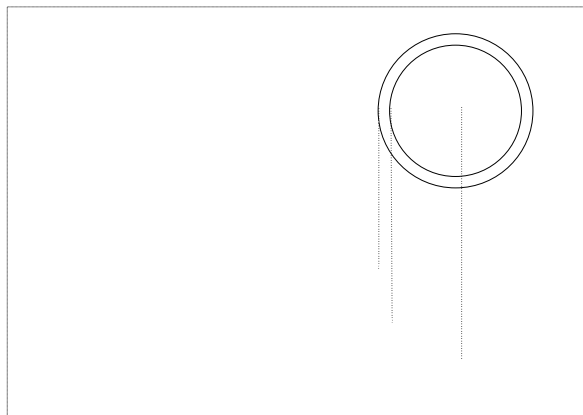
For Subtask 1.3, we will draw upon the related field of heterogenous catalysis to develop estimates of the magnitude of mass transfer effects. This will then allow us to determine 1. whether the fluid velocity is sufficient to eliminate external mass transfer resistances and 2. the impact of sorbent particle size and whether it needs to be reduced to reduce the concentration gradient in the particle. These estimation procedures have been developed by Satterfield[23] and can be directly applied.

**Task 2:          Treatment of Active Carbon for Enhanced Arsine Adsorption**

ASC Whetlerite is used for the removal of gases from streams of air. Most commonly, the Whetlerite is prepared by impregnating active carbon with copper and chromium. The adsorbent carbons used currently have their origins with these carbons developed as chemical warfare agents. We believe there is a some very relevant work being performed at defense laboratories which will find direct application for this semiconductor application. In particular, numerous reports are now appearing on the enhancement of these ASC Whetlerite carbons by doping or co-impregnation with a third component such as silver[24] Also there are recent patents by the Japanese[25] which describe other alkali metals such as K, Mg, and Fe in addition to the Cu and Cr. We see considerable opportunities for identifying other impregnants for the sorbent and sets the basis for the following work plan.

**Subtask 2.1** Improved Dispersion of Cu/Cr Oxides on Carbon

A common and usually successful way to improve the efficiency of heterogenous catalysts is to improve the dispersion of the supported metals so that the metals are not located in relatively large "dumps". We view this as a key way to improve the presently used arsine sorbent carbon. During the impregnation procedure it is necessary to carefully control pH and other factors so that the particles are uniformly impregnated; this pertains to either an eggshell effect or large crystallite clusters. Since much of the early work on auto exhaust treatment used base metal catalysts such as copper chromite on alumina, before the present noble metal systems were adopted, the numerous articles on these earlier catalytic systems should prove useful in developing strategies for better dispersion of Cu/Cr on activated carbon. We will probably try some limited laboratory work in this area to test out some of these ideas also.

**Subtask 2.2** Promoters to Enhance/Assist Cu/Cr Oxides

As mentioned above, Japanese patents are appearing more frequently on enhancements to the conventional Cu/Cr systems for improving arsine containment in the semiconductor industry. Silver has already been mentioned by Krishnan et al[11] as a dopant for the ASC whetlerite system. Furthermore, platinum and palladium are known to be effective dopants for the base metal Cu/Cr auto exhaust catalysts. Thus we think that there are reasonable possibilities that a simple modification of the existing arsine sorbents may lead to significant benefits. We plan to survey the literature in supported Cu/Cr on

alumina to develop leads for the activated carbon systems which could then be pursued and tested out under Phase II.

**Subtask 2.3** Alternative Metal Oxides

Impregnated metals other than copper/chromium combinations are also possible.
For example, a Japanese patent[26] reports on the activated carbon being sprayed with aqueous KI, $I_2$, and $FeSO_4$, dried and then used to adsorb arsine and phosphine. In another example, a Japanese patent[27] describes an active carbon containing NaOH and $HgCl_2$ which is effective for the trapping a semiconductor gas at high efficiency. These leads should be pursued further so see if these patents are valid and how well these alternative impregnated metals perform.

**Task 3:         Alternative Adsorbents for Arsine Adsorption**

We see considerable opportunity in this area for improving the existing arsine adsorbent system. Mega-Carbon Company has access to a novel superactivated carbon whose adsorption capacity is three times that of conventional carbons. This carbon has already been tested for chemical warfare by the Army's Natick laboratories[13] and with the following comment, "*We have found the superactivated carbon manufactured by a licensee of Amoco to be extraordinarily superior to any commercially available carbon we have evaluated in chemical protective fabrics and we are actively seeking a source of this carbon for larger scale testing*". This superactivated carbon is more expensive than commercial carbons but for specialty applications in the semiconductor industry, we think it is well suited. Additionally, other non-carbon adsorbents will be investigated.

**Task 3.1** High Surface Area Superactivated Carbon

indicated that this metal combination can be enhanced by
# Related Work

Dr. Ken Robinson, one of the Mega-Carbon team members, has been deeply     involved in developing drinking water treatment carbons for the last 5 years. He has been successful in obtaining a patent based on the granulation of the Amoco superactivated carbon powder so that it can be used in granular form. This background is very helpful as spin-off applications of the superactivated carbon will be for gas masks, air filters, and natural gas storage where a granular form is required.

Mr. Tom O'Grady, a consultant of the project, is one of the original inventors of the Amoco carbon and has considerable background applications and performance of activated carbons.

Dr. Frank Derbyshire, Mega-Carbon's Vice-President and other consultant, has considerable experience in the active carbon field. Frank has spent most of his professional in some aspect of carbons. He has also worked on the Amoco carbon, specifically, establishing its performance for natural gas storage and has written several articles on active carbons and how their properties related to performance.

# Research and Development

The successful completion of the process design of the 1 million lb/yr carbon plant under Phase I will set the basis for proceeding to Phase II in which a smaller module of the full-sized plant must be constructed and then operated to produce 4000 lbs of the superactivated carbon powder. Many of the technical hurdles facing the commercial plant will be the same for the smaller module, particularly regarding precalciner/calciner design (materials of construction, method of transport through the vessels such as auger, etc), and optimum policy for the time and temperature of the KOH-coke mixture in each vessel.

## Potential Post Applications

Although the US Government has currently viewed the superactivated carbon as an adsorbent powder to be used to manufacture chemical protection uniforms, it has far greater applications than this which would be beneficial to our country. It has already demonstrated its usefulness as an air filter for gas masks and air intake filters for tanks if it is in a granulated form. Additionally it can be used a detoxification agent for medical use in which a slurry of the powder when swallowed will significantly alleviate drug overdose and accidental poisoning for both human and animal use. Tests show that the granulated form of the superactivated carbon is also highly effective for drinking water treatment with the contaminant removal better and the time before carbon exhaustion about three times longer. Finally, the storage of natural gas on activated carbons looks very promising. It has been found that the Amoco carbon is highly effective for this application particularly on an equivalent weight basis but it is not yet dense enough on an equivalent volume basis. It still needs some improvement but strides are being made in making the carbon adsorbent denser for future use in natural gas fueled vehicles.

## Key Personnel

**Dr. Rodney L. Mieville** (Principal Investigator)

Ph.D. Physical Chemistry, 1964, University of Western Ontario, Canada, Thesis: Photo-Addition of Methyl Mercaptan to Olefins

ARIC Chemistry, 1953, Northern Polytechnic London University, England

**Experience:**

**1964-1992: Amoco Oil Research and Development**
Associate Research Scientist

Worked on a variety of projects including combustion kinetics, oil additives and catalysis, petroleum processes, adsorption, and inorganic membranes. The catalytic work involved all aspects of catalysis including reaction kinetics, coke and poisoning deactivation, synthesis and characterization and assessment of adsorbent and catalytic materials.

**1954-1961: British Petroleum Research and Development**
Research Chemist

Member of the ACS, RSC (Royal Society of Chemistry), NATAS (Thermal Society), and the Catalysis Society of North America. Chairman of Surface Acidity Task Group of D.32 Committee ASTM
6 Patents, 25 Publications

**Publications:**

1. D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, "*Photo-Initiated Reactions of Thiols and Olefins, I. The Thiyl Radical Catalyzed Isomerization of Butene-2 and 1,2-Ethylene-d2*," CANADIAN JOURNAL OF CHEMISTRY, Volume 42 (1964).

2. D. M. Graham, R. L. Mieville, R. H. Pallen, and C. Sivertz, "*Photo-Initiated Reactions of Thiols and Olefins, II. The Addition of Methanethiol to Unconjugated Olefins*," CANADIAN JOURNAL OF CHEMISTRY, Volume 42 (1964).

3. R. L. Mieville and Garbis H. Meguerian, "*Mechanism of Sulfur-Alkyllead Antagonism*," IND. & ENG. CHEMISTRY, Volume 6, No. 4, December 1967.

4. R. L. Mieville "*Measurement of Microporosity in the Presence of Mesopores*," JOURNAL OF COLLOID & INTERFACE SCIENCE, Vol. 41, No. 2, November 1972.

5.    R. L. Mieville "*Measuring Acidity by Temperature-Programmed Desorption*," JOURNAL OF CATALYSIS 74, 196-198 (1982).

6.    R. L. Mieville "*Studies on the Chemical State of Cu during Methanol Synthesis*," JOURNAL OF CATALYSIS 90, 165-172 (1984).

7.    R. L. Mieville "*Platinum-Rhenium Interaction: A Temperature-Programmed Reduction Study*," JOURNAL OF CATALYSIS 87, 437-442 (1984).

8.    H. Deligianni, R. L. Mieville, and J. B. Peri, "*State of Pd in Active Methanol Synthesis Catalysts*," JOURNAL OF CATALYSIS 95, 465-472 (1985).

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10.  R. L. Mieville, "*Coking Characteristics of Reforming Catalysts*," JOURNAL OF CATALYSIS 100, 482-488 (1986).

11.  R. L. Mieville, "*The Chemical State of Copper during Methanol Synthesis*," JOURNAL OF CATALYSIS 97, 284-286 (1986).

12.  R. L. Mieville, "*$N_2$ Adsorption Method for Measuring Certain Acid-Base Sites on Alumina*," JOURNAL OF CATALYSIS 105, 536-539 (1987).

13.  David F. Tatterson and Rodney L. Mieville, "*Nickel/Vanadium Interactions on Cracking Catalyst*," I&EC RESEARCH (1988), 27, 1595.

14.  R. L. Mieville and M. G. Reichmann, "*Temperature-Programmed Desorption Study of CO on Pt-Reforming Catalysts*," AMERICAN CHEMICAL SOCIETY (1989).

15.  R. L. Mieville, "*Coking Kinetics of Reforming*," CATALYST DEACTIVATION (1991).

16.  B. L. Meyers, R. S. Kurek, and R. L. Mieville, "*Microchemisorrption*," JOURNAL OF CATALYSIS, Volume 127, No. 2, (February 1991).

17.  R. L. Mieville, presentation at the Symposium on Effect of Pore Size on Catalytic Behavior Presented before the Division of Petroleum Chemistry, Inc., American Chemical Society in Miami Beach on September 10-15, 1976, entitled "*Temperature-Programmed Desorption Studies of Cracking Catalysts.  Relationship with Microporosity and Activity*."

18.  R. L. Mieville, presentation at the Symposium on Multimetallic Catalysts Presented before the Division of Petroleum Chemistry, Inc., American Chemical Society in Seattle on March 20-25, 1983, entitled "*Platinum-Rhenium Interaction: A Temperature-Programmed Reduction Study*."

19.  R. L. Mieville, presentation at the Symposium on Zeolite and Shape Selective Catalysis Presented at the AIChE Annual Meeting in Houston on March 29-April 2, 1987, entitled "*Interacrystalline Zeolite Diffusion*."

20.  R. L. Mieville and M. G. Reichmann, presentation at the Symposium on Preparation and Characterization of Catalysts Presented Before the Division of Petroleum Chemistry, Inc., American Chemical Society, Los Angeles Meeting on September 25-30, 1988, entitled "*Temperature-Programmed Desorption Study of CO on Pt Reforming Catalysts*."

21.  R. L. Mieville, D. M. Trauth, and K. K. Robinson, General Papers (Poster Session) Presented Before the Division of Petroleum Chemistry, Inc., American Chemical Society in Miami Beach on September 10-15, 1989, entitled "*Asphaltene Characterization and Diffusion Measurements*."

22.  R. L. Mieville, D. M. Trauth, and K. K. Robinson, presentation at the Symposium on Convection and Diffusion in Porous Catalysts at the AIChE Annual Meeting in San Francisco on November 5-10,

1989, entitled "*Asphaltene Characterization and Diffusion Measurements.*"

23. B. L. Meyers and R. L. Mieville, "A Comparative Study of TGA and TPR on Ni-W Hydroprocessing Catalysts," (Paper # 111, ACS Meeting).

24. H. Deligianni, R. L. Mieville and J. B. Peri, "*Possible Relationships of Sites for CO Adsorption with Methanol Synthesis Activity of Supported Pd Catalysts.*"

25. U. Balachandran, J. J. Picciolo, J. T. Dusek, R. A. Russell, R. B. Poeppel (Argonne National Laboratory) and R. L. Mieville, presentation at the 1992 International Gas Research Conference (IGRC 92), Orlando, Florida on November 16-19, 1992, entitled "*Fabrication of Ceramic Membrane Tubes for Direct Electrochemical Conversion of Natural Gas,*" July 1991.

**Patents:**

1. R. L. Mieville, "*Improvements in or Relating to the Production of Oxygenated Organic Compounds,*" US 882,863.

2. R. L. Mieville, "*Middle Distillate Fuel Oil Compositions Having Improved Pumpability,*" US 3,807,975.

3. R. L. Mieville, "*Middle Distillate Fuel Oil Compositions Having Improved Pumpability,*" US 3,807,990.

4. R. L. Mieville, "*Catalyst for Selective Hydrocracking of Alkylbenzenes,*" US 4,171,290.

5. R. L. Mieville, "*Reforming with a Catalyst Comprising Iridium, Zirconia, and Alumina,*" US 4,297,205.

6. R. L. Mieville, "*Methods to be Used in Reforming Processes Employing Multi-Metallic Catalysts,*" US 4,048,058.


**Dr. Ken Robinson**

D.Sc.  Ch.E.  1970, Washington University-St. Louis
M.S.   Ch.E.  1964, University of Michigan
B.S.   Ch.E.  1963, University of Michigan

Title of Thesis: "**Thermal Reforming by Means of Propylene-Propane Co-Pyrolysis**"

Experience-
**11/89 to 4/92: Amoco Corporation**
Manager, Technical University Relations

Technical liaison with major universities in the United States.  Technology transfer and coordination of external research.

**11/84-01/89:   Amoco Oil Company, Research and Development**
Research Associate

Exploratory process research on heavy oil conversion, asphaltene solubility-solids formulation, and coal resid coprocessing.  Engineering consultant to division.

**01/80-11/84:   Standard Oil (Indiana)**
Director, Coal Utilization

Manage and coordinate a variety of coal synfuel programs in the Synthetic Fuel Development

department.  Program areas include coal liquefaction-gasification, syngas conversion, solids-liquid separation of syncrudes.

**01/73-01/80:     Amoco Oil Company, Research and Development**
Project Manager
Petroleum Refining Research and Synfuels

**1/65-1/73:       Monsanto Company**
Senior Development Engineer

Member of AIChE, ACS, Chicago Catalysis Society
Professional Engineer in Illinois
5 Patents, 14 Publications

Publications:

1.      K. K. Robinson, and D. E. Briggs, "*Isothermal Pressure Drop Across Banks of Finned Tubes*," Heat Transfer-Los Angeles, Chemical Engineering Progress Symposium Series, Vol. 62, No. 64, 177 (1966).

2.      K. K. Robinson, A. Hershman, F. E. Paulik, and J. F. Roth, "*Catalytic Vapor Phase Hydroformylation of Propylene Over Supported Rhodium Complexes*," JOURNAL OF CATALYSIS, Volume. 15, No. 3, 245 (1969).

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5.      K. K. Robinson, A. Hershman, J. H. Craddock, J. F. Roth, "*Kinetics of the Catalytic Vapor Phase Carbonylation of Methanol to Acetic Acid*," JOURNAL OF CATALYSIS, Vol. 27, No. 3, 389 (1972).

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13. R. J. Bertolacini, J. M. Forgac, D. K. Kim, R. J. Pellet, and K. K. Robinson "*Catalytic Functionality for Cool Hydroliquefaction*," Third International Conference--The Chemistry and

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14. D. F. Tatterson, K. K. Robinson, R. Guercio, and T. L. Marker, "*Feedstock Effects in Coal Flash Pyrolysis*," Communication, I&EC, to be published (1990).

Patents:

1.     F. E. Paulik, K. K. Robinson, and J. F. Roth.
       "*Vapor Phase Hydroformylation Process*," US 3,487,112--British Patent   1,228,201.

2.     D. K. Kim, R. J. Bertolacini, L. C. Gutberlet, and K. K. Robinson, "*Process for Coal Liquefaction and Catalyst*," US 4,257,922.

3.     D. K. Kim, R. J. Bertolacini, L. C. Gutberlet, and K. K. Robinson, "*Process for Coal Liquefaction and Catalyst*," US 4,294,685.

4.     J. S. Meyer, K. K. Robinson, J. M. Forgac, and D. F. Tatterson, "*Rapid Hydropyrolysis of Carbonaceous Solids*," US 4,326,944.

5.     K. K. Robinson, "*Granulated Activated Carbon for Water Treatment*," US 4,954,469.


**Dr. Frank S.C. Lee**
Ph.D. Chemistry, University of California, Irvine, CA, 1974
B.S. Chemistry, National Taiwan Normal University, 1965
Post Doctoral, Environmental, University of California, Irvine, CA, 1976
Experience:

**1988-1992 Amoco Oil Company**, Naperville, IL
Senior Research ScientistAMOCO OIL COMPANY,                              Chemistry of petroleum and coal process/utilization
Environmental fate and Chemical characterization of organic pollutants     in wastewater, soil and oily sludge.

**1980-1987 Amoco Corporation,** Analytical Department

Analytical technology and chemistry of petroleum residdum and             synfuels derived from coal, tar sand, and shale.
Environmental trace analysis method development
Analytical liaison/specialist in heavy oil/synfuel areas

**1976-1980 Ford Motor Company**, Dearborn, Michigan

Research Scientist, Scientific Research Laboratories

Air pollution and automobile exhaust emission research
Atmospheric chemistry of particulate organic matter
Chemistry of polynuclear aromatic hydrocarbons
Member of a research team involved in the study of the health effects of diesel exhaust emissions.

Board of Directors, MACSTA (Mid-America Chinese Science & Technology Association), Chairperson, Chemical and Environmental Technology committee, MACSTA, Technical Director (environmental technology), Mt Jade Association of Technology and Enterprise (Mid-America),Technical Program Chairperson, 1991 Mid-America Chinese Professional Annual Convention, Chicago, May, 1991, Consultant and Lecturer on environmental chemistry at Central Research Institute of Ministry of Metallurgical Industries, Beijing, China, Sponsored by United Nation Development Programme, May-June, 1983

## Facilities/Equipment

Mega-Carbon is located in facilities adjacent to Xytel Corporation in Mount Prospect, IL, a suburb of Chicago; we have a business agreement with Xytel whereby we have access to design personnel and tools and can also share in the space for pilot plant construction. Mega-Carbon is housed in a 38,000 square foot office and plant facility, conveniently located near O'Hare Airport. Of the total covered area, approximately 10,000 square feet are used for offices and engineering with 28,000 square feet available for manufacturing and assembly. Support facilities include modern welding equipment, personal computers for every professional staff member, and a well supplied stock room of bulk direct and indirect materials.

The facilities provide a full service organization in which all resources are under one roof: chemical engineering, electrical engineering and electronics, computer technology, computer-aided drafting and design (CADD), process assembly, interface assembly and field service and maintenance.

Additionally Mega-Carbon is located near Northwestern University, in Evanston IL, where it is possible to have analyses run on the superactivated carbon to determine its surface area, examine its microstructure via scanning microscopy, and measure its adsorption capacity. All of these tools are currently applied to catalysts in Northwestern's Catalysis Center.


## Consultants

**Mr. Thomas O'Grady**

M.S. Chemical Engineering, 1951, University of Notre Dame
B.S. Chemical Engineering, 1950, University of Notre Dame

Present Position: Private Consultant

Experience:

52-89   Standard Oil(Ind), Amoco Corp. Amoco Oil Company
Research and Development Engineer, Supervisor
Background includes over 37 years of broad experience in process and product development. Manager of a major development for a new , unique active carbon. This involved laboratory, pilot plant development and marketing of this unique product. Prior to retirement from Amoco, research supervisor in the development of tar sand technology for recovery of syncrude from tar sands.

Publications:

1.      T.M. O'Grady, R.M. Alm and M.C. Hoff, "*Isomerization of Olefins with Sodium at Low Temperature*", Symposium on Carbanion Reaction and Processes of Hydrocarbons, ACS Meeting Sept 13-18, 1959

2.      T.M. O'Grady, "*Liquid-Liquid Equilibrium for the Benzene/n-Heptane/Water System in the Critical Solution Region*", J of Chem. Eng. Data, 12,9(1967)

3.      Marvin L. Deviney and Thomas M. O'Grady,"*Petroleum Derived Carbons*", ACS Symposium Series 21 (1976)

4.      H. Marsh, D. Crawford, T.M. O'Grady, and A.N. Wennerberg, "*Carbons of High Surface Area, A Study by Adsorption and High Resolution Electron      Microscopy*", Carbon 20 419 (1982)

5.      T.M. O'Grady and A. Wennerberg, "*High Surface Area Active Carbon*" 187th Meeting ACS, St. Louis, MO, (1984)

6.      H. Marsh, D.S. Yan, T.M. O'Grady, and A. Wennerberg, "*Formation of   Active Carbon from Cokes Using Potassium Hydroxide*", Carbon, 22,       603,(1984)

7.      O.P. Mahajan, K.K. Robinson, T.M. O'Grady, "*Amoco Carbon-The Super Adsorbent*", CAER

Workshop on Carbon Research, Lexington, KY June 20, 1991.

Patents

1. T.M. O'Grady, R.M. Alm, M.C. Hoff, "*Conversion Process*", US 3,257,415

2. T.M. O'Grady, A.N. Wennerberg, "*Method of Preparing a Catalyst Composition Consisting of Sodium, Sodium Carbonate, and Iron Oxide on       Alumina and the Product Thereof*", US 3,260,679

3. T.M. O'Grady, "*Unsaturated Hydrocarbon Dehydrogenation with Carbon Dioxide Activated Metal Oxide Catalyst*", US 3,329,733

4. T.M. O'Grady, R.M. Alm, M.C. Hoff, "*The Catalytic Isomerization of Unsaturated Acetals and Hydrocarbons*", US 3,437,698

5. A.N. Wennerberg and T.M. O'Grady,"*Active Carbon Process and Composition*", US 4,082,694

6. T.M. O'Grady, D.F. Tatterson, and R Coates,"*Shale Oil Stabilization with a Hydrogen Donor Quench*", US 4,536,277

7. D.F. Tatterson and T.M. O'Grady, "*Shale Oil Stabilization with a Hydrogen Donor Quench*", US 4,536,278

**Dr. Frank Derbyshire**

Ph.D.   Chemical Engineering, 1972, Imperial College , London
M. Eng. Chemical Engineering, 1968, MacMaster College, Ontario Canada
B.Sc.   Chemical Engineering, 1966, Manchester University, England

Present Position:
Director of Research, Center for Applied Energy Research, University of Kentucky, Lexington, KY and Vice-President of Mega-Carbon, Mt. Prospect, IL

Experience:
85-88 Sutcliffe Speakman Carbons, Std.
       Research Director

86-87 Private Business

82-86 Pennsylvania State University, Dept of Materials Science and Engineering
       Associate Professor in Fuel Science

79-82 Mobil R&D Corporation ,Central Research Division
       Associate and Group Leader

75-78   N.C.B. Coal Research Establishment,    Cheltenberg, England

**Dr. John B. Butt**

D.Eng. Ch.E.  1960, Yale University
M.Eng. Ch.E.  1958, Yale University
B.S.    Ch.E. 1963, Clemson University

Academic Experience-

**1969 to Present:**     **Northwestern University**, Department of Chemical Engineering, Professor. Walter P Murphy Professor

**1979, Spring:**   **University of California-Berkeley**, Visiting Professor

**1964-1969:**     **Yale University**, Department of Engineering and Applied Science, Associate Professor

**1963-1964:**     **Yale University,** Department of Engineering and Applied Science, Assistant Professor

**1961:**     **University of Texas**, Visiting Professor of Chemical Engineering

Member of AIChE, ACS, Chicago Catalysis Society
New York Academy of Sciences
American Society of Engineering Education
American Association for the Advancement of Science
Associate Editor, "Catalysis Reviews-Science and Engineering"
Registered Professional Engineer, Connecticut
Director of AIChE, 1975-1978
Editorial Board, Journal of Catalysis, 1976-
168 technical publications, 1 patent and 2 textbooks

No prior, current, or pending support for a similar proposal

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US Department of Defense
Small Business Innovation Research (SBIR) Program
**Cost Proposal**

1. Name: Mega-Carbon Company
2. Home office address: 801 Business Center Drive, Mt. Prospect, IL 60056
3. Location where work will be performed: 999 Chicago Avenue, Naperville,IL
4. Title of proposed effort: Development of High Performance Adsorbents for      Arsine Gas and Derivatives
5. Topic number and topic title: A931-044, Reduction of Environmental Hazards      Due to Arsine Gas and Derivatives

| | |
|---|---|
| 6. Total dollar amount | $49,687 |
| 7. Direct material costs: | $100 |
| 8. Material overhead : 5% x 100          = | $5 |
| 9. Direct labor:      hrs   x rate/hr     =<br>(PI)  R. Mieville    320        40        =<br>   K. Robinson    320        40        =<br>   F. Lee         50        35        =<br>   Technician    300        18        =<br>   Secretary    120        12        =<br>   Total direct labor              = | $12,800<br>$12,800<br>$1,750<br>$5,400<br>$1,440<br>$34,190 |
| 10. Labor overhead: rate      hour base<br>         35%      x   $34,190 | $11,966 |
| 11. Special testing:  none | |
| 12. Special equipment:<br>Rental of mainframe computer time | $500 |
| 13. Travel: none | |
| 14. Consultants:    hrs   x   rate/hr<br>   T. O'Grady      8        100<br>   F. Derbyshire   8         50<br>   J. Butt         8         50 | $800<br>$400<br>$400 |
| 15. Other direct costs: Publication Costs<br>Total estimated direct cost + overhead | $300 |
| 16. General and administrative cost  3% x 34,190 | $1026 |
| 17. Royalties: none      18. Fee or Profit: none | |
| 19. Total estimated cost(including fee) | $49,687 |
| 20. Responsible official<br>   Ken Robinson, President              Date | |
| 21a. no     21b. no     21c. no | |
| 22. Type of contract: firm-fixed price | |