

DEVELOPMENT OF A NEXT-GENERATION ENVIRONMENTAL CHAMBER FACILITY FOR CHEMICAL MECHANISM AND VOC REACTIVITY RESEARCH

Summary of Progress and Current Status August 20, 2002

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Introduction

The objective this EPA-funded project is to develop an environmental chamber facility that is needed for studies of photochemical air pollution formation under more realistic conditions and with more comprehensive measurements than previously has been possible. This facility can then be employed for evaluating gas-phase and gas-to-particle atmospheric reaction mechanisms, for determining how best to use ambient measurement data for predicting effects of control strategies, and for evaluating the reliability of ambient measurement instrumentation.

The project was initiated in late 1999 and the design and construction of the facility is now largely complete. Considerable research was conducted regarding chamber background effects to address the priority of conducting experiments at lower pollutant levels than previously employed, and approaches to minimize these effects were developed. As with many complex developmental projects, construction of the facility took longer and cost more than initially anticipated, but we believe the major design goals have been met. The remaining EPA funding, which we project will run out very early in 2003, will be used for chamber and instrumentation characterization experiments needed to use the facility for mechanism evaluation.

A research plan for use of the facility for priority research has been developed and is being reviewed by the U.S. EPA and the Reactivity Research Working Group (RRWG). Some funding to implement portions of this research plan is being provided by the California Air Resources Board (CARB), but additional funding will be needed to fully implement the research plan and utilize the facility to its full potential.

Summary of Progress

The program was initiated with a successful international workshop held in Riverside, California concerning atmospheric chemistry and environmental chamber research, where useful input concerning this project was obtained from researchers from the United States and Europe.

Near-term needs for measurement instrumentation were assessed, and equipment was purchased and evaluated. Extensive experiments were constructed using small test reactors to evaluate material for construction, to test design parameters, and to evaluate the new instrumentation. The results showed that if appropriate steps are taken it is possible to conduct experiments under NO_x conditions at least an order of magnitude lower than existing data, thereby providing results that better represents ambient air pollution. There was some skepticism when this project was proposed such low NO_x experiments might not be feasible.

Private sector funding was obtained to finance construction of a new building needed to house the chamber facility, with the chamber located on the second floor and the laboratory and offices underneath it. The chamber consists of a 16,000 cubic ft temperature-controlled “clean room” enclosure fitted with a 300 KW argon arc light source, with space for two up to 8,000 cubic ft reactors where the reactions will be monitored. The reactors are constructed of Teflon film fitted on specially designed moveable frameworks, with an associated high volume mixing system suitable for injecting low volatility materials, and a computer-controlled sampling and calibration system for the analyses. A high capacity air purification system is used to keep the enclosure clean and provide highly purified air for the experiments.

In addition to constructing and evaluating the new facility, a research plan was developed to utilize the new facility for priority research in the following areas:

- Improving our ability to predict effects of NO_x and the major types of VOCs on O₃ and PM formation under conditions more representative of ambient and near-attainment environments than current data, with varying temperature, humidity, and pollutant levels.
- Determining how best to use ambient measurement data for predicting effects of control strategies and evaluating the reliability of ambient measurement instrumentation.
- Evaluating ozone and PM impacts of VOC emissions from specific sources such as architectural coatings and low reactivity solvents being proposed for substitutions.

The RRWG is serving as an oversight group for assuring that the research effectively addresses regulatory priorities. An RRWG advisory committee for this project has been formed and is currently reviewing the detailed research plan that was prepared earlier this year.

The first experiment in the new facility, using a preliminary light source and reactor configuration, was carried out in February of 2002. The first experiment with the arc lights and the near-final configuration for a single reactor was conducted in July. The second reactor and the final mixing and sampling system is expected to be in place and operational by September. The initial experiments included evaluations of background effects, the performance of the light source, temperature control system, and analytical instrumentation in the current configuration. These characterization and performance evaluation studies, which are still underway, provide essential data needed for evaluating computer model predictions of the effectiveness of control strategy for reducing ozone and PM. Model evaluation experiments with simple chemical systems should begin in the fall of 2002, with simulations of more realistic systems beginning in early to mid 2003

A detailed report giving progress on this project through October of 2001 is available at <http://www.cert.ucr.edu/~carter/epacham/report1.pdf>. That report describes the facility design

and construction through that date, a discussion of the analytical instrumentation needs and equipment acquired, lists the experiments carried out and the analyses of the results obtained, and describes the problems encountered. The draft research plan that is now being reviewed by the EPA and the RRWG is included with that report.

Progress Since October, 2001

The work carried out and problems encountered in this project since the period covered by that report is briefly summarized below. A more complete discussion of the analysis of the results to date will be described in a subsequent report.

- A detailed quality assurance plan and standard operating procedure documents for conducting chamber experiments and for data processing were prepared and submitted to the EPA for review. These documents are available at <http://www.cert.ucr.edu/~carter/epacham>. Standard operating procedure documents for most of the instruments and major equipment were also prepared, with work on completing documentation of the remaining instruments and procedures ongoing.
- Several additional pure air experiments in the pillowbag reactor employed during the previous period were conducted to complement and fill out the data obtained previously. This included experiments using the new air purification system, where lower O₃ formation was observed, presumably due to the removal of methane.
- Significant problems were encountered with the Vortek light source after it was installed in September of 2001 that prevented it from being useable for environmental experiments until July of 2002. The major problems concerned the spectral filter system, which had to be specially designed to meet the spectral requirements for this project, and turned out to have design flaws that had to be corrected. The coated glass initially prepared for this filter did not have the proper spectrum, and the system broke after minimal use. Other components had problems that required considerable personnel time to deal with. However, most of the operational problems were corrected and eventually we were able to get a running system with a temporary spectral filter that does not exactly meet our specifications but is satisfactory for initial evaluation experiments. The new spectral filters that should meet our specifications have been delivered and are being installed now.
- Because of the problems with the Vortek light source, a temporary blacklight light source was installed in the new enclosure so experiments with larger reactors in the new enclosure could be carried out for evaluation. The lights came from the BTC chamber that was used in the experiments discussed in the first report, which was dismantled for this purpose.
- Initial characterization experiments were carried out in the new enclosure using the temporary blacklight system a large, ~40,000-liter pillowbag reactor that was temporarily installed for this purpose. These included background characterization experiments and some preliminary experiments with simple chemical systems. The results have not been fully analyzed, but a preliminary analysis indicates that even lower NO_x offgasing rates can be obtained in this reactor than observed previously in the smaller reactors.

- The initial experiments also indicated problems with formaldehyde and (to a much lesser extent) NO_x contamination in the new enclosure that could potentially affect the results of very low concentration experiments. The NO_x offgasing problem was solved and the formaldehyde offgasing was reduced after some holes in the low pressure region of the air handling system were found and patched. Levels of formaldehyde in the 20-30 ppb range still occur in the enclosure in irradiation experiments, though this appears to be declining with time.
- Considerable work was conducted to refine the design of the mixing system for the new reactors, so that they could be used for injection of low volatility material (as required in the CARB projects) as well as for mixing and exchange of reactants. A number of experiments were conducted with small pillowbag reactors to test for offgasing of contaminants from materials being considered for injection and mixing system for new reactor. Both dark offgasing and offgasing of materials upon irradiation were evaluated. Some materials were found to emit excessive formaldehyde and were therefore considered to be unsuitable. The materials to use for the system were selected in part based on the results of these experiments. The components for this system have been fabricated, and it should be installed and operational by September.
- Considerable design and engineering work was conducted to develop the movable frames to hold the Teflon reactors in a way that will seal the reactor to minimize leaks and to permit the reactor to collapse to permit rapid removal of pollutants between experiments. A design meeting these requirements was developed and a full-sized prototype was constructed and tested using polyethylene film. The prototype tests were successful and a functioning full sized, ~80,000-liter reactor was constructed with FEP Teflon film and installed in the enclosure. The enclosure has space for a second equivalent reactor, which will be installed by September.
- The design of the sampling system to be used with the facility was completed and the construction has been nearly completed. This system provides for computer-controlled sampling from different reactors, calibration sources, and zero air for the various sets of instruments connected to different sampling manifolds. Special provisions are made for the requirements of the TDLAS systems and for minimizing sampling artifacts for nitric acid. This system is scheduled to be completed and installed in late August or early September of this year.
- With the major design work for the framework and mixing system completed and a temporary spectral filter for the Vortek light source installed, the temporary blacklight system and pillowbag reactor was removed and a full sized reactor was installed on the new framework as indicated above. Construction of the second reactor for what will become a dual-reactor system was deferred until the performance of the system in the single-reactor mode can be assessed.
- Experiments were carried out with the Vortek light and the single reactor system in the near-final configuration beginning in July of 2002. The experiments consisted of pure air and CO – air background characterization runs, a formaldehyde – CO air irradiation to evaluate NO_x offgasing and measure the formaldehyde photolysis rate, a formaldehyde - NO_x run for preliminary model evaluation and characterization, and in-chamber NO₂ actinometry. The Vortek light successfully ran during these experiments for up to a full

24-hour period, and achieved an NO₂ photolysis rate of about 0.6 min⁻¹ when running at its maximum recommended power. This is comparable to or somewhat higher than the NO₂ photolysis rate calculated for direct overhead sunlight, which means that the Vortek light met its intensity specification. However, for routine use it would be better to run the system at a somewhat lower power level. In addition, some further reduction in the NO₂ photolysis rate is expected when the final Vortek spectral filter is installed, since the present temporary filter system is higher in the 300-400 nm region than called for in our spectral specification.

- Priority was given to conducting formaldehyde experiments with the current configuration to obtain information on how the results will change when the spectrum of the light source changes when the new spectral filter is installed. The formaldehyde consumption rate in the formaldehyde – CO experiment, which modeling analysis indicates should be almost entirely due to photolysis, was about $2.8 \times 10^{-3} \text{ min}^{-1}$. This is about 20% higher than predicted based on the results of the in-chamber actinometry runs, the measured spectral distribution, and the formaldehyde absorption cross sections and quantum yields used in the SAPRC-99 mechanism. Additional actinometry and experiments with the new spectral system will be needed to confirm if this is a consistent bias that will affect mechanism evaluation.
- The results of the characterization experiments in the new reactor with the Vortek light indicate that the NO_x offgasing rates are in the low end of the range observed with the smaller pillowbag reactors, but may be somewhat higher than was observed in the ~40,000-liter pillowbag reactor with the blacklights. However, the data have not been completely analyzed and further experiments will be needed to evaluate this.
- Background VOCs may prove to be a more difficult problem in the present system than background NO_x. Formation of a few ppb of formaldehyde was measured in the reactor in experiments where it should not be present. It is unclear whether this is due to the ~10-30 ppb of formaldehyde in the enclosure, due to some problem with the air purification system (whose catalytic converter has been removed for repair), or to contamination in the reactor itself. A few ppb of PAN was also observed in some experiments with NO_x but no other PAN precursors, and preliminary modeling of experiments sensitive to background VOCs suggest that there may be background VOCs beside the measured formaldehyde and CO and the background methane. This will not be a problem in experiments with added VOCs, but will need to be addressed before very low VOC experiments can be carried out for mechanism evaluation.

At the present time (late August, 2002) we are installing the new filter system for the Vortek and making other upgrades to that system, and are installing the second reactor and the mixing and sampling system. Repairs to the pure air system are also being made at this time. At the end of this period, or by early September, we should have the system in essentially its final configuration so we can begin the major work of chamber characterization in preparation for mechanism evaluation. The specific priorities for experiments will depend on whether additional Federal funding can be obtained to carry out the full research plan that has been developed, as discussed in the following section.

Current Funding Situation

As with most groundbreaking research and development projects, the time and cost required to construct the new facility was considerably greater than initially estimated. We had hoped to complete the facility in 2001 for about \$2 million, and use the remaining EPA funds to support operating the facility when conducting the research outlined above. However, we presently project that the Federal funds will be expended by January 2003, by which time we will have only begun conducting experiments of direct relevance to regulatory modeling.

We estimate that the annual cost of operating this facility at a minimal level to be approximately \$750K per year, with approximately \$1.5 - \$2 million per year being required to take full advantage of its unique capabilities. We do have approximately \$200K for a 3-year project from the California Air Resources Board (CARB) to conduct experiments on architectural coatings VOCs, and may obtain comparable funding from the California South Coast Air Quality Management District (SCAQMD) to conduct additional reactivity-related experiments. The SCAQMD has also expressed interest in possibly funding the radical measurement instrumentation needed to carry out some elements of the research plan, and a proposal to this effect (available at <http://www.cert.ucr.edu/~carter/epacham/radicals.pdf>.) is being submitted for their consideration. Private sector support related to ozone and PM impacts of specific solvents is expected once the EPA clarifies its regulatory policy concerning VOC reactivity, which is currently being re-evaluated.

However, the CARB funding was obtained with the expectation that the EPA funds would cover the costs of the needed characterization experiments and support the basic infrastructure, and the productivity of this and any future projects would be significantly reduced if project funds had to be used for this purpose. In addition, the public and private agencies with limited research funds may not be able to take advantage of this facility if their project had to support the full cost of operating this facility at its full capability.

We are requesting that the Federal investment in this facility continue at least \$1 million per year to assure continued operation of this facility and to fully leverage the support from the mission-oriented agencies and public sector groups. This would be used to cover the support staff and ongoing characterization and quality control, and permit continued acquisition and use of the advanced equipment needed for making critical measurements that would not otherwise be possible. The mission-oriented funding agencies will support for the focused experiments that address the specific policy-relevant research needs. Even if the Federal investment provides the majority of the funding for the facility, continued support from these groups is essential to assure that the most relevant and needed work is carried out.