

# **ENVIRONMENTAL EFFECTS OF SOLAR THERMAL POWER SYSTEMS**

**THE POTENTIAL PRODUCTION OF AIR POLLUTANTS  
NEAR STPS RECEIVER SURFACES**

SEPTEMBER 1981

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THE POTENTIAL PRODUCTION OF AIR POLLUTANTS  
NEAR STPS RECEIVER SURFACES

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## ABSTRACT

This report presents data and analysis addressing the potential production of air pollutants in the high temperature, high solar intensity beam environment adjacent to an STPS receiver. Results, (chemical equilibria, chemical kinetics, mass emission rates, transport and dispersion), indicate that some air pollutants may be produced as a result of operation of large scale central receiver STPS in quantities sufficient to be of regulatory concern. These will require steps toward management. Primary concern focuses on nitric oxide (NO), and its downstream potential pollutant products. In all likelihood the quantities produced will be small, and fully merit for solar its general recognition as an environmentally benign energy technology. Furthermore, for many solar configurations and modes of operation even this limited concern may not apply. Worst case conditions, however, are capable of leading to significant impacts from large scale high temperature STPS facilities.

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## 1.0 INTRODUCTION

At the height of the Arab oil embargo, as the lines for gasoline seemed to stretch interminably, the phrase "energy crisis" became all too well known. The use of the word "crisis" is revealing. The most similar Chinese word when literally translated means "risky opportunity". There are many "risky opportunities" among our choices of ways to approach our energy situation. There is no way that is risk-free, pollution-free, or investment-free. Since all have their associated costs, we must study these and choose an approach which on balance appears relatively more attractive. So it is with solar technologies.

It has been recognized that there could be potential for the production of atmospheric pollutants from chemical reactions at the high temperatures induced in the air surrounding solar receivers. In addition to thermal reactions, the intense solar radiation adjacent to receivers could facilitate photolytic processes. The purpose of this study has been to establish the significance of such possibilities; developing a reasonable understanding of the processes involved, their relative importance, and a measure of the ultimate air environmental impacts. An additional objective is to determine the level and direction of future research which may be needed.

The approach of this study encompassed nine steps.

- 1) From the mix of STPS technologies available for use — troughs, parabolic dishes, and central receivers (cavity and open face) — we select as a vehicle for consideration that likely to constitute a "worst-case" example. Focusing on the potential impacts of this example can resolve hypothetical questions of no real importance early, and focus attention on the few concerns meriting serious attention.
- 2) Selecting parameters representative of worst case application of the technology, such as large size or extreme temperatures, we establish rough measures of reaction conditions likely to be encountered: residence time for reaction to take place, and size of chemically reacting flows.
- 3) We utilize the literature and analysis to establish expected chemical equilibria between constituents in the atmosphere.
- 4) The probable mechanisms and rates of reactions involving key constituents (as suggested by equilibria) are established.
- 5) Some operations auxiliary to the primary STPS receiver are analyzed as potential sources for release of material and possible interaction.
- 6) Calculations are made to picture the transport and possible interaction of those pollutants most likely to be generated on a significant scale. The data used are for worst case circumstances, and therefore provide an upper-bound for possible impacts starting with essentially unpolluted air.
- 7) Data are collected and evaluated for actual air quality at nine U.S. DOE potential STPS sites. These data are analyzed for the potential for

conversion of "normal" constituents (by highly artificial processes) into maximal quantities of pollutants regulated by the National Ambient Air Quality Standards.

8) Scenarios for the possible enhancement of residence time (and thus reaction time and conversion potential) are developed and evaluated.

9) We draw conclusions from this work and suggest directions for further study of greatest value.

The remainder of the report addresses these topics. The primary data base, analytical detail and references essential to this technical work are included in a set of Appendices at the end of the report. The sections immediately following this introduction largely depict the systems and reactions of concern, explain how and why decisions were made regarding parameters of importance, and summarize results within each topic area.



## 2.0 SELECTION OF EXAMPLE TECHNOLOGY; WORST-CASE CONDITIONS

To evaluate all possible solar technologies under the wide variety of conditions possible for their operation would be a burdensome task and include a great deal of redundant effort. Thus, we have carefully focused our investigation on the path of solar use likely to lead to the worst possible outcome. If, after consistently choosing among the worst possible outcomes there are no resultant problems, then it follows that the unchosen paths would also lead to a predicted no-problem future. On the other hand, in those few sectors where potential problems appear likely, the methods of analysis and data developed can be used to more precisely define their relative importance, and to devise at as early a stage as possible means for problem avoidance.

During early stages of this study we briefly considered solar receiving troughs, parabolic dishes, and both open face and cavity central receivers. (Reasonably detailed comparisons of these technologies can be found in reference 1, including information needed as to how they will function.) In the present study we are primarily concerned with the potential of each technology for the production of pollutants released through the air environment. Thus operating temperatures and physical design characteristics that would lend themselves to pollutant production are a first concern. The potential for pollutant production was deemed greatest with the highest operating temperature and the design resulting in the longest residence/reaction time. Coincidentally, these characteristics may also represent the most efficient energy conversion system. Troughs and dishes generally do not concentrate as much solar power as does the central receiver design; i.e., the central receiver design operates at temperatures greater than those of troughs and some dishes. Point-focusing dishes may be an exception for temperature level, but these are generally small in scale and so reflect very short residence times. By contrast, the design of central receivers, being larger in scale and more open, allows a longer residence time and a greater amount of high temperature interface reaction volume. This is illustrated in Figure 2-1.

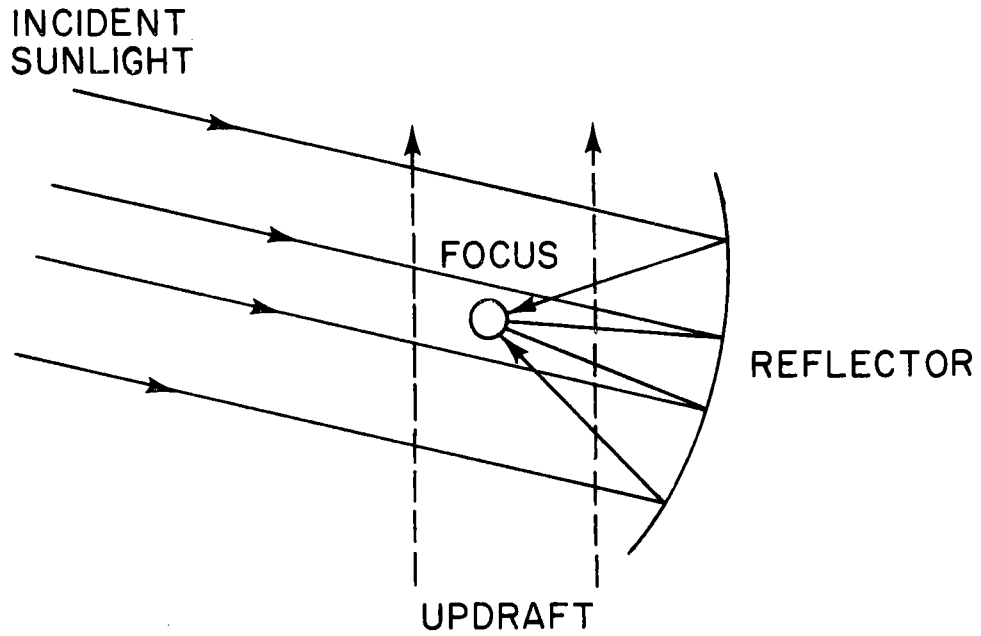
### 2.1 Central Receiver Design Characteristics of Interest

There are two common designs for central receivers; open face and cavity.

The open design is simpler and less costly. Its face is essentially smooth and flat. Solar energy is focused on the face and the heat transfer fluid circulating behind it is heated by conduction. While the open design is simpler and less costly, it is not capable of the efficiency of a cavity design. This is because the flat open face, even when coated to reduce the effect, loses thermal energy via reflection, reradiation, and also transport by adjacent air flow.

The cavity design uses selective coatings and geometric optical engineering design to increase overall efficiency by reabsorbing most all reradiated and reflected energy. Incidentally, this design may be more difficult to control in the event of loss of the heat transfer fluid -- an early, critical step in controlling a loss of fluid event (and preventing structural damage to the facility) is the defocusing of the heliostats. Without further solar heating, an open face, with its reradiative inefficiency, would cool faster than a cavity design and thus lead to quicker

CROSS-SECTION OF  
SOLAR TROUGH OR DISH



CROSS-SECTION OF  
OPEN FACE CENTRAL RECEIVER

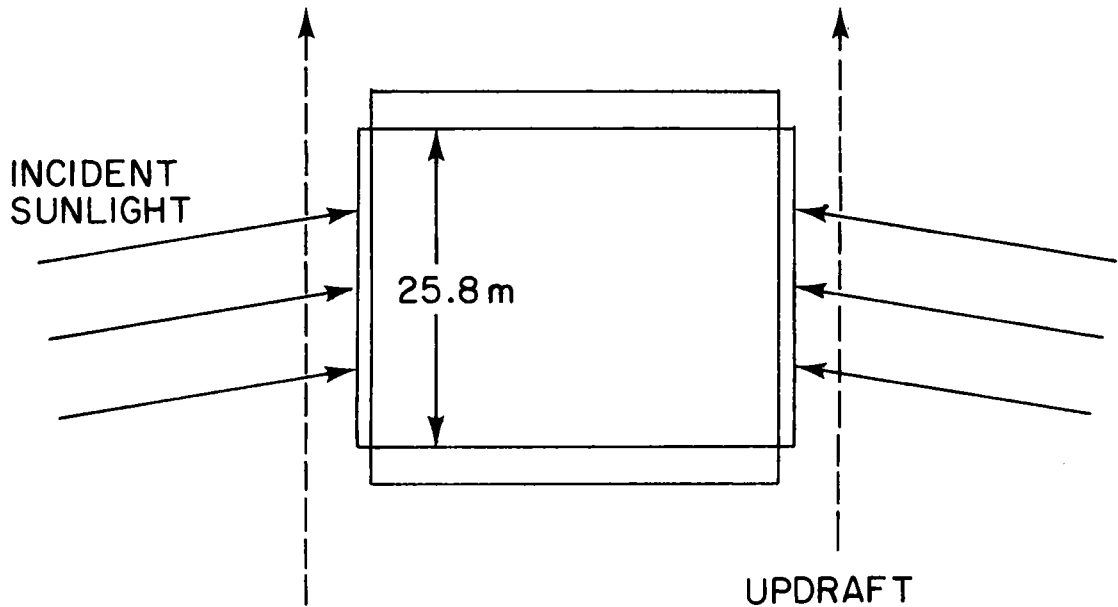


Figure 2-1

Comparison Showing Greater "Openness", Longer  
Reaction Zone of Central Receiver

control of the event. A simplified comparison of open and cavity designs illustrating features important to the present study is shown in Figure 2-2.

For reasons which will be detailed in subsequent portions of this report, we selected the open face receiver, herein referred to as "the central receiver", as the more likely producer of greater quantities of air pollutants.

At the face of the central receiver temperatures will range from 593°C (1100°F) to 2760°C (5000 °F). The worst case for pollution production is not ~~admittedly the best case~~ greater reaction rates, residence time. We will

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ions for a worst case design by the Rockwell output. This power is 61,000 heliostats in a central receiver with a tower 330 m (1083 ft)

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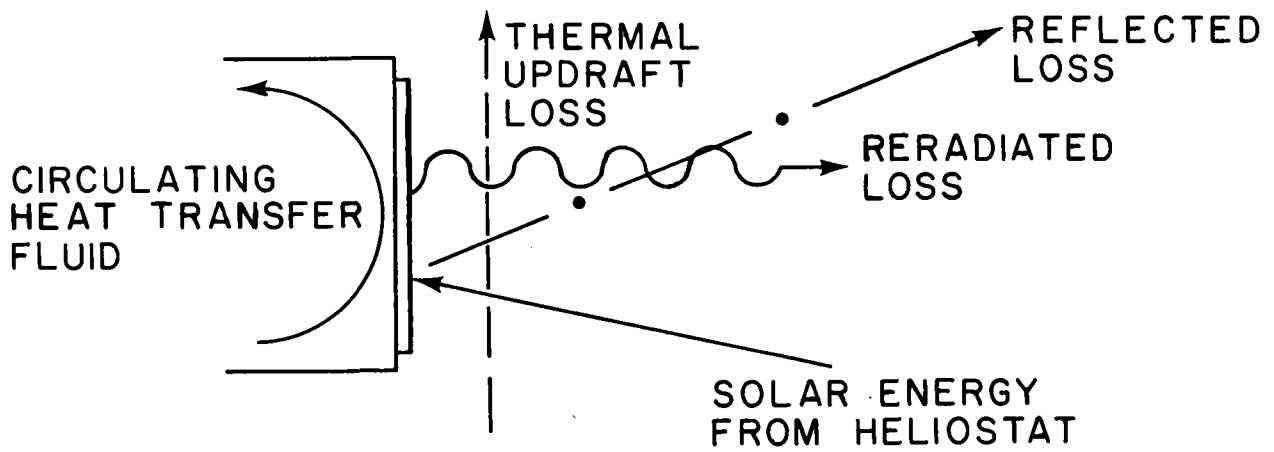
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ace, driven only by the  
thermal difference. It  
will traverse the face in the span of about 0.82 to 1.80 seconds, the former at 2760°C (5000°F) and the latter at 593°C (1100°F). At 2760°C (5000°F), the air parcel's average velocity is 35 m/s (80 mph), a common exit velocity for gases from a conventional combustion stack. Calculations leading to these results are detailed in Appendix 1.

At 2000°C (3632°F), within the range of current receiver temperatures, and with an atmospheric lapse rate typical of desert regions (3), the air parcel is expected to rise 500 - 600 m (1640 -1969 ft). If the lapse rate was virtually but not exactly adiabatic, the parcel would rise 1500 m (4921 ft) (4).

Of equal importance to the residence time of heated air near the receiver face, however, is the total quantity of the air mass experiencing this environment. Calculations (detailed in Appendix 1) provide a rough measure of this parameter. As the plume rises and is heated it expands, so that a greater bulk is represented. But accounting for the very substantial increase in vertical velocity noted above, the total cross-section required as a kind of open conduit shrinks to a small minimum at the top of the receiver. Our estimates, admittedly very crude, consider an annular space extending about 1.2 cm out from the receiver face at the top as the heated region within which reactions of interest are considered to occur.

The results for this very simple model are expected flow quantities of heated air: at 5000°F (3033°K), it is 77 m<sup>3</sup>/sec; and at 1100°F (866°K), it is 16 m<sup>3</sup>/sec.

RECEIVER: OPEN DESIGN



RECEIVER: CAVITY DESIGN

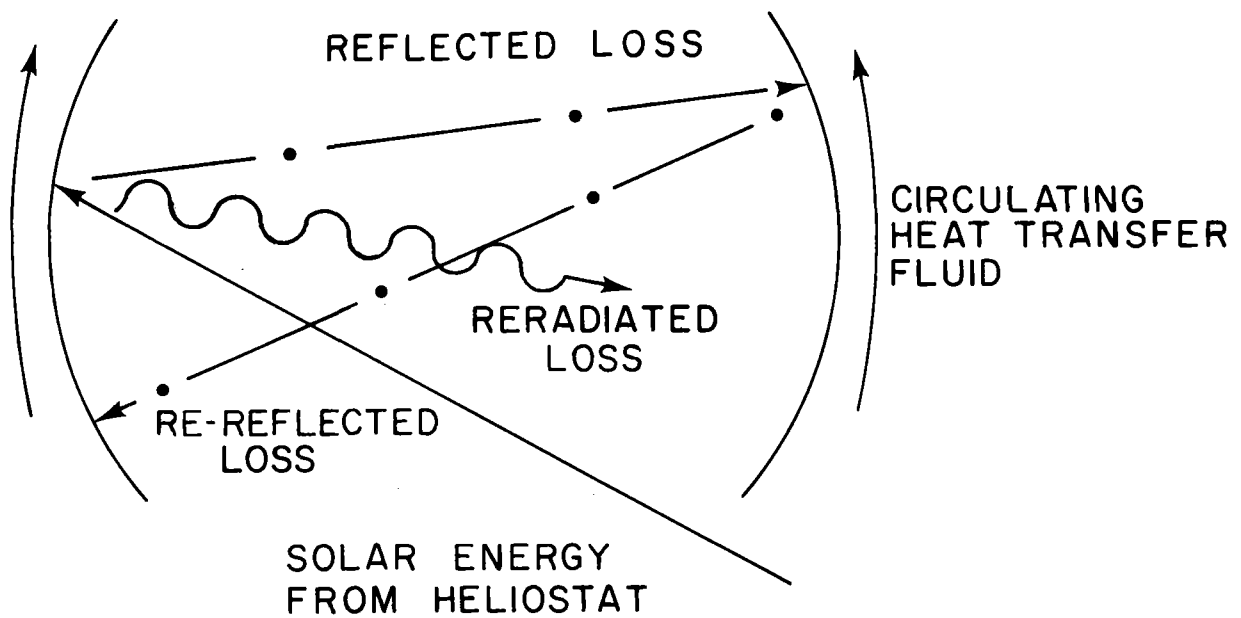


Figure 2-2

Comparison of Some Characteristics of Open and Cavity Receiver Designs

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For reasons which will be detailed in subsequent portions of this report, we selected the open face receiver, herein referred to as "the central receiver", as the more likely producer of greater quantities of air pollutants.

At the face of the central receiver temperatures will range from 593°C (1100°F) to 2760°C (5000 °F). The worst case for pollution production is not obviously the higher temperature with its accompanying greater reaction rates, since the lower temperature results in a longer residence time. We will therefore examine the situation for both temperatures.

The technology selected to provide specifications for a worst case example constitutes a high-power central receiver design by the Rockwell Corporation (2). The facility is rated at 430 MWe output. This power is generated by focusing the solar power collected by 61,000 heliostats in a field 3966 m (13,012 ft) by 4058 m (13,314 ft) onto a central receiver with a face measuring 28.5 m (94 ft) high, and sitting atop a tower 330 m (1083 ft) tall.

## 2.2 Anticipated Central Receiver Reaction Residence Times and Flow of Heated Air

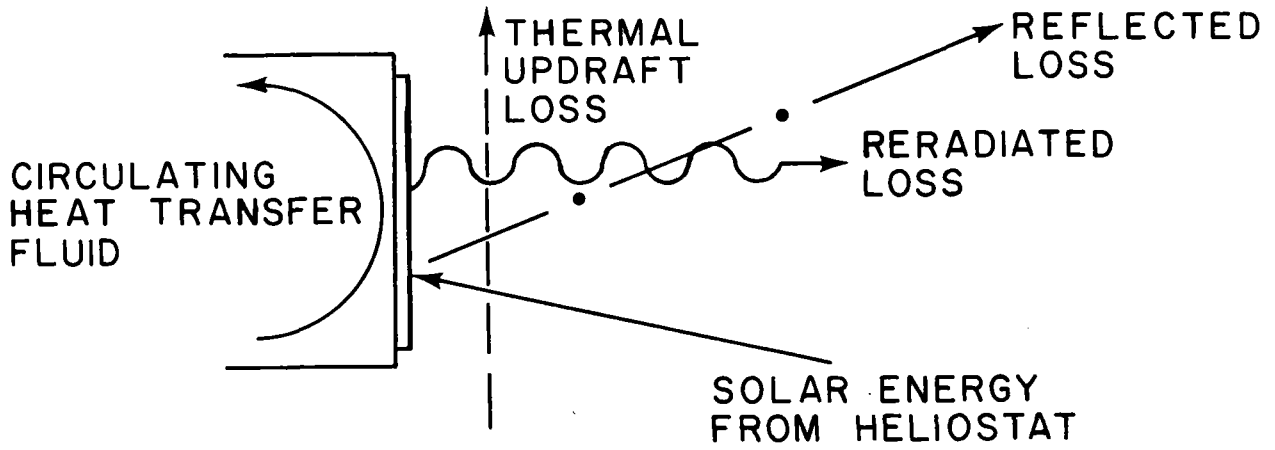
Assuming typical desert conditions and zero initial vertical velocity, an air parcel is expected to rise across the receiver face, driven only by the motive force arising from the ambient air/receiver thermal difference. It will traverse the face in the span of about 0.82 to 1.80 seconds, the former at 2760°C (5000°F) and the latter at 593°C (1100°F). At 2760°C (5000°F), the air parcel's average velocity is 35 m/s (80 mph), a common exit velocity for gases from a conventional combustion stack. Calculations leading to these results are detailed in Appendix 1.

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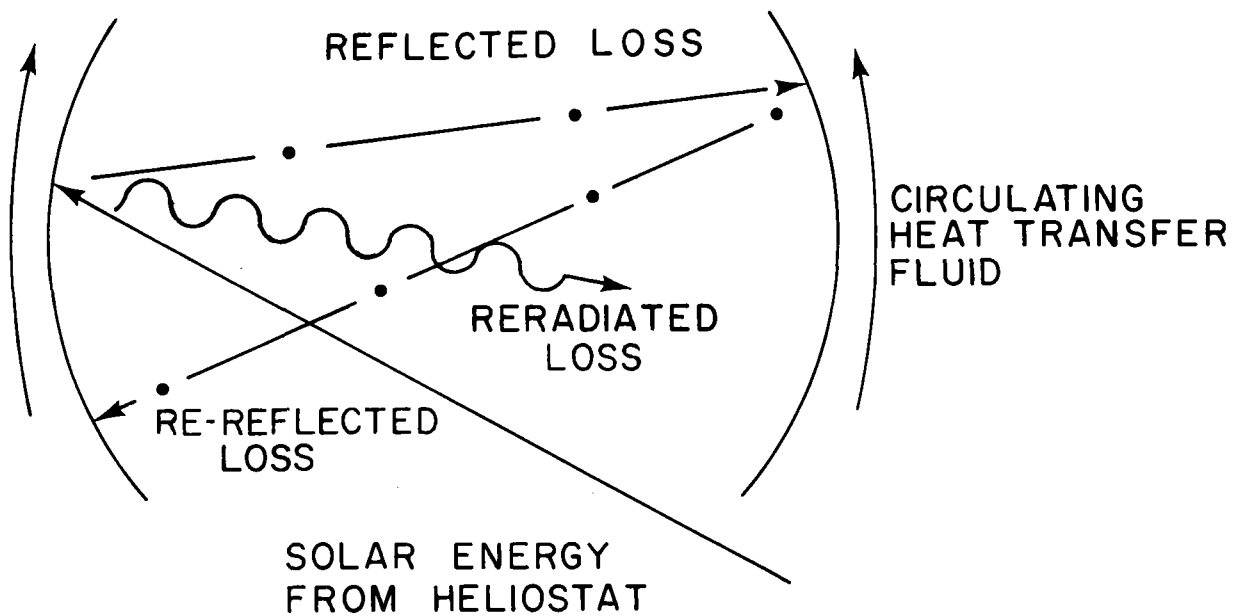


Figure 2-2

Comparison of Some Characteristics of Open and Cavity Receiver Designs

Reasonableness of results can be affirmed from several sources. First, as noted above, the computed average flow velocity is about that for typical power plant stacks. Second, for the model system (2) we would anticipate about a 197 MW total receiver heat loss. The heated plume we consider transports away 29 MW or 15 percent of this; a moderately large but not unreasonable share.

### 3.0 CHEMICAL CONVERSION PROCESSES

#### 3.1 Chemical Equilibria Resulting from Conversion Processes

As has been indicated in prior portions of this report, our intent is to focus on an expected few pollutants of possible concern in the operation of STPS devices. A most useful screen is chemical equilibrium. If at anticipated conditions all possible compounds of concern will not be present in quantities meriting that possible concern, we can rest assured that the solar design will be truly benign in operation.

From an initial screening of a large number of compounds (including free radicals and relatively unstable intermediates), we have focused on what appear to be the more important real concerns. Temperatures of 1100°F and 5000°F are assumed (together with intermediate values for some compounds), and equilibrium concentrations computed. For photolytic processes enhanced sunlight also is taken into account. (The data and calculations are presented in Appendix 2.)

Results are summarized in Table 3-1. It is clear that under the conditions encountered nitric oxide (NO), the traditional concern, is paramount. Nitrous and nitric acid data are included primarily because of concern for possible downwind acid rain consequences. It is clear, however, that it is the precursor nitric oxide which must be monitored (and perhaps managed) at the solar facility site. Ozone, at about 0.5 ppm at 5000°F and with intense sunlight, would represent a huge problem if this were an ambient level. However, the equilibrium values may never be achieved, and they also represent values which might be reached only in a thin annular sheath surrounding the very high temperature receiver face.

Table 3-1

Equilibrium Pollutant Concentration Estimates  
at Receiver Face\*

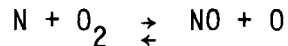
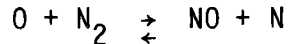
Temperature	Potential Concentration of Pollutant, ppm				
	NO	NO <sub>2</sub>	HNO <sub>2</sub>	HNO <sub>3</sub>	O <sub>3</sub>
1100°F	6.8	0.94	0.0012	3.3x10 <sup>-5</sup>	0.52
2000°F	650	5.2			
3000°F	6,500	12			
4000°F	27,000	18			
5000°F	47,000	22	0.17	1.8x10 <sup>-5</sup>	6.2x10 <sup>-4</sup>

\* Details presented in Appendix 2. Values represent only a very limited space adjacent to the solar receiver face.



### 3.2 Rates of Nitrogen Oxide Production

We have seen that nitric oxide (NO) is the potential pollutant of concern. It is most likely to be formed as a consequence of the cyclic chain process (Appendix 3):



Atmospheric oxygen atoms at equilibrium are sufficient to initiate the process. Formation of nitrogen dioxide (NO<sub>2</sub>), ozone (O<sub>3</sub>) and other possible compounds of ultimate concern seems quite likely to hinge on this first step. Thus we are led to address the rate at which this process will occur in our expected solar receiver environment.

The rate calculations can be quite complicated. However, very useful close approximations are available that adapt to present needs. We assume temperatures and residence times as developed earlier. The resulting data show a huge temperature dependence, indicating just how important actual receiver conditions rather than just those assumed by a simple model may prove to be. Results are summarized in Table 3-2 (all data and calculations are in Appendix 3).

Table 3-2

Production of Nitric Oxide  
at Receiver Face Conditions\*

<u>Temperature</u>	<u>[NO]/[NO]<sub>e</sub>, (fraction of equilibrium)</u>	<u>[NO], ppm</u>
1100°F	0.0	negligible
2000°F	0.0	negligible
3000°F	0.1	1,000
4000°F	1.0	30,000
5000°F	1.0	50,000

\* Results are exclusive of background. All values rounded, taking into account simplicity of flow model and approximation of actual conditions. Concentrations represent the inner core of the heated-air plume which will rise from the central receiver face.

### 3.2.1 Mass Emission Rates for Nitrogen Oxides

Combining the data for flow of solar receiver-heated air and the level of nitric oxide computed to be formed, we can generate figures for mass emission rates. It is clear that at the lower temperatures production will be negligible. AT 5000°F, however, we find a rate of 436 gm/sec (3460 lb/hr). This is nearly five times the quantity which would be permitted under California South Coast Air Quality Management District rules for a coal-fired electric power plant of equivalent size (see Appendix 3). At the much more moderate 3000°F temperature, though this might well be low for a high-technology, efficient design, expected emissions would approach about five percent of the District rule limitation. Even at this modest level, however, a regulatory accounting would appear essential in many air basins.

### 3.2.2 A Possible Hydrocarbon Source of Concern: TES Fluids

If a hybrid solar/fossil system is utilized, it is clear that some hydrocarbon sources may be involved. Plumes of nitrogen oxides and other effluents will interact, and the traditional problem will of necessity need to be addressed prior to final design and construction. We do not address that problem in the present report. (It has been treated in reference 5, however.)

At present we consider a small additional source of potential concern. Thermal energy storage fluids for many systems may be hydrocarbon-based. Example data for one such actual system (Appendix 4) suggest that modest but non-negligible concerns may derive from such usage.

Exposure of hydrocarbons to high temperatures leads to thermal degradation, creating low molecular weight hydrocarbons. These are normally combusted via incineration, providing a small on-site source of non-methane hydrocarbons; regulated compounds, of concern in the formation of photochemical smog.

For a 10 MWe system it is expected that about 44 gallons per day will be discarded and replaced by makeup fluid (Appendix 4). Analysis of the waste and specification of requirements for routine incineration projects a modest source: a 10MWe facility is the equivalent of operation of several hundred very "clean" automobiles; 0.87 gm/sec of non-methane hydrocarbons. Scaling up to our reference 430 MWe facility, we would project a 24-hour average emissions of 0.35 T/d. Such a source seems almost certain to be regulated. It suggests a need for early design consideration of on-site location to minimize NO<sub>x</sub> interaction and the potential to contribute to ozone production. It also suggests a need for consideration of the necessity for on-site incineration as contrasted with an alternative means for disposal.

### 3.3 Plume transport of Pollutants Released and Their Interaction

At this point it is clear that there are sources of pollutants of concern to be considered, even if they may represent modest inputs. Thus we proceed to compute the levels likely to be experienced downwind as a consequence, particularly at ground level. This very traditional task is addressed in Appendix 5.

Consistent with our initial worst case approach, parameters are selected

which tend to maximize near-ground levels. Thus meteorological assumptions include Turner "A" stability, a low wind speed of 0.9 m/sec, and effective reflection of all contaminants upward from the earth's surface. We also choose a quite low "effective" release point (294 m), and values which tend to minimize the rise of the heated plume.

### 3.3.1 Nitrogen Oxides

The resultant downwind values computed for NO<sub>x</sub> concentrations (as nitric oxide, NO) are presented in Table 3-3. As noted earlier, reactions in the atmosphere tend to convert NO to NO<sub>2</sub>. However, our simple approach does not permit addressing the very complex changing conditions for chemical equilibrium adjustment away from the somewhat constant temperature receiver face, and yet still well removed from ambient conditions. We know the strong equilibrium preference for nitric oxide at the receiver. As dilution and cooling take place, equilibrium shifts.

Table 3-3  
Estimated Downwind NO<sub>x</sub> Concentrations  
(Computed as NO)\*

Downwind Distance, m	At Ground Level		At Release Level	
	$\mu\text{g}/\text{m}^3$	ppm	$\mu\text{g}/\text{m}^3$	ppm
700	793	0.592	3560	2.660
1000	1090	0.813	1010	0.753
1200	718	0.537	634	0.474
1500	345	0.258	323	0.242
2000	124	0.093	121	0.091
3000	28	0.021	9	0.021

\* Worst case assumptions (Appendix 5)

The rate process at ambient conditions is quite slow, so that we expect only a gradual conversion of NO to NO<sub>2</sub> over substantial transport distances and so far removed from the solar facility site. At present the in between situation for conversion of NO to NO<sub>2</sub> is unclear. Thus in Table 3-3 we estimate data only as nitric oxide (NO), recognizing the nitrogen-atom equivalence for all species of NO<sub>x</sub> of interest.

In evaluating these data, it is particularly important to recognize that they are a consequence of sequential worst case assumptions. It is quite

likely that receiver face temperatures will not cause the surrounding annular air envelope to exceed 4000°F, even for advanced, high efficiency designs. This reduces both equilibrium and kinetic extremes. Further, heated air flow may well prove less. As a consequence, values more likely to be observed in the future might well be one-sixtieth those tabulated; still large enough to demand accountability, but of relatively minor concern.

It is also important to note that as materials released travel away from an STPS source, by the time they pass over the outer boundaries of the collector field they will most likely constitute a relatively thick vertical band of almost uniform concentration. Even with worst case emission levels as we compute them, at quite modest downwind distances augmented ambient levels would be difficult to distinguish from representative ambient levels for desert air (Appendix 7).

### 3.3.2 Hydrocarbons

Non-methane hydrocarbon concentrations have also been computed on the assumption that these can be treated as unreacting gases (Appendix 5). The levels are sufficiently low as to readily be lost in even low level background. However, if added to already contaminated air, even such small increments may assume some importance.

### 3.3.3 Ozone

Estimates for equilibrium ozone at worst case solar receiver face conditions are significant at 1100°F. However, this involves only concentrations within a limited space. Dilution and dispersion of this source, if computed as for nitric oxide, would quickly lead to values so low as to be of no importance at all. Atmospheric values of 0.04 ppm, for example, are commonplace in "clean" onshore breeze air polluted only by the Pacific Ocean.

## 3.4 Other Photolytic Reactions

Numerous chemical processes other than the few which have been noted above can take place, and a large number of these may be driven by energy from photons in sunlight. Some of the probably more important, considering pollutants which could be formed and which would be of ultimate concern, are addressed briefly in Appendix 6. Results can be summarized as indicating that while many reactions taking place in the unique environment adjacent to a receiver face may be of substantial theoretical interest, they appear very unlikely to pose any serious problem.

#### 4.0 "CREATIVE" CONVERSION OF TYPICAL DESERT AIR CONSTITUENTS

The preceding analyses of the potential air pollution consequences of the operation of STPS have been performed assuming the plant to be surrounded by an atmosphere of "clean" air. In this limited sense conclusions drawn can be said to represent "best-case" conditions. In actuality, background levels may add to on-site emissions sources (particularly  $\text{NO}_2$ ). Further, receiver conditions may stimulate enhanced conversion of constituents of polluted air, initially at tolerable levels, to create higher levels or new pollutants of concern.

The U.S. Department of Energy has compiled a list of possible solar repowering projects (6-19). Several sites and applications of central receivers are included. All the sites are in hot, well-insolated regions of the U.S.; the sites are generally in largely undeveloped areas, a fact of importance to land prices, pollutant concentrations, and degree of air quality monitoring. Climatology as well as general air quality background are important to the problems we address. Thus we have compiled wind data from monitoring stations as close as possible to the proposed solar facility sites (Appendix 7). The National Ambient Air Quality Standards (NAAQS) as of 1981 are also presented for reference in Appendix 7. Air quality data from monitoring observations for the regions are presented as fractions or multiples of the NAAQS. Finally, a chemical analysis of the Total Suspended Particulates (TSP) as observed from the Nevada region is presented (Appendix 7).

Since we are interested in establishing the worst-case scenario, we have taken the greatest concentration level for each pollutant from the various regions and combined the results to provide one hypothetical maximally polluted test-case site. Because the individual values represent past measurements they do not reflect what the pollutant concentrations could be with greater development and added (fossil) emission sources. But the test-case site does reflect the worst already-measured concentrations of pollutants in regions near the proposed solar central receiver facilities, hence representative of our worst-case technology. The hypothetical worst-case test site violates the NAAQS for all pollutants except  $\text{SO}_2$  (sulfur dioxide).

The literature abounds with listings and evaluative reviews of the chemical reactions involved in air pollution (4, 20-29). The worst case approach has led us to creative simplification for maximal effect. Many interactions are as yet unexplained. For example, the rate of disappearance of  $\text{SO}_2$  and the rate of aerosol formation increase when  $\text{SO}_2$  is photooxidized in the presence of  $\text{NO}_x$  and olefinic hydrocarbons, yet  $\text{SO}_2$  appears to slow down photochemical smog reactions. Humidity is an additional factor that can, especially at low levels, decrease aerosol formation with increasing levels of water vapor. In the lab, all of these processes require on the order of twenty-five minutes to begin showing measurable changes (reference 20, pg. 421).

Using our protocol of analyzing for the worst possible case, we have taken the chemical analysis of the Nevada TSP as if it were raw material available for creative conversion, and imagined it totally volatilized in the solar beam, thus contributing to measured pollutant loads. By this means we compute the absolute maximum additions to pollutants regulated under the NAAQS, acknowledging that overestimates of impacts will result.

As an example, we assume all non-methane hydrocarbons as equivalents to the olefin ethylene, and that this material is converted by partial oxidation in the receiver environment to carbon monoxide (CO). An extra 546  $\mu\text{g}/\text{m}^3$  is the most that can be contributed, even by this "creative" scheme, adding about five percent of the (1-hour) NAAQS permitted amount. Thus worst case levels would be raised from 0.9 to 0.95 times the standard (data for Albuquerque, New Mexico). The 8-hour average standard is already exceeded by a factor of 2.2, however. While an addition from any source to this level would appear unacceptable, the assumptions required to maintain unlikely processes over an extended period are too extreme to be considered credible.

In a somewhat similar fashion, sulfate ions from particulates could under reducing conditions be transformed into sulfur dioxide ( $\text{SO}_2$ ). The result would be at most two percent of the NAAQS (annual arithmetic mean) added to the current maximum of 0.88 (El Paso, Texas). Nitrate ions in particulates could be transformed under reducing conditions to nitrogen dioxide ( $\text{NO}_2$ ). The added pollutant load would represent about one percent of the NAAQS (annual arithmetic mean), raising exceedence from the historic worst-case 1.01 times the standard to 1.02 times this level (Clarence, Oklahoma); hardly of significance. Even more tenuously, it was noted that hydrocarbons and nitrogen sources just might convert ultimately to peroxyacylnitrates (PANs), which would worsen oxidant level from the 1.33 times the NAAQS level already observed (Barstow, California). However, the sequence of chemical changes required appear beyond any reasonable possibility.

Data and analysis for all of these "creative" possibilities are included in Appendices 7 and 8. An overall mitigating factor for any such processes is the limited residence time available for reaction. The imagined conditions require from several seconds to minutes or hours for any progress to be made. (Some are not likely to occur even with infinite time.) Thus under real conditions we find a basis to reject all the conjectures raised in this section.

## 5.0 EXTENDING THE RESIDENCE TIME

As shown in Chapter 2 and Appendix 1, we anticipate that the receiver face is effectively flushed by newly rising air parcels every 0.8 to 1.8 seconds. The significance of the possible production of pollutants at the receiver under some conditions is diminished by limited residence times in the reaction zone. Our worst-case protocol called for developing a possible mechanism by which the residence time could be increased.

### 5.1 The Model and Data Base

We first hypothesize a macroscale situation wherein the air surrounding the receiver face would initially rise, driven by the motive force arising from thermal, density, and buoyancy differences. It would then be cooled above the location of the solar beam, drifting slightly to one side, descending at a point outside the thermal updraft and being caught up again in the beam subsequently as "replacement air" bearing reactively-heightened pollutants. This situation is illustrated in the sketch of Figure 5-1.

The average wind speeds at the DOE project sites range from 10 - 18 km/hr (6.2 - 11.3 mph) (Appendix 7). Given the design and operating characteristics of the solar facility, if the wind were to blow at 14 km/hr (8.8 mph), the air from the receiver would travel beyond the heliostat field, a distance of 1983 m (6506 ft), in less than nine minutes. As noted in Chapter 2 of this report, the receiver-heated air (likely to be at 2000°C or 3632°F after leaving the receiver) is expected to rise between 500 and 1500 m (1640 to 4921 ft) above the receiver face height. Using the lower value of 500 m (1640 ft) above the receiver and a thermal acceleration of 61.8 m/s<sup>2</sup> for a 2000°C (3632°F) buoyant fluid, the air will reach its greatest altitude in about seventeen seconds; i.e., the heated air will rise to its maximum altitude of 830 m (500 m rise plus 330 m tower-receiver) a little over eight minutes before reaching the outer border of the heliostat field. The cooling air will then gain density and descend, traveling downwind and being further diluted all the while. Note that by comparison, the sketch of Figure 5-1 grossly underestimates the scale of the motions involved.

### 5.2 Macroscale Air Recycling

In order to increase the residence time and thereby augment the production of pollutants, the entrained pollutants, precursors, and intermediates would need to remain undiluted and would need to return to the reaction zone for another reaction period before losing their heightened reactivity, otherwise they would be like any virgin air parcel experiencing the beam for the first time. On a macroscale, the likelihood of an air parcel rising 500 m (1640 ft) while facing a constant horizontal wind of 14 km/hr (8.8 mph), not being diluted, and returning to the reaction zone prior to the entrained elements losing their heightened reactivities appears most unlikely. Thus at macroscale, increased residence time and solar-augmented pollution production via multiple passes through the reaction zone appears most unlikely. Unaugmented chemical reactions will occur in the moving, dispersing plume as is usual for all point-source emissions. If the air at the receiver is heated to either extreme of the design range, 593°C (1100°F) or 2760°C (5000°F), the counterbalancing effects of proportionately greater or lesser reaction rates and times, buoyancies and rates and distances of rise

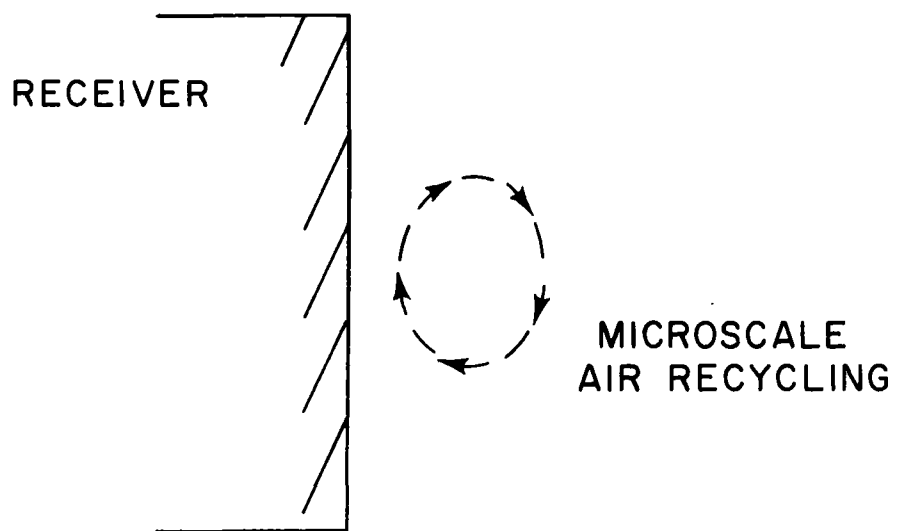
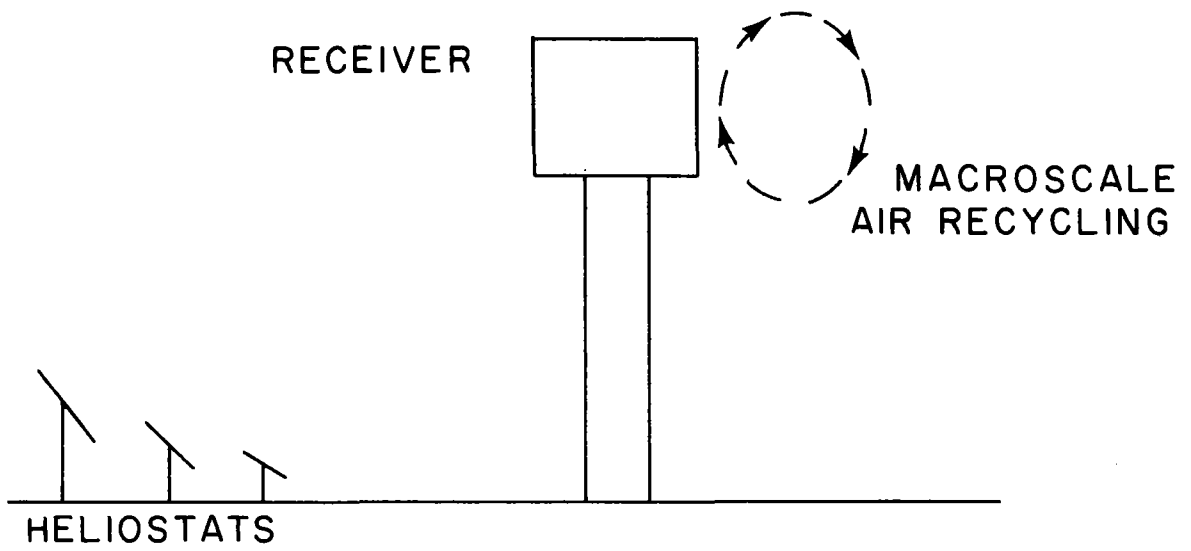


Figure 5-1  
Air Recycling Past Reaction Zone



act simultaneously allowing the same kind of analysis as just presented for the 2000°C (3632°F) condition and lead to much the same conclusion; that macroscale residence time extension is most unlikely.

There is additional information from research on rates of atmospheric reactions relevant to the processes under consideration, however (30). Extensive study indicates that under extreme photochemical conditions, even more extreme than experienced in the beam, nitrogen and sulfur oxides and hydrocarbons can react to form secondary particulate matter at a maximum rate of about ten-percent per hour. At such a maximum rate, only 1.5% conversion will have occurred as the air passes beyond the heliostat field in our example case. Thus macroscale extensions of reaction appear to be of very limited possible importance.

### 5.3 Microscale Air Recycling

On a microscale, a similar sort of mechanism can be imagined as a means for increasing the residence time. This situation is also illustrated in Figure 5-1. The heated air parcel with its load of pollutants, precursors, and intermediates would rise, drift away slightly due to turbulence or a puff of horizontal wind, cool and descend slightly, and be caught up again in the rising column of air, all with little or no dilution and rapidly enough to prevent loss of heightened reactivity. If feasible, this scenario could lead to multiple passes with an effectively increased residence time. However, it also might reduce peak temperatures that are experienced. Whether this happens or can happen in reality is an area worthy of further study.

### 5.4 Cavity Receivers

In Chapter 2 we stated our choice of the open face receiver as the more likely producer of greater quantities of air pollutants by comparison with the cavity design. Cavity designs may perhaps contribute a somewhat greater efficiency. The basic sources of efficiency, however, may work in the direction of reduced opportunity for an extension of residence times for heated parcels of air. On the macroscale, access of a "returning" parcel of air to the highest temperature, highest insolation cavity region would be made very much more difficult by the nature of cavity construction; access would tend to be shielded. On the microscale, small-scale, internal recirculation within the cavity region probably would be encouraged. This would mean that reactions, much like in a stirred-tank chemical reactor, could involve the same fluid parcel again and again. However, this increase in residence time is accomplished only at the expense of correspondingly large reductions in the exposure of masses of air to high temperature receiver surfaces. Because equilibrium provides a very real set of limits, this is likely to contribute an overall reduction in conversion to pollutant products below worst case results as computed earlier. Details of results could be highly dependent on design-specific factors. Thus what happens in reality in this instance is an area worthy of further study.

## 6.0 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

Data and analysis in this report have established that some air pollutants may be produced as a result of the operation of large scale STPS in quantities sufficient to be of regulatory concern. These will require steps toward management. Primary concern focuses on nitric oxide, (NO), and its downstream potential pollutant products. In all likelihood the quantities produced will be small, and fully merit for solar its general recognition as an environmentally benign energy technology. Furthermore, for many solar configurations and modes of operation even this limited concern may not apply. And, of course, use of solar may displace less clean fossil fuels. Worst case conditions, however, are capable of leading to quite large and thoroughly negative impacts from very large scale STPS facilities.

Additional results can be summarized as follows.

- 1) Of types of STPS, the technology providing greatest pollutant production opportunity is the solar central receiver.
- 2) Augmented production of pollutants is likely to be caused by thermal rather than primarily beam-photochemistry means.
- 3) Production of air pollutants is naturally limited as a consequence of brief residence times within regions of high temperature and insolation.
- 4) On-site incineration of waste, degraded hydrocarbon energy storage fluid is an example of a perturbing, pollutant-producing peripheral activity which could constitute a significant nuisance, and perhaps should be handled by other means.

Further study would be of value in the following areas.

- 1) A much better understanding is essential as to the flow, removal of heat, and mixing processes that occur in the annular sheath immediately surrounding the solar receiver surface (such research is underway); results will define the conditions for atmospheric reactions of concern.
- 2) Given a better information base, a more detailed look at the production of nitric oxide, (NO), and related chemical processes could prove worthwhile.
- 3) If results of efforts as suggested above show the production of air pollutants to be important for any likely STPS designs, steps can be devised to mitigate consequences.

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## APPENDIX 1. COMPUTATION OF RESIDENCE TIMES AND COMPUTATION OF FLOW OF HEATED AIR

The problem faced is to determine the residence time of an air parcel rising past a heated receiver face driven only by the buoyant force which results from the temperature difference between heated parcel air and ambient air, and to estimate the size of the resulting flow. Two receiver temperatures are selected to bound the values likely to be encountered in practice, while providing a picture of environmental worst case conditions. These are 1100 and 5000°F.

### A1.1 Facts, Assumptions

Receiver face 28.5 m (94 ft) high, 28.5 m diameter  
Ambient air temperature (T) 100°F (38°C, 311°K)  
Two instantaneously heated air parcel temperatures (T'); 1100°F (593°C, 866°K), and 5000°F (2760°C, 3033°K)  
Zero initial velocity ( $v_0$ ) 0 m/s  
Acceleration of gravity (g) 9.8 m/s<sup>2</sup>  
Distance travelled by an air parcel (d)  
Time in seconds (t)  
Velocity (v)  
Residence time ( $\tau$ )  
Ambient air density ( $\rho$ )  
Heated air parcel density ( $\rho'$ )  
Pressure (P)  
Gas constant (R)

### A1.2 Derivation

For a fluid element in static equilibrium:

$$dP = -\rho g dz$$

When heated, the parcel accelerates upward.

$$(dv/dt) = -g - (1/\rho') (dP/dz)$$

The pressure corresponds to the static equilibrium value for the parcel and ambient air. Substituting:

$$(dv/dt) = g(\rho - \rho')/\rho'$$

Using the ideal gas relationship:

$$P = \rho RT = \rho' RT'$$

Replacing  $\rho$  and  $\rho'$  with temperatures in the acceleration relationship:

$$(dv/dt) = g (T' - T)/T$$

### A1.3 Calculations

For the lower heated air parcel temperature (T = 1100°F):

$$(dv/dt) = 9.8(866 - 311)/311 = 17.5 \text{ m/s}^2$$

To rise across the face requires that a parcel move a distance  $d$  corresponding to the face height, starting from a height ( $d_0 = 0$ ), with an initial velocity ( $v_0 = 0$ ). Thus,

$$d = (dv/dt) t^2/2$$

$$28.5 = (17.5/2)t^2$$

Solving for  $t$ , which now represents the residence time for a fluid parcel traversing the entire heated face, bottom to top, we obtain for the residence time:

$$\tau_{1100}^{\circ\text{F}} = t = 1.8 \text{ seconds.}$$

For the higher heated air parcel temperature ( $T = 5000^{\circ\text{F}}$ ):

$$(dv/dt) = 9.8 (3033 - 311)/311 = 85.8 \text{ m/s}^2$$

And to rise across the entire heated face:

$$28.5 = (85.8/2) t^2$$

$$\tau_{5000}^{\circ\text{F}} = t = 0.82 \text{ seconds.}$$

#### A1.4 Flux of Heated Air

A terminal velocity is obtained by integrating the expression for  $dv/dt$ . Thus at the higher temperature ( $5000^{\circ\text{F}}$ ):

$$v_t = 9.8(3033 - 311) (0.82)/311 = 70 \text{ m/sec}$$

It is self-evident that as the heated plume rises and accelerates, a given air mass (or volume) can be accommodated within a continually diminishing horizontal cross-section serving to contain the flow. That is, a large bulk of slowly moving air must enter the space close to the hot receiver surface at its base in order to replace an equivalent quantity of rapidly rising air escaping at the top. One consequence is that portions of the actual air parcel leaving the solar receiver face may have experienced a somewhat shorter residence time than we have calculated.

A useful working result for the flow of heated air mass can be obtained by assuming some reasonable horizontal distance away from the face of the receiver up to which heating is effective. For the higher  $5000^{\circ\text{F}}$  example, we choose  $0.1 \text{ m}$ , measured after a vertical rise time of  $0.1 \text{ sec}$  and so  $0.43 \text{ m}$  (or about one foot) above the receiver base. Thus volume flow of heated air is estimated as the flux (at the higher  $5000^{\circ\text{F}}$  temperature) across a  $[(0.1 \text{ m}) (28.5 \text{ m}) (\pi)]$  cross section having a local vertical velocity of:

$$\begin{aligned} v &= [g(T' - T)/T]t \\ &= 9.8(3033 - 311) (0.1)/311 = 8.58 \text{ m/sec} \end{aligned}$$

The flow of heated air is thus estimated as  $77 \text{ m}^3/\text{sec}$  (at  $5000^{\circ\text{F}}$ , or

3033°K). It could theoretically be accommodated within a distance about 1.2 cm out from the face of the receiver after reaching terminal velocity. A corresponding flow estimate for the lower temperature (1100°F, 866°K) is 16 m<sup>3</sup>/sec.

#### A1.5 Commentary

The actual behavior of the heated boundary layer in open air adjacent to the very hot receiver face is extremely complex, not thoroughly understood, and hence the subject of active current research. In the absence of research results which would permit reasonably thorough analysis, the above very simple model has been developed and used to estimate worst case system behavior. Our goal includes estimating rates and equilibria for processes driven by conditions within this annular "reactor"; processes which by themselves are so complex as to necessitate simplification. Thus we are satisfied with a very simple heat transfer and flow model at this stage of understanding.

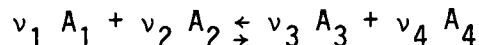
There are several points for comparison which permit a check on the reasonableness of the model for its intended purpose. First, the average velocity of the rising fluid parcel is expected on the basis of these computations to be about 35 m/s at the higher (5000°F) temperature. This is very close to the expected stack gas exit velocity for a hybrid fossil/solar facility (A 1). Second, the heat loss represented by the peak temperature portion of the escaping buoyant plume, as it is raised to the higher (5000°F) temperature, is about 29 MW by these computations. Thus it totals about 15% of the anticipated receiver heat loss (197 MW) for the reference 430 MWe hybrid system (A 1), and appears to be within reason.

If adjustments to these data are merited, it is likely that they will be in the directions of (a) lower peak temperatures realized, (b) correspondingly lower terminal velocity of the buoyant air plume, and (c) a smaller volumetric flow of air heated to the peak temperature. Larger quantities of air, on the other hand, may be heated but to substantially lower temperatures and so remain of lesser consequence. It appears highly unlikely that the effect of these estimates would be extreme by as much as a factor of ten.



APPENDIX 2. COMPUTATION OF CONCENTRATIONS OF POTENTIAL AIR POLLUTANTS  
AT THERMAL EQUILIBRIUM\*

If we are concerned with a reaction which may lead to the production of pollutants near the face of the receiver, the limiting possible result is to achieve chemical equilibrium. We consider an example reaction of the form:



where each  $A_i$  represents a reacting species and  $\nu_i$  is its stoichiometric coefficient within the reaction. At equilibrium we will find:

$$K = \left[ \frac{(y_3)^{\nu_3} (y_4)^{\nu_4}}{(y_1)^{\nu_1} (y_2)^{\nu_2}} \right] P^{(\nu_3 + \nu_4 - \nu_1 - \nu_2)}$$

In this relationship  $K$  is known as the equilibrium constant, the  $y$  values are mole fractions, and  $P$  is the pressure in atmospheres divided by one atmosphere. (Therefore both  $P$  and  $K$  are dimensionless).

The equilibrium constant  $K$  is readily obtained from the defined relationship:

$$\ln K = \frac{-\Delta G^0}{RT}$$

where  $R$  is the gas constant,  $T$  temperature, and  $\Delta G^0$  is known as the standard Gibbs-function (free energy) change of reaction, a function of temperature. This latter thermodynamic quantity is tabulated for common reactions in various handbooks. It also is given in terms of reactant and product thermodynamic parameters as:

$$\Delta G^0 = \nu_3 G^0_3 + \nu_4 G^0_4 - \nu_1 G^0_1 - \nu_2 G^0_2$$

Where direct sources of data are not available but data for related reactions may be, such relations permit construction of the needed standard Gibbs-function change by means of algebraic manipulation. Further, there is a useful relationship with the standard heat of reaction (enthalpy change). Thus:

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} = \frac{d}{dT} \left( \frac{-\Delta G^0}{RT} \right)$$

Heats of reaction, which also are temperature dependent, can be obtained by basic calorimetric observations such as the measurement of heat capacities. For conditions (such as high temperature) not readily achieved in the laboratory, needed data can also be calculated quite accurately from theory.

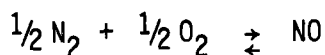
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\* The relationships found here are fully developed in most any thermodynamics text and also some air pollution literature. See, for example, references (A 2) to (A 5) at the end of these appendices.

As a result the kinds of data needed are tabulated in a number of sources, with one of the most useful the JANAF tables (reference A6).

Thus, making use of various sources of data and combining relations as needed through algebraic manipulation, the likely concentrations for chemical species of interest can be computed. The fact that all atmospheric pressures are unity assists in simplification. Mole fractions are conveniently equated to partial pressures in atmospheres, and results converted to other units as desired. Since in general our interests are satisfied with a close approximation to worst case results, many numerical values can be rounded and very small quantities neglected, greatly simplifying some algebra. Data for various reactions and product species are developed below.

### A2.1 Formation of Nitric Oxide



$$K_p = \frac{[NO]}{[N_2]^{1/2} [O_2]^{1/2}} = \frac{y}{(0.79 - y/2)^{1/2} (0.21 - y/2)^{1/2}}$$

where  $y$  is the partial pressure of NO in atmospheres. We first consider equilibrium at 1100°F (593°C, 866° R). Making use of the essentially linear relationship between  $(1/T)$  and  $\log K_p$ , we interpolate from the table below (data from reference A 6).

$T^\circ K$	$1/T$	$\log_{10} K_p$
800	0.00125	-5.243
900	0.00111	-4.587

For a temperature of 1100°F we obtain  $(1/T) = 0.00115$ , and interpolate for  $\log_{10} K_p$  to (-4.774), giving  $K_p = 1.68 \times 10^{-5}$ . Neglecting the terms in  $(y/2)$  to a first approximation:

$$y = (1.68 \times 10^{-5}) (0.79)^{1/2} (0.21)^{1/2} = 6.8 \times 10^{-6} \text{ atm.}$$

In a similar fashion, at 5000°F (2760°C, 3033°K, 5460°R), we can again interpolate from tabulated data (reference A 6).

$T^\circ K$	$1/T$	$\log_{10} K_p$
3000	0.000333	-0.913
3100	0.000323	-0.863

For a temperature of 5000°F we obtain  $(1/T) = 0.000330$ , and interpolate for  $\log_{10} K_p$  to (-0.898), giving  $K_p = 0.126$ . From this:

$$y = (0.126) (0.79 - y/2)^{1/2} (0.21 - y/2)^{1/2}$$

The equation is most conveniently solved starting with the assumption that  $y/2$  is small and to a first approximation can be neglected. This yields

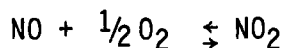
$y(1) = 0.051$ . Using  $y(1)$  to establish an estimate of  $y/2$  which is then included in the calculation, and so on, an iterative process leads to a final result:  $y = 0.047$  atm.

Thus, equilibrium amounts of nitric oxide at the two temperatures for which example calculations are shown, and also temperatures at 1000°F intervals between as a convenience, are given below.

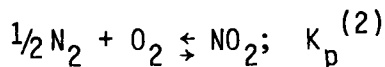
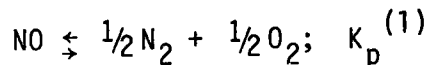
<u>T°F</u>	<u>[NO], ppm</u>	<u>T°F</u>	<u>[NO], ppm</u>
1100	6.8	4000	27,000
2000	650	5000	47,000
3000	6,500		

### A.2.2 Formation of Nitrogen Dioxide

We assume that the formation of nitrogen dioxide takes place following (and in equilibrium with) formation of nitric oxide.



Combining formation relations for the two nitrogen oxides involved:



The equilibrium constant  $K_p$  which is needed is obtained as:

$$K_p = \frac{K_p^{(2)}}{K_p^{(1)}} = \frac{[\text{NO}_2]}{[\text{NO}] [\text{O}_2]^{1/2}}$$

or alternatively:

$$\log K_p = \log K_p^{(2)} - \log K_p^{(1)}$$

Thus we can combine tabulated data (reference A 6) and interpolate to obtain the essential information.

<u>T°K</u>	<u>1/T</u>	<u>log<sub>10</sub> K<sub>p</sub><sup>(2)</sup></u>	<u>log<sub>10</sub> K<sub>p</sub><sup>(1)</sup></u>	<u>log<sub>10</sub> K<sub>p</sub></u>
800	0.00125	-5.417	-5.243	-0.174
900	0.00111	-5.185	-4.587	-0.598

Thus at a temperature of 1100°F (866°K),  $\log_{10} K_p = -0.457$ ,  $K_p = 0.349$ , and:

$$K_p = 0.349 = \frac{y}{([\text{NO}] - y) [\text{O}_2]^{1/2}}$$

where  $y$  represent partial pressure of  $\text{NO}_2$  in atmospheres. Substituting:

$$y = (0.349) (6.8 \times 10^{-6} - y) (0.21)^{1/2}$$

To compute a first approximation for  $y$ , we neglect  $y$  on the right hand side and obtain:  $y(1) = 1.09 \times 10^{-6}$ . Inserting this value on the right hand side and iterating, a final value reached is:  $y = 9.4 \times 10^{-7}$  atm.

In a similar fashion, at 5000°F, tabulated data are as follows.

$T^\circ\text{K}$	$1/T$	$\log_{10} K_p^{(2)}$	$\log_{10} K_p^{(1)}$	$\log_{10} K_p$
3000	0.000333	-3.864	-0.913	-2.951
3100	0.000323	-3.846	-0.863	-2.983

At a temperature of 5000°F (3033°K) we obtain  $(1/T) = 0.000330$ , interpolate for  $\log_{10} K_p$  to (-2.961), giving  $K_p = 1.09 \times 10^{-3}$ . From this:

$$y = (1.09 \times 10^{-3}) (0.047 - y) (0.186)^{1/2}$$

We note that in this instance the value of  $[\text{O}_2]$  is influenced by the significant prior conversion of  $\text{N}_2$  and  $\text{O}_2$  to  $\text{NO}$ . The result is:

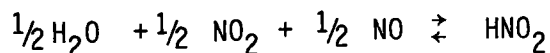
$$y = 2.21 \times 10^{-5} \text{ atm.}$$

Thus equilibrium amounts of nitrogen dioxide at the two temperatures for which example calculations are shown are given below, together with additional results at 1000°F intervals between. Equilibrium with nitric oxide as well as  $\text{N}_2$  and  $\text{O}_2$  is assumed.

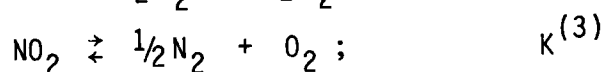
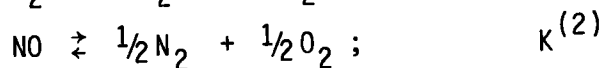
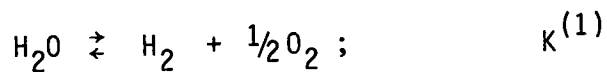
$T^\circ\text{F}$	$[\text{NO}_2]$ , ppm	$T^\circ\text{F}$	$[\text{NO}_2]$ , ppm
1100	0.94	4000	18
2000	5.2	5000	22
3000	12		

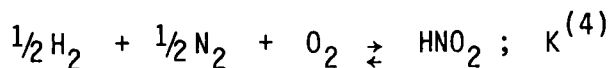
### A2.3 Formation of Nitrous Acid

Acid rain has been of growing concern, and in western regions this concern has encompassed the potential for formation of the several nitrogen oxide based acidic compounds. We assume that formation of nitrous acid may take place following (and in equilibrium with) formation of nitric oxide and nitrogen dioxide. Thus:



Combining formation relations for the molecules involved:





We can interpolate from the tabulated data (reference A 6).

$T^\circ\text{K}$	$1/T$	$-\frac{1}{2} \log_{10} K^{(1)}$	$-\frac{1}{2} \log_{10} K^{(2)}$
800	0.00125	-6.645	2.622
900	0.00111	-5.749	2.294

$T^\circ\text{K}$	$-\frac{1}{2} \log_{10} K^{(3)}$	$\log_{10} K^{(4)}$	$\log_{10} K_p$
800	2.709	-1.085	-2.399
900	2.593	-1.669	-2.531

For a temperature of 1100°F we obtain  $(1/T) = 0.00115$ , and interpolate for  $\log_{10} K_p$  to (-2.493), giving  $K_p = 3.21 \times 10^{-3}$ . Thus for  $y$  the partial pressure of nitrous acid in atmospheres:

$$K_p = 3.21 \times 10^{-3} = \frac{y}{[\text{H}_2\text{O}]^{1/2} [\text{NO}]^{1/2} [\text{NO}_2]^{1/2}}$$

To solve this equation we must specify the amount of moisture in the air. A reasonable upper limit value, likely to lead to an upper limit computed value for nitrous acid, is obtained by assuming air initially saturated from a source at 68°F (20°C). For this the partial pressure (vapor pressure) is 0.0231 atm. Substituting:

$$\begin{aligned} y &= (3.21 \times 10^{-3}) (0.0231)^{1/2} (6.8 \times 10^{-6})^{1/2} (9.4 \times 10^{-7})^{1/2} \\ &= 1.2 \times 10^{-9} \text{ atm.} \end{aligned}$$

In a similar fashion, at 5000°F, the tabulated data are as follows:

$T^\circ\text{K}$	$(1/T)$	$-\frac{1}{2} \log_{10} K^{(1)}$	$-\frac{1}{2} \log_{10} K^{(2)}$
3000	0.000333	-0.672	0.457
3100	0.000323	-0.601	0.432

$T^\circ\text{K}$	$-\frac{1}{2} \log_{10} K^{(3)}$	$\log_{10} K^{(4)}$	$\log_{10} K_p$
3000	1.932	-4.831	-2.899
3100	1.923	-4.871	-3.117

For a temperature of 5000°F we obtain  $(1/T) = 0.000330$ , and interpolate  $\log_{10} K_p$  to (-2.964), giving  $K_p = 1.09 \times 10^{-3}$ . From this:

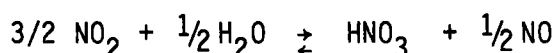
$$\begin{aligned} y &= (1.09 \times 10^{-3}) (0.0231)^{1/2} (0.047)^{1/2} (2.21 \times 10^{-5})^{1/2} \\ &= 1.69 \times 10^{-7} \text{ atm.} \end{aligned}$$

Thus, equilibrium amounts of nitrous acid at the two temperatures are:

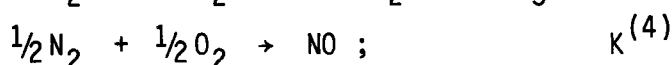
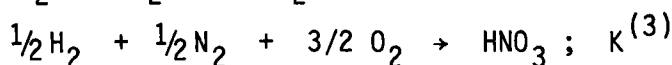
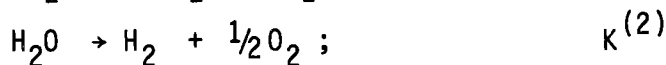
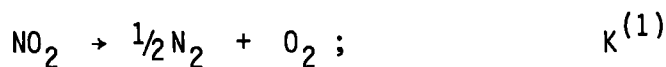
<u>T°F</u>	<u>[HNO<sub>2</sub>], ppm</u>
1100	0.0012
5000	0.17

#### A2.4 Formation of Nitric Acid

A reaction occurring within a homogeneous gas phase and leading to production of nitric acid is as follows.



Combining formation relations for the molecules involved:



We can interpolate from the tabulated data (reference A 6).

<u>T°K</u>	<u>1/T</u>	<u>-3/2 log<sub>10</sub>K<sup>(1)</sup></u>	<u>-1/2 log<sub>10</sub>K<sup>(2)</sup></u>
800	0.00125	8.126	-6.645
900	0.00111	7.778	-5.749

<u>T°K</u>	<u>log<sub>10</sub>K<sup>(3)</sup></u>	<u>1/2 log<sub>10</sub>K<sup>(4)</sup></u>	<u>log<sub>10</sub>K<sub>p</sub></u>
800	-1.980	-2.622	-3.121
900	-2.970	-2.294	-3.235

For a temperature of 1100 °F we obtain  $(1/T) = 0.00115$ , and interpolate for  $\log_{10}K_p$  to  $(-3.202)$ , giving  $K_p = 6.28 \times 10^{-4}$ . Thus for  $y$  the partial pressure of nitric acid in atmospheres:

$$K_p = 6.28 \times 10^{-4} = \frac{y[\text{NO}]^{1/2}}{[\text{NO}_2]^{3/2} [\text{H}_2\text{O}]^{1/2}}$$

Substituting:

$$\begin{aligned} y &= (6.28 \times 10^{-4}) (9.4 \times 10^{-7})^{3/2} (0.0231)^{1/2} (6.8 \times 10^{-6})^{-1/2} \\ &= 3.33 \times 10^{-11} \text{ atm.} \end{aligned}$$

In a similar fashion, at 5000°F, tabulated data are as follows:

<u>T°K</u>	<u>1/T</u>	<u>-3/2 log<sub>10</sub>K<sup>(1)</sup></u>	<u>-1/2 log<sub>10</sub>K<sup>(2)</sup></u>
3000	0.000333	5.796	-0.672
3100	0.000323	5.769	-0.601
<u>T°K</u>	<u>log<sub>10</sub>K<sup>(3)</sup></u>	<u>1/2 log<sub>10</sub>K<sup>(4)</sup></u>	<u>log<sub>10</sub>K<sub>p</sub></u>
3000	-8.277	-0.457	-3.610
3100	-8.343	-0.432	-3.607

For a temperature of 5000°F we obtain  $(1/T) = 0.000330$ , and interpolate for  $\log_{10}K_p$  to  $(-3.609)$ , giving  $K_p = 2.46 \times 10^{-4}$ . Thus for  $y$  the partial pressure of nitric acid in atmospheres:

$$y = (2.46 \times 10^{-4}) (2.2 \times 10^{-5})^{3/2} (0.0231)^{1/2} (0.047)^{-1/2}$$

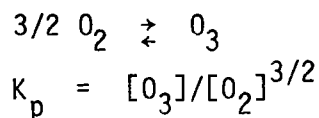
$$= 1.77 \times 10^{-11} \text{ atm.}$$

Thus, equilibrium amounts of nitric acid at the two temperatures are:

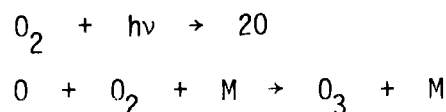
<u>T°F</u>	<u>[HNO<sub>3</sub>], ppm</u>
1100	$3.3 \times 10^{-5}$
5000	$1.8 \times 10^{-5}$

## A2.5 Formation of Ozone

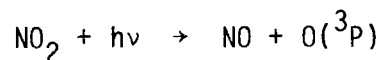
In "pure" air, without consideration of extraneous reactions or other interference, an equilibrium value of ozone content of the atmosphere can be computed.



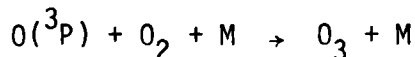
However, actual production of ozone is not this direct or simple. At high altitudes where energetic photons have not yet all been absorbed:



where M represents any third body able to remove excess energy from reaction products. At lower altitudes, however, the absence of photons with sufficient energy means that other processes must be responsible for the ozone found to be present. Formation usually is attributed to the photolytic cycle operating with less energetic (longer wavelength) photons and involving nitrogen dioxide (A 7). With radiation below 430 nm:



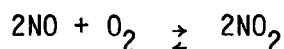
which, since the triplet-P oxygen atom is highly reactive, is quite naturally followed by:



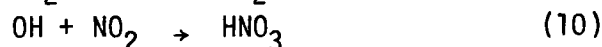
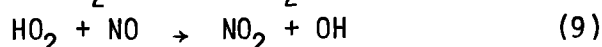
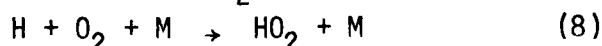
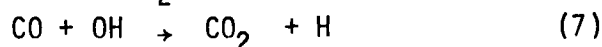
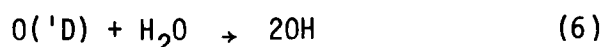
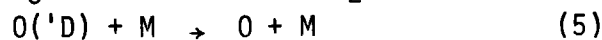
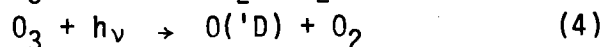
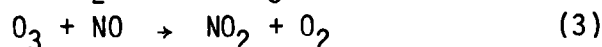
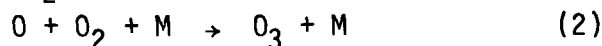
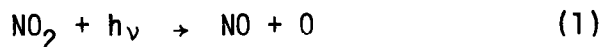
At conditions typical of a somewhat polluted atmosphere:



An initial source of nitrogen dioxide can be provided by the very much slower thermally driven process, perhaps from a remote source:



If we consider an atmosphere remote from urban sources of hydrocarbons, but perhaps influenced by not too distant sources of the combustion-derived pollutants CO and NO<sub>x</sub>, the following reactions encompass the most likely processes (A 7).



Assuming that concentrations of O<sub>2</sub>, CO and H<sub>2</sub>O are constant, and that the pseudo-steady state approximation commonly used within chemical kinetics may be applied for active centers such as O, O(^1D), H, OH, HO<sub>2</sub>, and O<sub>3</sub>, we can write the following algebraic relations between rates (R<sub>n</sub>) for the numbered (n) elementary reaction steps given above.

$$R_2 - R_3 - R_4 = 0$$

$$R_1 - R_2 + R_5 = 0$$

$$R_4 - R_5 - R_6 = 0$$

$$2R_6 - R_7 + R_9 - R_{10} = 0$$

$$R_8 - R_9 = 0$$

$$R_7 - R_8 = 0$$

Solving these equations simultaneously for the concentrations of steady state species, we find:



$$[O_3] = k_1 [NO_2] / (k_3 [NO] + C)$$

$$\text{where: } C = k_4 k_6 [H_2O] / (k_5 [M] + k_6 [H_2O]).$$

Generally the magnitude of the function C is relatively small, and for practical purposes (or as a "worst case"), it can be neglected. The rate constant  $k_1$  incorporates a measure of the incident solar intensity.

Observations indicate that the actual value of the effective ( $k_1/k_3$ ) ratio for normal intensities and other conditions is less than  $25 \mu\text{g}/\text{m}^3$  (or 0.015 ppm) (reference A 5, pg. 410). In the present case we are concerned with much-enhanced solar intensities: very likely 2000 times a "normal" sun, and perhaps more for advanced systems. This will enlarge  $k_1$ , and to incorporate this fact we need to multiply ( $k_1/k_3$ ) by an appropriate factor. On the other hand, temperatures are high, speeding the reverse process (enlarging  $k_3$ ). We can take these facts into consideration as follows.

At  $1100^\circ\text{F}$  we use an assumed 4000-times solar enhancement, and the approximately 2.5 Kcal/mole energy of activation for reaction step 3 (A 8). Designating ( $k_1/k_3$ ) as the value for  $1100^\circ\text{F}$  at the solar receiver and ( $k_1^0/k_3^0$ ) as that for typical ambient conditions:

$$\begin{aligned} (k_1/k_3)_{1100^\circ\text{F}} &= (0.015 \text{ ppm}) \left( \frac{k_1 / k_3}{k_1^0 / k_3^0} \right) \\ &= (0.015)(4000) \exp \{ (2500/1.987) [(1/866) - (1/298)] \} \\ &= 3.76 \text{ ppm} \end{aligned}$$

Incorporating this value in the approximate equilibrium expression:

$$[O_3]_{1100^\circ\text{F}} = (3.76)[0.94]/[6.8] = 0.52 \text{ ppm.}$$

In a similar fashion, at  $5000^\circ\text{F}$ :

$$\begin{aligned} (k_1/k_3)_{5000^\circ\text{F}} &= (0.015)(4000) \exp \{ (2500/1.987) [(1/3033) - (1/298)] \} \\ &= 1.33 \text{ ppm.} \end{aligned}$$

And for ozone equilibrium:

$$[O_3]_{5000^\circ\text{F}} = (1.33)[22]/[47000] = 6.2 \times 10^{-4} \text{ ppm.}$$

It should be noted that incorporation of appropriate values for the function C as in the initial expression would reduce both estimates of equilibrium ozone.

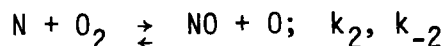
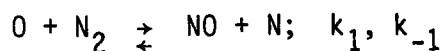
The general picture presented by these results, though much simplified, probably is realistic as a worst case example. Comparison of computed results with urban smog and laboratory smog chamber experience, however, shows that ambient concentrations of CO are not sufficient to account for observed ozone production rates (A 7). Addition of atmospheric hydrocarbons as actually may occur permits a parallel peroxy-oxyl cyclic series to operate, utilizing a pool of chemical species with unpaired electrons (free radicals). The end result is more rapid conversion of NO to  $NO_2$ , and hence more rapid production of ozone. A possible source of the free radicals essential to initiation of

the process is nitrous acid. Rate processes and the likelihood of achieving equilibrium will be addressed in subsequent appendices.

### APPENDIX 3. RATES OF PRODUCTION OF NITROGEN OXIDES

There are many potential air pollutants which one might speculate could be produced in enhanced quantities within the high temperature space adjacent to the face of a solar receiver. Equilibrium data such as those presented in Appendix 2 of this report provide a useful screen, eliminating possibilities which are unimportant. However, for those species which may be potentially important, equilibrium is only approached asymptotically after long times. Potential pollutants may not be produced simply because the rate of production is too low, even with favorable equilibrium.

Equilibrium calculations suggest that nitric oxide is the one species of real importance most likely to be generated in significantly enhanced quantities as a result of solar thermal operation. The kinetics are generally believed to depend primarily on the cyclic chain (reference A 5):



in which  $k_1, k_2$  represent the forward and  $k_{-1}, k_{-2}$ , the reverse rate constants.

When the usual rate expression is derived for these reaction steps, the nitrogen atom concentration  $[N]$  is assumed to remain at a quasi-steady state, and also the equilibrium constant for the overall reaction is given as  $K_{pNO}$ :

$$K_{pNO} = [NO]/[N_2]^{1/2} [O_2]^{1/2}$$

we obtain the expression below for the rate of the chemical process.

$$\frac{d[NO]}{dt} = \frac{2k_1[O][N_2] \{1 - ([NO]^2/K_{pNO}^2 [N_2][O_2])\}}{1 + (k_{-1}[NO]/k_2[O_2])}$$

A generally useful assumption is that oxygen atom concentration  $[O]$  may be obtained from its equilibrium value; readily calculated (data from reference A 6). The rate equation can be written in the form (reference A 5, pg 384):

$$\frac{dY}{dt} = \frac{M(1 - Y^2)}{Z(1 + CY)}$$

where:  $Y = [NO]/[NO]_e$ , thus defining  $[NO]$  as a fraction of the equilibrium value  $[NO]_e$ . Of the other parameters,  $C$  and  $M$ ,  $C$  can be shown to have little influence on computed results; values between 0 and 1 appear appropriate. Values for  $M$  can be obtained from experimental and calculated data. An expression defining  $M$  is:

$$M = 5.7 \times 10^{15} T^{-1} P^{1/2} \exp(-58,400/T)$$

with  $M$  in  $\text{sec}^{-1}$ ,  $P$  in atm, and  $T$  in  $^\circ\text{K}$ .

Treating the solar heated annular space within which the reactions take place as a constant-temperature region, the solution to the rate equation then

becomes:

$$(1 - Y)^{C+1} (1 + Y)^{C-1} = \exp(-Mt)$$

Substituting values of interest to the present application, the parameter M is given at the two temperatures by the values below.

$$T = 1100^{\circ}\text{F} : \\ M = (5.7 \times 10^{15}) (866)^{-1} (1)^{1/2} \exp(-58,400/866) = 3.4 \times 10^{-17}$$

$$T = 5000^{\circ}\text{F} : \\ M = (5.7 \times 10^{15}) (3033)^{-1} (1)^{1/2} \exp(-58,400/3033) = 8.1 \times 10^3$$

It is obvious that at 1100°F the value of M is essentially zero, and the only feasible solution for Y at any reasonable residence time t is vanishingly small. Thus at 1100°F we would anticipate no observable conversion of atmospheric N<sub>2</sub> and O<sub>2</sub> to NO within the solar heated space adjacent to a solar receiver in the time available.

At 5000°F the value of M is substantial. If we choose to approximate C as C = 0, on substituting:

$$(1 - Y)/(1 + Y) = \exp [(-8.1 \times 10^3) (1.8)] \approx 0$$

where 1.8 seconds represents the residence time computed for heated, buoyant reactants. The solution for Y is a value approaching one, and so representing conversion approaching equilibrium. If a value for C is chosen as C = 1:

$$(1 - Y)^2 = \exp [(-8.1 \times 10^3) (1.8)] \approx 0$$

Again conversion approaching equilibrium is projected. In fact, the cyclic chain process is so fast at 5000°F that even for a 0.001 second residence time, conversion to reach about 0.999 of the equilibrium product is predicted.

In between temperature values demonstrate kinetics lying between these extremes. With temperatures reduced from the peak 5000 to 4000°F, for example, equilibrium is still almost completely achieved. At 3000°F we anticipate reaction to about ten percent of the equilibrium value in the residence time available. At 2000°F, on the other hand, reaction would be negligible.

### A3.1 Calculation of Mass Emission Rates for Nitrogen Oxides

It is apparent from the kinetic data that at the lower (1100°F) temperature formation of nitrogen oxide air pollutants by conventional processes is unlikely to occur as a result of operation of the solar system. At 5000°F, lasting as long as a millisecond, on the other hand, we anticipate near equilibrium conversion to form nitric oxide (NO); a partial pressure of about 0.047 atm. This occurs within an annular slab of space adjacent to the solar receiver through which heated air is drawn; a flow estimated as perhaps 77 m<sup>3</sup>/sec. A mass emission rate (Q) is computed as follows for this situation.

$$Q = \frac{(77 \text{ m}^3/\text{sec})(10^3 \text{ 1/m}^3)(30 \text{ gm/mol})(0.047 \text{ fraction})(273^{\circ}\text{K})}{(22.4 \text{ 1/mol})(3033^{\circ}\text{K})}$$

= 436 gm/sec (3460 lb/hr)

We note that this is nearly five times the 0.092 Kg/sec (730 lb/hr) which would be permitted under California South Coast Air Quality Management District Rule 475/1135.1 for a 430 MWe coal-fired power plant (A 9).

These results indicate that production of the potential conventional pollutant likely to be of greatest concern, nitric oxide (NO), is very strongly temperature dependent. Exposed to the face of a central receiver and heated sufficiently, air will be converted in substantial quantities to NO; enough to be of concern. Products will drift from the solar receiver face as a buoyant plume. These may subsequently enter into other reactions, causing further impacts downwind of the solar facility.

## APPENDIX 4. DISCHARGES OF HYDROCARBON-CONTAINING THERMAL ENERGY STORAGE FLUIDS

It is anticipated that hydrocarbon-based fluids will be used for thermal energy storage (TES) within many solar thermal energy systems. Exposure of hydrocarbons to high temperature leads to thermal degradation, with the decomposition products of concern low molecular weight hydrocarbons (A 10). Data based on 600 hours of testing provide an analysis of the hydrocarbon-containing waste mixture which it is intended would be burned off at the site. These data are listed in the following Table A4-1.

It was determined that the TES fluid partially decomposes under the stresses of thermal cycling. The lighter molecular weight degradation products impair the efficiency of the TES fluid and increase its flammability and explosive potential. Because the degradation products are of low molecular weights, and because they comprise only a fraction of the total TES fluid weight, loss of the degradation products does not significantly affect the viscosity and usefulness of the remaining TES fluid.

It is anticipated that about 44 gallons/day of make-up TES fluid will be added, and thus a corresponding amount of material needs to be discharged. The waste analysis data indicate an average molecular weight of 28.9 gm/mole. Scenarios for discharge from the 10 MWe facility are tabulated below (Table A4-2). It is anticipated that a propane-fueled pilot would burn continuously to remove  $H_2$ , avoiding hazard, and that "full" combustion of the discharge gases to  $CO_2$  and  $H_2O$  would be implemented (A 10). The worst case discharge rate is 109 lb/hr, or, taking into account the chemical composition of wastes, 1710 gm-moles/hr for a 10 MWe small field-scale system. The "worst case" discharge represents about 4 times the peak typical daily rate, and 8 times the 24-hour average discharge rate.

### A4.1 Thermal Incineration Design

Thermal incineration of a mixture such as this waste can be an effective means of disposal. However, a high temperature such as 1450°F is required over a residence time such as 0.5 second, with an excess of oxygen and with turbulence (mechanical mixing) to assure complete contact of oxygen with fuel. With basically sound design and operation, about 95% efficiency of removal can be assured. (A 5).

Thus the worst case discharge scenario we assume starts with the peak discharge rate of 109 lb/hr of the mixture as analyzed, and assumes incineration with propane as a fuel added in sufficient quantity to achieve the desired flame temperature. We also assume a ten percent excess of oxygen over stoichiometric (at 100 percent conversion), and 95 percent waste/fuel conversion to  $CO_2$  and  $H_2O$  products. Heat loss from the device accounts for a further assumed ten percent of the heat derived from combustion.

The first step in the required calculations is to establish the effluent composition after incineration, aside from added propane fuel and its products. The next step then is to establish what share of the needed heat can be provided by combustion of the waste itself. These data are provided in Table A4-3. Heat capacity data are obtained from standard thermochemical data

Table A4-1  
Analysis of Gas to be Burned Off\*

<u>Component</u>	<u>Molecular Weight (gm/mol)</u>	<u>Mole Fraction x 100 (Volume %)</u>
N <sub>2</sub>	28	2.0
CO	28	2.4
CO <sub>2</sub>	44	2.0
H <sub>2</sub>	2	20.8
O <sub>2</sub>	32	0.2
CH <sub>4</sub>	16	20.5
C <sub>2</sub> H <sub>6</sub>	30	19.3
C <sub>2</sub> H <sub>4</sub>	28	0.5
C <sub>3</sub> H <sub>8</sub>	44	12.3
C <sub>3</sub> H <sub>6</sub>	42	2.0
n-C <sub>4</sub> H <sub>10</sub>	58	8.1
i-C <sub>4</sub> H <sub>10</sub>	58	2.4
n-C <sub>5</sub> H <sub>12</sub>	72	6.0
i-C <sub>5</sub> H <sub>12</sub>	72	0.4
H <sub>2</sub> O	18	1.0
<hr/>		
Average Molecular Weight	28.9	

\* Reference A 10. 10MWe facility

Table A4-2

Scenarios for Discharge of Hydrocarbon-Containing Fluids\*

Typical discharge Rate

<u>Time Period</u>	<u>Discharge (lb)</u>	<u>Discharge Rate (lb/hr)</u>
6 PM - 6 AM	131.0	10.9
6 AM - 7 AM	6.6	6.6
7 AM - 8 AM	2.2	2.2
8 AM - 1 PM	62.8	12.6
1 PM - 4 PM	81.9	27.3
4 PM - 6 PM	38.2	19.1
	Total: 322.7 lb	Average: 13.4 lb/hr

Worst-Case discharge Rate\*\*

<u>Time Period</u>	<u>Discharge (lb)</u>	<u>Discharge Rate (lb/hr)</u>
6 PM - 6 AM	655.5	54.6
6 AM - 8 AM	163.9	82.0
8 AM - 6 PM	1092.5	109.3
	Total: 1911.9 lbs	

\* Reference A 10. 10 MWe facility.

\*\* Assumes the tank (1000 gal) thermally charged (580°F) and held overnight.



Table A4-3

## Discharge Parameters after 95% Incineration\*

<u>Component</u>	<u>Moles Component per Mole Total Waste</u>	<u>"Worst Case" Emission Factors, gm-moles/hr</u>	<u><math>\Delta h</math>, Kcal/hr, to reach 1450° (<math>\Delta T = 750^{\circ}\text{C}</math>)</u>
N <sub>2</sub>	12.916	22,086	124,600
CO	0.0012	2.1	12
CO <sub>2</sub>	1.726	2,952	27,140
H <sub>2</sub>	0.0104	17.8	95
O <sub>2</sub>	0.470	804	4,846
CH <sub>4</sub>	0.0102	17.4	197
C <sub>2</sub> H <sub>6</sub>	0.0097	16.6	322
C <sub>2</sub> H <sub>4</sub>	0.0003	0.5	8
C <sub>3</sub> H <sub>8</sub>	0.0062	10.6	295
C <sub>3</sub> H <sub>6</sub>	0.0010	1.7	39
n-C <sub>4</sub> H <sub>10</sub>	0.0041	7.0	253
i-C <sub>4</sub> H <sub>10</sub>	0.0012	2.1	76
n-C <sub>5</sub> H <sub>12</sub>	0.0030	5.1	226
i-C <sub>5</sub> H <sub>12</sub>	0.0002	0.3	13
H <sub>2</sub> O	2.546	4354	30,300

---

Total: 188,400 Kcal/hr

\* This table considers wastes discharged plus 110% stoichiometric air, but not added propane fuel. Discharge rate: 1710 moles/hr waste (10 MWe facility).

sources, for the specific components of interest and at appropriate elevated temperatures (A 11, pg D-132; A 12). The quantity assumed discharged is 1710 gm-moles/hour (109 lb/hr).

We anticipate that the heat needed cannot be provided by unaided combustion of waste. Data establishing this firmly are given in Table A4-4. The heats of combustion for each component can be obtained from standard reference sources (A 11, pg D-230).

With these data we can compute the quantity of propane needed to fuel incineration and maintain a temperature of 1450°F so that the process approaches completion. The assumptions made include that there is a ten percent heat loss which must be allowed for, and that added propane also must be accompanied by 110 percent stoichiometric air (at 100 percent conversion). If we let  $x$  = gm-moles/hr of propane which must be added:

$$\begin{aligned} & \left(x \frac{\text{gm - mole}}{\text{hr}}\right) \left(526.3 \frac{\text{Kcal}}{\text{mole}}\right) + 27,800 \frac{\text{Kcal}}{\text{hr}} = 1.1 \left\{188,400 \frac{\text{Kcal}}{\text{hr}} \right. \\ & + (x) (750^{\circ}\text{C}) \left[ \left(0.03708 \frac{\text{Kcal}}{\text{mol-}^{\circ}\text{K}}\right) + \left(5 \frac{\text{O}_2}{\text{C}_3\text{H}_8}\right) (1.1) (0.00804 \frac{\text{Kcal}}{\text{mol-}^{\circ}\text{K}}) \right. \\ & \left. \left. + \left(18.81 \frac{\text{N}_2}{\text{C}_3\text{H}_8}\right) (1.1) (0.00752 \frac{\text{Kcal}}{\text{mol-}^{\circ}\text{K}}) \right] \right\} \end{aligned}$$

The solution given by this equation is:  $x = 542.3$  gm-mole/hr.

Thus, adding in the propane needed for combustion to maintain the required temperature and so an assumed 95% conversion, we can compute the residuals which actually will be discharged. These are given in Table A4-5. It is important to remember that these data are for a 10 MWe facility. It is anticipated that scale-up to a larger facility would cause correspondingly larger releases. For example, we would expect that a 430 MWe facility, delivering 80 percent of its power from solar, would discharge  $(430/10) (0.8) (0.87) = 30$  gm/sec of non-methane hydrocarbons to the atmosphere under worst-case conditions. The corresponding 24-hour average is a small but not-insignificant 0.35 T/d. A second pollutant of concern included in the tabulation is carbon monoxide, for which 10 MWe facility emissions total 0.016 gm/sec. This value is sufficiently small to generally be of no significance.

Table A4-4

Heat Contributed by Incineration of Discharge\*

<u>Component</u>	<u>Kcal/hr from Waste Combustion</u>
N <sub>2</sub>	-
CO	142
CO <sub>2</sub>	-
H <sub>2</sub>	609
O <sub>2</sub>	-
CH <sub>4</sub>	3,668
C <sub>2</sub> H <sub>6</sub>	6,115
C <sub>2</sub> H <sub>4</sub>	166
C <sub>3</sub> H <sub>8</sub>	5,579
C <sub>3</sub> H <sub>6</sub>	833
n-C <sub>4</sub> H <sub>10</sub>	4,792
i-C <sub>4</sub> H <sub>10</sub>	1,362
n-C <sub>5</sub> H <sub>12</sub>	4,275
i-C <sub>5</sub> H <sub>12</sub>	242
H <sub>2</sub> O	-
	<hr/>
Total	27,800 Kcal/hr

\* Discharge rate: 1710 moles/hr of waste (10 MWe facility)

Table A4-5

Tabulation of Estimated Worst Case Discharge Derived  
from Thermal Storage Fluids\*

Components	gm-mole/hr	Emission Factors	
		gm/sec	lb/hr
N <sub>2</sub>	33,310	259.1	2,054
CO	2.1	0.016	0.13
CO <sub>2</sub>	4,467	54.6	433
H <sub>2</sub>	17.8	0.0099	0.078
O <sub>2</sub>	1,210	10.8	86
CH <sub>4</sub>	17.4	0.077	0.61
C <sub>2</sub> H <sub>6</sub>	16.6	0.14	1.1
C <sub>2</sub> H <sub>4</sub>	0.5	0.0039	0.031
C <sub>3</sub> H <sub>8</sub>	37.7	0.46	3.6
C <sub>3</sub> H <sub>6</sub>	1.7	0.020	0.16
n-C <sub>4</sub> H <sub>10</sub>	7.0	0.11	0.87
i-C <sub>4</sub> H <sub>10</sub>	2.1	0.034	0.27
n-C <sub>5</sub> H <sub>12</sub>	5.1	0.10	0.79
i-C <sub>5</sub> H <sub>12</sub>	0.3	0.006	0.048
H <sub>2</sub> O	6,415	32.1	255

Emissions of Particular Concern\*

Non-Methane Hydrocarbons, total: 0.87 gm/sec

Carbon Monoxide: 0.016 gm/sec

\* 10 MWe facility.

## APPENDIX 5. NITROGEN OXIDE AND NON-METHANE HYDROCARBON PLUME TRANSPORT AND INTERACTION; OZONE TRANSPORT

Data developed in other appendices show that significant quantities of nitrogen oxides may result from exposure of an annular sheath of air to the high temperatures experienced by some solar receivers. Also, organic thermal storage fluids may need to be discharged, with post-incineration releases to the atmosphere. The worst-case consequence of these requirements is developed below.

We assume that release of nitrogen oxides (primarily as NO) takes place at the elevation of the receiver on its tower, and that post-incineration hydrocarbon emissions are released at essentially the same location. Thus they are carried as a buoyant plume together, up to elevation and downwind, with a potential for photochemical reaction over time and hence production of oxidant. However, if the input from the solar system is kept quite small, releases may only add to background sources and marginally enhance photochemical reaction.

### A5.1 Plume Modeling

We assume a Gaussian atmospheric dispersion model (A 1, A 13). Considering the scale of the solar facility and the surroundings likely to be influenced, and also the relatively slow, complex reactions within the field of interest, the initial approach is to treat releases as if they were unreactive. Worst-case meteorological assumptions include Turner "A" stability for a complex of reasons, but primarily because these will demonstrate maximum ground level and near ground level impacts (A 1). We choose a low wind speed, 0.9 m/sec. and assume all air contaminants are effectively reflected upward again after they reach the earth's surface.

With these assumptions, a downwind concentration value,  $\chi$ , in units of gm/m<sup>3</sup>, can be computed from the relation (A 13):

$$\chi = \frac{Q}{2\pi\sigma_y\sigma_z u} \left[ \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \right] \left\{ \exp\left[-\frac{(z+H)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right] \right\}$$

where: Q = source emission rate, gm/sec  
u = wind speed (0.9 m/sec)  
H = effective stack height (m)  
 $\sigma_y$  = horizontal dispersion coefficient (m), a function of downwind distance  
 $\sigma_z$  = vertical dispersion coefficient (m), a function of downwind distance

At ground level  $z = 0$ , which reduces the above relation to:

$$\chi \text{ (at } z=0) = \frac{Q}{\pi\sigma_y\sigma_z u} \left[ \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \right] \left[ \exp\left(-\frac{H^2}{2\sigma_z^2}\right) \right]$$

H represents the sum of the height to the actual release point, which we choose as about 294 m, and  $\Delta H$  (in m), the height of rise of the heated plume above the release point:

$$\Delta H = (v_s d/u) [1.5 + 2.68 \times 10^{-3} Pd(T_s - T_a)/T_s]$$

Where:  $v_s$  = vertical velocity of the plume on its release (m/s)

$d$  = inside stack diameter at the point of release (m)

$u$  = wind speed (0.9 m/sec)

$T_s$  = stack gas temperature ( $^{\circ}K$ )

$T_a$  = air temperature ( $301^{\circ}K$ )

$P$  = atmospheric pressure (937.9 mb)

Continuing the selection of parameters, we choose 35 m/sec as the value for  $v_s$ , representing the average rise velocity from our example calculation for heated air flowing adjacent to a receiver face heated to  $3033^{\circ}K$  ( $5000^{\circ}F$ ). The appropriate value for  $d$ , (inside stack diameter), is not clearly established with an external flow. We choose a geometric mean of the two linear dimensions developed in earlier example heated air balance calculations:  $d = 1.0$  m. At the very least this represents a reasonable value. For  $T_s$ , of course, we choose  $3033^{\circ}K$ . Thus, substituting:  $\Delta H = 146$  m. Using 294 m as the release point (alongside the receiver face):  $H = 146+294 = 440$  m. In developing this estimate we have deliberately selected values so as to keep the ultimate value of  $H$  low, and so provide maximum ground level exposure from the resultant plume. This represents a worst case situation.

For assumed atmospheric stability (Turner "A"), dispersion coefficients are functions of downwind distance as shown in Table A5-1 (A 13).

Table A5-1

Selected Atmospheric Dispersion Coefficients

<u>Distance Downwind (m)</u>	<u><math>\sigma_y</math> (m)</u>	<u><math>\sigma_z</math> (m)</u>
700	103	210
1000	195	450
1200	260	660
1500	375	1100
2000	610	2000
3000	1250	4600

With these data we can substitute in the equations above and determine what quantity of either NO<sub>x</sub> (as primarily NO) or non-methane hydrocarbons to expect (with the species mix indicated in Appendix A-4). Values can be obtained for either ground- or release-level locations. We choose as an example the 436 gm/sec source rate for NO computed in Appendix 3 (5000°F receiver temperature case), and the 30 gm/sec source rate for non-methane hydrocarbons (Appendix 4; 80% solar capacity from 430 MWe facility, discharge of thermal storage fluid waste case). We look only at data directly downstream from the point of release: thus y = 0. Results of calculations are presented in Tables A5-2 and A5-3.

Table A5-2

Estimated Downwind NO<sub>x</sub> Concentrations  
(Computed as NO)

<u>Downwind Distance, m</u>	<u>At Ground Level</u>		<u>At Release Level (440 m)</u>	
	<u>μg/m<sup>3</sup></u>	<u>ppm</u>	<u>μg/m<sup>3</sup></u>	<u>ppm</u>
700	793	0.592	3560	2.660
1000	1090	0.813	1010	0.753
1200	718	0.537	634	0.474
1500	345	0.258	323	0.242
2000	124	0.093	121	0.091
3000	28	0.021	9	0.021

Table A5-3

Estimated Downwind Non-Methane Hydrocarbon Concentrations

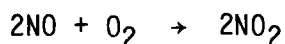
<u>Downwind Distance, m</u>	<u>At Ground Level</u>		<u>At Release Level (440 m)</u>	
	<u>μg/m<sup>3</sup></u>	<u>ppm</u>	<u>μg/m<sup>3</sup></u>	<u>ppm</u>
700	55	0.028	245	0.123
1000	75	0.038	69	0.035
1200	50	0.025	44	0.022
1500	24	0.012	22	0.011
2000	8	0.004	8	0.004
3000	2	0.001	2	0.001

## A5.2 Commentary

These data provide much useful information. But in evaluating these data, it is essential from the start to recognize that the basis for their development was selection of worst case conditions. Thus, for example, we recognize that nitrogen oxide formation is highly sensitive to temperature, both from the standpoint of equilibrium and of kinetics. Very possibly the maximum temperature experienced by a parcel of air for even advanced designs can be made to never exceed 3000°F. If so, downwind worst case concentrations need to be scaled downward to less than one-sixtieth those tabulated; a very important difference. Similarly, hydrocarbons from burnoff of thermal storage fluids are readily enough managed by the expedient of release at a continuous average rate rather than peak release rates followed by reduced rates. By this means worst case hydrocarbon releases can be reduced to about one-eighth of those tabulated. In a similar fashion, release and transport process assumptions have been quite conservative. Thus the worst case "overestimate" of the problem may quite readily constitute more than one order of magnitude.

Given these caveats, nitric oxide (NO) levels near the source are projected as significant by comparison with typical background. Levels drop very rapidly, so that on passing a probable facility boundary (2 to 3 km) they become modest though readily observable. A careful accounting and all reasonable means for mitigation would appear essential.

A key concern would be conversion to nitrogen dioxide (NO<sub>2</sub>). Nitrogen dioxide represents a much less acceptable form both because of its visibility (color) and distinct, disagreeable odor, and because of its ability to harness sunlight and initiate the photochemical chain leading to oxidants. The equilibrium data (Appendix 2) indicate that at high temperatures near the source NO<sub>2</sub> levels will remain quite low by comparison with those for NO. Without added conversion of NO to NO<sub>2</sub>, dispersion would make levels unobservable at a facility boundary several kilometers distant. The thermal conversion process for NO:



occurs quite slowly at a rate governed by the rate constant of  $k = 7.62 \times 10^{-10} \text{ ppm}^{-2} \text{ min}^{-1}$  (A 14), under standard atmospheric conditions. Starting from worst case data, at source elevation and 700 m downwind, the conversion is thus indicated as:

$$\begin{aligned} \frac{d[\text{NO}_2]}{dt} &= (7.62 \times 10^{-10}) (2.66)^2 (2.1 \times 10^5) \\ &= 1 \times 10^{-3} \text{ ppm/min} \end{aligned}$$

Hours are then needed for significant conversion to take place. At 1000 m distance the rate drops by another order of magnitude. Of even greater potential importance, if worst case estimates merit reduction to 1/10 or less tabulated values as discussion above has indicated, conversion rates are reduced by 1/100. Thus it appears that a combination of equilibrium limits and subsequent rate limits will bound the levels of NO<sub>2</sub> actually experienced. The NO<sub>x</sub> "problem" thus becomes the traditional concern for addition to other possible regional sources, and its contribution to large-



scale, low-level pollutant masses.

### A5.3 Ozone Transport

The estimates for equilibrium ozone ( $O_3$ ) in the plume of effluent air exposed to solar receiver temperatures are quite low by comparison with nitrogen oxides (Appendix 2), though above most all ambient levels. Dispersion, as was computed for  $NO$ , would reduce these to below observable incremental quantities.

There is a further concern, however. The combined nitric oxide/non-methane hydrocarbon plume could accommodate reaction to form added ozone. Two factors mitigate this potential. First, the ratio  $NO/nmHC$  is very large, and at low hydrocarbon values, this insures low near-source ozone maxima (reference A 7 pg 43). Second, the rate process is quite slow, and with representative values requires induction periods such as ten hours. Thus ozone (and oxidant) should not be of major concern.

## APPENDIX 6. OTHER PHOTOLYTIC REACTIONS

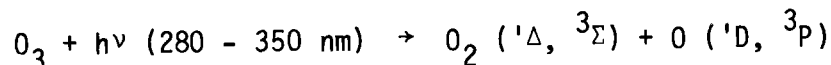
A truly unique aspect of the large-scale production of energy from solar sources is the fact that intense beams of sunlight - up to several thousand times a "normal" sun - will be created and used. This, in turn, creates the possibility of photolytic chemical reactions assuming a unique importance. Some such reactions have been addressed earlier. A huge body of knowledge has been accumulated, with large portions summarized in sources such as references A 7 and A 8. Several generalizations emerge.

- (1) While solar energy may utilize intense beams, the energy of an individual photon penetrating to the earth's surface is rather small, limiting the kinds of reactions which can be initiated.
- (2) Multiple photon processes are feasible and may combine sufficient energy to drive processes of great interest, but then lower statistical likelihood lessens their practical importance.
- (3) Many photolytic processes, if initiated in a "clean" environment, are part of a system which spontaneously reverts to much the original equilibrium composition once the driving energy of the sun is removed.

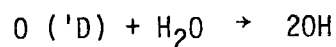
Summary observations regarding several photolytic reactions of particular interest follow.

### A6.1 Ozone Photolysis

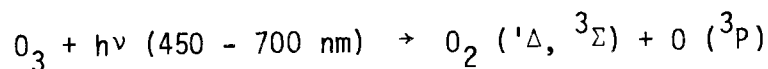
Some consideration of ozone photolysis has already been included in Appendix 2. Reaction products depend on the wave length of incident light. For example:



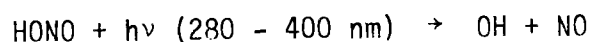
The singlet-D species of oxygen atom is considerably more reactive than the ground state triplet-P atom. For example, it may react with water:



Thus creating a free radical chain branching opportunity. Furthermore, the OH radical provides a particularly active intermediate for a host of possible reactions (A 7). At longer wavelengths:

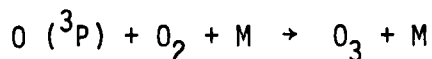
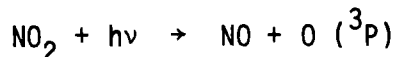


### A6.2 Nitrous Acid Photolysis



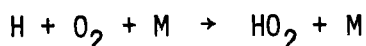
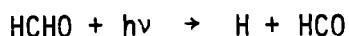
This reaction represents an alternative source of reactive OH radical, though limited by the quantity of source nitrous acid. However, (Appendix 2), equilibrium data indicate that the compound will be formed.

### A6.3 Nitrogen Dioxide Photolysis

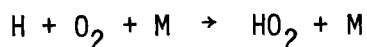


As noted earlier, photolysis of nitrogen dioxide is the key step in the process by which solar energy converts residuals from combustion and other processes into photochemical smog.

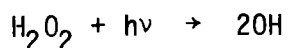
### A6.4 Aldehyde Photolysis



Peroxy radicals share the characteristics of OH radicals, leading to generally similar chains of product reactions. The chains may be convertible. For example, in an atmosphere containing carbon monoxide:

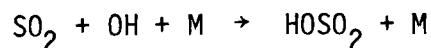
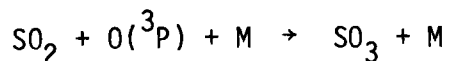


And also:



### A6.5 Other Effects

The products of photolytic reactions may assist in the transformation of pollutants:



In this instance photolysis may speed up an otherwise very slow reaction, raising the oxidation state of sulfur.

One of three or more species must be present, it appears, before the initial photolytic trigger can cause the photochemical conversion chain to proceed and to produce smog: carbon monoxide, ozone, or formaldehyde. All are likely to be present in at least trace quantities in the gases heated adjacent to a solar receiver. As we have noted, characteristic system reaction rates appear slow enough (A 7, A 8) so that short exposure time will provide only limited enhancement.

## APPENDIX 7. ESSENTIAL DATA

To be useful the calculations and analyses included in this report must be based on data suited to likely sites for solar facilities. This appendix presents data for several such sites; specifically wind data, and data on the observed incidence of criterion atmospheric pollutants. These latter are referenced to National Ambient Air Quality Standards (also included). Chemical analysis of particulate matter for one site also is included. Data sources represent references A 15 to A 23, inclusive.

### A7.1 Wind Data

The following Table A7-1 lists wind velocities, giving average velocity first (on the left) and then peak velocity (on the right). Values in miles per hour are given in parentheses (mph), and other values are in km/hr.

Table A7-1  
Wind Data for Possible Solar Sites

	<u>March</u>	<u>June</u>	<u>September</u>	<u>December</u>	<u>Annual</u>
Tucson, Arizona	(7.4,27) 12,43	(8.9,34) 14,55	(9,31) 14,50	(8.4,35) 14,56	(8.4,32) 14,51
Reno, Nevada	(6.9,34) 11,55	(8.4,34) 14,55	(5.7,23) 9,37	(3.7,30) 6,48	(6.2,30) 10,48
Albuquerque, New Mexico	(10.5,42) 17,68	(9.7,38) 16,61	(8.2,43) 13,69	(7.1,35) 11,56	(8.9,40) 14,64
Clarence, Oklahoma (near Tulsa)	(12.7,29) 20,47	(11.2,31) 18,50	(6.4,20) 10,32	(9.2,29) 15,47	(9.9,27) 16,43
Lubbock, Texas*	(14,37) 23,60	(11,23) 18,37	(11.6,35) 19,56	(8.5,31) 14,50	(11.3,31) 18,50
Amarillo, Texas*	(13.1,32) 21,51	(11.6,37) 19,60	(6.4,17) 10,27	ND	(11.3,31) 18,50

\* Site is midway between these locations.

### A7.2 National Ambient Air Quality Standards

Table A7-2 presents the National Ambient Air Quality Standards in effect as of 1981.

Table A7-2

## National Ambient Air Quality Standards

<u>Pollutant</u>	<u>Averaging Period</u>	<u>Concentration</u>	
		<u><math>\mu\text{g}/\text{m}^3</math></u>	<u>ppm</u>
Total Suspended Particulate (TSP)	annual geometric mean	75	
	24 hour arithmetic mean	260	
SO <sub>2</sub>	annual arithmetic mean	80	0.03
	24 hour arithmetic mean	365	0.14
NO <sub>2</sub>	annual arithmetic mean	100	0.05
CO	8 hour average	10,000	9
	1 hour average	40,000	35
O <sub>3</sub>	1 hour average (post 1979)	235	0.12
	1 hour average (pre 1979)		0.08
Non-methane Hydrocarbons (HC)	6-9 AM average	160	0.24

A7.3 Observed Pollutant Levels in Region with Solar Potential

Table A7-3 incorporates ambient air quality data for sites near which solar facilities are likely to be constructed. The data are in each case presented as fractions of the (1981) National Ambient Air Quality Standards tabulated above. Appropriate averaging periods are utilized.

Table A7-3

Ambient Air Quality Data as a Fraction  
of National Standards

Site/ Pollutants	Averaging Period						
	Annual Geometric mean	24 hour Geometric mean	Annual Arithmetic mean	24 hour Arithmetic mean	8 hour mean	1 hour mean	6-9AM
<u>Albuquerque NM</u>							
TSP	0.99	0.99					
SO <sub>2</sub>			0.13	0.13			
NO <sub>2</sub>			0.36				
CO <sup>2</sup>					2.20	0.90	
O <sub>3</sub>						1.14	
HC							ND*
<u>Abilene TX</u>							
TSP	0.81	0.77					
SO <sub>2</sub>			0.16	0.15			
NO <sub>2</sub>			0.21				
CO <sup>2</sup>					ND	ND	
O <sub>3</sub>						ND	
HC							ND
<u>Lubbock TX</u>							
TSP	0.81	0.84					
SO <sub>2</sub>			0.14	0.06			
NO <sub>2</sub>			0.20				
CO <sup>2</sup>					ND	ND	
O <sub>3</sub>						ND	
HC							ND
<u>Odessa TX</u>							
TSP	0.91	1.12					
SO <sub>2</sub>			0.24	0.18			
NO <sub>2</sub>			0.26				
CO <sup>2</sup>					0.36	0.30	
O <sub>3</sub>						0.25	
HC							2.08
<u>E1 Paso TX</u>							
TSP	1.37	1.53					
SO <sub>2</sub>			0.49	0.88			
NO <sub>2</sub>			0.30				
CO <sup>2</sup>					0.21	0.05	
O <sub>3</sub>						0.17	
HC							2.92

Table A7-3 (Continued)

Site/ Pollutants	Averaging Period						
	Annual Geometric mean	24 hour Geometric mean	Annual Arithmetic mean	24 hour Arithmetic mean	8 hour mean	1 hour mean	6-9AM
<u>Tulsa-Clarence OK</u>							
TSP	0.88	ND*					
SO <sub>2</sub>			ND	ND			
NO <sub>2</sub>			1.01				
CO <sup>2</sup>					1.15	ND	
O <sub>3</sub>						1.16	
HC							ND
<u>near Tucson AZ</u>							
TSP	1.76	1.83					
SO <sub>2</sub>			0.08	0.17			
NO <sub>2</sub>			0.30				
CO <sup>2</sup>					0.70	0.30	
O <sub>3</sub>						0.87	
HC							3.41
<u>near Reno NV</u>							
TSP	0.78	ND					
SO <sub>2</sub>			ND	ND			
NO <sub>2</sub>			ND				
CO <sup>2</sup>					ND	ND	
O <sub>3</sub>						ND	
HC							ND
<u>Barstow CA</u>							
TSP	0.88	1.18					
SO <sub>2</sub>			ND	ND			
NO <sub>2</sub>			0.66				
CO <sup>2</sup>					1.12	0.34	
O <sub>3</sub>						1.33	
HC							ND
<u>High values</u>							
TSP	1.76	1.83					
SO <sub>2</sub>			0.49	0.88			
NO <sub>2</sub>			1.01				
CO <sup>2</sup>					2.20	0.90	
O <sub>3</sub>						1.33	
HC							3.41

\* indicates not determined

#### A7.4 Analysis of total Suspended Particulate Matter

Chemical analysis of total suspended particulate matter collected in Nevada, averaged over 1979, and likely to be representative of southwestern solar sites is as follows.

Table A7-4  
Analysis of Particulates

<u>Element</u>	<u>Amount, <math>\mu</math> g/m<sup>3</sup></u>
Mg	2.81
Fe	0.75
Cu	0.09
Zn	0.13
As	0.01
Cr	0.008
Pb	0.09
Cd	0.001
SO <sub>4</sub> <sup>-2</sup>	2.60
NO <sub>3</sub> <sup>-1</sup>	1.14
Other Constituents	<u>50.8</u>
TSP	58.4



## APPENDIX 8. "CREATIVE" CONVERSION OF AMBIENT AIR POLLUTANTS

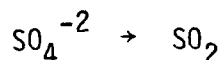
Data in Appendix 7 provide a picture of the kinds and quantities of pollutants to be expected in ambient air near representative solar thermal facility sites. If we disregard many details of chemical kinetics and chemical equilibrium, we can imagine "creative" processes by which constituents in the atmosphere are converted so as to provide worst case quantities of specific pollutants of concern. In principal, the high intensity solar beam could provide conditions such that, for example, desert dust could be volatilized. Evaluation from this extreme point of view, should it suggest the absence of serious problems, is totally reassuring. The only presently available chemical analyses of total suspended particulates are from Nevada. The data are presented in Appendix 7.

### A8.1 Carbon Monoxide

We assume that all non-methane hydrocarbons are olefins, specifically ethylene, and that all this material is converted by partial oxidation to carbon monoxide. The molecular weights are equal at 28. Thus at the non-methane hydrocarbon worst case concentration of  $546 \mu\text{g}/\text{m}^3$ , an extra  $546 \mu\text{g}/\text{m}^3$  CO is the absolute maximum that can be contributed. By comparison with the National Ambient Air Quality Standard of  $40,000 \mu\text{g}/\text{m}^3$  (1 hour average), this is an added 5 percent. If added to the observed worst case level of 0.90 times the 1-hour average standard (Albuquerque), it could cause levels of 0.95 times the standard to be reached. It seems totally unlikely that meeting the 8-hour average standard, already exceeded by a more serious factor of 2.2, could be influenced. Assumptions needed are too extreme.

### A8.2 Sulfur Dioxide

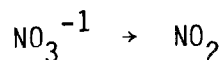
Sulfate ions contained in particulates, under total volatilization or under reducing conditions, could be transformed to sulfur dioxide:



Thus sulfate, with a molecular weight of 96, is converted to sulfur dioxide at molecular weight 64. Starting with a worst case  $2.60 \mu\text{g}/\text{m}^3$ , we could expect no more than an added  $(64/96)(2.60) = 1.73 \mu\text{g}/\text{m}^3$  of  $\text{SO}_2$ . Stated another way, total suspended particulate could contribute at most an additional 2 percent of the National Ambient Air Quality Standard (annual arithmetic mean). By so doing it would raise the observed peak from 0.88 times the standard (El Paso) to about 0.90 times the standard; certainly of no significance.

### A8.3 Nitrogen Dioxide

Nitrate ions contained in particulates, if also exposed to total volatilization or reducing conditions, could be transformed to  $\text{NO}_2$ :

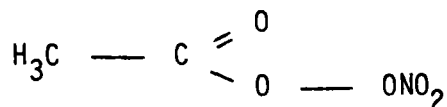


Thus nitrate, with a molecular weight of 62, is transformed to nitrogen dioxide of molecular weight 46. Starting with a worst case  $1.14 \mu\text{g}/\text{m}^3$ , we could expect no more than an added  $(46/62)(1.14) = 0.85 \mu\text{g}/\text{m}^3$  of added  $\text{NO}_2$ . Thus total suspended particulate could contribute at most an additional 1

percent of the National Ambient Air Quality Standard (an annual arithmetic mean). By so doing it would raise the observed peak from 1.01 times the standard to 1.02 times this level; very likely not to be observable, and of no significance.

#### A8.4 Peroxyacylnitrates

The most tenuous conversion process which can be conceived is the transformation of ethylenic hydrocarbons together with nitrogen dioxide to form PANs; peroxyacylnitrates, the simplest form of which is:



Suppose all non-methane hydrocarbon, as ethylene (molecular weight 28), is converted to the molecular weight 75 intermediate:  $\text{C}_2\text{H}_3\text{O}_3$ . In this case the worst case oxidant level, already 1.33 times the National Ambient Air Quality Standard, could be significantly exceeded. However, the chemical changes required are unreasonable to expect under any likely conditions.

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