# Sulfur and the World Trade Center Disaster

by

F. R. Greening

## 1.0 Introduction

Appendix C of the well-known FEMA Report on the collapse of buildings at the WTC on September 11th, 2001, focuses on two samples of badly corroded structural steel removed from the WTC debris field, /See Ref 1/. The authors of Appendix C, namely J. Barnett, R.R. Biederman and R.D. Sisson Jr., describe metallographic sectioning and EDS (X-ray fluorescence) analyses of two samples and show that iron sulfide, FeS, surface deposits are associated with the severe corrosion of the steel. In an interview published in the Spring 2002 issue of *WPI Transformations*, Barnett et al. speculate *how* the steel was sulfided in the manner observed, but note that:

"*The important questions are how much sulfur do you need, and where did it come from? The answer could be as simple--and this is scary- as acid rain…… We may have just the inherent conditions in the atmosphere so that a lot of water on a burning building will form sulfuric acid, hydrogen sulfide or hydroxides, and start the eutectic process as the steel heats up,*"

Barnett et al. note that the sulfur could also have come from the contents of the burning buildings, such as rubber or plastics, or ocean salts, such as sodium sulfate, which is known to catalyze sulfidation reactions on turbine blades of jet engines. However, at the time of writing, (Feb, 2006), Barnett et al. have not published any additional information on the sulfidation of steel at the WTC.

S. W. Banovic et al. at NIST have also observed sulfiding of structural steel components recovered from the WTC rubble pile /2/. These researchers report the results of EDS analysis of three samples, two of which (K-16 and C-115), showed the presence of iron sulfides in areas exhibiting severe corrosion/erosion. Banovic et al. suggest that the severe corrosion was initiated by sulfur ingress into the material but note that:

"*As sulfur was not readily available in large amounts in the steel, an external source must have supplied this specie.*"

In this report we investigate possible sources of sulfur in the WTC and discuss possible mechanisms for the observed sulfidation of the structural steel.

## 2.0 Sources of Sulfur in the WTC

Although sulfur is a relatively common constituent of materials found in typical urban environments, it is difficult to quantify all the sources of this element in a complex structure such as the WTC. Certainly we know that the A36 structural steel used throughout the WTC contained less than 0.04 wt % sulfur. However, this sulfur is chemically bound in sulfide inclusions such as MnS and is essentially immobile. More labile forms of sulfur are found as additives or natural impurities in common workplace materials such as paper, wood and plastics. For example, wood contains up to 0.05 wt % sulfur, while vulcanized rubber may contain up to 5 wt % sulfur.

In the present context it is not simply the presence, but the *mobility*, of sulfur in the WTC that is of interest. In view of the nature of the WTC disaster it is clear that the fires provided a mechanism for the transfer of sulfur containing species from their various sources in the buildings to the surface of structural steel members, thereby creating an environment favorable to sulfiding. We therefore need to consider the effects of the WTC fires on sulfur containing materials in the Trade Center buildings.

## 3.0 The Production of $SO_2$ in the WTC Fires

Practically all sulfur-containing materials emit sulfur dioxide, $SO_2$, when heated to a sufficiently high temperature in air. However, because of the wide range of sulfur bond strengths in common sulfur compounds, (e.g. sulfates, sulfides, thiols, etc), there is potentially a very wide range of temperatures, typically from 300 to 1300 °C, over which release of $SO_2$ is possible. Nevertheless, measurable levels of $SO_2$ are always generated by the combustion of trace sulfur in carbonaceous materials such as plastic or wood.

In the case of the WTC disaster, the Boeing 767 aircraft that hit the Twin Towers were carrying about 30,000 kg of kerosene of which about 25 % ignited *inside* the buildings releasing about 300 Gigajoules of chemical energy. Office furniture, paper, plastics, carpeting, etc, provided additional fuel with an estimated energy content of about 280 Megajoules/$m^2$ of floor space, /See, for example, Ref 3 /. As a result, intense fires raged inside the Twin Towers for up to an hour after the aircraft impacts and sustained heat release rates of at least 10 MW over an effective area of about 1000 $m^2$ in each Tower. There has been considerable debate with regard to the temperatures that were reached at the height of these fires, but values of *at least* 600 °C, and as high as 1000° C in localized "hotspots", are likely. Thus, there can be no doubt that the fires in the WTC on 9-11 provided the appropriate conditions for the release of $SO_2$ from the combustion of sulfur containing materials on affected floors.

Unfortunately there appears to be very little published data on measured concentrations of $SO_2$ in real or simulated building fires. Nevertheless, based on known or assumed inventories of materials in the WTC it is possible to estimate the potential release of $SO_2$ from the two significant sources of sulfur: *live load materials* and *dead load materials*. Live load materials are those items that are moveable within the building such as people, office furniture, wall hangings, computers, telephones, printers, paper, etc. Dead load materials are the permanent structural components, such as steel beams and columns, concrete floors, gypsum wallboards, etc, used in the construction of buildings.

### (i) Live Load Materials

As noted above, the live load materials that were present in the WTC would be very similar to the materials found in offices or dwellings in any modern urban environment. In fact, researchers investigating airborne particulate over New York City in October 2001 observed that the plume of smoke and dust released during the WTC disaster "*resembled in many ways those seen from municipal waste incinerators*", /4/. It follows that levels of $SO_2$ created by live load materials subjected to the WTC fires may be estimated from reports on gaseous emissions from the incineration of municipal waste /5/. These reports show that typical municipal solid waste (MSW) consists of 36 wt % paper and paperboard, 13 wt % glass and metal, 11 wt % plastics, 11 wt % food waste, 6 wt % wood, 5 wt % rubber, 4 wt % textiles - a mixture that is probably close to the composition of combustible material in most office buildings. In Reference /5/ it is reported that ultimate analysis of dried composite MSW shows the presence of 0.2 wt % sulfur, 1.3 wt % N and 0.7 wt % chlorine.

The live load in the WTC buildings is estimated to be no more than 100 kg/$m^2$ of usable floor space. Thus we conclude there was a *maximum* of about 0.2 kg of sulfur per square meter of floor space available for the production of $SO_2$ from the combustion of live load materials. If we assume that in a one-hour fire, 10 % of the live load sulfur was released as $SO_2$ from an effective floor area of 1000 $m^2$, about 40 kg of $SO_2$ would have been released within each WTC Tower. If we further assume that the combustion gases accumulated in a volume of 10,000 $m^3$ and the effective air exchange rate was four floor-volumes per hour, the *maximum* concentration of $SO_2$ from the combustion of live load materials in the Twin Towers was 1 gram / $m^3$, equivalent to 350 ppm of $SO_2$ (by volume).

By way of comparison we note that D. O. Albina et al. have studied the composition of flue-gases from the combustion of MSW, (See, for example, Ref /6/), and report data for Cl, N and S containing species:

"*The calculated flue-gas composition upon combustion of 1 kg (dry) NYC MSW was 7.4 % $CO_2$, 11 % $H_2O$ and 7.2 % excess $O_2$ and the balance $N_2$ with 334 ppm HCl, 210 ppm, NO and 227 ppm $SO_2$. These results are in relatively good agreement with flue-gas compositions obtained in the combustion chambers of present WTE facilities. Typical HCl concentrations in combustors were in the range 200 – 900 ppm while $SO_2$ concentration were in the range of 10 – 300 ppm….. Concentrations of gaseous $SO_2$ were observed to increase at 600 °C and to peak at 900 °C.*"

We conclude, based on these experimental and theoretical estimates, that sulfur released by the combustion of live load materials in WTC 1 & 2 generated local $SO_2$ concentrations up to about 350 ppm within fire-affected zones in these buildings.

WTC 1, 2 & 7 had an important additional source of live load sulfur contained in tanks of diesel fuel oil located in the basement (WTC 1 & 2) or on the ground floor (WTC 7) of these buildings. This fuel was stockpiled for emergency electrical power generation /1/. Diesel fuel oil typically contains about 0.2 % sulfur impurity. A significant portion of the diesel fuel stored in WTC 1 & 2 was recovered during recovery operations after 9-11. However, FEMA have reported that up to 40,000 kg of diesel fuel may have been consumed in fires that burned for over five hours in WTC 7 on 9-11, releasing about 60 MW of heat energy. Thus we conclude that diesel fuel may have added up to 160 kg of $SO_2$ emissions to the lower floors in WTC 7.

(ii) Dead Load Materials

Structural A36 steel accounted for more than 50 % of the WTC building's dead load and sulfur was certainly present at low concentrations in the A36 steel. Nevertheless, this potential source of $SO_2$ may be discounted because this sulfur was essentially immobilized in sulfide inclusions and not subject to release by oxidation.

There is, however, a potential source of $SO_2$ in another major dead load material, gypsum wallboard, which is essentially pure calcium sulfate di-hydrate, $CaSO_4.2H_2O$, and therefore rich, (~ 19 % by wt), in sulfur. Gypsum wallboard was used extensively in the Twin Towers, including locations conventionally reserved for concrete such as the lining of stairwells and elevator shafts. In fact, after steel and concrete, gypsum was the third most widely used construction material in the Twin Towers and contributed about 20 $kg/m^2$ to the building dead load. Thus we estimate that there was about 4 kg of sulfur per square meter of floor space available for the production of $SO_2$ from this source, or about 20 times the amount of sulfur available from all live load materials combined. The question remaining, of course, is: could gypsum wallboard, in regions of the WTC buildings that were exposed to fires, have released a significant amount of sulfur as $SO_2$?

Chemists have investigated the thermal decomposition of gypsum, $CaSO_4.2H_2O$ or anhydrite, $CaSO_4$, since the early 1900s because of its potential for making sulfuric acid by the liberation of $SO_2$ or $SO_3$ from a plentiful and inexpensive starting material /7/. It was known at this time that the direct reaction:

$$CaSO_4 \rightarrow CaO + SO_3 + \tfrac{1}{2} O_2$$

(followed by: $SO_3 + H_2O \rightarrow H_2SO_4$), only proceeds at an acceptable rate at temperatures ~ 1400 °C. However, early research showed that the above reaction could be accelerated by additives such as clay and, more importantly, the *reduction* of $CaSO_4$ to CaO and $SO_2$ by reaction with solid carbon or gaseous carbon monoxide was found to be possible at temperatures well below 1000 °C /8/. In these cases $CaSO_4$ was decomposed by two novel reactions:

$$2CaSO_4 + C \rightarrow 2CaO + CO_2 + 2SO_2$$

and,

$$CaSO_4 + CO \rightarrow CaO + CO_2 + SO_2$$

Since the 1980s there been renewed interest in these reactions because of their role in the removal of $SO_2$ from combustion gases by contact with lime (CaO) in so-called flue gas desufurisation processes, (See, for example /9/ and references contained therein.). As a consequence, the chemistry of calcium sulfate reduction has been investigated over a wide range of conditions. Thus, for example, R. Kuusik and co-workers (See Ref/10/), have reported details of the thermal decomposition of calcium sulfate in carbon monoxide/nitrogen mixtures and note that in 10 - 20 % CO/ $N_2$, calcium sulfide, CaS, and carbon dioxide are formed at temperatures in the range 780 - 850 °C, while at CO concentrations below 10 %, calcium oxide, CaO, carbon dioxide and sulfur dioxide are formed above 900 °C. Kuusik et al. also note that the presence of impurities such as $SiO_2$ in the calcium sulfate lower the decomposition temperatures by up to 100 °C.

Published data /11/ on the kinetics of the reduction of calcium sulfate indicate that about 0.1 % per minute conversion to $SO_2$ would occur for $CaSO_4$ maintained at 900 °C in an atmosphere containing 1 % CO. If we assume that similar temperature and carbon monoxide impurity concentrations prevailed for 30 minutes in the combustion gases from the WTC fires, about 240 kg of $SO_2$ would have been released within each WTC Tower by decomposition of gypsum wallboard. If we further assume, as was done for the live load production of $SO_2$, that the decomposition gases accumulated in a volume of 10,000 $m^3$ and the effective air exchange rate was four floor-volumes per hour, the *maximum* concentration of $SO_2$ from the decomposition of gypsum was 12 grams / $m^3$, equivalent to 0.42 vol % $SO_2$.

## 4.0 Special Cases of $SO_2$ Production at the WTC on 9-11

In view of the extraordinary circumstances of the tragic events of 9-11 it is worth considering even the most unusual or controversial sources of sulfur in WTC 1, 2 & 7. In this category we place the following:

(i) Thermite/Thermate Reactions

The proposition that deliberately placed thermite/thermate "cutter charges" were used in a controlled demolition of WTC buildings 1, 2 & 7 has been discussed in great detail in /12/. We will not consider the problems associated with how such incendiaries may have been placed; suffice it to say that a typical "thermite " formulation, consisting of a mixture of 25 wt. % aluminum metal powder, and 75 wt. % ferric oxide powder, undergoes the exothermic reaction:

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe \; ; \qquad \Delta H = -853.5 \text{ kJ/mole},$$

However, because of the great difficulty in igniting thermite, iron-thermite is typically not used alone as an incendiary mixture. It is more commonly used in multi-component thermite-incendiary compositions, in which another oxidizer and binder are included together with thermite. Thermate-TH3, a mixture of thermite and pyrotechnic additives, is reported to be superior to thermites and is adapted for use in incendiary hand grenades. Its composition by weight is typically thermite 68.7%, barium nitrate 29.0%, sulfur 2.0% and binder 0.3%. S. Jones has suggested that sulfur additives to the thermite formulations supposedly used in the demolition of WTC 1, 2 & 7 could account for the sulfiding of steel /12/.

In order to estimate the total amount of sulfur that could have been released by firing thermate charges placed at pre-selected locations in the WTC we need to know how much thermate was used on 9-11. If we assume that a single thermate cutter charge consists of about 20 kg of reagents and 100 charges were needed per building, we conclude that a total of 2000 kg of thermate was used to demolish each WTC building. This implies that the production of $SO_2$ from thermate was no more than about 40 kg per building.

### (ii) Molten Aluminum Reactions

The presence of molten aluminum in the Twin Towers during 9-11 was first documented by FEMA /1/. Reports of spontaneous, and sometimes highly energetic, reactions between molten aluminum and gypsum, known to be present in large quantities of wallboard used at the WTC, are noted in /13/. While it is well known that molten aluminum is very reactive to oxides, it is also reactive to sulfates. Hence consideration should be given to the possible role of molten aluminum in producing $SO_2$ through the reaction:

$$3CaSO_4 + 2Al \rightarrow 3CaO + Al_2O_3 + 3SO_2$$

This reaction only occurs between *__molten__* aluminum and finely divided $CaSO_4$ and therefore requires crushed wallboard material exposed to sustained temperatures of at least 550 °C. The presence of molten aluminum in the Twin Towers has been discussed in /13/, where it was shown that the airframes of the Boeing 767 aircraft that crashed into WTC 1 & 2 on 9-11 represent a source of about 10,000 kg of molten aluminum. Reports of spontaneous, and sometimes highly energetic, reactions between molten aluminum and materials present on the Twin Towers such as pulverized concrete and gypsum are noted in /13/. If we assume that the molten aluminum reacted with equal efficacy with these materials, we estimate that up to 1000 kg of aluminum may have reacted with $CaSO_4$. The stoichiometry of this reaction then implies that as much as 3500 kg of $SO_2$ could have been released in WTC 1 & 2 by reactions between $CaSO_4$ and molten aluminum.

### (iii) Automobile Fires in WTC 1 & 2 Underground Parking

It has been well documented that the February 1993 terrorist bombing of the WTC started many fires involving maintenance areas, tenant storage and parked automobiles located in the basement levels of WTC 1 & 2 /14/. There can be little doubt that similar, but more extensive fires occurred during 9-11. The parking garage under the WTC held nearly 2,000 automobiles, each tank holding an estimated five gallons of gasoline. When recovery workers reached the lower levels of the WTC they found the remains of exploded and burned vehicles. Automobile tires weigh about 10 kg and contain an average of 1.5 wt. % sulfur. If 1000 tires were burnt in fires in the lower levels of WTC 1 & 2 during 9-11, a release of about 300 kg of $SO_2$ is expected from this source.

## 5.0 Post 9-11 Detection of Sulfur Compounds at or Near the WTC Site

We have presented data to suggest that $SO_2$ was present at concentrations up to 0.4 vol % in areas exposed to the WTC fires prior to the collapse of the respective buildings. Nonetheless, it is reasonable to ask: Is there *any* physical evidence for the presence of sulfur-containing gases or particulate at the WTC site in the aftermath of 9-11? The answer to this question is a definite "Yes" based on air sampling data recorded by the New York State Department of Health (NYSDOH) in October 2001 /15/, and by aerosol science researchers in October to December 2001 /4/.

The NYSDOH data include measurements of acid gases and airborne particulate concentrations above the WTC debris pile on October 31st, 2001, or *50 days after the WTC disaster*. The particulate sulfate concentration was 56.5 $\mu g/m^3$, while 58.7 $\mu g/m^3$ of $SO_2$, and 33.9 $\mu g/m^3$ of HCl were detected; these values are ~ 10 times higher than typical concentrations of these species measured at locations 1 km or more from the WTC site.

As previously noted, T.A. Cahill and co-workers collected many airborne particulate samples at a site 1.8 km NNE of the WTC rubble pile after the WTC disaster /4/. The first samples available for chemical analysis were collected 31 days after 9-11 and show that sub-micron particles, with diameters in the range 0.26 to 0.09 μm, contained ~ 30% organic matter and ~ 29% sulfuric acid with only minor, (less than 2 %), amounts of species containing Si, Cl, K, Ca and Fe.

These results are very significant since they show that sulfur-containing species were more abundant than chlorine-containing species in the gases and particulate material emanating from the WTC rubble pile even though chlorine is estimated to be at least three times more abundant than sulfur in the combustible, live load, materials in the WTC – see Section 3.0 above and ref /5/. This strongly argues in favor of the presence of large additional sources of labile sulfur in construction, (dead load), or other materials at the WTC.

## 5.0 The Sulfidation of Structural Steel in $SO_2$

In this Section we present a brief discussion of steel sulfidation in $SO_2$ in relation to the conditions prevailing in the WTC on 9-11. The corrosion of structural steels such as ASTM A36 is dominated by the chemistry of pure iron since these steels contain at least 97 % iron with only small additions of elements such as carbon, silicon and manganese. T. Flatley et al. have published an excellent review of the corrosion of iron in atmospheres containing $SO_2$ /16/. These authors note that many studies have been undertaken to investigate the corrosion of mild steel in the temperature range 300 – 1300 °C in atmospheres chosen to simulate the combustion products of fuel oil, coke oven gas or producer gas with additions of $SO_2$ up to 3 vol %. These studies show that corrosion rates, as measured by the weight of scale formed on the metal substrate, always increase when sulfur dioxide is added to a so-called 'neutral' atmosphere typically consisting of 80 % $N_2$; 10 % $CO_2$ and 10 % $H_2O$. The resulting corrosion scales contain an iron sulfide-iron oxide eutectic between the metal and the outer oxide layers.

Flatley et al. also report that iron disks, 12 mm in diameter, scale at a rate of about 0.5 $mg/cm^2/min$ in atmospheres containing 0.25 vol % $SO_2$ flowing at 100 $cm^3/min$ at 800 °C. Calculation of the rate at which $SO_2$ was being supplied to the iron show that ***all*** of the $SO_2$ was being consumed by conversion to FeS and FeO, indicating how reactive $SO_2$ is towards iron under these conditions.

## 6.0 Discussion

In this report a variety of observations and quantitative data have been presented that demonstrate the presence of unexpectedly high levels of sulfur-based gases and particulate material at the WTC during and immediately after the events of September 11th, 2001. Chemical considerations suggest that $SO_2$ is the likely precursor of volatile sulfur and the heat of reaction of WTC materials the likely liberating agent. We are therefore left with the problem of identifying the source(s) of the sulfur.

Potential sources of sulfur in the WTC buildings were reviewed in Sections 2.0 - 4.0 of this report. Based on data from the incineration of municipal solid waste it is estimated that live load materials in typical office buildings contain about 0.2 wt % sulfur. Complete release of this sulfur by combustion of host materials such as office furniture, computers, paper, etc, is estimated to lead to concentrations of $SO_2$ of no more than 400 ppm by volume. On this basis, emissions of $SO_2$ from the WTC fires should have been *less* than emissions of other gases such as HCl, $NH_3$, $NO_x$, etc. However, analysis of aerosols collected in Lower Manhattan after 9-11 shows that sulfur-based emissions were much higher than expected and indicate the presence of other sources of sulfur in the WTC besides typical live load office materials. One such source was identified in the form of sulfur-containing diesel fuel oil stored for emergency purposes in large tanks on the ground floor of WTC 7.

Sources of sulfur in dead load materials are considered in part (ii) of Section 3.0 where it is shown that the large quantities of gypsum wallboard used throughout the WTC, containing 19 wt % sulfur, represented a potentially significant source of $SO_2$ emission. This potential is realized when wallboard is exposed to sufficiently high temperatures in a reducing environment. It is proposed that carbon monoxide, CO, from incomplete combustion of hydrocarbon fuel and debris in the WTC fires, generated an environment favorable to the reaction:

$$CaSO_4 + CO \rightarrow CaO + CO_2 + SO_2,$$

thereby liberating large, (> 100 kg), quantities of $SO_2$. Literature data show that this reaction propagates rapidly at temperatures above 800 °C and in CO concentrations of at least 1 vol %.

In Section 4.0 special consideration is given to two additional sources of sulfur release at the WTC:

(i) Thermite/thermate cutter charges that *may* have been placed in WTC 1, 2 & 7. These charges have the potential to release significant (~ 40 kg) quantities of $SO_2$ from the oxidation of sulfur additives in these incendiary devices.

(ii) Reactions between molten aluminum and the $CaSO_4$ present in wallboard used throughout the WTC. These reactions could release very significant (~ 3500 kg) quantities of $SO_2$.

Table 1 presents a summary of these potential sources of $SO_2$ in the WTC buildings on 9-11. The Table shows that the most significant release of $SO_2$ from materials present in WTC 1 & 2 during 9-11 would have been from reactions involving the $CaSO_4$ present in wallboard. On the other hand, sulfur in the diesel fuel oil stored in large tanks in the lower floors appears to be the most significant source of $SO_2$ released in WTC 7.

**Table 1:** **Summary of Major Sources of $SO_2$ in WTC Buildings on 9-11**

| Source | Total $SO_2$ Released (kg) | |
|---|---|---|
| | WTC 1 & 2 | WTC 7 |
| Live Load Materials – furniture, paper, plastic | 40 | 40 |
| Dead Load Materials – gypsum wallboard | 240 | 80 |
| Diesel Fuel Oil For Emergency Power | ? | 160 |
| Termite/Thermate In “Cutter Charges” | 40 | 40 |
| Molten Aluminum Reactions with gypsum | 3500 | - |
| Automobile Fires in WTC 1 & 2 | 300 | ? |

Having identified the various sources of sulfur release in the WTC during 9-11 we need to consider one more question: Did the sulfiding observed in WTC steel occur only in the fires in the buildings or did it also occur in the rubble pile? In order to answer this question we need to consider the potential for sulfur release in these two environments:

### (i) Sulfur release in the WTC fires prior to building collapse

NIST's *Final Report* on the WTC disaster discusses the nature of the WTC fires in some detail /17/. Thus in Section 3.1.4 of NIST NCSTAR 1-5 it is noted that if the floors of the Towers were airtight there would have been sufficient oxygen for only about 2 % of the combustibles to burn and the fires would have died-out in about 2 minutes. NIST conclude that:

> "*Since the fires burned longer than this and since they thus consumed far more of the combustibles, the rate at which fresh air became available played a major role in determining the duration of the fires.*"

NIST add that, prior to the aircraft impacts, only a modest flow of additional air would have reached the office space on any given floor but, *after the impacts*, these conditions changed because hundreds of windows were broken. Nevertheless, the copious quantities of dark, sooty, smoke that rose from the Twin Towers almost immediately after the aircraft impacts show that the WTC fires were always under-ventilated and thus starved for oxygen – a condition favorable to the generation of carbon monoxide.

Although data based on direct measurement of carbon monoxide in the Twin Towers are obviously lacking it is possible to estimate approximate CO concentrations using data from building fire simulations: See for example /18, 19/. These, and similar reports, show that partially ventilated fires involving combustion temperatures of at least 700 °C typically generate about 0.1 g of CO per gram of fuel consumed. Estimates given by NIST in ref /17/ indicate that about 2000 kg of combustibles were burned per hour per WTC floor. The CO production in the WTC fires is therefore predicted to be about 200 kg per hour per floor. If we assume that the combustion gases were released into 10,000 $m^3$ of floor space, the maximum CO concentration would have been 1.6 vol %. Thus we conclude that the 1 vol % target concentration of CO required for rapid calcium sulfate reduction to $SO_2$ was theoretically possible about 40 minutes into the WTC fires.

Data on CO production in actual WTC fire simulation tests are now available in the NIST *Final Report* on the WTC disaster /20/. 2 MW fires, primed with several liters of heptane to simulate spilt jet fuel, and ignited in multiple workstation office modules, appear to provide the most realistic simulations of the WTC fires carried out to date. These tests show that temperatures over 800 °C were attained near the ceiling of the test compartment only 4 minutes after ignition and remained at, or up to 200 ° above that level for 30 minutes. Carbon monoxide production was erratic but showed peak concentrations up to 4 vol % during periods of oxygen depletion. We conclude that the conditions necessary for the reduction of calcium sulfate to $SO_2$, namely temperatures above 800 °C and CO concentrations above 1 vol %, were present at locations within the WTC fires.

### (ii) Sulfur release in the rubble pile

The condition of the vast quantities of material in the rubble pile at ground zero in the days after the attacks on the WTC remains one of the great mysteries of 9-11. There is, however, ample evidence that at least some areas of the rubble pile were still very hot or even of fire for many days after the collapse of WTC 1, 2 & 7. Thus airborne infrared thermal imaging of the rubble pile showed the presence of three major hot spots with temperatures in the range 625 – 750 °C, *five* days after 9-11 /21/. These hot spots were located along the former south wall of WTC 1, the east wall of WTC 2 and the east end of WTC 7. It would be reasonable to assume that these hot spots correspond to locations where burning debris fell, and was buried as the respective buildings collapsed. However, it has also been suggested that these hot spots were created by thermite incendiaries placed prior to, and ignited during 9-11 with the intention of destroying WTC 1, 2 & 7 /12/. We shall now examine these alternative explanations of the hot spots in relation to the production of heat in the rubble pile.

Heat was generated in the rubble pile, at least initially, in the same way it was generated in the WTC buildings just prior to their collapse, namely by combustion of building live load material. Although the jet fuel spilt in the WTC was completely burnt long before the buildings collapsed, this excellent "lighter fuel" started fires involving combustible materials such as paper, wood, textiles, plastics, furniture, etc that burnt for up to an hour within the Twin Towers. When the buildings collapsed, burning material together with a large amount of this type of "fuel" was dumped into the debris pile along with hot structural steel, aluminum, crushed concrete, gypsum wallboard, etc. This mixture then settled and smoldered like ashes in an abandoned barbeque pit.

The maximum amount of heat that such a smoldering pile of rubble could generate may be determined if the total mass of combustible material in the WTC is known. Based on typical live load data for office buildings we assume WTC 1, 2 & 7 each contained 5 kg/m$^2$ of combustible material. (See, for example, /22/) Such material is capable of releasing 20 MJ/kg of heat energy. For the combined WTC 1 & 2 office floor space of about 400,000 m$^2$ this implies a maximum theoretical heat energy release of $4.0 \times 10^{13}$ J. It may be estimated that this amount of energy, released within 1,000,000,000 kg of material with an average heat capacity of 0.5 J/g K, would raise the *average* temperature of the rubble pile by 80 °C assuming no heat losses.

As previously noted, proponents of the use of incendiary devices in a controlled demolition of WTC 1 , 2 & 7 have estimated that 4000 kg of thermite/thermate would be sufficient to bring down these buildings. However, because the heat released by the thermite reaction is 4 MJ/kg, ignition of 4000 kg of thermite/thermate releases no more than $1.6 \times 10^{10}$ J of heat energy or less than 0.1 % of the energy available from the combustion of live load material. Thus, if thermite was used in the amounts suggested, its thermal signature would be insignificant in comparison to the heat released by the combustion of available live load material. It is also important to note that 4000 kg of thermite/thermate would contribute relatively minor amounts of $SO_2$ compared to other sources of this gas in the rubble pile.

Before concluding this discussion it is worth considering claims for the presence of molten metal in the WTC rubble pile. The evidence for molten metal is entirely anecdotal; however, S. Jones in Ref /12/ suggests that the "pools of molten metal" observed within the rubble pile are in fact molten iron or steel produced by the thermite/thermate incendiary devices supposedly used in a controlled demolition of WTC 1, 2 & 7. In support of Jones' hypothesis it is readily calculated that the $1.6 \times 10^{10}$ J of heat energy released by the ignition of 4000 kg of thermite/thermate would be capable of melting about 6,000 kg of structural steel which would then be at a temperature of 1539 °C. And we can readily agree that complete combustion of all carbon-based materials in the WTC buildings, including jet fuel, diesel oil, wood, plastics and fabrics would be incapable of generating such temperatures. Nonetheless, there are a number of reasons not to accept Jones' "thermite" theory.

First, and most importantly, the thermal imaging data noted above and discussed in Ref /21/ shows that five days after 9-11 the *maximum* near-surface temperature in the rubble pile was *less than 800 °C*. Since the original WTC fires were mainly in the upper floors of these buildings, the hottest regions of the freshly-formed rubble pile would have been near the top. This observation alone precludes the presence of molten steel in the WTC rubble pile at the time of the reported sightings of "pools of molten metal". Thus we must seek alternative explanations for the nature of these hot spots. One possibility would be that the molten metal was in fact aluminum, which melts at 660 °C, and was reported to be produced by the action of the jet fuel fires on the airframes lodged in WTC 1 & 2 /13/. Moreover, molten aluminum is very reactive and would undergo exothermic reactions with many materials it would contact. However, we believe there is another explanation for the presence of "molten pools" in the WTC rubble pile in the days after 9-11, as we shall now explain.

It has been well documented that the combustion of materials (such as coal) that naturally contain small amounts of sulfur, chlorine, sodium and potassium salts and/or calcium-alumino-silicates, leads to the formation of low viscosity melts or *slags*. These slags, which form in various regions of the combustion train, have melting points as low as 400 °C *and are known to be extremely corrosive to steel surfaces* - see Refs /23 – 26/.

Waste incinerators and fossil-fuelled boilers frequently exhibit severe corrosion of their low alloy steel heat exchangers from exposure to molten slag. Affected surfaces, upon cooling, are covered with thick, enamel-like, layers of adherent material formed by deposition of molten fly ash. These sulfur and chlorine-rich deposits tend to form fluxes with the protective iron oxide scale that cause accelerated wastage of the base metal. Studies have shown that the tendency to form deposits *increases* under reducing conditions when CO (carbon monoxide) is present. Under these circumstances deposition rates as high as 1g of deposit per kilogram of fuel are possible. We therefore suggest that some areas of the WTC rubble pile were exposed to conditions comparable to those in a furnace chimney where hot combustion gases rich in CO, carrying particles of alkali sulfates, impinged on steel surfaces. This led to the formation of hot (up to 800 °C) corrosive slags that initiated exothermic reactions with steel and other surfaces, thereby sustaining the slag's molten state. These slags could subsequently flow like volcanic lava in the debris pile and collect in pools. Such pools could easily be mistaken for molten metal.

We finally note that, under reducing conditions, sulfur may be converted to hydrogen sulfide, $H_2S$, which is more corrosive to steel than $SO_2$. Thus we see that there were many mechanisms for the mobilization of sulfur at the WTC during 9-11 including formation of gaseous $SO_2$ and $H_2S$ as well as molten sulfates. These sulfur-containing species are reactive towards iron at temperatures as low as 400 °C thus making it inevitable that sulfiding of structural steel, although initiated *prior to* the collapse of the WTC buildings, continued in the hot rubble pile for many days after 9-11.

## 6.0 Conclusion and Recommendations

In this report it is shown that sulfur, especially in its most common oxidized form, $SO_2$, had many potential emission sources in the WTC prior to 9-11. These sources have been quantified and rated according to their potential to release $SO_2$ under conditions prevailing in buildings 1, 2 & 7 during and after 9-11.

It is concluded that sulfur emissions from the combustion of typical live load materials such as furniture, paper, plastics, textiles, etc, were relatively small compared to sulfur emissions from more unconventional sources, including those involving diesel fuel for emergency power generation in WTC 7 and $CaSO_4$ in gypsum wallboard used in WTC 1 & 2. Sulfur emissions from thermite/thermate are shown to be quite small compared to these sources.

By way of verifying these conclusions it is suggested that the NIST fire tests, which were conducted on simple office module simulations, should be repeated using more realistic environments that include shredded aluminum alloy 2024, crushed concrete and gypsum, water, rusted steel, aviation fuel, plastics, etc. In this way better estimates of the rates of production of $SO_2$ and the degree of sulfidation of steel could be established.

F. R. Greening
February 26th, 2006
Greening@sympatico.ca

(This version, which includes a corrected reference on page 1, was issued May 15th, 2006.)

## References

1. "*World Trade Center Building Performance Study*." FEMA Report 403, May 2002.
2. "*Final Report on the Federal Building and Fire Safety Investigation of the World Trade Center Disaster. – Damage and Failure Modes of Structural Steel Components*." NIST NCSTAR 1-3C, 2005.
3. "*Progress Report on the Federal Building and Fire Safety Investigation of the World Trade Center Disaster.*" Appendix J, NIST Special Publication 1000-5, June 2004.
4. T. A. Cahill et al. "*Analysis of Aerosols from the World Trade Center Collapse Site, New York, October 2 to October 30, 2001.*" Aerosol Science and Technology 38, 165, (2004)
5. "*Municipal Solid Waste in the United States: Facts and Figures.*" USEPA Report No. EPA530-R-03011, (2003).
6. D. O. Albina et al. "*Effects of Feed Composition on Boiler Corrosion in Waste-to-Energy Plants.*" 12th North American Waste to Energy Conference (NAWTEC 12), 2004.
7. W. Q. Hull et al. "*Sulfuric Acid from Anhydrite.*" Industrial and Engineering Chemistry, 49(8), 1204 (1957).
8. T.D. Wheelock et al. "*Reductive Decomposition of Gypsum by Carbon Monoxide.*" Industrial and Engineering Chemistry 52(3), 215, (1960).
9. A. Lyngfelt et al. "*Model of Sulfur Capture in Fluidised-Bed Boilers Under Conditions Changing Between Oxidizing and Reducing*." Chemical Engineering Science 48(6), 1131, (1993).
10. R. Kuusik et al. "*Thermal Decomposition of Calcium Sulfate in Carbon Monoxide.*" Journal of Thermal Analysis 30, 187, (1985).
11. A. Lyngfelt et al. "*Sulfur Capture in Fluidized Bed Boilers: the Effect of Reductive Decomposition of* $CaSO_4$." Chemical Engineering Journal 40,59, (1989).
12. S. Jones. "*Why Indeed did the WTC Buildings Collapse?*" Report available at www.scholarsfor911truth.org, posted January 2006.
13. F.R. Greening. "*Aluminum and the World Trade Center Disaster.*" Report available at www.911Myths.com, posted January 2006.
14. W. A. Manning (Ed). "*The World Trade Center Bombing: Report and Analysis.*" FEMA Report TR-076, 1993.
15. "*Report on Air Sampling Near the World Trade Center Site.*" New York State Department of Health, October 30th and 31st, 2001.
16. T. Flatley et al. "*Oxidation of Iron in Atmospheres Containing Sulfur Dioxide.*" Journal of the Iron and Steel Institute 209, 523, (1971).
17. "*Final Report on the Federal Building and Fire Safety Investigation of the World Trade Center Disaster. - Reconstruction of the Fires in the World Trade Center*." NIST NCSTAR 1-5, 2005.
18. W.M. Pitts "*Algorithm for Estimating Carbon Monoxide Formation in Enclosed Fires.*" Proceedings of the 5th International Symposium on Fire Safety Science, pages 535-546, 1997.
19. B.Y. Lattimer et al. "*Transport of High Concentrations of Carbon Monoxide to Locations Remote the Burning Compartment.*" NIST Report No. GCR 97-713, April 1997.
20. "*Final Report on the Federal Building and Fire Safety Investigation of the World Trade Center Disaster. – Experiments and Modeling of Multiple Workstations Burning in a Compartment.*" NIST NCSTAR 1-5E, 2005.
21. R. N. Clark "*Images of the World Trade Center Site Show Thermal Hot Spots on September 16th and 23rd, 2001.*" USGS OFR 01-0429, 2001.
22. "*Final Report on the Federal Building and Fire Safety Investigation of the World Trade Center Disaster. – Building Interiors and Combustibles*." Chapter 3, NIST NCSTAR 1-5, 2005.
23. K. Natesan et al. "*Fireside Corrosion of Alloys for Combustion Power Plants.*" U.S. D.O.E Report Under Contract W-31-109-Eng-38. 2001.
24. A. Karlsson et al. "*Iron and Steel Corrosion in a System of* $O_2$, $SO_2$ *and Alkali Chloride. The Formation of Low Melting Point Salt Mixtures.*" Corrosion Science 30, 153, (1990).
25. H. J. Grabke et al. "*The effects of Chlorides, Hydrogen Chloride, and Sulfur Dioxide in the Oxidation of Steels Below Deposits.*" Corrosion Science 37, 1023, (1995).
26. D. A. Shifler. "*High-Temperature Gaseous Corrosion Testing.*" ASM Handbook Vol 13A: Corrosion Fundamentals, Testing and Protection, pp 657 – 678, ASM International, 2003.