# Health Consultation

Review of 2002 Accidental Catalyst Release

WYOMING REFINERY COMPANY

NEWCASTLE, WESTON COUNTY, WYOMING

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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Agency for Toxic Substances and Disease Registry
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## Health Consultation: A Note of Explanation

An ATSDR health consultation is a verbal or written response from ATSDR to a specific request for information about health risks related to a specific site, a chemical release, or the presence of hazardous material. In order to prevent or mitigate exposures, a consultation may lead to specific actions, such as restricting use of or replacing water supplies; intensifying environmental sampling; restricting site access; or removing the contaminated material.

In addition, consultations may recommend additional public health actions, such as conducting health surveillance activities to evaluate exposure or trends in adverse health outcomes; conducting biological indicators of exposure studies to assess exposure; and providing health education for health care providers and community members. This concludes the health consultation process for this site, unless additional information is obtained by ATSDR which, in the Agency's opinion, indicates a need to revise or append the conclusions previously issued.

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# HEALTH CONSULTATION

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## NEWCASTLE, WESTON COUNTY, WYOMING

Prepared by:

U.S. Department of Health and Human Services
Agency for Toxic Substances and Disease Registry
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## 1.0 Summary

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| **INTRODUCTION** | The Agency for Toxic Substances and Disease Registry's (ATSDR's) purpose is to serve the public by using the best science, taking responsive public health actions, and providing trusted health information to prevent people from coming into contact with harmful toxic substances. |
| **CONCLUSION** | ATSDR concludes that breathing vanadium pentoxide in the outdoor air for the majority of the 6-hour Wyoming Refinery Company (WRC) accidental catalyst release in 2002 is not expected to harm people's health. However, ATSDR finds that respiratory effects (e.g., coughing, wheezing) are plausible for residents who were downwind and outside during the 10:35 pm to 11:00 pm time-frame. |
| **BASIS FOR DECISION** | In April 2004, the U.S. Environmental Protection Agency (EPA) requested that ATSDR conduct a review of data related to a March 24, 2002, accidental catalyst release to the air at the WRC facility in Newcastle, Wyoming.<br><br>No air samples were collected during this non-routine release at WRC. ATSDR completed a modeling analysis and toxicological evaluation to address the exposure concerns related to the catalyst release.<br><br>1. Given that time of the release (10:00 pm to 4:00 am) occurred when most people were likely not outside, that the modeled estimates for the majority of the 6-hour event were below lowest adverse health effect levels and healthy worker exposure levels, and that ATSDR's assumptions likely resulted in overstating the potential exposure concentrations, ATSDR does not believe the catalyst release to have dispersed vanadium concentrations that would cause an adverse impact to a healthy person.<br>2. However, ATSDR finds that respiratory effects (e.g., coughing, wheezing) are plausible for residents who were downwind and outside during the 10:35 pm to 11:00 pm time-frame of the catalyst release. These respiratory effects are expected to be short-lived and reversible. ATSDR recognizes that if people with respiratory illness (such as asthma and chronic bronchitis) were outside during the event, they would have been more likely to experience a reversible health effect such as coughing and wheezing. |

| | |
|---|---|
| **NEXT STEPS** | ATSDR determined no further public health actions are needed with regard to the 2002 catalyst release. |
| **FOR MORE INFORMATION** | You can call ATSDR at 1-800-CDC-INFO and ask for information on the Wyoming Refiner Company site. |

## 2.0 Statement of Issues

In April 2004, EPA requested ATSDR evaluate the possibility of whether the community's inhalation exposure to vanadium pentoxide from a 2002 WRC catalyst release may have contributed to or may have induced adverse health effects such as asthma, chronic bronchitis and lung fibrosis. EPA noted the catalyst contained magnesium and zinc too [EPA 2004a]. EPA and ATSDR chose to focus on vanadium pentoxide exposures because of the higher concentration of vanadium in the catalyst sample and vanadium pentoxide's toxicity characteristics compared to the other catalyst constituents.

In June 2004, ATSDR completed its preliminary evaluation, but the results were inconclusive. However, the agency indicated it would conduct a follow-up review of the available information. In 2006, ATSDR completed the follow-up review of available information and proposed air modeling. In 2010, ATSDR completed a modeling analysis and toxicological evaluation to address the exposure concerns related to the catalyst release. See Appendix A, Table 1, for additional information about ATSDR's activities related to this site.

In this health consultation, ATSDR

1. reviews information known about the catalyst release,
2. discusses the quality of the emissions data that are available for the modeling analysis,
3. presents the air dispersion modeling analysis parameters and the modeling results, and
4. evaluates whether exposure to the catalyst containing vanadium might have caused respiratory effects in the exposed population.

## 3.0 Background

WRC's Newcastle facility is located in the western portion of Newcastle, Wyoming. Former names of this facility include Gray Oil Company, Sioux Oil Company, and Tesoro Crude Oil Company. The WRC facility spans approximately 46 acres and consists of a refinery production and processing area, evaporation ponds, storage tanks, boilers, heaters, and other unit operations typically found at petroleum refineries. Online aerial photographs of Newcastle indicate that residential areas are located along the northwestern, northern, northeastern, and southeastern boundaries of the facility. Most residential areas of Newcastle are located within ½-mile of the WRC facility boundary.

The refinery previously produced a range of products from locally derived crude oil, but currently specializes in the production of "light-end" or "middle" products, such as butane, propane, diesel fuel, JP-4 jet fuel, gasoline, and fuel oil [WDEQ 2006]. As of January 1, 2008, the WRC Newcastle facility had a crude distillation capacity of 14,000 barrels per calendar day, making this one of the smaller refineries in the United States

[DOE 2008]. This crude distillation capacity represents less than 0.08 percent of the total U.S. crude distillation capacity.

The 2002 accidental release that is the focus of this evaluation occurred at WRC's "Stack S-21," through which emissions from the facility's fluidized catalytic cracking unit are vented. Accordingly, the rest of this section focuses on fluidized catalytic cracking operations, even though WRC has an additional process for refining crude oil.

"Catalytic cracking" is a general term for petroleum refining processes that use a solid catalyst to break down large hydrocarbons found in crude oil into smaller hydrocarbons desired for various petroleum products. The catalysts are most commonly aluminum oxide and silicon dioxide, but may also be made of other materials and contain various impurities.

"Fluidized catalytic cracking" (FCC) is a term used to describe a catalytic cracking operation in which the crude oil is cracked in the presence of very fine catalyst particles that, when aerated, essentially act as a fluid [EPA 1995]. Most refineries that employ FCC technology have multiple integrated unit operations, such as the FCC operation that brings together the crude oil (or other feed) with the catalyst, a fractionation operation that separates the cracked products, and a catalyst regeneration step that reactivates spent catalyst before returning it to the process. Overall, the main input to this process is crude oil, and the main outputs are the fractionated products. Air emissions can include particulate matter, sulfur dioxide, carbon monoxide, hydrocarbons, nitrogen oxides, ammonia, and other chemicals [EPA 1995]. Catalyst added to the system is constantly regenerated, though fresh catalyst must be added periodically.

Because the FCC operation is essentially a closed system, air emissions of (and potential exposures to) the catalyst are typically limited. However, catalyst can be emitted during process upsets and other accidental release scenarios. In these cases, air emissions will not only include the catalyst, but also will include chemicals found in the crude oil and cracking products. Such a release from the WRC facility is the focus of this evaluation. This release occurred following a 16-hour shutdown of the FCC unit in March 2002 and apparently resulted from a malfunctioning valve [News Letter Journal 2002a].

## 4.0 Discussion

When evaluating potential air exposures, ATSDR generally prefers to assess exposures using direct measurements of exposure concentrations. In cases where air sampling data are not available, ATSDR will sometimes use air dispersion models to assess potential inhalation exposures to air contaminants. Because no air samples were collected during the 2002 accidental catalyst release at WRC (as is often the case for non-routine release scenarios), ATSDR proposed air dispersion modeling to estimate the level vanadium pentoxide from the catalyst released in the air. The modeled estimate could then be used to evaluate whether exposure to vanadium pentoxide might have caused respiratory effects that the exposed population is concerned about.

In this section, ATSDR first discusses the quality of the emissions data that are available for the modeling analysis, such as the potential breakdown products of the catalyst (i.e., what could have been emitted during the accident). ATSDR then discusses the air dispersion modeling analysis parameters and the modeling results. Following this, the toxicological properties of vanadium oxides are described and the likelihood of potential harmful effects resulting from exposures are evaluated.

### *4.1 2002 Catalyst Release*

To determine the quality of the emissions data that are available for the modeling analysis, numerous information sources were reviewed regarding the 2002 catalyst release. These sources included information originally compiled by EPA and WRC such as the soil sampling results taken after the accidental release, Material Safety and Data Sheets (MSDS) for the spent catalyst, and documentation of communications between EPA and WRC. Other sources of information included EPA's compilation of Air Pollution Emission Factors (commonly referred to as AP-42) for information on emissions from FCC units and searches of the scientific literature (e.g., *Oil and Gas Journal*) for information pertaining to FCC operations and catalyst composition. The following text summarizes the information reviewed. Appendix B provides additional information.

- **Total catalyst released.** Estimates of the total amount of catalyst released to the air range from 8 tons to 33 tons. Because none of the documentation provided information on how these estimates were calculated, the accuracy of these estimates cannot be evaluated. The most current estimate, which is also the largest estimate, indicates that 33 tons (or 65,975 pounds) of spent catalyst were released between 10:00 pm on March 24, 2002, and 4:00 am on March 25, 2002. Table 2, Appendix B, provides the time-resolved catalyst emission rates for the 33-ton estimate. As a conservative measure, ATSDR chose to use these time-resolved catalyst emission rates in its evaluation.

- **Percent of vanadium in the catalyst release.** No direct measurements are available to quantify the vanadium content of the spent catalyst that WRC emitted into the air in March 2002. However, insights into the potential vanadium quantity can be gleaned from other sources such as MSDS for the spent catalyst and spent catalyst samples analyzed following the accidental release. For the spent catalyst, a 1998 W.R. Grace MSDS reported a range of 0.004% to 0.75% vanadium by weight, and a 2002 WRC MSDS documents a vanadium concentration of <0.1% by weight [WR Grace 1998, WRC 2002]. EPA contractors analyzed eight surface soil samples, two spent catalyst samples from locations where dusts from the event reportedly settled, and one spent catalyst sample submitted by WRC. Of all the EPA analyses, the sample submitted by WRC had the greatest concentration. Therefore, ATSDR considers the analysis of the spent catalyst sample provided by WRC following the release event (0.14% vanadium) the best estimate of the actual vanadium content of the catalyst released in March 2002. Appendix B provides further information. This estimate (0.14% vanadium), combined with the best estimate of total catalyst released (65,975 pounds), suggests that the March 2002 event released 92 pounds of vanadium into the air. ATSDR's modeling is based on the time-resolved estimated emission rates multiplied by the assumed vanadium composition of 0.14% (see Table 5, Appendix C).

- **Chemical speciation of vanadium in the catalyst release.** Vanadium is known to exist in multiple oxidation states (-2 to +5), which may be of significance for the WRC event because vanadium toxicity varies with oxidation state. However, no measurements are available characterizing the chemical speciation of vanadium in air emissions from WRC and ATSDR found no information quantifying emissions of different vanadium species from comparable FCC units at other petroleum refineries. Review articles suggest that the oxidation state most commonly encountered in ambient air is pentavalent vanadium (+5 oxidation state or vanadium pentoxide). Appendix B provides further information. Given that these literature reviews suggest that vanadium emitted into the atmosphere is typically in the pentavalent form and that the pentavalent form is more toxic, ATSDR assumed the vanadium in the emissions is 100% vanadium pentoxide in its modeling analyses for this site.
- **Particle size distribution of emissions.** No measurements quantified the particle size distribution of emissions during the March 2002 event. WRC data may not be representative of the non-routine operating conditions during the accidental release. As a result, any estimate of the particle size distribution for this particular event is highly uncertain. Therefore, the modeling analysis of the WRC event assumed that 100% of the vanadium emitted to the air was in the respirable form.

## *4.2 Air Dispersion Modeling Analysis*

Air modeling analyses can be classified into two very general categories: screening evaluations and refined evaluations. A screening modeling evaluation is typically based on relatively simple models and is used to gain initial insights on potential levels of air contamination resulting from a single source of air emissions. Refined evaluations use much more sophisticated models and are therefore far more resource intensive.

### 4.2.1 Model Selection

In this section, ATSDR provides a brief summary of air modeling conducted by EPA. Then, ATSDR provides the basis for its air dispersion modeling analysis.

- **EPA's Modeling Effort.** It is important for ATSDR to be aware of the critical assumptions and input parameters used in EPA's previous work so that differences between model outputs can be adequately explained. EPA's previous work was based on a "box model," which assumes that a given quantity of emissions instantly disperses in a fixed volume of ambient air. This model is essentially a calculation: the estimated emissions (in pounds) are divided by the volume of air (in cubic feet), followed by some unit conversions to arrive at an estimated ambient air concentration (in micrograms per cubic meter ($\mu g/m^3$)). EPA assumed that 20 tons (40,000 pounds) of dry catalyst were emitted during the release event. EPA also assumed that the catalyst contained 0.08% vanadium. Based on these assumptions, the mass estimate of vanadium in the plume was 14,600 grams of vanadium released. EPA next assumed the following dimensions for its box: lateral dimensions were 8,000 feet by 8,000 feet, and the vertical dimension was 400 feet. Using these parameters, EPA estimated the air concentration of vanadium in the catalyst plume was 20 µg/$m^3$.

- **ATSDR's Modeling Effort:** ATSDR considered multiple air dispersion models, including AERMOD and SCREEN3. After careful evaluation of the available data, ATSDR chose SCREEN3 to model the 2002 accidental catalyst release because this model:
    1. provides a more realistic depiction of actual dispersion characteristics than a box model,
    2. provides a meaningful and health-protective assessment of plume dispersion without the need for more refined modeling,
    3. is a screening model that EPA has recommended for use in evaluating air quality impacts from stationary sources in simple terrain [EPA 1992, EPA 1995, EPA 2005], and
    4. is capable of estimating worst-case air quality impacts for this site.

### 4.2.2 Model Parameters

When running SCREEN3, modelers must make several assumptions and assign values to key input parameters. Tables 4 and 5, Appendix C, list the key decisions that were made when running the model. Generally, ATSDR relied on information in the site files when specifying model inputs. However, in cases where important parameters did not have reliable data (e.g., the chemical composition of vanadium, the particle size distribution of emissions), ATSDR assumed values that would likely overstate ambient air concentrations, as is standard for screening analyses.

ATSDR ran the model using "rural" dispersion coefficients (which tend to predict higher air quality impacts than "urban" coefficients) and simple terrain, both of which are reasonable assumptions given the land use in the immediate vicinity of the WRC facility.

First, ATSDR ran SCREEN3 using the "full meteorology" option. In this option, the model examines potential vanadium concentrations associated with 54 different combinations of meteorological conditions. The model assumes that winds constantly blow in one direction and then predicts air quality impacts at fixed distances from the emission source. The model determines the worst-case meteorological scenario, which typically involves unstable atmospheres and calm winds (i.e., winds equal to 1.0 meter/second (m/s), or 2.2 miles/hour).

Second, because the release occurred during the night when atmospheric stability is typically either neutral or stable, ATSDR performed additional model runs to account for different atmospheric variations and to further characterize the potential concentrations of vanadium. ATSDR ran SCREEN3 for all 54 possible combinations of the model's stability classes and wind speeds. Table 6, Appendix C, shows the results for each of the model runs. Overall, this table describes the different combinations of atmospheric stability and wind speed, the predicted the maximum ground-level concentrations for each of the time-resolved emission rates, and the distances from the stack base where the concentrations were found to occur.

### 4.2.3 Model Results

Based on the assumptions and input parameters described in the previous sections and listed in Tables 4 and 5, the SCREEN3 modeling analysis predicted a maximum ground-level vanadium pentoxide concentration of 79 $\mu g/m^3$ for the WRC event. According to the model, this concentration was predicted to occur 773 meters (approximately ½ mile) from the base of the stack that released the spent catalyst. This maximum concentration was predicted for the highest emission rate of 13.2 grams per second (g/s) and for a class A atmosphere (highly unstable) with wind speeds of 1.0 m/s (or 2.2 miles/hour).

Table 6, Appendix C, summarizes the complete data set of model runs. For the highest emission rate (13.2 g/s) that occurred for about 25 minutes of the 6-hour event, the estimated ambient air vanadium pentoxide concentrations for the 54 modeling simulations ranged from 12 $\mu g/m^3$ (which was predicted to occur during a class D (neutral) atmosphere with wind speeds of 1.0 m/s) to 79 $\mu g/m^3$ (which was predicted to occur during a class A (highly unstable) atmosphere with wind speeds of 1.0 m/s). For the lowest emission rate (0.6 g/s) that occurred for about 4 hours of the 6-hour event, the estimated ambient air vanadium pentoxide concentrations for the 54 modeling simulations ranged from 0.5 $\mu g/m^3$ to 4 $\mu g/m^3$.

For reference, meteorological data collected in Gillette, Wyoming (approximately 75 miles from Newcastle) indicate that winds were blowing at approximately 10 miles per hour (or 4.5 m/s) during the time of the WRC release event. The estimated ambient air vanadium pentoxide concentrations for this particular wind speed range from 0.8 $\mu g/m^3$ to 51 $\mu g/m^3$, depending on the atmospheric stability and emission rate.

The maximum vanadium pentoxide concentration output by the model (79 $\mu g/m^3$) is an upper-bound estimate of the highest offsite vanadium concentration, based on the highest estimated emission rate during the 6-hour event. At other times during the 6-hour event, off-site concentrations at this location would be expected to be lower than this value. This vanadium concentration (79 $\mu g/m^3$) was predicted to occur at the offsite location where air quality impacts were expected to be greatest. Average concentrations at all other offsite locations would also be expected to be lower.

### 4.2.4 Uncertainties

ATSDR's analysis presents a reasonable upper-bound estimate of exposure concentrations during the WRC release event. The modeling analysis was based on multiple assumptions that likely overstated potential exposures. The following text presents these uncertainties.

- Given the magnitude of wind speeds during the WRC event (i.e., approximately 10 miles/hour), airborne vanadium likely dispersed rapidly after the emissions at WRC were brought under control.
- The SCREEN3 model does not account for wind direction. Rather, the model assumes that winds blow exclusively in the direction from the source to the downwind receptor of interest. For longer duration exposure events, this particular feature can cause the model to overstate ambient air concentrations,

given that wind directions are known to fluctuate over time. However, the extent to which the model overstates concentrations for acute exposure durations is limited, given the possibility (or perhaps the likelihood) that winds may blow in a single direction over short time frames, like the 6-hour duration of the WRC event.

- SCREEN3 does not account for particle deposition. As a result, emissions are assumed to remain airborne, which will cause the model to overstate actual ambient air concentrations that may have occurred.
- In the model, ATSDR assumed that 100% of the emitted vanadium was in the respirable form. Exposure concentrations would be proportionally lower if one were to assume a certain fraction of emissions were particles larger than the respirable range. Limited information provided by WRC suggests that a large portion of the vanadium emitted might not have been respirable, but this information is poorly documented and may not be representative of the non-routine operating conditions during the accidental release.
- ATSDR assumed the analysis of the spent catalyst sample provided by WRC following the release event (0.14% vanadium) offers the best estimate of the actual vanadium content of the catalyst. EPA's modeling was based on the assumption that vanadium accounts for 0.08% of the catalyst that was released into the air. After reviewing additional information on spent catalyst properties, including sampling data for spent catalyst and the material that deposited in Newcastle, ATSDR decided to use a 0.14% vanadium composition. This composition (0.14%) is the upper bound of all direct measurements of catalyst conducted in Newcastle in the weeks following the release event.
- ATSDR assumed the vanadium composition was 100% vanadium pentoxide. Although the exact chemical composition of vanadium compounds released during the WRC event is not known, is likely not 100% vanadium pentoxide.
- The estimated upper-bound exposure concentration (79 $\mu g/m^3$) would be expected to occur roughly around 10:35 pm to 11:00 pm, near the time of the peak emissions from the WRC release event. Ambient air concentrations likely rapidly declined after the emissions ceased. Accordingly, only those people who were outdoors during this time frame would have been exposed to the peak concentrations.
- Because the release event occurred during the middle of a cold early spring night (25$^{o}$ F), most residents were likely indoors with their windows closed. Accordingly, infiltration of emissions to indoor environments was likely to be minimal during the time that catalyst was released. This document does not attempt to quantify the indoor air concentrations that may have occurred.

### 4.3 Vanadium Toxicity and Health Evaluation

This section briefly summarizes and highlights the literature review that ATSDR conducted, as well as provides ATSDR's public health evaluation of the modeled results.

#### 4.3.1 Vanadium Toxicity

Of note, this review of vanadium toxicity focuses on studies of inhalation exposure to vanadium compounds and identifies studies that might characterize the relative toxicity (via inhalation exposure) for individual vanadium compounds. Given the nature of this particular release and the fact that the chemical form of the vanadium emissions is not known, ATSDR focused on identifying and evaluating studies that evaluated the health implications of acute inhalation exposure to various vanadium compounds, and this review was not limited to any single vanadium compound. Accordingly, this section does not present detailed information on exposures via non-inhalation routes and inhalation exposures of chronic duration.

ATSDR examined four reviews of vanadium toxicity:

1. EPA's health assessment for vanadium pentoxide posted to the agency's web site for the Integrated Risk Information System (IRIS) [EPA 1988].
2. The World Health Organization's (WHO) most recent Chemical Assessment Document for vanadium pentoxide and other inorganic vanadium compounds [WHO 2001].
3. ATSDR's Toxicological Profile for Vanadium and Compounds (draft for public comment) [ATSDR 2009].
4. The International Agency for Research on Cancer's (IARC) 2006 monograph on the carcinogenicity of metal compounds, which includes non-cancer toxicity data presented on vanadium pentoxide.

The following statements are consistent with the information that ATSDR gathered and reviewed when developing this toxicity section (see Appendix D for further information):

- Vanadium toxicity varies with exposure dose, duration, and route.

- Vanadium can be present in several oxidation states and hundreds of chemical forms. Limited information on relative toxicity suggests that vanadium toxicity increases with oxidation state (i.e., pentavalent compounds are more toxic than tetravalent compounds) and that vanadium pentoxide is the most toxic of the vanadium compounds that have been studied to date. However, no experimental studies were identified that systematically studied the relative inhalation toxicity of a broad range of vanadium compounds.

- Multiple review articles identify respiratory effects as the endpoint of greatest concern following inhalation of vanadium compounds. However, effects to other organs (e.g., ocular, discoloration of the tongue) have been identified in humans exposed to extremely high levels of vanadium compounds.

- Several occupational exposure studies and a controlled (experimental) exposure study among healthy volunteers reported various respiratory effects (e.g., coughing, wheezing, bronchitis) following acute inhalation exposure to various vanadium compounds. The reported effects were short-lived and reversible. ATSDR's Toxicological Profile reports a no-observed-adverse-effect-level (NOAEL) and lowest-observed-adverse-effect-level (LOAEL) of 100 µg vanadium/$m^3$ and 600 µg vanadium/$m^3$, respectively, from the controlled exposure study [ATSDR 2009, Zenz and Berg 1967]. In this study, a productive cough without any subjective complaints, alterations in lung function, or impact on daily activities were observed in five subjects exposed to vanadium pentoxide dust at 100 µg vanadium/$m^3$. For the same study, a persistent cough lasting for 8 days developed in two subjects exposed to vanadium pentoxide dust at 600 µg vanadium/$m^3$.

- ATSDR's acute inhalation minimal risk level (MRL) for vanadium is 0.8 µg/$m^3$. This acute MRL is based on a study where groups of 40–60 female rats were exposed to varying amounts of vanadium pentoxide 6 hours/day, 5 days/week for 16 days [NTP 2002]. The endpoint for the MRL derivation was an increase in the incidence of lung inflammation in rats exposed to 560 µg vanadium/$m^3$ as vanadium pentoxide for 13 days. The human equivalent concentration (HEC) for this LOAEL is 73 µg vanadium/$m^3$.

- For reference, the following list identifies other regulations, permissible exposure levels, or advisories pertaining to inhalation exposure to vanadium in the workplace. Note that the estimated exposure level for the release event (79 µg/$m^3$) was the upper bound estimate for a 25-minute exposure and some of the levels that follow are for longer exposure durations.

  - WHO air quality guideline = 1 µg/$m^3$ (vanadium): According to WHO, it is believed that below 1 µg/$m^3$ (averaging time 24 hours) environmental exposure to vanadium is not likely to have adverse effects on health.
  - National Institute for Occupational Safety and Health's (NIOSH) recommended exposure limit (REL) ceiling value = 50 µg vanadium/$m^3$: RELs are exposure limits recommended by NIOSH for workers. NIOSH recommends a ceiling value REL (15 minute) not be exceeded at any time during the workday.
  - Occupational Safety and Health Administration's (OSHA) permissible exposure limit (PEL) ceiling value = 500 µg/$m^3$ (vanadium pentoxide): PELs are the maximum concentration of a chemical that a worker may be exposed to under OSHA regulations. According to OSHA, at no time during the workday should a ceiling value be exceeded.
  - American Conference of Governmental Industrial Hygienist's (ACGIH) threshold limit value (TLV) = 50 µg/$m^3$ (vanadium pentoxide): TLVs are time-weighted average concentrations for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

- Immediately Dangerous to Life or Health (IDLH) concentration = 35,000 μg/m$^3$ (vanadium): IDLH is defined as an atmosphere that poses an immediate threat to life, would cause irreversible adverse health effects, or would impair an individual's ability to escape from a dangerous atmosphere.

### 4.3.2 Health Evaluation

The SCREEN3 model indicates that estimated ambient air concentrations of vanadium pentoxide for the 10:35 pm to 11:00 pm time-frame during the WRC release event likely ranged from 12–79 μg/m$^3$. These values exceeded ATSDR's acute MRL of 0.8 μg/m$^3$, and the highest estimated value is comparable to the LOAEL (73 μg/m$^3$) for vanadium pentoxide on which the MRL was based. This estimated range was below the NOAEL and LOAEL (100 μg/m$^3$ and 600 μg/m$^3$, respectively), established for the controlled exposure study among healthy volunteers. The upper bound exposure estimate (79 μg/m$^3$) approaches the NOAEL (100 μg/m$^3$) from the controlled human exposure study and is comparable to the LOAEL-HEC (73 μg/m$^3$) from the animal study that the MRL is based on.  Therefore, ATSDR finds that respiratory effects (e.g., coughing, wheezing) are plausible for residents who were downwind and outside during the 10:35 pm to 11:00 pm time-frame of the catalyst release. These respiratory effects are expected to be short-lived and reversible.

The highest estimated vanadium pentoxide concentration (79 μg/m$^3$) was predicted for about a ½ hour of the 6-hour event. For the remaining 5 ½ hours of the 6-hour event when the emission rate was lower, the estimated vanadium pentoxide concentrations ranged from 0.5–16.2 μg/m$^3$ (see Table 6, Appendix C). These values exceeded ATSDR's MRL of 0.8 μg/m$^3$, but were lower than the LOAEL-HEC (73 μg/m$^3$) from the animal study that the MRL is based on and the NOAEL and LOAEL (100 μg/m$^3$ and 600 μg/m$^3$, respectively) established for the controlled exposure study among healthy volunteers. All modeled estimates were also below healthy worker exposure levels (NIOSH, OSHA and ACGIH). Therefore, for the majority of the release event, ATSDR finds that breathing vanadium pentoxide in the outdoor air is not expected to harm people's health. However, ATSDR does recognize that if people with respiratory illness (such as asthma and chronic bronchitis) were outside during the event, they would have been more likely to experience a reversible health effect such as coughing and wheezing. Of note, this evaluation focuses on vanadium pentoxide exposures; ATSDR acknowledges that the air emissions during the accidental release will not only include vanadium pentoxide, but also will include other chemicals.

Of note, ATSDR's assumptions likely resulted in overstating the potential vanadium pentoxide exposure concentrations, such as assumptions related to

- the particle size of vanadium—likelihood that a certain fraction of emissions were particles larger than the respirable range,
- the vanadium oxidative state—likelihood that there were multiple oxidative states of vanadium in the plume, and
- particle deposition—likelihood that emissions did not all remain airborne.

## 5.0 Child Health Considerations

ATSDR recognizes the unique vulnerabilities of children from exposure to hazardous substances in their environment. Children are at greater risk than are adults from certain kinds of exposures to hazardous substances because they often have greater exposure than do adults. Children also are more active and have higher heart and respiratory rates, causing them to have higher peak and mean exposures. If toxic exposure levels are high enough during critical growth stages, the developing body systems of children can sustain permanent damage. Children are also smaller than adults, resulting in higher doses of chemical exposure per body weight. Most important, children depend completely on adults for risk identification and management decisions, housing decisions, and access to medical care. Based on the site specific scenario, exposure to children during the release is likely to be minimal because children would probably not be outside during the time of the release (10:00 pm to 4:00 am) and the temperature (25° F) was too cold to encourage outside play. Therefore, the exposure risk for a child during the WRC release is low.

## 6.0 Conclusions

ATSDR was asked to evaluate the possibility of whether the community's inhalation exposure to vanadium pentoxide from a 2002 catalyst release at the WRC facility may have contributed to or may have induced adverse health effects such as asthma, chronic bronchitis and lung fibrosis. No air samples were collected during this non-routine release scenario.

Because no air samples were collected during the 2002 accidental catalyst release at WRC, ATSDR estimated the level vanadium pentoxide from the catalyst released in the air using the model SCREEN3. For the majority of the 6-hour WRC accidental catalyst release event, ATSDR concludes that breathing vanadium pentoxide in the outdoor air is not expected to harm people's health. Given that time of the release occurred when most people were likely not outside, that the modeled estimates for 5 ½ hours of the 6-hour event were below NOAEL and LOAEL values, and that ATSDR's assumptions likely resulted in overstating the potential vanadium pentoxide exposure concentrations, ATSDR does not believe the catalyst release to have dispersed vanadium concentrations that would cause an adverse impact to a healthy person.

However, based on modeling estimates, ATSDR finds that respiratory effects (e.g., coughing, wheezing) are plausible for residents who were downwind and outside during the 10:35 pm to 11:00 pm time-frame of the catalyst release. These respiratory effects are expected to be short-lived and reversible. In addition, ATSDR recognizes that if people with respiratory illness (such as asthma and chronic bronchitis) were outside during the event, they would have been more likely to experience a reversible health effect such as coughing and wheezing.

Of note, these conclusions are based on a modeling analysis that has inherent uncertainties. All model inputs were based on what was judged to be the best available data and many model input parameters were intentionally selected to overstate air quality impacts. However, some inputs have limited supporting data (e.g., the vanadium composition in spent catalyst) and their uncertainties cannot be reduced by any further evaluation or sampling. ATSDR also acknowledges there is some uncertainty in these health findings because the agency only considered the effects of vanadium pentoxide and not other potential catalyst constituents released during the event.

## 7.0 Recommendations

ATSDR determined no further public health actions are needed with regard to the 2002 catalyst release.

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# Appendix A. ATSDR Activities

| Table 1. Timeline of ATSDR Activities | |
|---|---|
| April 2004 | • EPA requests that ATSDR conduct a review of data related to a March 24, 2002, accidental catalyst release.<br>• EPA requests ATSDR focus on vanadium pentoxide exposures. |
| June 2004 | • ATSDR responds to EPA that a preliminary evaluation of the available information was inconclusive.<br>• ATSDR states it will conduct a follow-up review. |
| September 2006 | • ATSDR completes a follow-up review of available information and finds that air dispersion modeling may address concerns about vanadium exposures.<br>• ATSDR indicates it will conduct a modeling analysis. |
| August 2008 | • ATSDR completes its review of the quality of the emissions data (ex., total catalyst released, composition and speciation of vanadium in the release, and particle size distribution) to be used in a dispersion modeling analysis. |
| September 2008 | • ATSDR completes its initial review of vanadium toxicity focusing on studies of inhalation exposure to vanadium compounds. |
| October 2008 | • ATSDR documents the assumptions made and input parameters selected for the modeling.<br>• ATSDR completes its initial modeling analysis. |
| March 2010 | • ATSDR finishes drafting a health consultation document that summarizes all facets of its modeling analysis and toxicological evaluation.<br>• ATSDR sends the draft document for internal agency review and independent review. |
| September 2010 | • ATSDR completes updates to the draft health consultation per comments received though the internal agency and independent review process.<br>• These updates include changing input parameters (emission rates) used in the model to be more protective of public health as well as completing additional modeling analyses.<br>• ATSDR submits the updated health consultation document into its formal electronic clearance system. |

# Appendix B. Estimates of Vanadium Emissions

## Appendix B. Estimates of Vanadium Emissions

In this appendix, ATSDR provides supporting information that addresses the quality of the available emissions data used in the modeling analysis.

### Total Catalyst Released

By all accounts, the accidental release at WRC began on Sunday, March 24, 2002, and ended on Monday, March 25, 2002. The records provided to ATSDR include multiple and varying estimates of the total amount of catalyst released over the entire course of the event.

- **7 tons**: Immediately following the event, WRC estimated that 7 tons of catalyst were emitted during the accidental release [News Letter Journal 2002b]. After consulting with the designer of the FCC unit, WRC noted that "…18 to 20 tons of catalyst were probably released," with the majority of the material released between 11:00 pm and 11:30 pm on Sunday, March 24, 2002.
- **18-20 tons**: An initial analysis by representatives from EPA's Office of Inspector General specifies that "…an estimated 18-20 tons of dry catalyst" were emitted during the accidental release [EPA 2004a].
- **20 tons**: A letter from the EPA Ombudsman to ATSDR indicated that the accidental release consisted of 20 tons of catalyst [EPA 2004b].
- **33 tons**: A representative of WRC provided ATSDR with time-resolved catalyst emission rates (see Table 2). These data included emission rates for four distinct time frames between 10:00 pm on Sunday through 4:00 am on Monday, which suggest a total release of 33 tons of catalyst over the course of the event.

  ATSDR does not know how these data were estimated because supporting information were not available. In summary, site documents provide four different estimates of the amount of catalyst that WRC released to the air during the 2002 event. The most current estimate indicates that 33 tons of spent catalyst were released. Table 2 summarizes how the emission rates varied with time.

***Table 2. Total Catalyst Emission Rates***

| Time Frame | Emissions Data | | |
|---|---|---|---|
| | Pounds Per Minute | Total Pounds | Total Tons |
| 10:00 pm – 10:35 pm | 255 | 8,925 | 4.46 |
| 10:35 pm – 11:00 pm | 1,250 | 31,250 | 15.63 |
| 11:00 pm – 12:00 am | 198 | 11,880 | 5.94 |
| 12:00 am – 4:00 am | 58 | 13,920 | 6.96 |
| **Total emissions over the entire event:** | | 65,975 | 32.99 |

**Concentration of Vanadium in the Catalyst Release**

To evaluate potential exposures to vanadium during the 2002 event, ATSDR not only needs information on the total catalyst released, but also on the concentration of vanadium within the spent catalyst. Vanadium in spent catalyst may originate from at least three sources: (1) the original catalyst, (2) the crude oil that was processed in the FCC unit, and (3) other compounds that WRC may have added to its process for various purposes. The exact concentration of vanadium in the spent catalyst released to the air in March 2002 was not measured directly (i.e., in the stack), largely because petroleum refineries are generally not required to monitor vanadium in their air emissions.

Estimates of the vanadium in the spent catalyst can be gleaned from other sources of information.

- **Material Safety Data Sheets (MSDSs) (0.004–0.75% vanadium, by weight):** WRC provided ATSDR with two MSDSs that document the percent of vanadium in the spent catalyst. The first MSDS was prepared in 1998 by W.R. Grace for "spent (used) fluid cracking catalyst" and reported a range of vanadium concentrations of 40 to 7,500 ppm (0.004% to 0.75% vanadium, by weight) [WR Grace 1998]. The other MSDS was prepared by WRC and documents a vanadium concentration of "<0.1%," by weight [WRC 2002]; of note, this MSDS was issued after the 2002 event. The two MSDSs offer insights into the potential range of vanadium content in spent catalyst; however, from the MSDSs, there is no way to determine where in the potential range of vanadium concentrations the composition of catalyst released on March 24-25, 2002 event fell.

- **WRC sampling (0.09% vanadium, by weight):** Following the March 2002 accidental release, WRC reported collecting a sample of the catalyst that fell and having it analyzed for concentrations of several metals. WRC communicated the measured vanadium concentration (902 ppm or 0.09% vanadium, by weight) to the local newspaper [News Letter Journal 2002b].

- **EPA catalyst sampling (0.14% vanadium, by weight):** Less than 2 weeks following the March 2002 event, EPA mobilized an emergency response team to characterize the environmental impacts of the release [URS 2002]. As part of this investigation, EPA contractors analyzed eight surface soil samples, two spent catalyst samples from locations where dusts from the event reportedly settled, and one spent catalyst sample submitted by WRC. Vanadium concentrations in surface soil ranged from not detected to 39 ppm. Vanadium concentrations in dust collected from surface accumulation in a resident's front yard and from a resident's deck contained 440 ppm and 470 ppm, respectively. Also, WRC provided a catalyst sample to the EPA contractors. This sample reported a vanadium concentration of 1,400 ppm (or 0.14% vanadium, by weight). Documentation of this investigation is extensive, including thorough attention to data quality. ATSDR considers the best representation of conditions during the accidental release to be the analyses of the catalyst samples, and chose to use the greater value (0.14% vanadium, by weight) in its analysis.

In summary, no direct measurements are available to quantify the vanadium content of spent catalyst emitted from the WRC stack in March 2002. Considering all data points available, the vanadium content of spent catalyst is likely between 0.004% and 0.75%, by weight. ATSDR considers the best estimate of the vanadium content is 0.14% (by weight), as quantified in a sample of spent catalyst measured during EPA's sampling effort after the accidental release[1]. This estimate (0.14% vanadium), combined with the best estimate of total catalyst released (65,975 pounds), suggests that the March 2002 event released 92 pounds of vanadium into the air.

**Chemical Speciation of Vanadium in the Catalyst Release**

Vanadium is known to exist in multiple oxidation states (-2 to +5), which may be of significance for the WRC event because vanadium toxicity may vary with oxidation state. However, no site-specific information is available to characterize the oxidation state of the vanadium that WRC released to the air. This lack of data is not unusual because many laboratory analytical methods routinely used for environmental sampling (e.g., X-ray fluorescence, inductively coupled argon plasma spectroscopy) are designed to detect the concentration of the parent metal present, without providing information on the chemical form or oxidation state of the metals that are detected.

Without direct measurements of the chemical speciation of vanadium at WRC, a literature review for additional insights into the forms of vanadium that were most likely emitted was conducted. Relevant observations from that review follow:

- In the opening paragraph of a review article of vanadium toxicity, researchers have reported that "…in the presence of oxygen, air, and oxidizing agents, or in oxygenated blood, vanadium is always in the +5 oxidation state" [Sitprija and Eiam-Ong 1998].

- Another review article notes that airborne vanadium from fossil fuel combustion is emitted primarily as oxides, with several specific examples given: VO, $V_2O_3$, $VO_2$, and $V_2O_5$ [Crans et al. 1998].

- ATSDR's draft Toxicological Profile for Vanadium states that "…generally, lower oxides formed during combustion of coal and residual fuel oils, such as vanadium trioxide, undergo further oxidation to the pentoxide form, often before leaving the stacks" [ATSDR 2009].

- The World Health Organization (WHO) published a review of toxicity information on vanadium compounds in 2001. The authors further support the prevalence of pentavalent vanadium: "The most common commercial form of vanadium is vanadium pentoxide" [WHO 2001]. This review further notes that vanadium pentoxide is formed in the combustion of fossil fuels in boilers and

[1] Of note, a review of additional publications and information resources (e.g., EPA's AP-42 document, EPA's "SPECIATE" database, peer-reviewed journals, Web searches) for further data on typical vanadium content in spent FCC catalyst was also conducted. However, those supplemental reviews failed to generate insights on emissions scenarios comparable to those that occurred during the March 2002 event at WRC.

heaters. Of note, this observation may not relate directly to the FCC unit at WRC, which heats crude oil rather than burns it.

In summary, no measurements are available that determine the chemical speciation of vanadium in air emissions from WRC, both during routine and non-routine release scenarios. Review articles suggest that the oxidation state most commonly encountered in ambient air is pentavalent vanadium (+5 oxidation state). Given that these literature reviews suggest that vanadium emitted into the atmosphere is typically in the pentavalent form, ATSDR assumed the emissions are 100% vanadium pentoxide in its modeling analyses for this site.

**Particle Size Distribution of Emissions**

No site-specific measurements are available on the particle size distribution of emissions from the FCC unit, whether during routine operations or accidental releases. WRC's air permit offers no insights on particle size distributions for FCC emissions [WDEQ 2007]. The only site-specific information available on the particle size of the spent catalyst is documented in a 2004 memo from a WRC official to ATSDR. Following is the information that WRC provided in this communication:

> "The size distribution data we have for catalyst preceding the release is in the following table. These data represent actual physical particle size from a Malvern analysis performed by Grace Division's labs. These are not aerodynamic diameters. The apparent density of the catalyst was 0.82 grams per cubic centimeter."

***Table 3. Particle Size Distribution of the Spent Catalyst***

| Size Range | 0 – 20 µm | 0 – 40 µm | 0 – 80 µm |
|---|---|---|---|
| Mass Fraction | 2% | 7% | 66% |

Data source: WRC 2004.

µm = micrometer

The average size reported was 70 micrometers (µm). Although the previous information might imply that the majority of the vanadium released was in particle size ranges greater than 20 µm (and therefore not respirable), no supporting information was provided. ATSDR does not know (1) whether this distribution represents "fresh" catalyst or "spent" catalyst, (2) whether the measurements were taken under conditions similar to those during the release event (i.e., heated to several hundred degrees Centigrade), or (3) whether the measurements were characteristic of exhaust from the FCC's pollution controls that may have been operating during the release.

To fill this data gap, a broader review was conducted of particle size distribution data in the peer-reviewed literature, of the EPA emission factor guidance, of review articles, and of other information resources. Although numerous publications have reported particle size distributions for a wide range of fossil fuel combustion sources, no articles were located that present particle size information for accidental releases from catalyst regeneration operations at FCC units.

Overall, no direct measurements quantified the particle size distribution of emissions during the March 2002 event, and the limited particle size distribution data subsequently provided by WRC may not be representative of the non-routine operating conditions during the accidental release. As a result, any estimate of the particle size distribution for this particular event is highly uncertain. Therefore, for the modeling analysis of the WRC event, ATSDR assumed that 100% of the vanadium emitted to the air was in the respirable form.

# Appendix C. Modeling Assumptions, Input Parameters and Results

**Table 4. SCREEN3 Modeling Assumptions and Input Parameters***

| Assumption/Parameter | Value Used | Units | Comments |
|---|---|---|---|
| Total vanadium emissions | 92 | pounds | This value is based on the best information available and may understate or overstate the actual emissions value. This value was obtained from the total mass released estimated by WRC (65,975 pounds) and a vanadium composition of 0.14% (see Appendix B). |
| Chemical composition of vanadium emissions | 100% vanadium pentoxide | (—) | Without reliable information available on the chemical speciation of vanadium in the catalyst release, an initial assumption that 100% of the release is in the form of vanadium pentoxide, which the scientific literature suggests is the most toxic chemical form likely to be found in the environment. This assumption will overstate the health risks associated with the release event. |
| Particle size distribution | 100% respirable | (—) | Given the lack of reliable information on the particle size distribution in the stack emissions during the release event, an initial assumption that all of the vanadium emitted into the air was in the respirable form. Model results based on this assumption will overstate the actual exposures that likely occurred. |
| Stack height | 37.5 | meters | Data reported by WRC [WRC 2004]. |
| Stack inside diameter | 1.52 | meters | Data reported by WRC [WRC 2004]. |
| Stack exit velocity | 11.12 | meters/second | The average exit velocity over the duration of the event, based on stack readings provided by WRC [WRC 2004]. |
| Exit temperature | 477 | Kelvin | Data reported by WRC as 400$^{o}$ F, which is 477 Kelvin. [WRC 2004]. |
| Ambient temperature | 269 | Kelvin | Meteorological data collected at 1:55 AM at a meteorological monitoring station in Gillette, Wyoming, indicated an ambient temperature of 25$^{o}$ F, or 269 Kelvin. |

* Simple terrain, rural dispersion coefficient and full meteorology mode were selected to run the SCREEN3 model.

| Time Frame | Total Catalyst Released in Pounds Per Minute* | Vanadium Released in Pounds per Minute† | Emission Rate In Grams per Second‡ |
|---|---|---|---|
| 10:00 pm – 10:35 pm | 255 | 0.357 | 2.7 |
| 10:35 pm – 11:00 pm | 1,250 | 1.75 | 13.2 |
| 11:00 pm – 12:00 am | 198 | 0.277 | 2.1 |
| 12:00 am – 4:00 am | 58 | 0.0812 | 0.6 |
| Averaged over entire timeframe (10 pm to 4 am) | 183 | 0.256 | 1.9 |

***Table 5. Catalyst Emission Rates in used in SCREEN3***

* WRC provided ATSDR with these time-resolved catalyst emission rates.
† ATSDR assumed 0.14% vanadium composition.
‡ Emission rate parameter used in SCREEN3.

| *Table 6. SCREEN3 Models Results* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Scenario** | **Stability Class** | **Wind Speed (m/s)** | **Estimated Vanadium Concentrations (µg/m$^3$)** | | | | | **Distance from Stack Base (m)** |
| | | | **Emission Rate 2.7 g/s** | **Emission rate 13.2 g/s** | **Emission Rate 2.1 g/s** | **Emission Rate 0.6 g/s** | **Emission Rate 1.9 g/s** | |
| 1 | A | 1.0 | 16.2 | 79.4 | 12.6 | 3.6 | 11.43 | 773 |
| 2 | A | 1.5 | 11.2 | 54.7 | 8.7 | 2.5 | 7.88 | 606 |
| 3 | A | 2.0 | 11.7 | 57.3 | 9.1 | 2.6 | 8.25 | 545 |
| 4 | A | 2.5 | 11.9 | 58.4 | 9.3 | 2.7 | 8.40 | 496 |
| 5 | A | 3.0 | 12.1 | 59.2 | 9.4 | 2.7 | 8.52 | 461 |
| 6 | B | 1.0 | 9.4 | 46.1 | 7.3 | 2.1 | 6.63 | 1,886 |
| 7 | B | 1.5 | 7.7 | 37.7 | 6.0 | 1.7 | 5.42 | 1,214 |
| 8 | B | 2.0 | 8.7 | 42.5 | 6.8 | 1.9 | 6.12 | 995 |
| 9 | B | 2.5 | 9.4 | 45.8 | 7.3 | 2.1 | 6.59 | 861 |
| 10 | B | 3.0 | 9.8 | 48.0 | 7.6 | 2.2 | 6.91 | 770 |
| 11 | B | 3.5 | 10.1 | 49.5 | 7.9 | 2.2 | 7.12 | 705 |
| 12 | B | 4.0 | 10.3 | 50.4 | 8.0 | 2.3 | 7.25 | 655 |
| 13 | B | 4.5 | 10.4 | 50.8 | 8.1 | 2.3 | 7.31 | 616 |
| 14 | B | 5.0 | 10.4 | 51.0 | 8.1 | 2.3 | 7.34 | 585 |
| 15 | C | 1.0 | 6.9 | 33.9 | 5.4 | 1.5 | 4.88 | 3,685 |
| 16 | C | 1.5 | 6.5 | 31.7 | 5.0 | 1.4 | 4.56 | 2,156 |
| 17 | C | 2.0 | 7.5 | 36.9 | 5.9 | 1.7 | 5.31 | 1,706 |
| 18 | C | 2.5 | 8.3 | 40.6 | 6.5 | 1.8 | 5.85 | 1,440 |
| 19 | C | 3.0 | 8.9 | 43.4 | 6.9 | 2.0 | 6.24 | 1,265 |
| 20 | C | 3.5 | 9.3 | 45.2 | 7.2 | 2.1 | 6.51 | 1,140 |
| 21 | C | 4.0 | 9.5 | 46.5 | 7.4 | 2.1 | 6.70 | 1,047 |
| 22 | C | 4.5 | 9.7 | 47.4 | 7.5 | 2.2 | 6.82 | 975 |
| 23 | C | 5.0 | 9.8 | 47.9 | 7.6 | 2.2 | 6.89 | 918 |

Table 6 continued.

***Table 6. SCREEN3 Models Results***

| Scenario | Stability Class | Wind Speed (m/s) | Estimated Vanadium Concentrations (µg/m$^3$) | | | | | Distance from Stack Base (m) |
|---|---|---|---|---|---|---|---|---|
| | | | **Emission Rate 2.7 g/s** | **Emission rate 13.2 g/s** | **Emission Rate 2.1 g/s** | **Emission Rate 0.6 g/s** | **Emission Rate 1.9 g/s** | |
| 24 | C | 8.0 | 9.9 | 48.2 | 7.7 | 2.2 | 6.94 | 714 |
| 25 | C | 10.0 | 9.7 | 47.4 | 7.5 | 2.2 | 6.82 | 640 |
| 26 | D | 1.0 | 2.4 | 11.9 | 1.9 | 0.5 | 1.71 | 12,560 |
| 27 | D | 1.5 | 3.2 | 15.5 | 2.5 | 0.7 | 2.23 | 6,179 |
| 28 | D | 2.0 | 4.0 | 19.7 | 3.1 | 0.9 | 2.84 | 4,414 |
| 29 | D | 2.5 | 4.7 | 23.2 | 3.7 | 1.1 | 3.34 | 3,463 |
| 30 | D | 3.0 | 5.3 | 26.0 | 4.1 | 1.2 | 3.74 | 2,984 |
| 31 | D | 3.5 | 5.7 | 28.0 | 4.5 | 1.3 | 4.03 | 2,596 |
| 32 | D | 4.0 | 6.0 | 29.5 | 4.7 | 1.3 | 4.25 | 2,315 |
| 33 | D | 4.5 | 6.3 | 30.7 | 4.9 | 1.4 | 4.42 | 2,103 |
| 34 | D | 5.0 | 6.5 | 31.5 | 5.0 | 1.4 | 4.54 | 1,938 |
| 35 | D | 8.0 | 7.1 | 34.5 | 5.5 | 1.6 | 4.97 | 1,373 |
| 36 | D | 10.0 | 7.2 | 35.0 | 5.6 | 1.6 | 5.04 | 1,186 |
| 37 | D | 15.0 | 6.8 | 33.3 | 5.3 | 1.5 | 4.79 | 1,000 |
| 38 | D | 20.0 | 6.1 | 29.9 | 4.8 | 1.4 | 4.30 | 942 |
| 39 | E | 1.0 | 7.2 | 35.2 | 5.6 | 1.6 | 5.06 | 6,077 |
| 40 | E | 1.5 | 6.1 | 29.6 | 4.7 | 1.3 | 4.26 | 5,195 |
| 41 | E | 2.0 | 5.3 | 26.1 | 4.1 | 1.2 | 3.75 | 4,672 |
| 42 | E | 2.5 | 4.8 | 23.5 | 3.7 | 1.1 | 3.38 | 4,314 |
| 43 | E | 3.0 | 4.4 | 21.5 | 3.4 | 1.0 | 3.10 | 4,051 |
| 44 | E | 3.5 | 4.1 | 19.9 | 3.2 | 0.9 | 2.87 | 4,001 |
| 45 | E | 4.0 | 3.8 | 18.6 | 3.0 | 0.8 | 2.68 | 4,001 |

Table 6 continued.

| ***Table 6. SCREEN3 Models Results*** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Scenario** | **Stability Class** | **Wind Speed (m/s)** | **Estimated Vanadium Concentrations (µg/m³)** | | | | | **Distance from Stack Base (m)** |
| | | | **Emission Rate 2.7 g/s** | **Emission rate 13.2 g/s** | **Emission Rate 2.1 g/s** | **Emission Rate 0.6 g/s** | **Emission Rate 1.9 g/s** | |
| 46 | E | 4.5 | 3.6 | 17.4 | 2.8 | 0.8 | 2.51 | 3,879 |
| 47 | E | 5.0 | 3.4 | 16.6 | 2.6 | 0.8 | 2.39 | 3,735 |
| 48 | F | 1.0 | 5.0 | 24.3 | 3.9 | 1.1 | 3.50 | 11,230 |
| 49 | F | 1.5 | 4.2 | 20.6 | 3.3 | 0.9 | 2.96 | 9,518 |
| 50 | F | 2.0 | 3.7 | 18.1 | 2.9 | 0.8 | 2.60 | 8,498 |
| 51 | F | 2.5 | 3.3 | 16.3 | 2.6 | 0.7 | 2.35 | 7,816 |
| 52 | F | 3.0 | 3.1 | 14.9 | 2.4 | 0.7 | 2.15 | 7,307 |
| 53 | F | 3.5 | 2.8 | 13.8 | 2.2 | 0.6 | 1.99 | 7,000 |
| 54 | F | 4.0 | 2.7 | 13.2 | 2.1 | 0.6 | 1.90 | 7,000 |

g/s grams per second
m meters
m/s meters per second
µg/m³ micrograms per cubic meter

# Appendix D. Vanadium Toxicity

## Appendix D. Vanadium Toxicity

This review of vanadium toxicity focuses on studies of *inhalation* exposure to vanadium compounds to identify studies that might characterize the relative toxicity (via inhalation exposure) for individual vanadium compounds. Because of the short-term nature of the WRC catalyst release, this review focuses on identifying and evaluating studies that evaluated the health implications of *acute* inhalation exposure to various vanadium compounds. This review was not limited to any single vanadium compound. Of note, because this health consultation is focused on short-term inhalation exposures, ATSDR's review does not present detailed information on exposures via non-inhalation routes and inhalation exposures of chronic duration.

## Summary of Relevant Publications

ATSDR examined four reviews of vanadium toxicity:

1. EPA's health assessment for vanadium pentoxide posted to the agency's web site for the Integrated Risk Information System (IRIS) [EPA 1988].
2. The World Health Organization's most recent Chemical Assessment Document for vanadium pentoxide and other inorganic vanadium compounds [WHO 2001].
3. ATSDR's Toxicological Profile for Vanadium and Compounds (draft for public comment) [ATSDR 2009].
4. The International Agency for Research on Cancer's (IARC) 2006 monograph on the carcinogenicity of metal compounds, which includes non-cancer toxicity data presented on vanadium pentoxide.

The following text provides information from ATSDR's review.

### EPA IRIS Profile on Vanadium Pentoxide

EPA has developed an IRIS profile for vanadium pentoxide [EPA 1988], but not for vanadium or any other vanadium compound. The IRIS summary file (available from EPA's IRIS Web site) documents limited information on effects associated with oral exposure to vanadium pentoxide, but presents no information on effects associated with inhalation exposure. EPA has not developed a reference concentration or any other health guideline on inhalation exposure levels. While EPA's IRIS profile provides some insights on vanadium toxicity following ingestion exposures, that information is not reviewed here because this health consultation was developed primarily to review inhalation toxicity.

### WHO Concise International Chemical Assessment Document

In 2001, WHO issued Concise International Chemical Assessment Document (CICAD) #29, which addressed the toxicity of vanadium pentoxide and other inorganic vanadium compounds [WHO 2001]. The following key points were either stated in the CICAD report or are consistent with its findings:

- CICAD reports that vanadium pentoxide is found in numerous by-products of fossil fuel combustion (e.g., fly ash, soot), but does not identify other vanadium compounds formed in these processes. The document also notes that airborne vanadium from fossil fuel combustion tends to be found in finer particles.

- Health effects reported in humans exposed to vanadium pentoxide are consistent with those reported in the ATSDR Toxicological Profile: delayed bronchial effects (e.g., cough, excessive mucus production) in a group of volunteers following a single inhalation exposure; eye, nose, and throat irritation among workers with prolonged exposures to vanadium pentoxide fumes and dusts; and isolated skin reactions following patch testing. Note, however, that evidence for dermal reactions was mixed across studies, and the report ultimately concluded "the potential for vanadium and vanadium compounds to produce skin irritation on direct contact is unclear" [WHO 2001]. Green discoloration of the tongue has also been observed in "highly exposed" workers, but the clinical significance of this effect is not entirely clear. The effects reported in humans following acute inhalation exposures all resolved within a few days after exposures ceased, and no evidence of long-term health effects in humans were noted following acute inhalation exposures. While studies in occupational settings provide some insights on vanadium toxicity, the inferences that can be drawn from these studies are limited due to inherent limitations in study design (e.g., lack of control for confounding factors, concurrent exposures to multiple pollutants, inadequate characterization of exposure doses).

- Overall, the CICAD report concludes that respiratory tract irritation and genotoxicity are the "toxicological endpoints of concern" for humans exposed to vanadium compounds. Genotoxic effects are not expected to be important for ATSDR's evaluation of the WRC release, given the short duration of exposures.

- The concluding section of the CICAD report notes that WHO has established a 24-hour average "air quality guideline" for vanadium of 1 $\mu g/m^3$, which is based on a reported LOAEL derived from an occupational study (20 $\mu g/m^3$) and an uncertainty factor of 20. The report does not clearly identify the study from which this guideline was derived, but it appears to be an occupational study of inhalation exposures to vanadium pentoxide that occurred over 6 months [Lewis 1959]. If that indeed is the basis of the WHO air quality guideline, the underlying study has an exposure duration that is not directly comparable to that for the study ATSDR used to derive its acute inhalation MRL.

- Based on a review of toxicity values ($LD_{50}$, or lethal dose-50% kill) reported in multiple studies of oral exposures in rats, the CICAD report concludes that pentavalent vanadium compounds tend to be more toxic than tetravalent vanadium compounds; and, among the pentavalent compounds considered, vanadium pentoxide exhibits the greatest toxicity via ingestion. Note that the finding of pentavalent vanadium compounds being more toxic than tetravalent vanadium compounds is supported by more recent *in vitro* studies [e.g., Worle-Knirsch et al. 2007].

- The CICAD report did not identify any studies conclusively linking vanadium exposures to cancers in humans. Specifically, the CICAD report states: "No useful information is available on the carcinogenic potential of any form of vanadium via any route of exposure in animals or in humans" [WHO 2001]. However, the lack of data on carcinogenicity of vanadium compounds should not be viewed as a serious limitation for ATSDR's evaluation of the WRC release event, given the limited duration of inhalation exposure.

- The CICAD report indicates that the overall information base on the toxicity of vanadium and vanadium compounds is limited.

**ATSDR's Toxicological Profile for Vanadium and Compounds (draft for public comment)**

ATSDR's Toxicological Profile presents information on the toxicology of vanadium and its compounds [ATSDR 2009]. One of the opening paragraphs in the "Health Effects" chapter of the profile states that the toxicologically significant compounds are vanadium pentoxide ($V_2O_5$), sodium metavanadate ($NaVO_3$), sodium orthovanadate ($Na_3VO_4$), vanadyl sulfate ($VOSO_4$), and ammonium vanadate ($NH_4VO_3$) [ATSDR 2009].

Focusing on *inhalation* exposure, the draft 2009 profile's table on "levels of significant exposure" reviews the findings of five studies addressing acute exposures to vanadium pentoxide. These studies evaluated health effects in animals (one study of rabbits, one study of rats, one study of mice, and two studies of monkeys). Of all five studies, the lowest effect level identified was 560 µg vanadium/$m^3$. For this study, groups of 40–60 female rats were exposed to varying amounts of vanadium pentoxide 6 hours/day, 5 days/week for 16 days [NTP 2002]. The endpoint was an increase in the incidence of lung inflammation in rats exposed to 560 µg vanadium/$m^3$ as vanadium pentoxide for 13 days. The human equivalent concentration for this lowest-observed-adverse-effect-level (LOAEL) is 73 µg vanadium/$m^3$. ATSDR derived its acute inhalation Minimal Risk Level (MRL) of 0.8 µg/$m^3$ from this study.

Although a number of studies have reported respiratory effects in humans exposed to vanadium, in particular vanadium pentoxide, very few provide reliable quantitative exposure data. ATSDR's Toxicological Profile reports a no-observed-adverse-effect-level (NOAEL) and a LOAEL of 100 µg vanadium/$m^3$ and 600 µg vanadium/$m^3$, respectively, for a controlled (experimental) exposure study [ATSDR 2009, Zenz and Berg 1967]. In this study, a productive cough without any subjective complaints, alterations in lung function, or impact on daily activities was observed in five subjects exposed to vanadium pentoxide dust at 100 µg vanadium/$m^3$. For the same study, a persistent cough lasting for 8 days developed in two subjects exposed to vanadium pentoxide dust at 600 µg vanadium/$m^3$.

ATSDR's Toxicological Profile notes that several occupational studies, particularly among boilermakers and other occupations known or suspected to have elevated vanadium exposures, have linked both acute and chronic inhalation exposures to various health effects in humans. These include respiratory outcomes (e.g., cough, wheezing, chest pain, sore throat), ocular effects (eye irritation), and skin rashes. The Toxicological Profile notes that the respiratory symptoms observed in these occupational settings "…are reversible within days or weeks after exposure ceases" [ATSDR 2009]. Though these occupational studies offer some insights into potential vanadium-related health effects following inhalation exposures, none of the studies included sufficient exposure data to establish dose-response relationships. Moreover, the effects noted in these studies might also have resulted from other factors (e.g., exposures to other substances) or may not be conclusively attributed to vanadium due to the lack of control populations. Overall, the human studies reviewed in ATSDR's Toxicological Profile indicate that inhalation exposure to various forms of vanadium can lead to respiratory, ocular, and dermal effects; though the exposure levels associated with most of these non-cancer outcomes in humans have not been rigorously quantified.

In summary, ATSDR's Toxicological Profile reviews findings from occupational studies and animal studies pertaining to inhalation exposure of various vanadium compounds. The profile concludes that "studies of health effects on people who have inhaled vanadium in the workplace clearly show that the target organ is the respiratory system" [ATSDR 2009]. All information in the Toxicological Profile implies that health effects following acute inhalation exposures to vanadium are relatively short-lived and reversible.

No studies were identified on cancers in humans or animals following inhalation of vanadium compounds; however, the lack of carcinogenicity data may not be relevant to this evaluation given the short duration of exposure following the WRC event.

**IARC Review**

In 2006, IARC issued a monograph (Volume 86) on the carcinogenicity of multiple metal compounds, including vanadium pentoxide [IARC 2006]. While the IARC monograph focuses on the carcinogenic potential of vanadium pentoxide, it also reviews the chemical's toxicity. Of particular note, the monograph provides insights from a past case report [Musk and Tees 1982] that was identified in some of the earlier reviews (e.g., ATSDR's Toxicological Profile, the CICAD document) but not necessarily interpreted in the same fashion.

More specifically, the IARC monograph includes a section that reviews findings from various studies of workers exposed to vanadium compounds. This section is based on several of the same studies that were considered in the other review articles. The monograph explains that Musk and Tees (1982) presents information from four case reports of workers at a "vanadium pentoxide refinery" located in western Australia. For one of these workers, respiratory effects (wheezing, primarily during the morning hours) reportedly occurred for at least 8 weeks after inhalation exposures to vanadium pentoxide ceased. This particular worker was a smoker and was reportedly "predisposed to developing more severe manifestations of exposure by virtue of his family history of asthma and positive prick skin tests to common allergens." The worker was exposed to vanadium compounds (and apparently other pollutants, given that he was working in a "de-amonniation shed") for approximately 5 days and then did not return to work. Though the study did not include measurements or estimates of potential exposure levels, the fact that this worker developed green discoloration of the tongue (an outcome observed only in the most highly exposed occupational workers) suggests that the exposures were extremely elevated. Ultimately, the authors of these case reports conclude: "…vanadium compounds appear to be capable of inducing asthma in previously normal subjects" [Musk and Tees 1982].

This finding from one case report is not consistent with the many other studies and review articles that all concluded that health effects associated with acute inhalation exposures of vanadium are short-lived and reversible. The IARC monograph presents the following overall interpretation of the occupational studies: "While the majority of the above studies have noted reversibility of these acute pulmonary effects, asthma [now possibly labeled 'reactive airways dysfunction syndrome'] has been reported to develop as a sequela to high, acute exposure to vanadium in some exposed workers." The Musk and Tees study (1982) is cited for the statement regarding the possibility of asthma developing in some exposed workers.

The IARC monograph provides additional general observations regarding vanadium toxicity of direct relevance to ATSDR's evaluation of the WRC site. For instance, the monograph notes that vanadium toxicity tends to be greatest for the pentavalent state, with vanadium pentoxide apparently being the most toxic form. However, this observation appears to be taken directly from earlier review articles [WHO 2001] and not necessarily the result of additional or independent analyses. Further, the monograph reiterates an important conclusion noted in other toxicity reviews: "The major non-cancer health effect associated with inhalation exposure to vanadium pentoxide involves acute respiratory irritation, characterized as 'boilermakers bronchitis.' This clinical effect appears to be reversible" [IARC 2006].

Though this memo does not focus on carcinogenicity, given the nature of exposures that occurred following the WRC release event, it should be noted that IARC concluded that vanadium pentoxide is "possibly carcinogenic to humans" based on "inadequate evidence" in humans and "sufficient evidence" in experimental animals [IARC 2006].