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Saturation Point Model for the Formation of Metal Nitrate in Nitrogen Tetroxide Oxidizer

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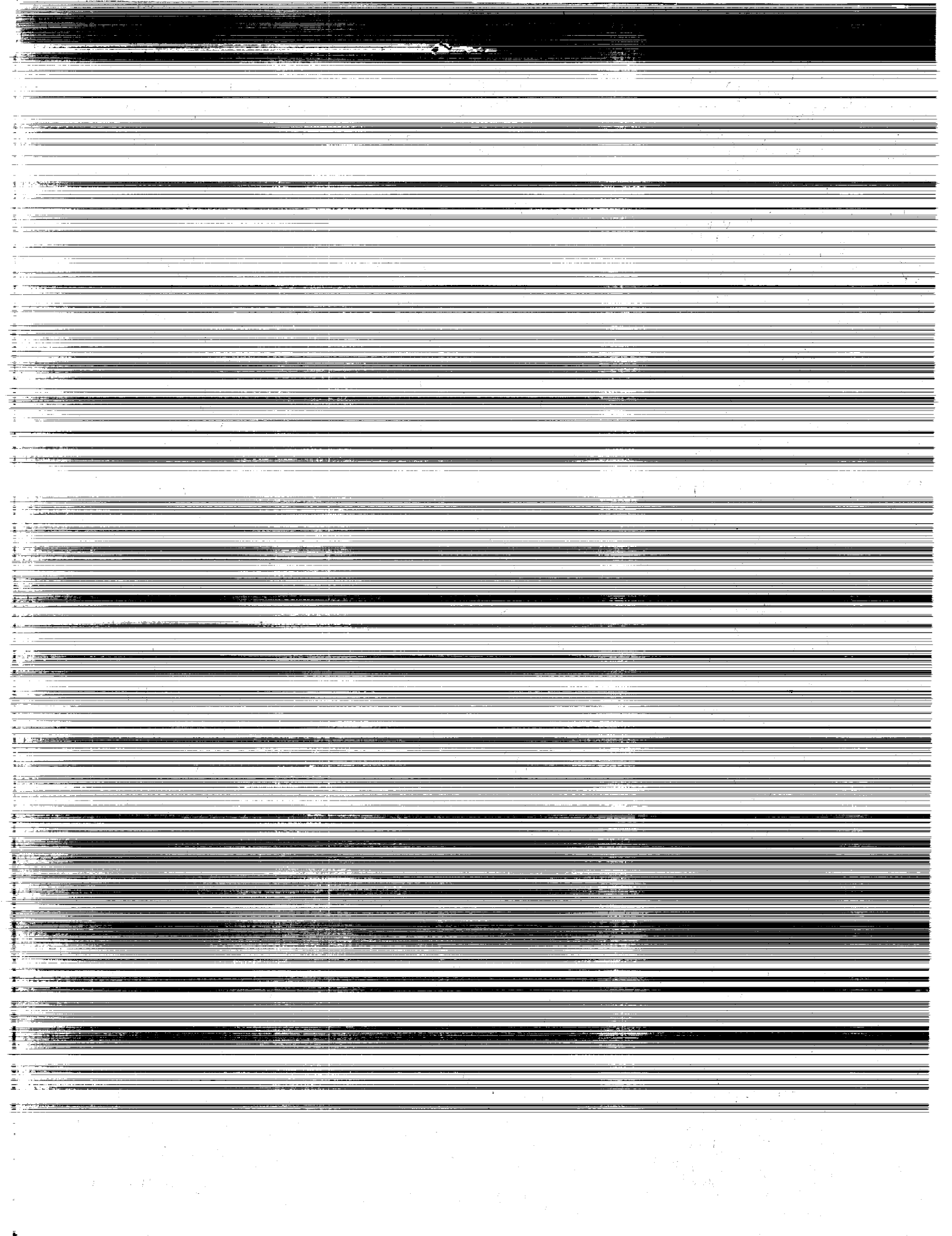
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THE FORMATION OF METAL NITRATE IN NITROGEN
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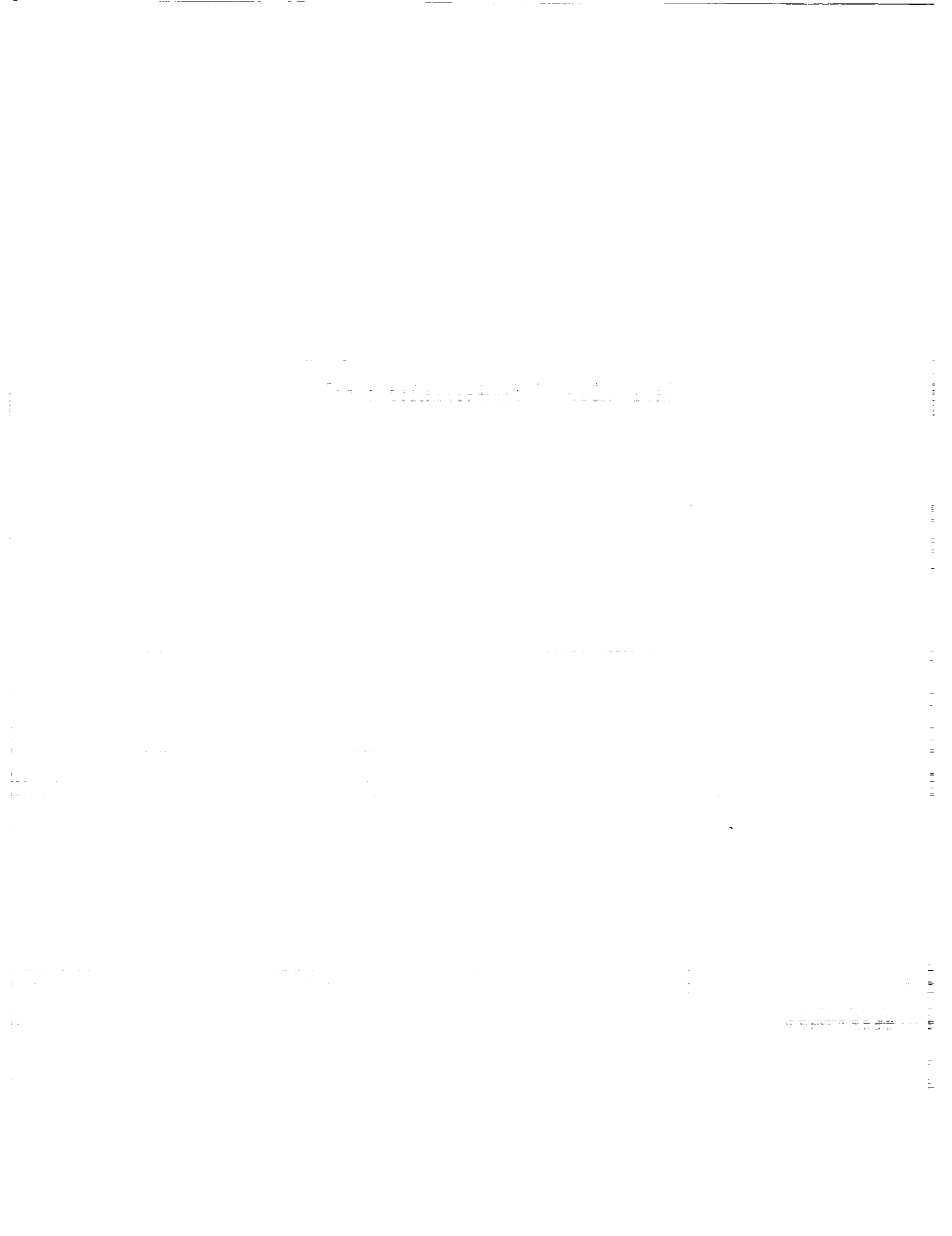
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**Saturation Point Model
for the Formation of
Metal Nitrate in Nitrogen
Tetroxide Oxidizer**

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National Aeronautics and
Space Administration
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SUMMARY

A model has been developed for the formation of metal nitrate precipitation in nitrogen tetroxide oxidizer. ("N₂O₄" refers to the pure compound, and "oxidizer" refers to nitrogen tetroxide and all other constituents.) The basis of this model is the saturation point of metal nitrate in the oxidizer. This basis is chosen mainly because of White Sands Test Facility's (WSTF) experience with metal nitrate in the oxidizer. Means of reaching the saturation point are discussed, and a relation is made for the reaction/formation rate and diffusion rate of metal nitrate in the oxidizer. Also, an example shows the calculations that may be used to correlate a given corrosion rate to the saturation point. If the saturation point is achieved, metal nitrates will precipitate and become a potential problem. Metals and alloys suitable for use with the oxidizer can thus be determined experimentally. This model (figure 1) can be expressed by the following equation.

$$\begin{array}{l} \text{[MN]} > \text{[MN]} = \text{[MN]}_0 + \text{[MN]}_{\text{RXN}} - \text{[MN]}_{\text{DIFFUSION}} \\ \text{Precipitation} \quad \text{Critical} \\ \text{Point,} \quad \text{Surface,} \\ \quad \quad \quad \text{in System} \end{array}$$

The basic model is that for a "critical" surface (a surface or location that cannot tolerate metal nitrate precipitate), the concentration of metal nitrate in the oxidizer at that surface or location must be below the precipitation point. The concentration of metal nitrate in the oxidizer at that surface or location is equal to the initial concentration [MN]₀ plus any metal nitrate formed by reaction [MN]_{RXN} minus any metal nitrate that diffuses away [MN]_{DIFFUSION}.

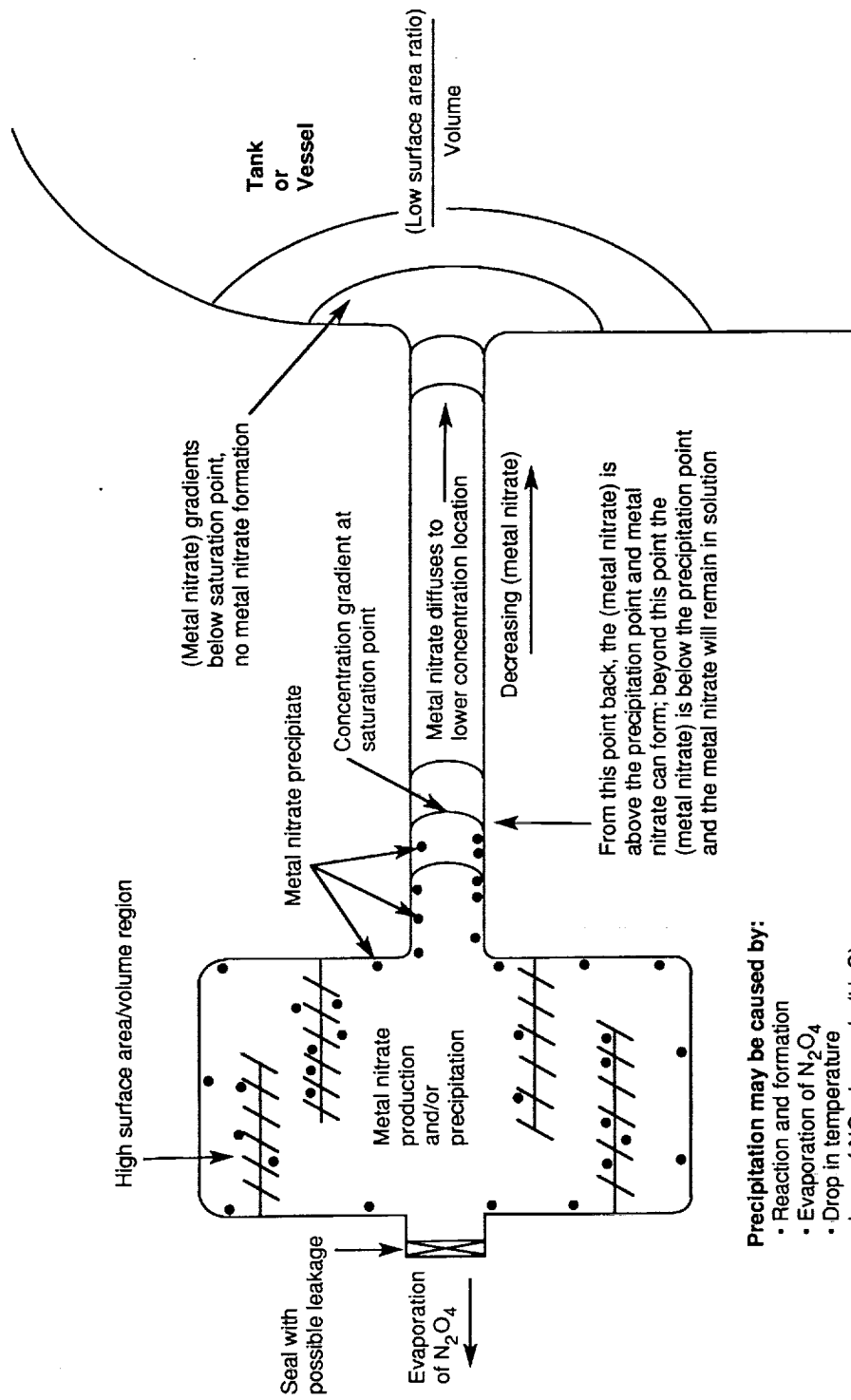
The metal nitrate formation model is on page 2 (figure 1).

INTRODUCTION

In May 1990 a Tiger Team was formed to investigate Post STS-26 Reaction Control System (RCS) oxidizer valve failures that have been attributed to the formation of metal nitrate in the oxidizer valve. This paper was prepared as a result of participating in the Tiger Team investigation. I want to thank Stan Bibie, Pat Meyer, Regor Saulsberry, and I. D. Smith for their help and review of this paper.

SATURATION POINT OF METAL NITRATE IN THE OXIDIZER

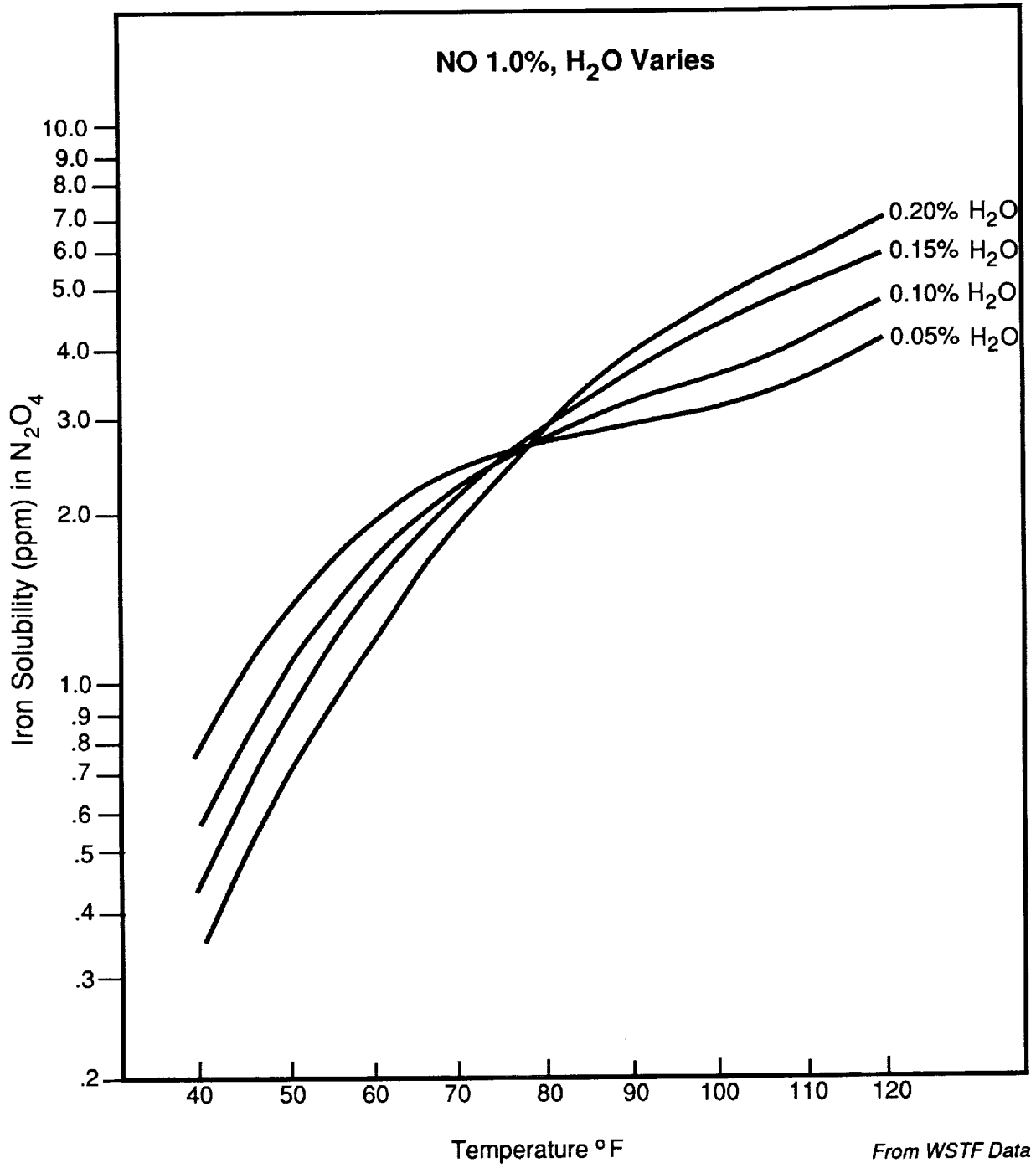
In 1981, WSTF conducted a study (TR-268-001) to establish the conditions under which metal nitrate formation occurs. (WSTF refers to metal nitrate as metal nitrate or, in particular, iron nitrate flow decay material—the nitrogen tetroxide adduct of iron nitrate [Fe(NO₃)₃ 1-1.5 N₂O₄]—in some form. Iron nitrate forms when nitrogen tetroxide is in contact with iron-bearing alloys.) The study revealed that metal nitrate formation occurred ONLY when the specification grade oxidizer was saturated with metal nitrate. In other words, metal nitrate in the oxidizer does not precipitate below the saturation point. This is an important observation because this means that even though metal nitrate may be in the oxidizer at some low concentration all the time, it is not a problem (does not precipitate) until the saturation point is reached. Therefore, the model developed for metal nitrate formation (causing subsequent problems with system operations) is based on the saturation point. It is, therefore, important to understand the saturation point for metal nitrate in oxidizer and the factors involved. Since WSTF has demonstrated that problems occur when the saturation point is reached, a good approach to this dilemma is to look closely at the saturation point and the various ways in which the saturation point can be achieved. (Saturation point graphs are on pages 3 through 8.)

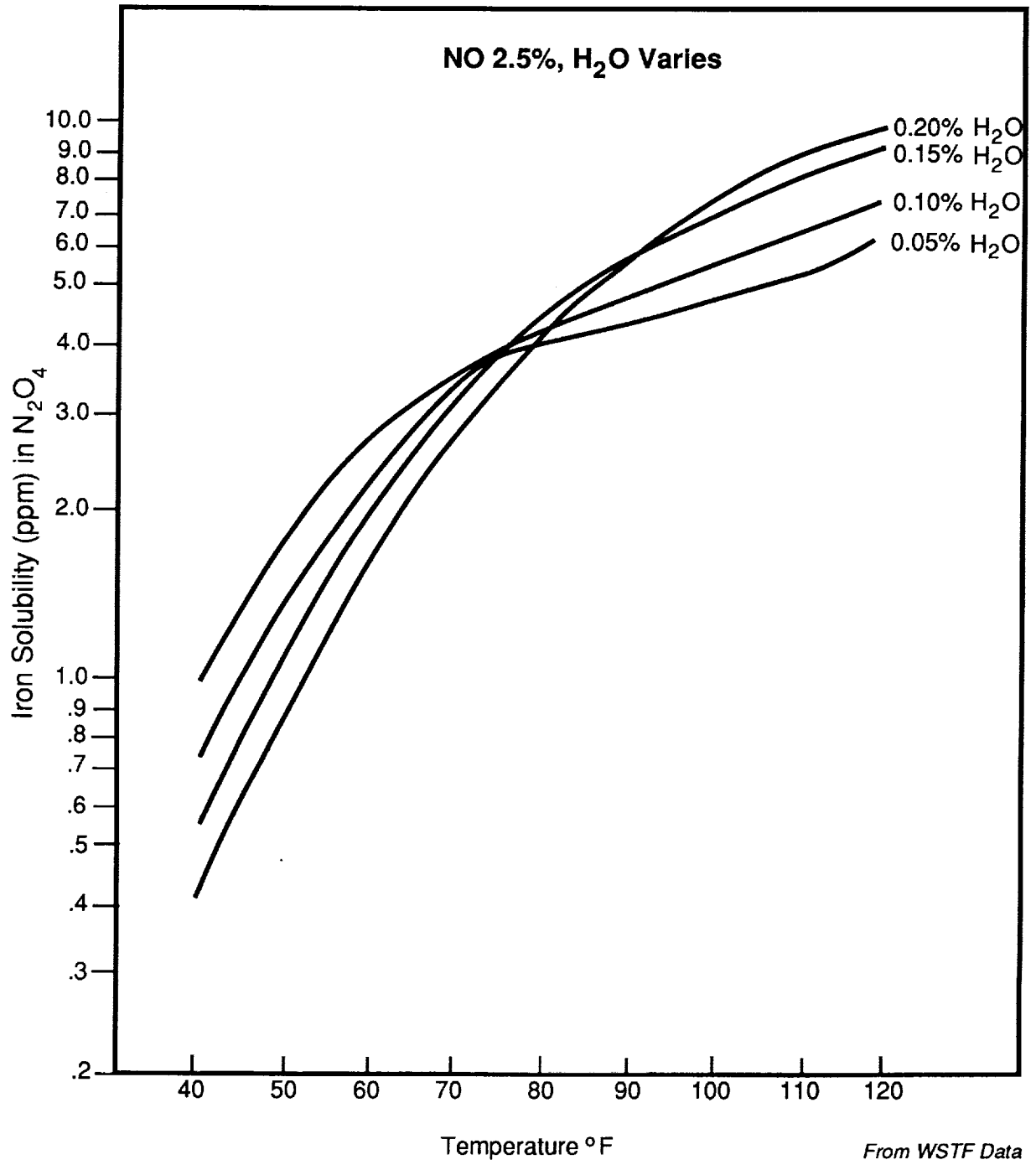


Precipitation may be caused by:

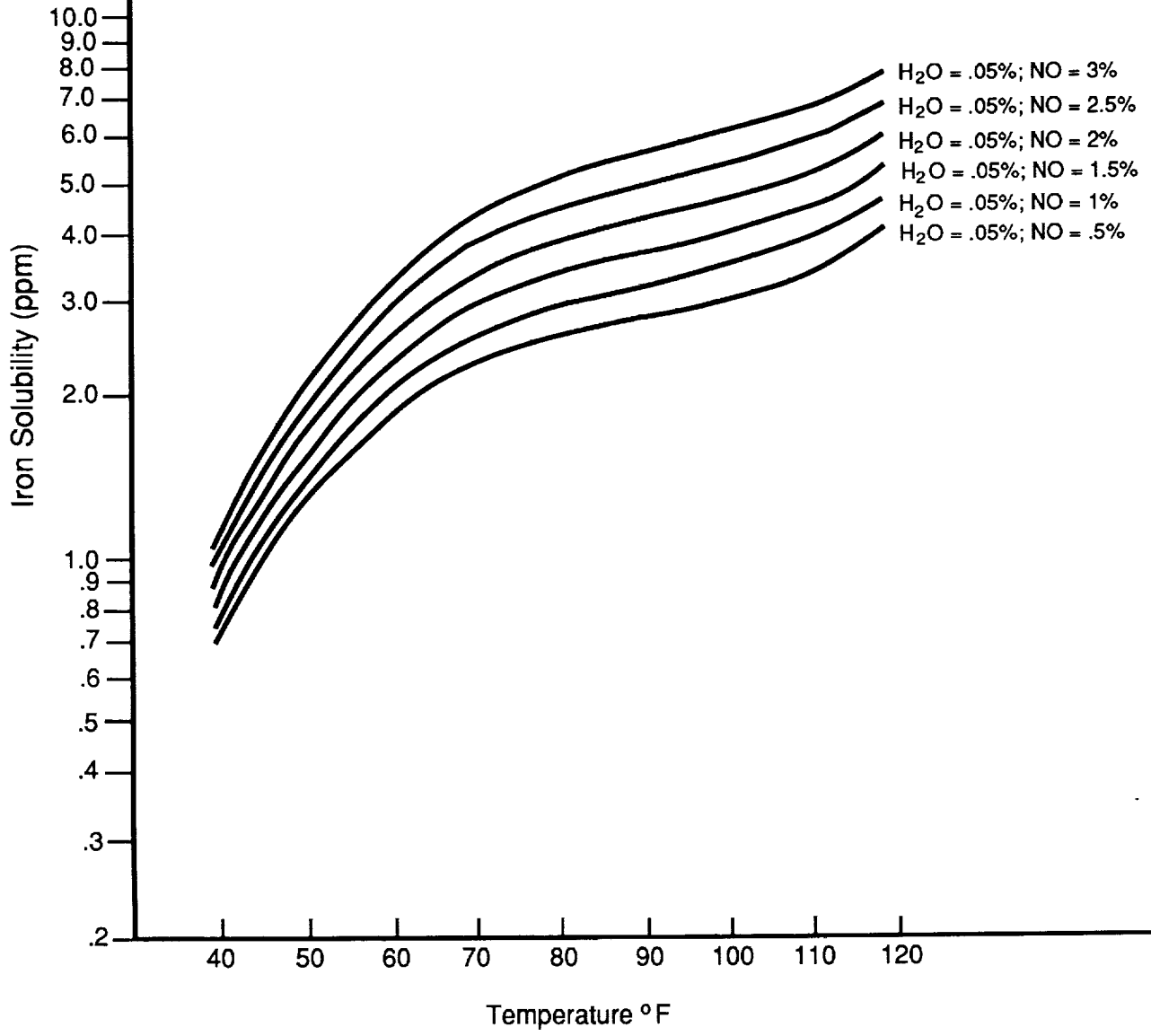
- Reaction and formation
- Evaporation of N_2O_4
- Drop in temperature
- Loss of NO ; change in (H_2O)

Figure 1. Metal Nitrate Formation Model

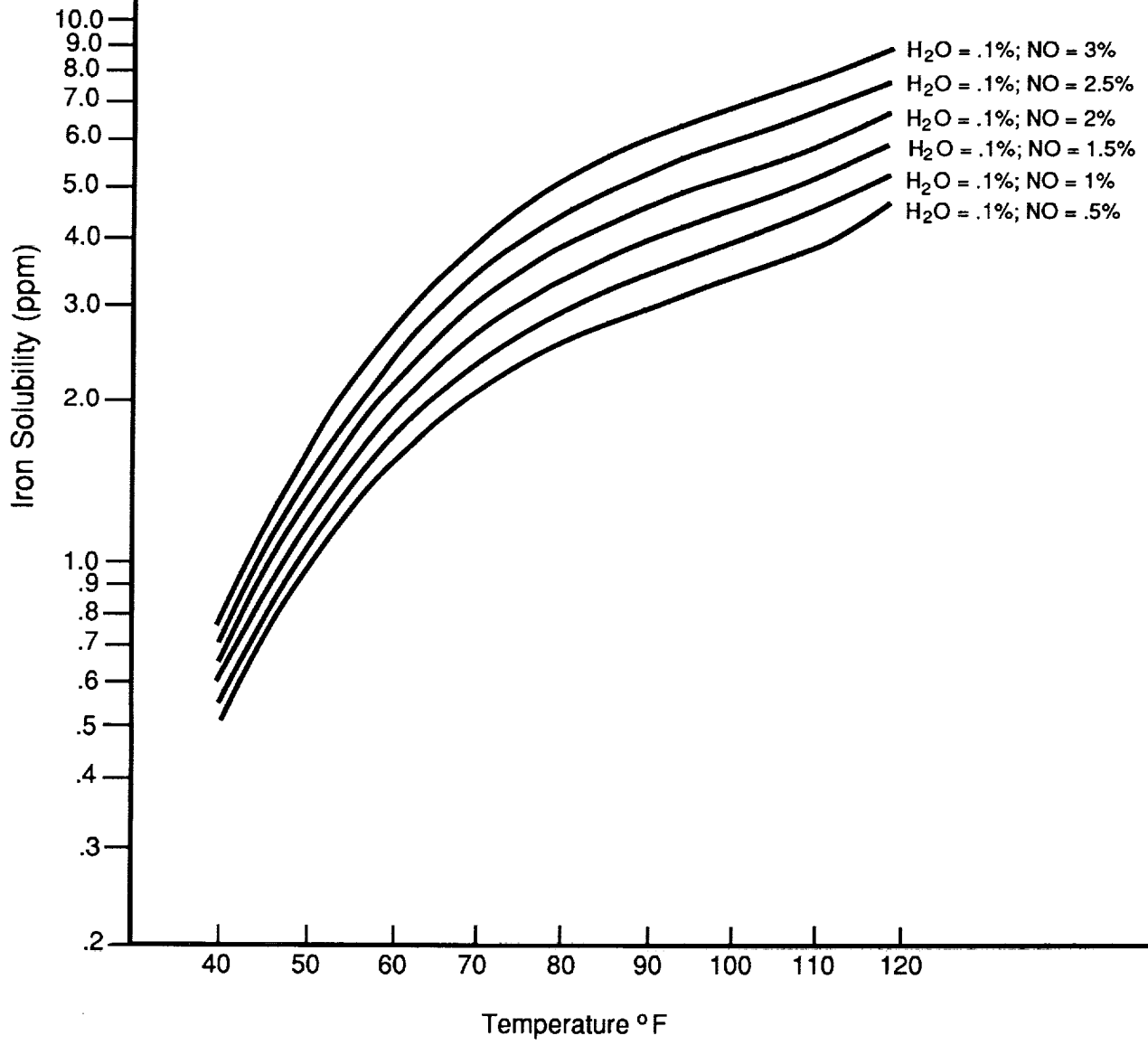




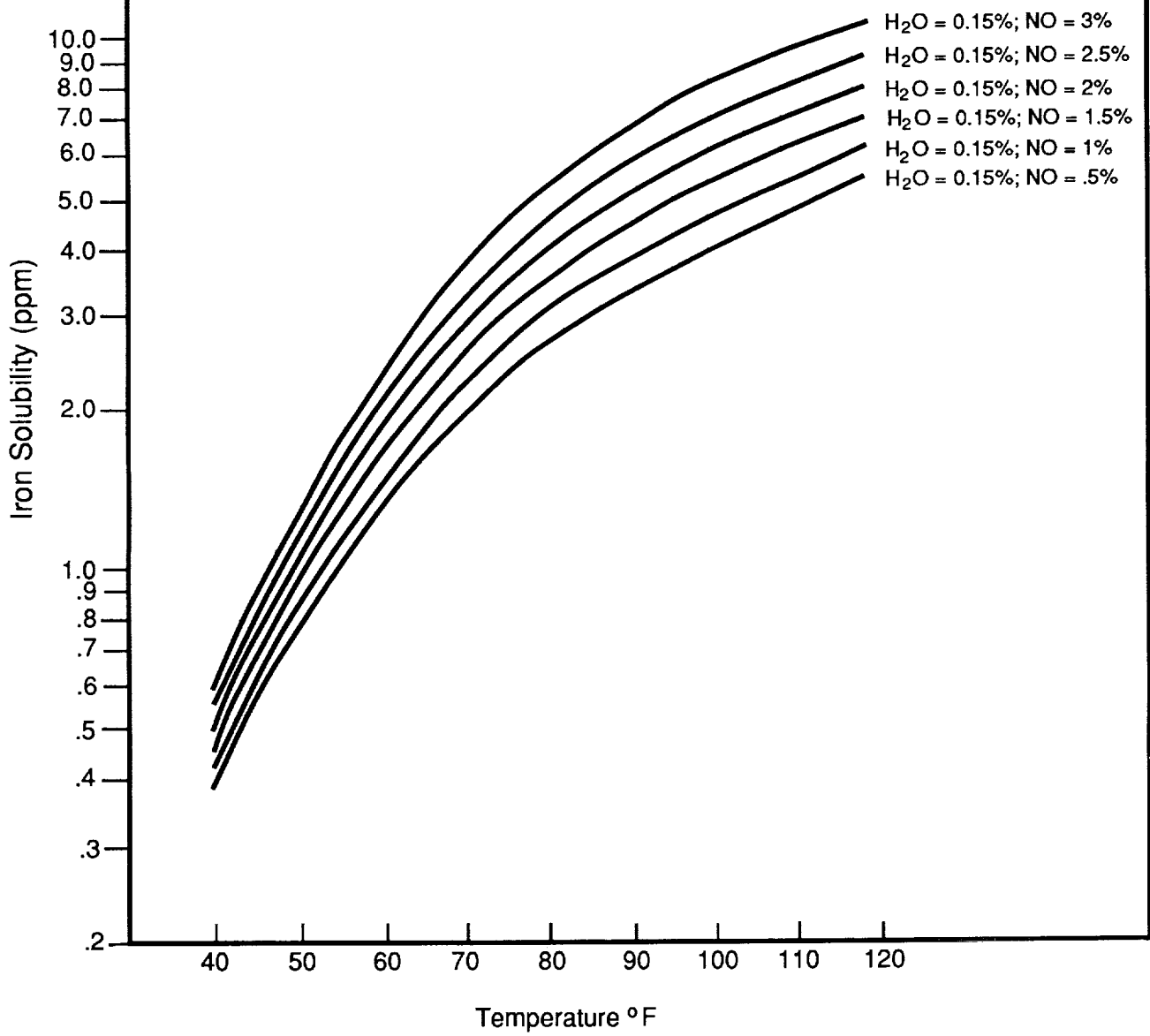
Iron Nitrate Concentration in N₂O₄



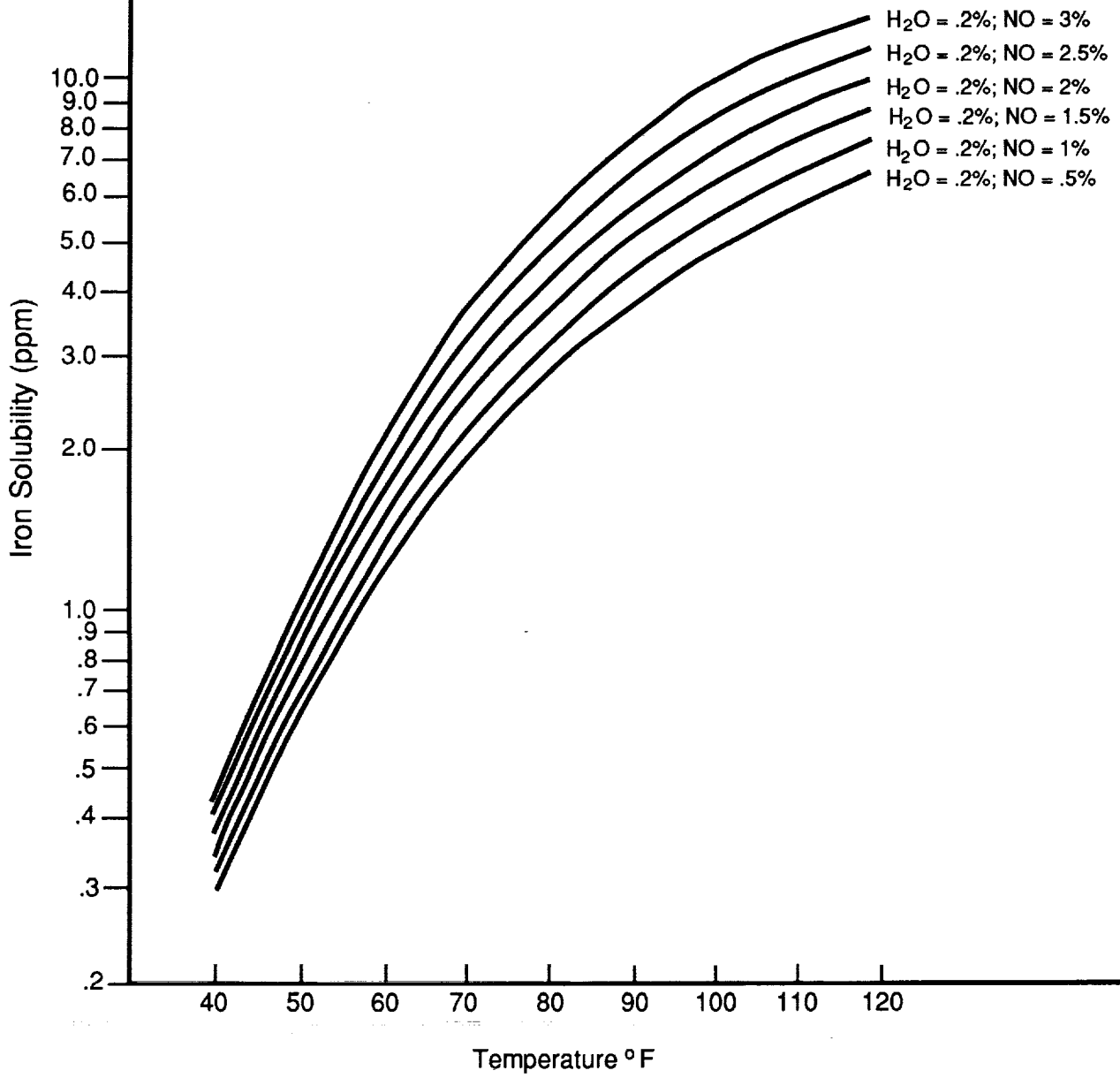
Iron Nitrate Concentration in N_2O_4



Iron Nitrate Concentration in N_2O_4



Iron Nitrate Concentration in N_2O_4



SATURATION POINT OF METAL NITRATE IN OXIDIZER AND FACTORS

The saturation point of metal nitrate in specification grade oxidizer depends on the temperature and concentration of the constituents that make the oxidizer, and on the relationship between temperature and the constituents. The following table, derived from a WSTF Tiger Team handout, shows the relationship for temperature versus the compounds N_2O_4 , NO (nitric oxide), and H_2O (water) for the given concentration ranges.

Solubility of Metal Nitrate in Oxidizer vs. Temperature
[] denotes concentration

Compound	Concentration Range	Metal Nitrate Solubility
N_2O_4	High	Directly related to temperature
NO	0.5 to 10.0%	Increases as [NO] increases
H_2O	0.05 to 0.2%	Decreases below 80°F as [H_2O] increases About the same at around 80°F as [H_2O] varies Increases above 80°F as [H_2O] increases

Note that the NO concentration metal nitrate solubility effect is more dramatic than the H_2O concentration metal nitrate solubility effect over the given concentration ranges. Also, below 80°F, higher concentrations of water actually lower the metal nitrate solubility slightly. (Water as such does not exist in oxidizer.)

MODEL FOR METAL NITRATE FORMATION (PRECIPITATE FORMATION)

Several mechanisms (some of which are interrelated) are possible for metal nitrate precipitate formation. They include lowering the temperature of the oxidizer, evaporation of N_2O_4 , lowering of [NO], variation of [H_2O] (depending on temperature), and chemical reaction and production of metal nitrate. These mechanisms will be discussed in relation to the model: The model being that to form metal nitrate, the precipitation point of the oxidizer must be reached. Below the precipitation point, the metal nitrate that is not precipitate in solution does not impede system performance.

- a. Lowering the temperature of the oxidizer: If we observe the WSTF saturation curves (iron solubility versus temperature) for the oxidizer, we see that a direct relationship exists between metal nitrate solubility and temperature. Furthermore, as the [H_2O] increases for temperatures below 70°F, the iron solubility decreases. For oxidizer consisting of 0.2 percent H_2O and 0.5 percent NO, at 60°F the iron solubility is only 1.1 ppm. The Pad A STS-35 oxidizer loaded into the orbiter was 1.0 ppm iron according to one of the two analyses. This means that if STS-35 RCS temperatures dropped below 60°F, iron nitrate probably precipitated. WSTF's experience was that once iron nitrate precipitates, the precipitate does not easily dissolve back into solution. Thus, temperature alone may be responsible for the precipitation of iron nitrate.

- b. Evaporation of N_2O_4 : A small leak can result in the evaporation of N_2O_4 , NO, H_2O , and other volatiles, but not metal nitrate and other nonvolatiles. Two things can occur from a leak.
- If only the volatiles evaporate, the nonvolatiles (which includes metal nitrate precipitate) will stay behind and build up. Therefore, the metal nitrate concentration will increase and can even reach the saturation point at and near the leak. If the leak rate is small and the diffusion rate of metal nitrate in oxidizer is high enough, the metal nitrate attempting to accumulate should diffuse away from the leak and back into other components or vessels without precipitation.
 - If evaporation occurs, the heat of vaporization will lower the temperature of the structure and oxidizer in the vicinity of the leak. The lower temperature means a lower precipitation point and a slower diffusion rate.
- c. Lowering of [NO]: The [NO] is directly related to the saturation point of metal nitrate. If [NO] preferentially evaporates at a faster rate than nitrogen tetroxide from a leak or if for some reason nitrous oxide slowly escapes from the oxidizer, the precipitation point will be lowered.
- d. Variation of [H_2O]: As mentioned in the solubility table, an increase in [H_2O] below 70°F will lower the solubility of metal nitrate in oxidizer. This effect, however, is not as profound as the temperature effect alone. In other words, it is important to keep the oxidizer system at least above 60°F. If this is done, the water effect is small. Positive system pressure should keep water and other chemical intrusion from occurring even with small leaks. Water intrusion is thought to cause adverse chemical reactions (see subparagraph e).
- e. Chemical reaction and production of metal nitrate: While corrosion rates for some metals in the oxidizer have been determined experimentally and documented, the exact steps for the production and eventual precipitation of metal nitrate apparently have not been established. Some steps and some important observations will be discussed in the next paragraph.

THE "FLOW DECAY MATERIAL" PHENOMENON

At the first Tiger Team meeting, WSTF presented a discussion of the formation of metal nitrate in small orifices in metal after oxidizer was flowed through the orifice. This metal nitrate formation, termed "flow decay material," formed only in the orifice and not on the flat metal plate at the opening to the orifice. WSTF thought this metal nitrate formation might be due to the pressure drop through the orifice. This could be true if a gas phase reaction is occurring; WSTF is studying this possibility. However, if the reaction is a liquid phase reaction and if the oxidizer remains a liquid while flowing through the orifice, the oxidizer flowing is essentially an incompressible fluid and the temperature will remain constant even if a pressure drop occurs. Furthermore, liquid phase chemical reactions are generally expressed in terms of concentrations and temperature and not pressure. (Gas phase reactions are also expressed in terms of temperature and concentrations, although sometimes partial pressures of gases are used in modeling the reaction.) The reaction mechanism (illustrated in figure 2 on page 12) is proposed for the formation of metal nitrate.

- STEP 1: Reactant approaches the metal surface from the oxidizer mixture. (The exact reactant—nitric acid, water, or nitrogen tetroxide—is not specified here. This chemistry is not well established.
- STEP 2: Reactant diffuses through a passive layer to the surface (if any passive layer is present).
- STEP 3: Reactant diffuses through the surface to the surface site where free or weak bonded iron metal is available.
- STEP 4: Chemical reaction occurs; a complex is formed.
- STEP 5: Complex diffuses away from the surface.
- STEP 6: If the metal nitrate in the oxidizer is below the saturation point and if the complex can diffuse farther away from the surface to other regions, precipitation will not occur. If the oxidizer is at the saturation point, the complex will precipitate or attach to other precipitate already formed.

As already stated, the exact chemistry is not well established: The exact role of water in the formation reaction is not known. Chemical reactions (if any) caused by water need to be experimentally determined. What is known is that the precipitate is found primarily at the inlet and outlet interfaces of the RCS system, and should be occurring due to one or more of the following mechanisms.

- a. Lowering of temperature to the saturation point
- b. Intrusion of water followed by chemical reaction
- c. Chemical reaction due to high surface area to volume ratio and inferior metal surfaces
- d. Evaporation of oxidizer
- e. Change of oxidizer composition (loss of NO)

Experimentally, we know that high chromium alloys tend to have lower corrosion rates, and that the surface area to volume oxidizer ratio does affect the corrosion production concentration.

BRIEF FAILURE ANALYSIS OF RCS VALVES

The RCS valve failure can be attributed to the metal nitrate causing the pilot poppet and main poppet to stick and not open within the specified time. The pilot poppet appears to have been the cause in at least four of the five failures. Metal nitrate buildup is heavy on the poppet and beside and below the teflon seals. In the photographs from the failure investigations, metal nitrate appears to be oozing out from under the seals and onto the teflon seal/poppet interface. The surface under the seal has an extremely high surface area to volume ratio and is, therefore, susceptible to achieving the saturation point with just moderate corrosion rates. Furthermore, the seals interface with the atmosphere and may, therefore, be susceptible to water intrusion. One failure, however, S/N 220, appears to be attributable to pits (perhaps manufacturing defects) on the poppet surface that have produced metal nitrate. The photographs show these pits, which have high surface area to volume ratios and may lack in proper passivation. Numerous inlet quick disconnects have failed at the Cape and at WSTF due to metal nitrate buildup.

Liquid Phase Reaction

- STEP 1** Reactant approaches surface
- STEP 2** Reactant diffuses through passive layer to surface
- STEP 3** Reactant diffuses to surface site of weak bonded iron
- STEP 4** Chemical reaction occurs, "complex" formed
- STEP 5** "Complex" diffuses away from surface
- STEP 6** "Complex" precipitates or diffuses to other regions

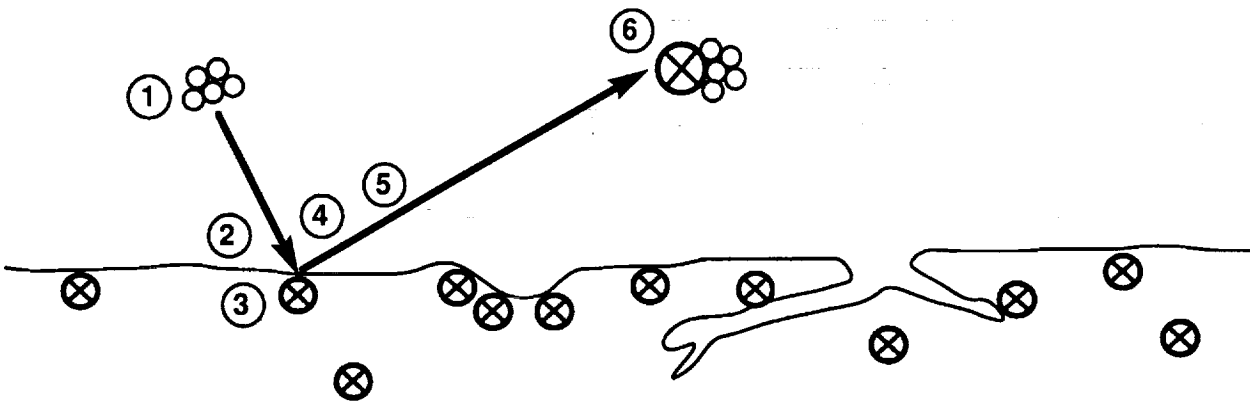


Figure 2. Liquid Phase Reaction Mechanism

SUGGESTIONS FOR PREVENTION OF METAL NITRATE FORMATION

- a. Maximize the concentration of NO in oxidizer. The WSTF solubility data shows that the NO has a fairly dramatic effect on the solubility of metal nitrate in oxidizer. The NO concentration could be increased to a level that would ensure the oxidizer retained excellent hypergolic properties yet would allow metal nitrate concentrations to be as high as 5 ppm (or even higher) without precipitation under usage conditions. However, recent WSTF tests have shown that increasing the NO concentration also increases the oxidizer reactivity with metals. WSTF has formulated and completed various experiments with high NO concentrations.
- b. Develop and use "point-of-use" metal nitrate filters to minimize the metal nitrate in nitrogen tetroxide loaded from Pads A and B at the Cape. The molecular sieve, developed at WSTF and used by the oxidizer supplier (Cedar Chemical), is typically 0.2 ppm or less in metal nitrate concentration at tank truck loading. Yet Pad A and B analysis indicates the metal nitrate is typically 0.5 to 0.6 ppm. (The analysis for STS-35 was the highest at 1.0 ppm.) Ensuring that a minimum metal nitrate concentration is initially loaded into the orbiters will increase the possibility for avoiding the saturation point. If the tank truck and Pad A and B values are real, point-of-use filters should be considered.
- c. Ensure that RCS valve temperatures do not drop below the saturation temperature (around 60°F) during all operations including orbiter ferrying. Allowing the temperature of the oxidizer to drop below the saturation point should be avoided under all circumstances. WSTF testing has shown that the precipitation point of metal nitrate is proportional to temperature, dropping to below the 1.5 ppm metal nitrate level for specification grade oxidizer at around 60°F.
- d. Better understand the basic (kinetic) chemical reactions occurring to produce metal nitrate. Basic kinetic equations were not demonstrated during the Tiger Team review apparently because the basic mechanism for the formation of metal nitrate is not well understood. Water intrusion with subsequent nitric acid formation is thought to be the major cause for corrosion, yet no proof or rate of reaction data has been established. The higher chromium alloys in general seem to be more corrosion resistant. For many metals, corrosion rates and passivation techniques seem to be fairly well established. Minimizing water intrusion (by using the universal throat plug and better handling techniques) and leaving systems wetted with nitrogen tetroxide (not water!) should help reduce corrosion. It is important, however to establish the basic kinetic equations showing the exact results of water, acid, nitrous oxide, free chlorides, and metals in nitrogen tetroxide in order to understand how metal nitrate is formed. If the basic equations cannot be established, individual metals and alloys can be tested and corrosion rates established to build corrosion tolerant systems in the future. Passivation and other corrosion prevention techniques should be experimentally proven.

EXAMPLE (NOT AN ACTUAL CASE) CORRELATING CORROSION RATE TO SATURATION POINT, WITH DETERMINATION OF A MAXIMUM SURFACE AREA (SA) TO VOLUME (VOL) RATIO

The following example (with calculations):

- Demonstrates how the corrosion rate and the saturation point may be correlated
- Is mainly intended to demonstrate appropriate calculations and terms for determining metal nitrate formation
- Provides the calculations for a maximum SA to VOL ratio (the maximum that should be used on any manufactured component to avoid reaching the saturation point and precipitation of metal nitrate)
- Uses the corrosion rate of unpassivated 304L stainless steel (data provided to Tiger Team by WSTF) which will probably have corrosion rates higher than metals and alloys generally used on flight components
- Does not assume any diffusion of produced (pre-precipitate) metal nitrate to less concentrated oxidizer (For instance, a region below a seal or a region with a very long and very thin diameter passage to the next component would, in either instance, have slow diffusion rates and, therefore, little chance of lowering the metal nitrate concentration by diffusion.)

The Fe production rate for unpassivated 304L in MON-3 N₂O₄, after 20 days, is about 1×10^{-6} grams Fe/in x inches SA. The temperature (not given in WSTF handout) is probably ambient. Note that the corrosion rate is very low after 20 days for unpassivated 304L. Corrosion rates will vary for metals, N₂O₄ composition, and temperature.

IRON PRODUCTION RATE = 1.0×10^{-6} grams Fe/in x in surface

Surface roughness, passivation, and composition affect corrosion rate. Some high chromium alloys have demonstrated superior corrosion resistance.

The maximum solubility of metal nitrate, without precipitation, at 70°F is about 3 ppm. (Worst case for 70°F from Kennedy Space Center samples of flight nitrogen tetroxide was STS-33C at 2.8 ppm.)

MAXIMUM METAL NITRATE SOLUBILITY, 70°F = 3.0 ppm:

(three Fe molecules per 1,000,000 N₂O₄ mixture molecules)

The nitrogen tetroxide loaded into the orbiter already has some metal nitrate in solution. (Worst case was Pad A STS-35 at 1.0 ppm.) Thus, the net solubility available to absorb any metal nitrate produced is the difference between the precipitation point and the initial metal nitrate concentration.

3.0 ppm total - 1.0 ppm initially = 2.0 ppm net available

Thus, another 2.0 ppm Fe could be added to solution before saturation would occur.

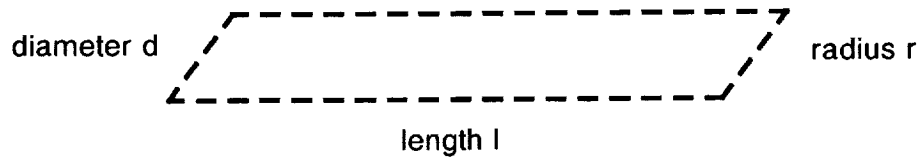
For the unpassivated 304L, the highest SA of metal to VOL of oxidizer that will not cause the solubility limit to be exceeded can now be calculated.

MW Fe = 56
 MW N₂O₄ mixture = MW N₂O₄ = 88
 density N₂O₄ = 1.45 g/cc

cm x cm (SA)
 ----- = maximum =
 cm x cm x cm (VOL) (70°F)

$$\begin{aligned}
 & \frac{\text{cm x cm (SA)}}{0.2 \times 10^{-6} \text{ g Fe}} \times \frac{56 \text{ g Fe}}{\text{gmole Fe}} \\
 = & \frac{\text{cm x cm x cm (VOL)}}{1.45 \text{ g N}_2\text{O}_4} \times \frac{88 \text{ g N}_2\text{O}_4}{\text{gmole N}_2\text{O}_4} \times \frac{1,000,000 \text{ gmole N}_2\text{O}_4}{2.0 \text{ gmole Fe}} \\
 = & 56 \times 1.5 \times 2.0 / 0.2^{-6} \times 1.0^{+6} \times 88 \text{ (cm)} \\
 = & 9 \text{ cm x cm} / \text{cm x cm x cm, maximum (SA) / (VOL) ratio}
 \end{aligned}$$

For an open-ended cylinder (a tube)



$$(SA) = 2 \times \pi \times r \times l$$

$$(VOL) = \pi \times r \times r \times l$$

$$(SA) / (VOL) = 2 / r \text{ cm}$$

$$9 \text{ cm} = \frac{2}{r} \text{ or less}$$

$$\text{or, } \frac{\text{cm}}{9} = \frac{r}{2} \text{ or greater}$$

The minimum radius needs to be 1/4.5 cm, or about 0.1 inches.

For this example with no diffusion, an unpassivated 304L tube filled with 1.0 ppm MON-3 N₂O₄, at 70°F, left stagnant for 20 days, would begin to precipitate metal nitrate if the tube radius was 0.1 inch or less.



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