

DECONTAMINATION OF MMH- AND NTO/MON –PROPELLANT TANKS

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ABSTRACT

Decontamination of liquid propellant tanks, namely MMH and NTO/MON tanks, due to emergency off-loading of a spacecraft can cause damage to the propellant tank material if safety precautions are not taken into account. MMH (Mono-Methyl Hydrazine) reacts with water with an exothermic reaction that causes temperature rise and hydrous reaction product formation. NTO and MON (Nitrogen Tetroxide Oxidiser / Mixed Oxides of Nitrogen) react with water forming nitrous and nitric acid, which may cause corrosion and enhance Stress Corrosion Cracking (SCC) in the titanium tank material. To avoid these problems, a new procedure with a numerical prediction tool for decontamination of MMH tank has been developed, used and assessed to decontaminate the MMH tank of the ESA Rosetta spacecraft successfully. The ESA proposed procedure for MON oxidiser tank emergency off-loading and decontamination is also presented.

1. INTRODUCTION

This paper presents the hazards of existing decontamination procedures [2, 3] to the reaction control system, namely to MMH and MON tanks, and gives a proposal to decontaminate MMH and MON tanks safely.

2. MMH TANK DECONTAMINATION

2.1 Hazards of MMH Tank Decontamination with Water and Isopropyl Alcohol

According to the decontamination procedure [2, 3] after off-loading the MMH liquid propellant, the propellant tank is filled and off-loaded with water, thereafter the tank is filled and off-loaded with IPA and finally dried with nitrogen gas purges.

MMH reacts with water similarly to hydrazine forming a hydrate compound. The standard heat of formation for an equimolar mixture of MMH and water is $\Delta H^\circ(298K) = -239.7 \text{ kJ/mol}$ [1]. Assuming a

completely stoichiometrically reacting mixture (containing 72 weight-% MMH and 28 weight-% H_2O) and the heat capacity of the reacting mixture as weight average of the reacting compounds, the temperature would rise 55K by adiabatic process.

At the end of water insertion, the liquid in the propellant tank will be a weak aqueous solution of MMH hydrate.

After off-loading the liquid water that contains MMH in hydrous solution, Isopropyl Alcohol (IPA) is introduced to the tank. By chemical similarity, the aqueous solution of MMH hydrate dissolves in liquid IPA. Neither a vigorous reaction nor a temperature rise can be predicted to occur in this case.

According to [3, 2] the decontamination is completed with the IPA off-loading and nitrogen gas purge cycling is performed in order to vaporise and reduce IPA and water residuals to an acceptable level. It is uncertain whether the hydrous reaction products will be vaporised and expelled with the IPA and water during the gas purges or whether residuals can remain in the tank.

The identified hazards of the procedure [2] are 1) temperature rise can be harmful for the system and 2) uncertainty of cleanliness level after removal of water and IPA by gas purging due to reaction product formation.

2.2 MMH Tank Decontamination with Nitrogen Gas Purges - Modelling

In order to avoid the hazards of water and IPA insertion in the MMH tank, it has been investigated whether liquid MMH propellant residuals can be removed from the tank effectively with nitrogen gas purges only. MMH is not known to dissociate and it has a high enough vapour pressure to allow for this procedure to be effective.

Simple and partly experimental equations were developed to simulate MMH removal efficiency with gas purges. The removed propellant pressure from the

tank volume with one gas purge can be computed with the equation 1:

$$P_{prop,rem} = \frac{P_{high} - P_{low}}{P_{high}} P_{prop,tank} \cdot k \quad (1)$$

Where $P_{prop,rem}$ = pressure of the removed propellant [bar], P_{high} = high purge pressure (created with nitrogen pressurisation) [bar], P_{low} = low purge pressure (after depressurisation) [bar], $P_{prop,tank}$ = pressure of the propellant remaining in the tank [bar] and k = removal efficiency constant [-].

As long as there is liquid propellant in the tank $P_{prop,tank}$ equals to the vapour pressure of the propellant. The removed mass of propellant can be calculated from the removed pressure in the tank volume. The residual propellant mass is then calculated by deducting the removed propellant masses from the known or assumed initial residuals.

The formulation of equation 1 is based on the assumption that the removed propellant vapour is relative to the ratio of pressure drop in the tank and to a removal efficiency k . The removal efficiency is assumed to be constant. In this paper k is derived from the ROSETTA's IPA drying curve [4] and equals $k=0.7$. The value is also in accordance with the measurement from the MMH tank drying with nitrogen gas purges of the ESA Artemis spacecraft [5]. It should be noted that since k has been evaluated based on two cases only, the model is approximate.

2.3 MMH Tank Decontamination with Nitrogen Gas Purges – Application to ROSETTA

The removal of liquid and gaseous MMH from the ROSETTA propellant tank has been evaluated with equation 1 with following parameters: high purging pressure $P_{high} = 3.5$ bar, low purging pressure $P_{low} = 1.5$ bar, tank volume $V=1.108$ m³, liquid propellant residual 0.13dm³ and temperature $T = 295$ K. It was considered that four gas purges could be done per day. Figure 1 presents the results computed with equation 1 for modelling propellant pressure in the tank in function of number of gas purges and time.

According to the computation (Fig.1) the liquid propellant residual is all in vapour form after three purge cycles and it would take a total of 28 gas purge cycles to reach a MMH concentration of 0.1 ppm [6, 6].

The ROSETTA MMH tank was decontaminated with nitrogen and helium gas purges [8], Fig 1. After 27 nitrogen gas purge cycles the measured MMH level was between 0.5 and 3 ppm, which is well in accordance with the prediction. It was then decided to change nitrogen gas to helium gas in order to achieve a high concentration of helium at the end of decontamination process. Yet, the measurements made on samples taken after a total of 28 and 30 gas cycles were indicating MMH concentrations between 4 and 13 ppm, which was confusing. Later it became obvious that the Dräger tubes that were used to determine the MMH level, gave a higher response with helium than with nitrogen.

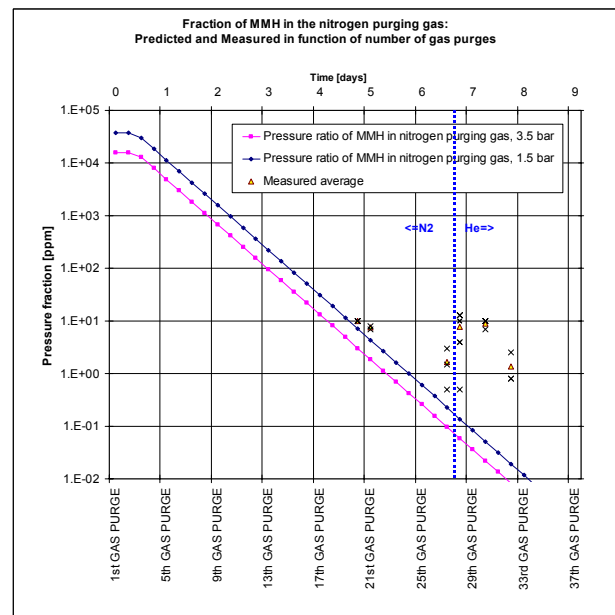


Figure 1: Pressure ratio of MMH vapour in nitrogen purging gas: predicted and measured. Predicted: The partial pressure ratio of the MMH propellant in the tanks is assumed to be constant during one purge operation, but since the purging pressure varies between 1.5 bar and 3.5 bar, the pressure ratio of MMH in the purging gas actually varies: when the purging pressure is high the ratio of MMH vapour pressure is low. Measured: The “x” signs on the graph indicate the measured values in ppm in 1 bar, the yellow triangle is the average of the measured values.

Although the finally measured MMH concentrations in helium gas (2.5, 0.8, 0.8 ppm) were higher than expected, the MMH concentration level was considered acceptable and the tank was pressurized to blanket pressure.

Lessons learned [8]:

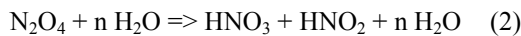
- MMH tank decontamination with nitrogen gas cycling is feasible and results are in good agreement with predictions (efficiency factor k) provided that tank internal configuration is not too complicated and strict discipline is adhered to.
- S/C heaters for tank and connected piping may not be needed provided that the ambient temperature in the facility can be raised to 24-25°C
- The Dräger tube readings were different when using helium gas as compared to readings with nitrogen gas. It is therefore advisable to complete the decontamination process with nitrogen gas before any gas exchange to helium.
- It is recommended to use a “virgin” ground half coupling and a (very) short adaptor pipe for sampling once a low level of contamination, say better 10 ppm, has been achieved. The ground half coupling and connections on the Ground Support Equipment (GSE) include filters and soft seal material that – during off-loading – can become soaked with or locally retain higher concentration of propellant that may negatively affect the sampling results.

3. NTO/MON TANK DECONTAMINATION

3.1 Hazards of MON Tank Decontamination with Water

The oxidiser used on Rosetta is Nitrogen Tetroxide (NTO, N_2O_4) containing one percent Nitrogen Monoxide (NO), therefore the oxidiser is called Mixed Oxides of Nitrogen MON-1.

NTO, which is the major part of MON-1 reacts with water in large excess and forms nitric acid (HNO_3) and nitrous acid (HNO_2) according to equation 2: [10]



Nitrous acid may undergo decomposition according to equation 3.



It has been reported on several occasions that nitric acid HNO_3 and in particular Red Fuming Nitric Acid (RFNA) causes Stress Corrosion Cracking (SCC) in titanium alloys [10], [11], and [12]. RFNA is nitric acid that contains 0.5-20% dinitrogen oxide NO_2 and 2-3 % free water.

3.2 Hazards of NTO/MON Tank Decontamination with Nitrogen Gas Purges

Because of the high liquid vapour pressure of MON-1 (1.12 bar @ 22 °C), most of the MON-1 propellant can be removed by vaporisation with nitrogen gas purge cycles similarly to MMH.

The MON-1 pressure decay can be predicted applying MON-1 liquid vapour pressure in equation 1 and having the low and high purging pressures as previously (from 1.5 bar to 3.5 bar), see figure 2. It had been assumed that MON-1 off-loading leaves $0.13dm^3$ liquid residual with its vapour pressure in the tank; hence the total mass of MON-1 residuals is 4.8 kg.

Since the nitrogen purging gas contains 11ppmv water as impurity, nitric acid formation is possible in gas phase. In Fig. 2 the nitric acid (HNO_3) level had been computed as a worst-case of nitric acid formation, assuming that all the available water and nitrogen tetroxide form HNO_3 .

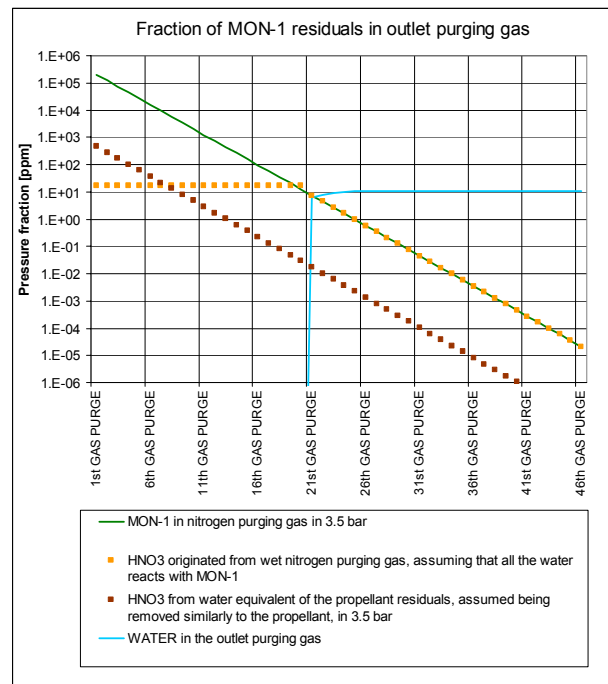


Figure 2: Decontamination of ROSETTA MON-1 tank with nitrogen gas purges.

As modelled in Fig. 2, after 20 gas purges the MON-1 vapour concentration is in the same order of magnitude as that of water. At this point, although the gas concentrations are weak, it may be possible to have a situation where the majority of the nitrogen tetroxide reacts with water and forms nitric acid, in other words the situation is approaching red fuming nitric acid (RFNA) conditions. Then the condition may become

favourable for SCC in the micro crevices of the propellant tank, which were formed during manufacturing of the tank and widened during its pressurization.

Since nitric acid enhances SCC in titanium alloys and insertion of water (liquid or vapour) in the MON-tank forms nitric acid, a decontamination procedure that minimises nitric acid formation and hence reduces SCC risk to the Reaction Control System (RCS) is introduced.

3.3 NTO/MON Tank Decontamination with Water and Isopropylalcohol (IPA)

As a precaution against having favourable conditions for SCC, a decontamination procedure with gaseous nitrogen, liquid water and liquid IPA purges is proposed to avoid the identified risks.

The MON-tank emergency Off-loading and Decontamination procedure proposed for ROSETTA consists of the following activities 1 to 8:

1. Liquid oxidant off –load: Depressurisation of the MON-1 tank from flight level (about 14.4 bar) to about 9 bar, off-loading of the liquid MON-1 oxidant and further reduction in tank pressure to 1.5 bar. This will leave about 0.13dm³ liquid MON-1 and MON-1 vapour in the tank.

2. Four nitrogen gas exchange cycles: As modelled in Figure 2, most of the residual oxidant can be removed with nitrogen gas purge cycles. The assumed 0.13dm³ liquid residual can be removed with one gas purge cycle (pressurising the tank to 3.5 bar and depressurising it to 1.5 bar). Four nitrogen gas purge cycles are proposed in order to remove all the liquid propellant and to minimise the remaining propellant in vapour form before inserting liquid water to the tank. With four gas purge cycles there is no danger of RFNA conditions.

3. Tank loading with water: Loading of the tank with water to 97 % fill level. Any possible liquid residuals on the tank inner surfaces are being taken up and diluted by the water. It had been reported [13] that the reactions 2 and 3 are slow in vapour phase. Therefore, the remaining MON-1 vapours most likely reside on the top of the liquid water in the ullage volume and are expelled through the tank gas port on top as liquid water is being introduced to the tank through the liquid port at the bottom. This way the MON-1 content in the tank is reduced to about 3% of the value at the start of the water loading.

4. Nitrogen gas exchange cycles in the ullage: The small ullage volume on top of the liquid water is purged with 11 nitrogen gas purge cycles in order to further reduce the propellant vapour concentration on top of the water and to minimise the total amount of oxidant residuals (and nitrous and nitric acid).

5. Water off-load: Water is off-loaded from the tank leaving 0.13dm³ liquid residual.

6. Tank loading with IPA: Because water has a low vapour pressure at room temperature, it would be a lengthy process to remove water (and nitric acid) residuals with nitrogen gas purges. Therefore, after liquid water removal the tank is filled with IPA to 97 % fill level. It is assumed that all the liquid water residuals containing MON oxidant residuals in the form of NHO₃ become dissolved and diluted in IPA.

7. IPA off-load: IPA is off-loaded, leaving 0.13dm³ liquid residual in the tank. This IPA residual contains a fraction of water residual and a (very) small fraction of oxidant residuals.

8. Nitrogen gas purge cycles: According to [6] CSG require tank decontamination to 3 ppm MON before permission can be given for the transfer of the spacecraft to building S1. This level would be achieved after IPA off-loading. The maximum permitted values for IPA is 25 ppm and for water 10 ppm. Approximately 20-25 gas cycles will be needed in order to achieve required cleanliness level [9].

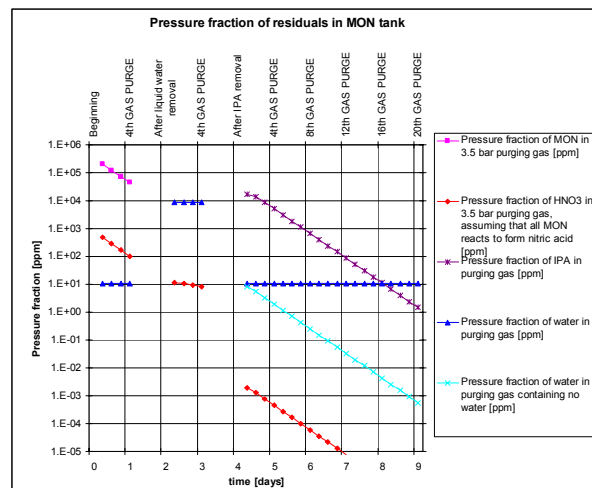


Figure 3 Pressure fraction of oxidant, water and IPA residuals in function of decontamination operations. HNO₃ level is as worst case, assuming all available water and oxidant react to form HNO₃.

Figure 3 presents the residuals levels in the oxidant tank in function of decontamination operations and time. As a worst-case approximation, it is assumed that all the oxidant vapour residuals are dissolved in water during water fill-up (action no 3.). In practise, the majority of the oxidant residuals will be removed with nitrogen gas purge cycles in the ullage on top of liquid water. It is assumed that IPA residuals can be removed with gaseous nitrogen purge cycles according to the equation 1 and that the water residuals in IPA (containing oxidant residuals) are removed at the same rate as IPA.

4. CONCLUSIONS

A procedure for the decontamination of the MMH tank with nitrogen gas cycles has been developed and assessed to decontaminate the ROSETTA MMH tank successfully. The number of nitrogen gas cycles needed to reach the required cleanliness level can be approximated with the equation presented.

A new procedure for MON tank decontamination has been developed and proposed in order to minimize tank damage potential, since water and nitrogen tetroxide react to form nitrous and nitric acid, which can cause stress corrosion cracking in titanium alloys. The proposed procedure suggests removing most of the oxidant with nitrogen gas exchange cycles before inserting liquid water and performing gas exchange cycles in the small ullage volume on top of the water. Water residuals will then be dissolved, diluted and removed with IPA. Final drying of the tank will then be performed with nitrogen gas cycles.

The lessons learned during the MMH tank decontamination shall be taken into account and incorporated in future decontamination procedures.

5. REFERENCES

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