**GENERAL DYNAMICS**
Ordnance and Tactical Systems–Canada Valleyfield

# Quantitative safety assessment of handling and storage of NG spent acid

Mario Paquet, Ian Levac and Louis-Étienne Boudreau

### The main safety concerns of NG spent, in order of priority, are the following

1 -The dissolved NG can come out of solution in the storage tank
2 -Heat from the outside: Acid can be heated to the point of self-sustained decomposition (unsafe fume-off event)
3 -Heat from the inside: Acid can start self-heating to the point of self-sustained decomposition (unsafe fume-off event)
4 -The acid can freeze in the storage tank

*All of these concerns can be safely controlled individually, collectively it is more complex*

## The foremost danger is the separation of NG from nitrating spent acid

### Proper equipment/conditions/procedures should provide:

-appropriate separation/extraction of emulsified NG from spent acid before reaching NG spent acid storage tank
-maximize NG solubility in spent acid for storage
-establish the minimum storage temperature base on spent acid composition

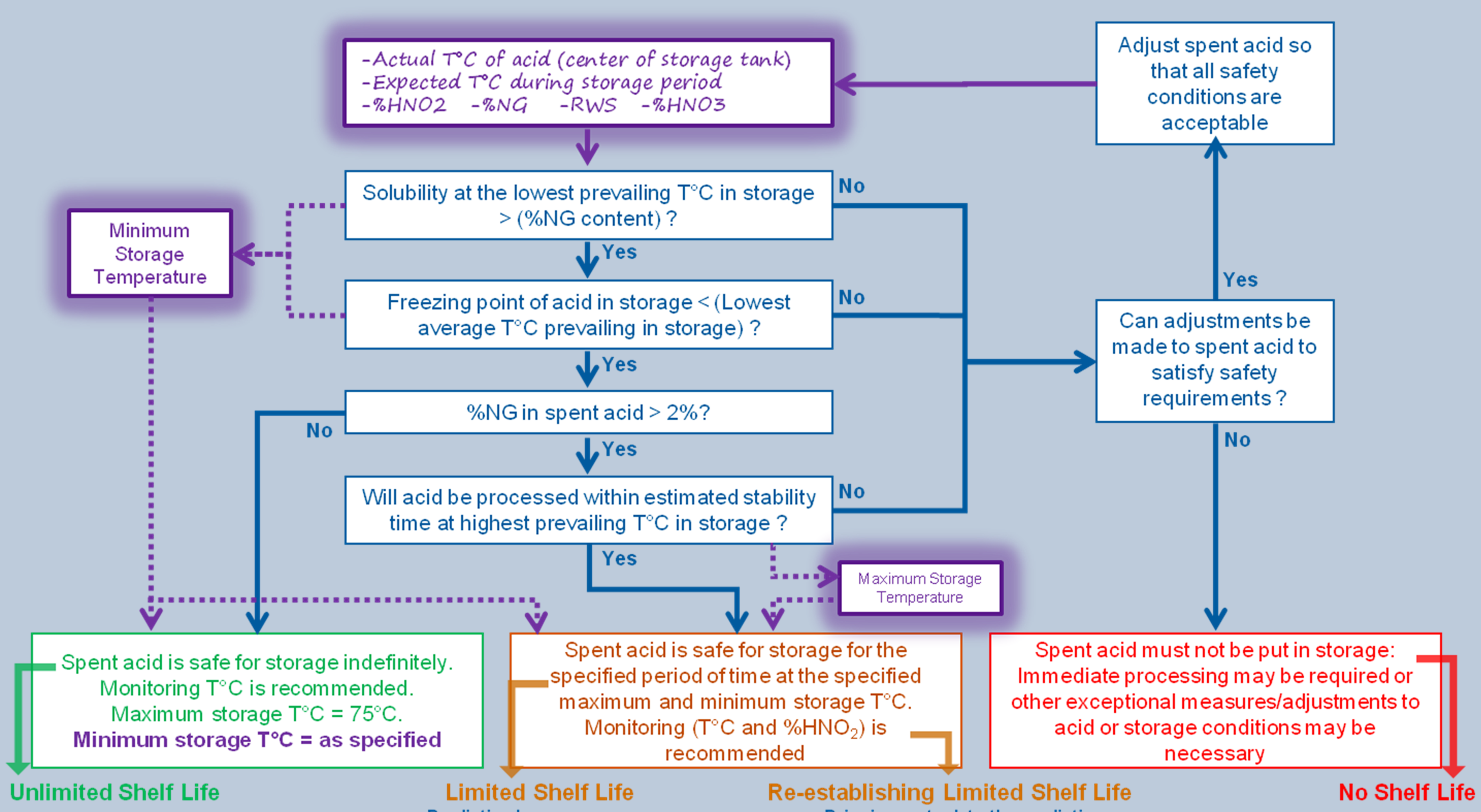
### In circumstances where NG is floating on spent acid in storage tank, a facility should be able to:

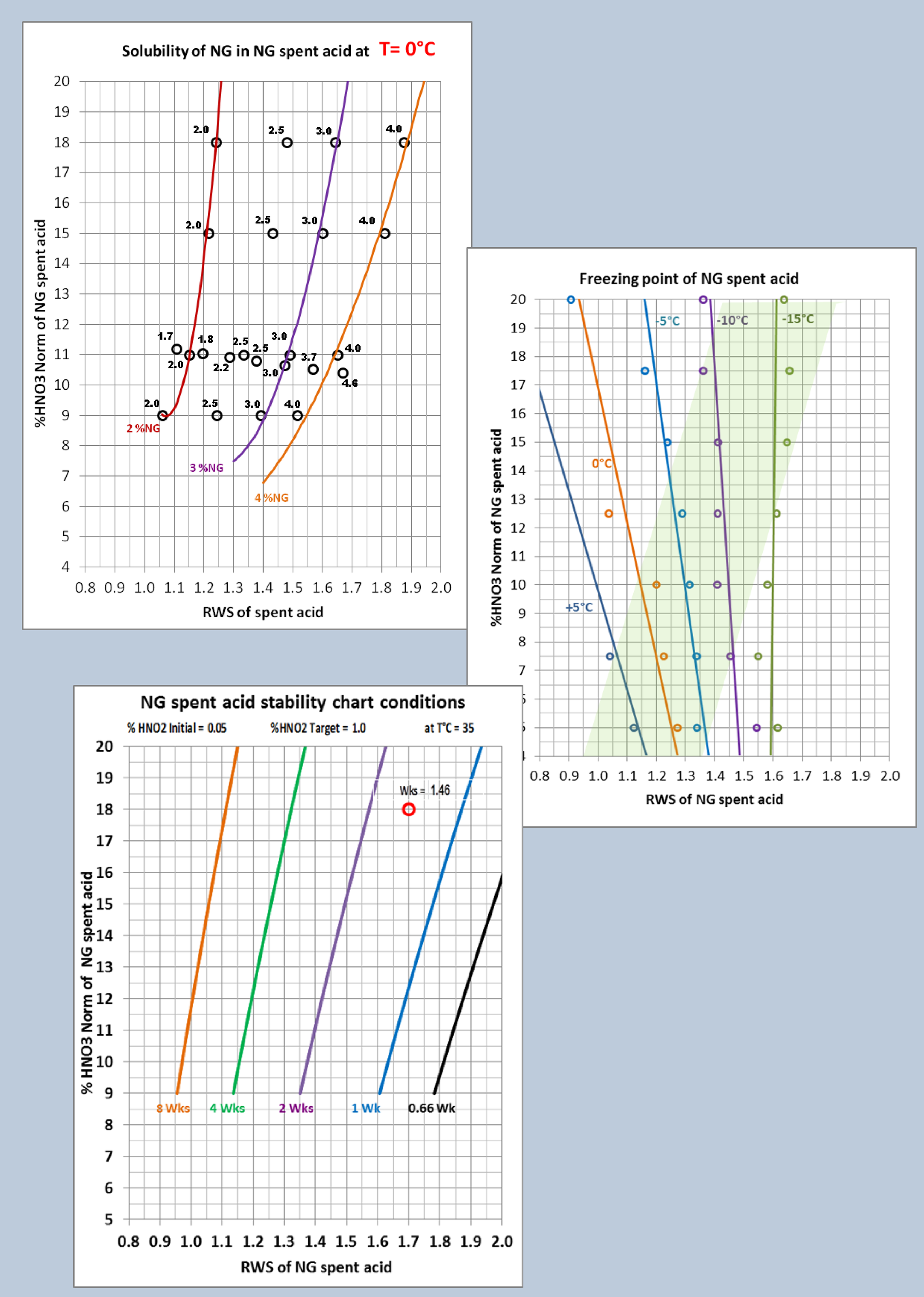
-confirm if NG is floating on top of spent acid in a storage tank and how much
-rank the hazard base on conditions and amount of NG floating
-handle properly and safely the situation

*The NG plant staff should be prepared (procedure/equipment/…) and trained to do so*

## Main safety concerns of NG spent acid

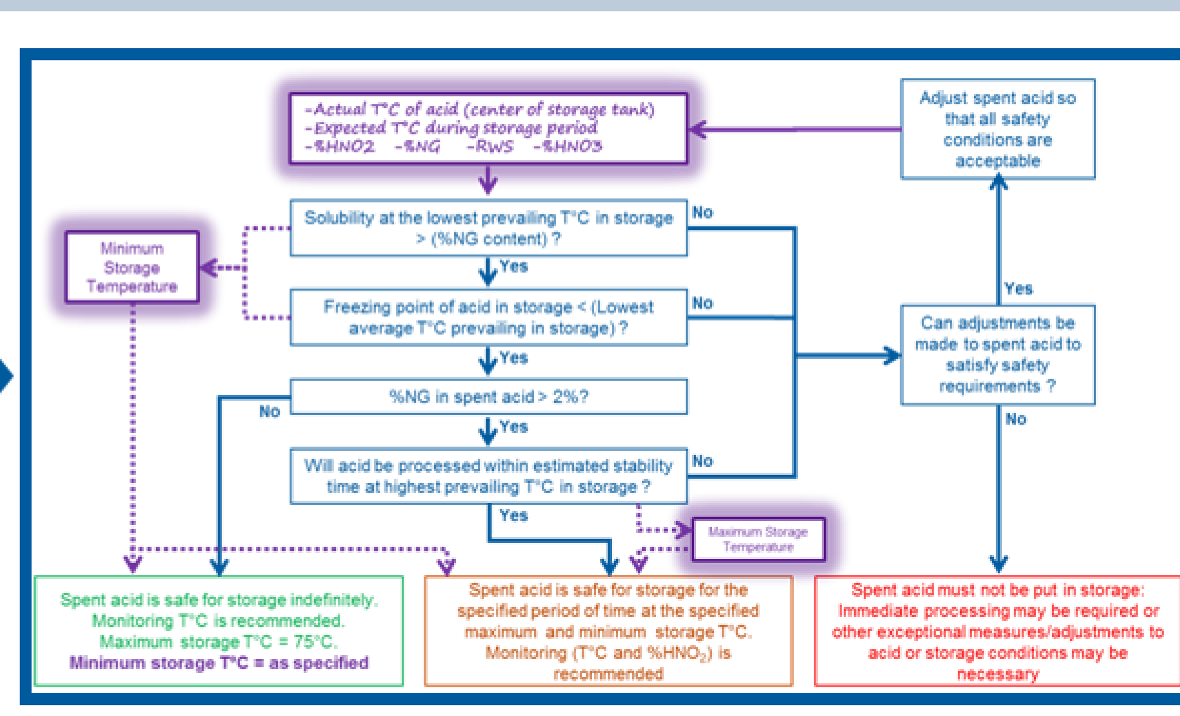
### For NG spent acid with no evidence of NG separation in storage




## INPUT

NG spent acid data:
RWS
%HNO3
%HNO2
%NG
T°C Center
T°C Ambient



## OUTPUT

NG storage condition specification:
Minimum T°C
Maximum T°C
Maximum storage time

**Information required to perform safety assessment:**

- **Solubility of NG in spent acid at various T°C**
- **Freezing T°C of NG spent acid**
- **Effect of %NG on spent acid decomposition energy** — *Severity ∝ %NG in spent acid*
- **NG spent decomposition kinetics** — *Taking into consideration acid composition (RWS,%HNO3), T°C, initial %HNO2*
- **Thresholds in decomposition kinetics** — *In order to estimate time to reach a target*
- **Non-isothermal storage conditions vs isothermal** — *Models are isothermal, real life is non-isothermal*

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# Quantitative estimation of hazard rating of NC and other nitrate ester spent acids

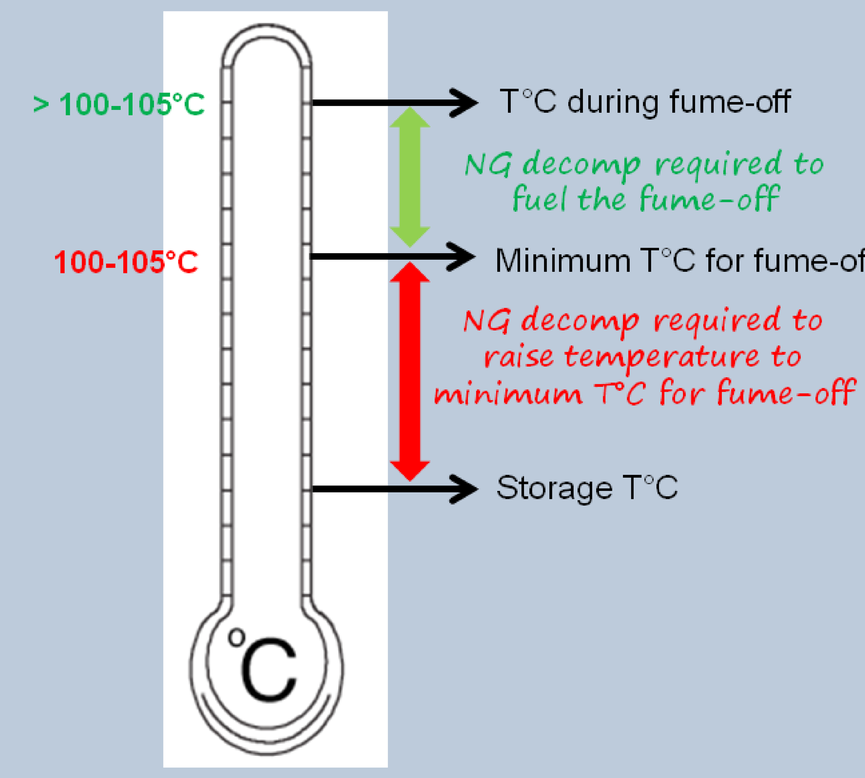
Mario Paquet, Ian Levac and Louis-Étienne Boudreau

The ability of NG spent acid to self-heat is essentially related to the total content and nature of the organic matter in the spent acid.

The NG in solution must be present in quantity sufficient to bridge the temperature gap between the external temperature and the temperature required to activate a fume-off (>90°C, near 100-105°C).

In addition: there must be enough NG left to fuel the fume-off. Temperature will rise significantly above 100-105°C threshold

*Note: Typically 120-130°C when 2-3% NG remains after reaching 100°C.*
*Can well be above 150°C when organic content is higher*




## There is a threshold below which the NG spent will be safe under all prevalent conditions possible in storage

The energy of a decomposition under adiabatic conditions produces the maximum possible temperature increase and can be estimated

$$\Delta T_{ad} = \frac{Q'}{C'_P}$$

$\Delta T_{ad}$ = *Adiabatic temperature rise in °C*
$Q'$ = *Heat of decomposition in kJ/kg*
$C'_P$ = *Specific heat capacity in kJ/(kg °C)*

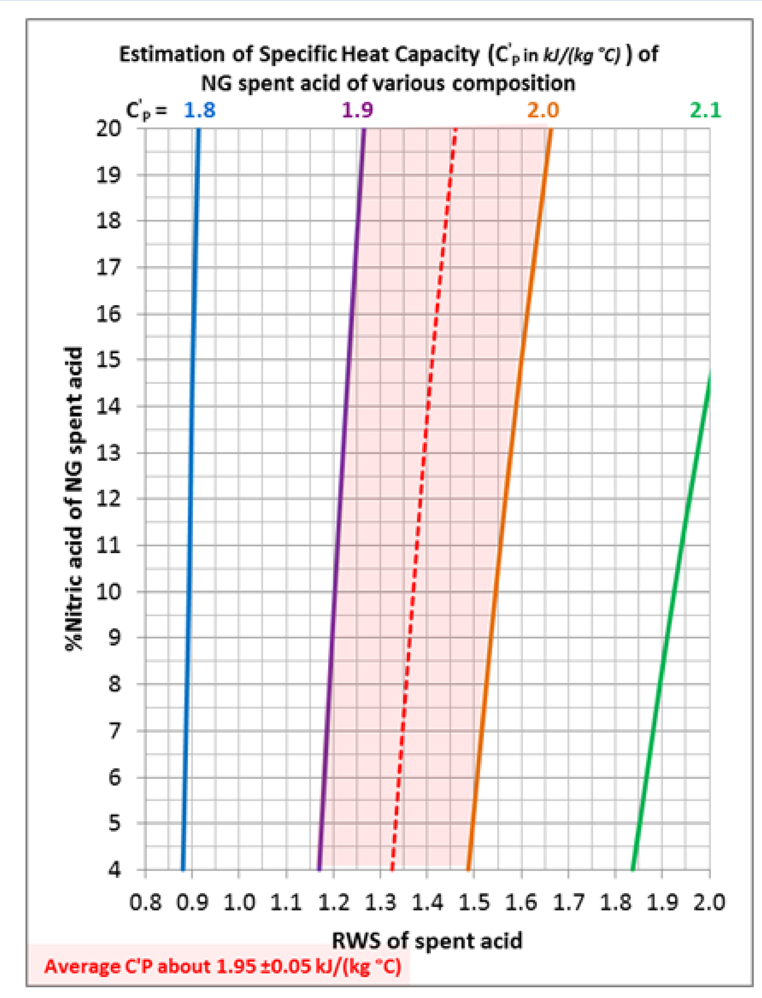
Estimation of specific heat capacity of NG spent acid of various composition since it is the mass weighted average of $C_p$ or:

$$C_P = \frac{\sum_i M_i C_{P\,i}}{\sum_i M_i} = \frac{\%Nitric}{100} C_{p\,Nitric} + \frac{\%Sulfuric}{100} C_{p\,Sulfuric} + \frac{\%Water}{100} C_{p\,Water}$$

*Where %Nitric + %Sulfuric + %Water = 100%*

| kJ / (kg K) | kJ / (kg K) | kJ / (kg K) |
|---|---|---|
| Cp Water | Cp Nitric | Cp Sulfuric |
| 4.183 | 1.744 | 1.417 |

*Rule of thumb: The average $C_P$ for most NG spent acid compositions is about 1.95 ±0.05 kJ/(kg °C)*




**Note: Cp of NG spent acid =1.744*%Nitric/100+4.183*((100-%Nitric)/((98/18)/RWS+1))/100+1.417*((100-%Nitric)/(RWS/(98/18)+1))/100**

$$\Delta T_{ad} = \frac{Q'}{C'_P}$$ → 34.8°C x 2.068 kJ/(kg °C) = about 72.0 kJ/kg NG spent acid

$$\Delta T°C_{Adiabatic} = 32.5°C \pm 2.5°C$$

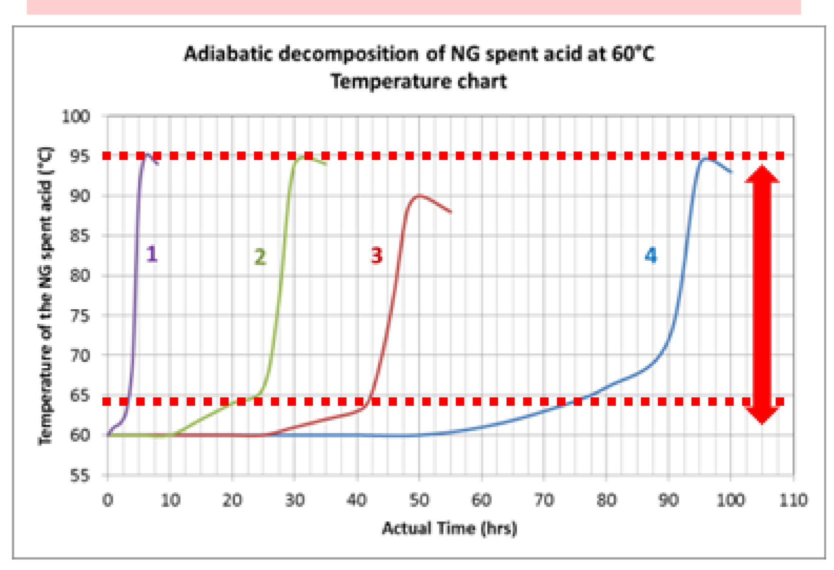
Since the concentration of NG is about 2.0%
→ Heat of reaction about -3598 kJ/kg NG in solution

*Rule of thumb:*

*Maximum Temperature Rise (MTR) (in °C) that a NG spent acid can produce by self-heating is about 17°C X %NG in solution*

**Maximum safe storage temperature is approximately:**
*Safe storage T°C →* 90°C – MTR (in °C)
*Maximum storage T°C →*105°C – MTR (in °C)

**Note: Based on the actual fume-off critical temperature of about 100-105°C**




| Curve # | 1 | 2 | 3 | 4 | Average |
|---|---|---|---|---|---|
| %HNO3 | 18.3 | 18.1 | 18.0 | 18.1 | |
| RWS | 1.93 | 1.39 | 1.40 | 1.25 | |
| %NG | 2.0 | 2.1 | 2.2 | 2.2 | |
| T°C increase | 34.8 | 35 | 30.5 | 34.5 | 34 |
| $C_p$ | 2.068 | 1.937 | 1.94 | 1.899 | 2.0 |
| $H_{react}$ of spent acid | -72.0 | -67.8 | -59.2 | -65.5 | -66 |
| $H_{react}$ of organic | -3598 | -3228 | -2690 | -2978 | -3124 |
| T°C increase/%NG | 17 | 17 | 14 | 16 | 16 |

-The concentration in nitrate ester group is proportional to the nitrogen content of the solubilized nitrate ester explosive
-The thermal decomposition of nitrate ester group of different nitrate ester explosives is similar in term of heat of decomposition and to some extend kinetic

| | | Storage time: | Indefinite Maximum temperature of storage 70°C | To be determined Temperature monitored and upper limit set | Storage not recommended (or requires an efficient and reliable temperature control) |
|---|---|---|---|---|---|
| | | Rating of thermal safety hazard | None | Important | Critical |
| Nitrate ester | %Nitrogen | T°C Adiabatic Max (T°C/% nitrate ester) | % Nitrate ester required for a **35°C** maximum increase under adiabatic condition | % Nitrate ester required for a **50°C** maximum increase under adiabatic condition | % Nitrate ester required for a **75°C** maximum increase under adiabatic condition |
| NG | 18.5 | 17 | 2.1 | 2.9 | 4.4 |
| Di-NG | 15.3 | 14 | 2.5 | 3.6 | 5.3 |
| EGDN | 18.4 | 17 | 2.1 | 3.0 | 4.4 |
| NC Grade B | 13.5 | 12 | 2.8 | 4.0 | 6.0 |
| NC Grade A | 12.6 | 12 | 3.0 | 4.3 | 6.5 |

*Suspended matter is similar to solubilized matter in term of thermal contribution to self heating of spent acid*

*Matter floating on top of the spent acid is not similar to suspended matter in term of thermal contribution to self heating of spent acid*

**The rule of thumb T°C Adiabatic Max is 12°C / % NC in spent acid (soluble and suspended)**
**< 3 % NC in spent acid is safe under all prevailing conditions (max adiab T°C increases: 35°C)**
**> 3.5 % NC in spent acid, safety is strongly dependent on stability of acid (max adiab T°C increases: 42°C)**
**> 4 % NC in spent acid, safety is extremely dependent on stability of acid (max adiab T°C increases: 50°C)**
**> 6 % NC in spent acid, safety is considered critical (max adiab T°C increases: 75°C)**

1 réservoir 300 m³ à 30 °C

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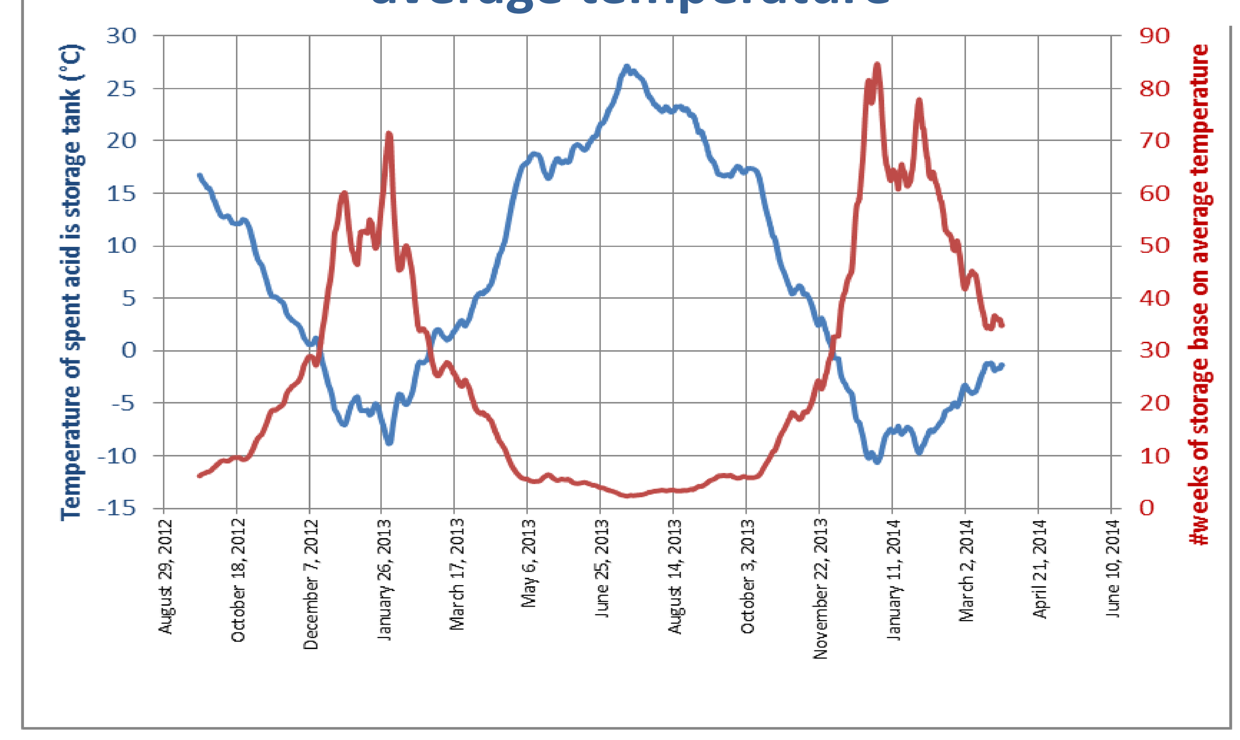
# … and if NG spent acid becomes unstable?

Louis-Étienne Boudreau

## Obtain/review available data:

-How old is the spent acid?
-What is the temperature in the spent acid (center)?
-What is the tank temperature (external surface, shade/sun, cooling,…)?
- What is the latest compositional analysis of spent acid?
-How much time available before the % $HNO_2$ reaches 0.5%?
-…

**Estimation of NG spent stability using the average temperature**




## Possible measures to correct the situation

**Dilute the acid with low spent, add virgin NG acid mix in spent acid → reduce % $HNO_2$ / change composition**

| | |
|---|---|
| Pros | Stop self heating reaction rapidly |
| Cons | Use raw material ($) |
| | Higher volume to eliminate ($) |

**Reduce temperature by spraying water on the external wall of the tank**
**Agitation of spent acid in addition to cooling by water spraying**

| | |
|---|---|
| Pros | Stop self heating reaction gradually |
| Cons | Water treatment, water vs tank containment dike system |

**Use air bubbling to reduce the % $HNO_2$ → reset the self -heating reaction**

| | |
|---|---|
| Pros | Reset the decomposition clock to zero |
| Cons | Use compressed air, handling of NOx and SOx venting |

### *Air bubbling efficiency depends on several factors:*

*-Type of air injection, size of bubbles*
*-Distribution of air bubbles along tank*
*-Quantity of acid in the tank*
*-Amount of organic matter added*

### Prevention / operating devices of a spent acid tank

Temperature reading (bottom and middle of the tank)
Level reading
Normal vent design
Explosion vent design
Water cooling system
Alarm and warning control
Frequent laboratory analysis (weekly)

## For Valleyfield:

Below 2% in NG content; the acid stability is not an important risk factor because under prevailing storage conditions, the acid is never able to reach the decomposition temperature. The only concern is NOx as an airborne contaminant.

Spent acid would need to be heated by an external source above 78°C.

Maximum average temperature of spent acid reached during summer is about 25°C.

Assuming all the NG would decompose instantaneously and adiabatically, the maximum increase in temperature would be about 25°C above ambient.