

Fire protection concept for the storage of pyrophoric materials

Dr. Armin Heyn, Bayer Technology Services GmbH, Leverkusen, Germany

Typically metal alkyl compounds are used within the chemical industry as catalysts in many organic chemical reactions. They are usually pyrophoric, i.e. upon contact with air they lead to self-ignition with the formation of harmful gases which are often irritating to the respiratory system. Metal alkyl compounds tend to react extremely vigorously with water generating intense heat and releasing flammable gases. Such fires are often poorly extinguished and can only be contained with dry chemical agents such as dry powder, vermiculite or sand. Due to the enormous heat radiant output firefighting of larger fires is limited to the cooling of adjacent plant / equipment with water spray. However it should be ensured that no water is ever allowed to enter the metal alkyl fire as water reacts very violently with metal alkyls.

In this paper graphs are presented, with which one can estimate the radiant heat output of aluminium alkyl solution fires depending on the leak rate and the distance to the fire.

Furthermore, a realized fire protection concept for the storage of aluminium alkyl solutions is presented, based on a combination of leakage prevention and radiation shielding.

Pyrophoric substances

As pyrophoric (Greek, from pyr = fire and phorein = carry) substances are referred to, which react violently with oxygen at room temperature in air. The energy released in this oxidation is so high that the materials ignite themselves. Pyrophoric substances often react violently with moisture and water.

Pyrophoric substances may be solids (powders), liquids, solutions in inert solvents or gases. The main pyrophoric substance groups are listed in Table 1

Pyrophoric substance group	Typical examples
Metal alkyls and aryls	Trimethylaluminium, (n-, sec-, tert-) butyllithium, diethylzinc, dimethylcadmium
Grignard Reagents	RMgX (R=alkyl, X=halogen), methylmagnesiumbromide
Metal carbonyls	Iron pentacarbonyl, nickel tetracarbonyl
Metal hydrides	Sodium hydride, lithium aluminium hydride
Non-metal alkyls	R3B, R3P, R3As, tributylphosphine
Non-metal hydrides	Diethylarsine, diethylphosphine
Metal powders (finely divided)	Cobalt, iron, zinc, zirconium, hafnium
Alkali and partially alkaline earth metals	Lithium, sodium, potassium, rubidium, caesium; Calcium, strontium, barium
White phosphorus	
Pyrophoric gases	(Mono- di-)silane, dichlorosilane, diborane, phosphine, arsine

Table 1: Pyrophoric substance groups and typical examples

Due to the diversity of the substances shown in Table 1, this discussion will focus mainly on alkyl-aluminium compounds, which are one of the most common pyrophoric liquids. Explanations can be largely applied to other pyrophoric liquids, too.

Properties of aluminium alkyls

According to the GHS classification aluminium alkyls are pyrophoric substances of category 1 with the following physical-chemical hazard information

- H250: Catches fire spontaneously if exposed to air and
 - H260: In contact with water releases flammable gases which may ignite spontaneously.
 - EUH014: Reacts violently with water
- and includes a health hazard statement
- H314: Causes severe skin burns and eye damage.

Hazardous reactions can occur with organic acids, esters, alcohols, aldehydes / ketones, amines / amides, ethers, hydrogen halides, etc.

By dissolving aluminium alkyls in inert solvents such as aliphatic and aromatic hydrocarbons, the solution can be diluted below the

- Self-ignition-limit (limiting concentration above which the solution ignites itself) or
- Non-pyrophoric-limit (limiting concentration < self-ignition-limit above which cellulose-containing material in a standard 'filter paper test'¹ does not show charring / browning)

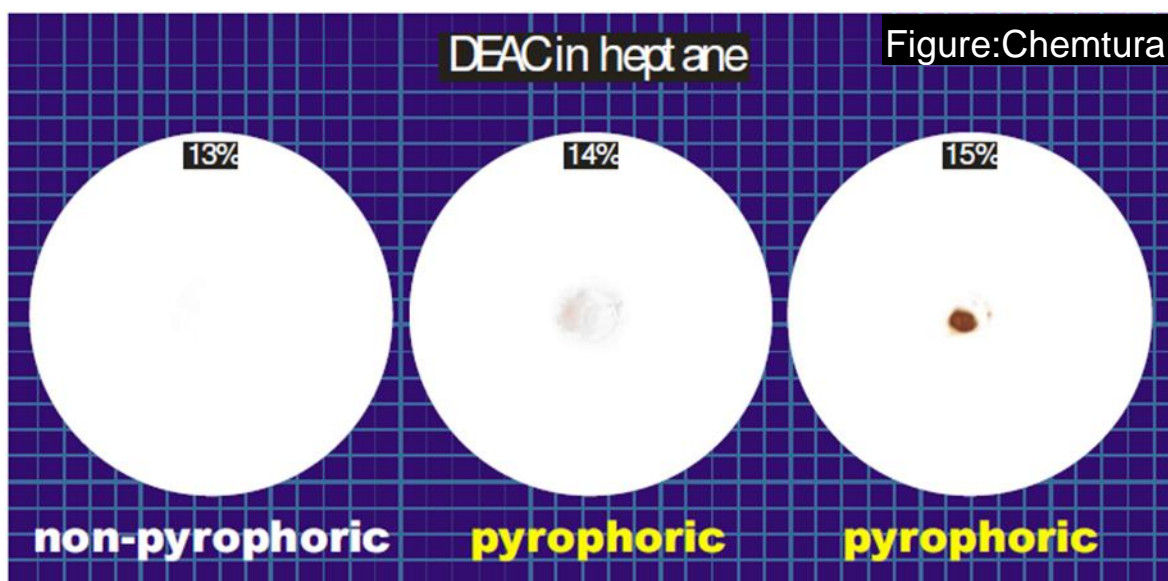


Figure 1²: 'Filter paper test' for diethyl aluminium chloride dissolved in heptane

In figure 1, the 'filter paper test' of diethyl aluminium chloride dissolved in heptane is shown. Up to a concentration of 13% DEAC in heptane does not show browning on the cellulose. From 14% browning begins. Thus the non-pyrophoric-limit is 13%.

The Transport labelling of aluminium alkyls (Figure 2) differs, depending on whether they are transported above or below the non-pyrophoric-limit.

Transport-Labeling

- **Spontaneously Combustible (Class 4.2) if > NPL**

X333

3394

SPONTANEOUSLY COMBUSTIBLE
4

DANGEROUS WHEN WET
4

UN # new: 3394 = Organometallic substance, liquid, pyrophoric, water-reactive UN # old: 3051 = Aluminium alkyls
- **Water-reactive substances/Dangerous when wet materials (Class 4.3) if < NPL**

X323

3399

DANGEROUS WHEN WET
4

FLAMMABLE LIQUID
3

UN # new: 3399 = Organometallic compound, liquid, flammable, water-reactive UN # old: 3207 = Organometallic compound or compound solution / dispersion water reactive, flammable, N.O.S

Figure 2²: Transport labelling for aluminium alkyls depending on the non-pyrophoric-limit

According to table 2 the non-pyrophoric-limit depends on the alkyl chain length of the aluminium alkyl. Note that the lowest value, i.e. most-pyrophoric is for the triethyl and not the trimethyl aluminium. With alkyl chain lengths from dodecyl on, the aluminium alkyl is non-pyrophoric. Furthermore, the non-pyrophoric-limit increases with an increasing number of by halide atoms, substituted alkyl chains and with an increasing chain length of the inert solvent.

Tradename	Formula	Solvent	NPL [wt.%]	Source: Chemtura
TMA	(CH ₃) ₃ Al	Heptane	14	
TEA	(C ₂ H ₅) ₃ Al	Heptane	12	
TBA	(n-C ₄ H ₉) ₃ Al	Heptane	27	
THA	(n-C ₆ H ₁₃) ₃ Al	Heptane	49	
TOA	(n-C ₈ H ₁₇) ₃ Al	Heptane	61	
TDDA	(n-C ₁₂ H ₂₅) ₃ Al		non-pyrophoric	
DEAC	(C ₂ H ₅) ₂ AlCl	Heptane	13	
EASC	(C ₂ H ₅) ₃ Al ₂ Cl ₃	Heptane	15	
EADC	C ₂ H ₅ AlCl ₂	Heptane	29	
TEA	(C ₂ H ₅) ₃ Al	Pentane	10	
TEA	(C ₂ H ₅) ₃ Al	Hexane	12	
TEA	(C ₂ H ₅) ₃ Al	Nonane	13	

Table 2²: Dependence of the non-pyrophoric-limit of various parameters

Solutions of aluminium alkyls above the self-ignition-limit show beyond spontaneous combustion in air an even more violent reaction with water. Large quantities of combustible gases which usually ignite spontaneously are released in an explosive reaction.³

Below the self-ignition-limit the oxidation in air causes an increase in temperature resulting in a more rapid evaporation of the solvent. As the evaporation of the solvent increases the reaction speeds up, but spontaneous combustion does not occur. Again, on contact with water the solution shows a much more violent reaction. This hydrolysis reaction releases heat and causes fast solvent evaporation, without leading to self-ignition. Here too a potentially explosive gas air mixture is formed.³

Fighting of aluminium alkyl fires

Firefighting of aluminium alkyl fires is limited because the radiant heat is very high and the fire cannot be realistically extinguished because air contact reignites the fire immediately.

Therefore firefighting is limited to the attenuation of the fire dynamics and radiated heat by cutting off the air supply to the burning surface, and by cooling of adjacent facilities with water spray. At this point it has to be ensured that no water aerosols enter the fire and reinforce it due to the violent reaction of aluminium alkyls with water.³

For firefighting dry extinguishing powders of classes A, B, C and B, C are well suited and should be applied if possible with applicators onto the burning surface. In order to guarantee controlled burn out 5 - 10 kg of dry powder is required per kg of aluminium alkyl. As an alternative to dry powder vermiculite can also be used. The light absorbent material is particularly suited for large fires. Vermiculite-filled plastic sacks are usually used in burning-trenches and -pits. After the sacks melt the material spreads over the surface and reduces the oxygen supply. But caution must be exercised, as there may still be active material under the surface which must be made to react under controlled conditions.³

For fighting larger fires, in addition to the normal fire brigade clothing, a special protective suit must be kept ready which can also be worn over breathing apparatus. This consists of aluminized trousers and a jacket with integral hood made of the same material. The heat resistant visor is a gold coated glass pane.³

Calculation of the radiant heat of aluminium alkyl fires

For the development of an adequate fire protection concept, the knowledge of the heat flux as a function of the size of the fire respectively the size of the leakage and the distance from the fire is essential.

According to the 'Yellow Book'⁴ the radiation heat of an aluminium alkyl pool fire can be calculated in the following steps:

1. Determination of the burning rate
2. Calculation of the average flame length
3. Calculation of the flame tilt angle
4. Calculation of the elongated flame diameter
5. Calculation of the flame surface emissive power (SEP)
6. Calculation of atmospheric transmissivity (radiation permeability)
7. Calculation of the view factor
8. Calculation of the heat flux

Step 1: Determination of the burning rate

If the burning rate was not measured, the best correlation to predict the rate of burning of a combustible liquid (single component) under ambient conditions is by Burgess [1974]⁴

$$m'' = c_8 \cdot \frac{\Delta H_c}{\Delta H_v + c_p \cdot (T_b - T_a)} \left(\frac{kg}{m^2 \cdot s} \right) \quad c_8 = 0,0006 \left(\frac{kg}{m^2 \cdot s} \right) \quad (1)$$

- with: m'' = Burning rate under still weather conditions in $kg/(m^2 \cdot s)$
- ΔH_c = Heat of combustion
- ΔH_v = Heat of vaporization
- c_p = Specific heat capacity of the liquid
- T_b = Boiling temperature
- T_a = Ambient temperature
- c_8 = The original value of 0.001 was adapted to the fire tests of AkzoNobel⁵ to 0.0006

An aluminium alkyl solution is a mixture of an inert solvent with an aluminium alkyl. The burning rate of the mixture is determined by the evaporation of the two components in the combustion zone.

Due to their different volatilities the burning rate of the solvent is much higher than that of the aluminium alkyl as shown in Figure 3

This phenomenon was confirmed by fire tests of AkzoNobel⁵.

According to figure 4 aluminium alkyl solutions show a maximum burning rate at the beginning which decreases continuously with increasing duration of the fire.

Table 3 shows for a typical 20 - 30% solution of aluminium alkyl in n-hexane a measured max burning rate for a pool fire of $m'' = 0,073 \text{ kg/m}^2 \cdot \text{s}$.

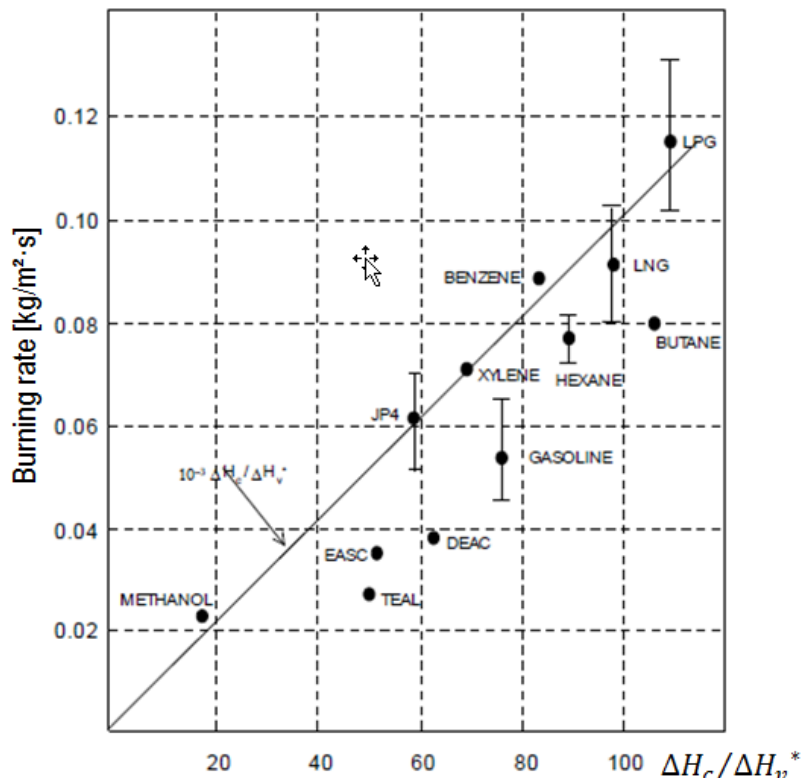


Figure 3: Relationship between burning rate and $\Delta H_c / \Delta H_v^*$ by Burgess & Zabitakis⁴

Product	Max. Burning rate ($kg/m^2 \cdot s$)
11% TEAL/Isopentane	0,083 - 0,033
22% TEAL/Isopentane	0,078 - 0,030
20% TEAL/n-Hexane	0,073 - 0,037
50% TEAL/n-Hexane	0,072 - 0,037

Table 3: Measured burning rates of TEAL / isopentane and TEAL / n-hexane solutions; Source: AkzoNobel⁵

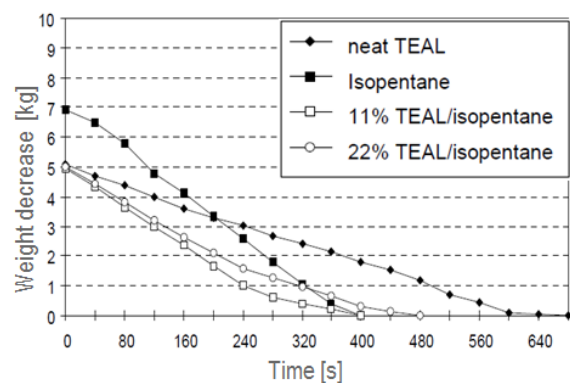


Figure 4: Measured contribution of isopentane and TEAL to the burning rate of TEAL / isopentane solutions; Source: AkzoNobel⁵

Step 2: Calculation of the average flame length

From the characteristic wind velocity u_c :

$$u_c = (g \cdot m'' \cdot D / \rho_{air})^{1/3} \quad (2)$$

- with: u_c = Characteristic wind velocity in m/s
- g = Gravitational acceleration 9,81 m/s²
- m'' = Burning rate at still weather conditions in kg/(m²·s)
- D = Pool diameter in m
- ρ_{air} = Density of air 1,2 kg/m³

and the scaled wind velocity u^* :

$$u^* = u_w / u_c \quad (3)$$

- with: u_w = Wind velocity in 10 m height in m/s

the average flame length L is calculated to:

$$L/D = 55 \cdot (m'' / (\rho_{air} \cdot (g \cdot D)^{1/2}))^{0,67} \cdot u^{*0,21} \quad (4)$$

- with: L = Average flame length in m

From Figure 5 and Table 4 in conjunction with Figure 4 and Figure 3 the dependency of the flame length from the burning rate is visible. Figure 6 shows the calculated flame height as a function of the pool area.

Product	measured (m)	calculated (m)
DEAC	2,3	2,7
EASC	2,2	2,6
TEAL	2,0	2,2
Isopentane	4,0	4,9
n-Pentane	3,5	4,4
n-Hexane	3,1	4,1
n-Heptane	3,0	3,8

Table 4: Comparison of measured and calculated flame height of a 1 m² pool fire; Source: AkzoNobel⁵



Figure 5: Flame height of a 1 m² pool fire of neat TEAL and 11% TEAL / isopentane solution; Source AkzoNobel⁵

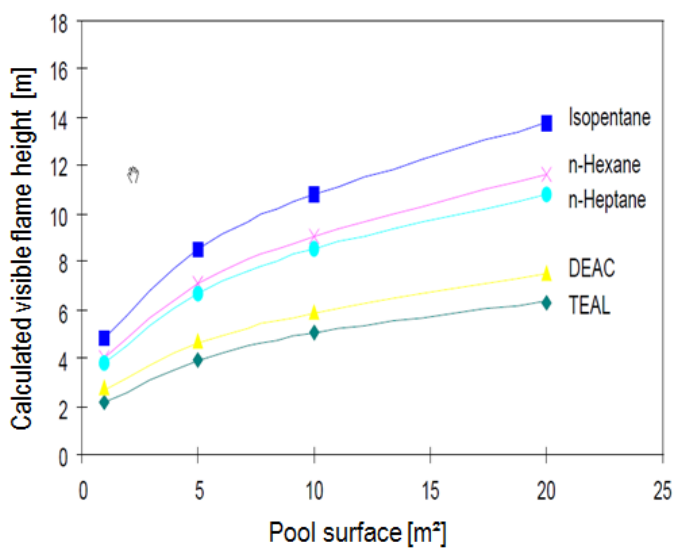


Figure 6: Calculated visible flame heights of big pool fires of neat Al-alkyls and solvents; Source: AkzoNobel⁵

Step 3: Calculation of the flame tilt angle

From the Froude number Fr_{10} :

$$Fr_{10} = u_w^2 / (g \cdot D) \quad (5)$$

with: Fr_{10} = Froude number for wind velocity at a height of 10 m

and the Reynolds number

$$Re = u_w \cdot D / \nu \quad (6)$$

with: ν = Kinematic viscosity of air in m^2/s

the flame tilt angle function is calculated to:

$$\tan \theta / \cos \theta = 0,666 \cdot Fr_{10}^{0,333} \cdot Re^{0,117} \quad (7)$$

with: θ = Flame tilt angle in degrees

With $\tan \theta / \cos \theta = c$ the flame tilt angle θ (figure 7) can be calculated analytically to:

$$\theta = \arcsin(((4 \cdot c^2 + 1)^{1/2} - 1) / (2 \cdot c)) \quad (8)$$

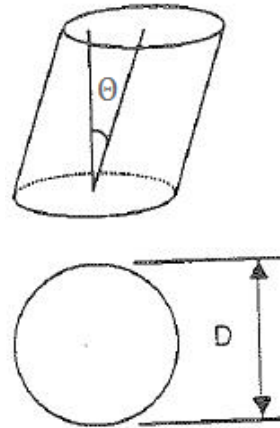


Figure 7: Tilt angle θ of a cylindrical flame

Step 4: Calculation of the elongated flame diameter

With the influence of wind, the flame is compressed on the leeward side to the ground before it rises from the floor (flame-drag). This increases the flame base surface and stretches it to an elliptical form. The stretched diameter D' (Figure 8) increases the flame surface and reduces the distance to the irradiated object on the leeward side. It is calculated for a cylindrical flame form to:

$$D' / D = 1,5 \cdot Fr_{10}^{0,069} \quad (9)$$

with: D = Pool diameter in m

D' = Actual elongated flame base diameter in m

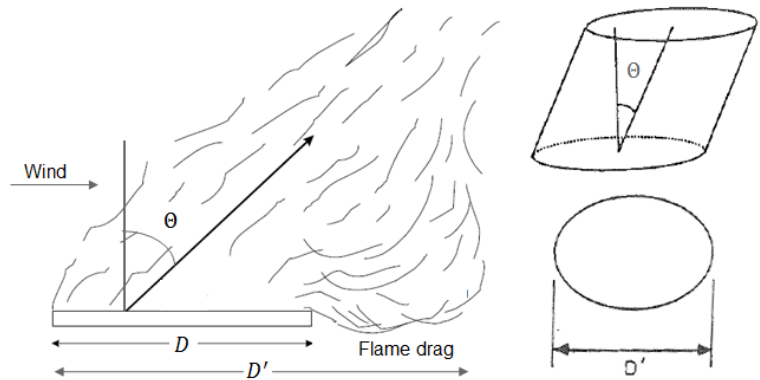


Figure 8: Due to wind elongated flame base diameter D'

Step 5: Calculation of the flame surface emissive power (SEP)

The flame surface emissive power (SEP) is calculated for an inclined cylindrical flame to:

$$SEP_{max} = F_s \cdot m'' \cdot \Delta H_c / (1 + 4 \cdot L / D) \quad (J / (m^2 \cdot s)) \quad (10)$$

with: SEP_{max} = Maximum Surface Emissive Power from a flame without soot production in $J/(m^2 \cdot s)$

F_s = Fraction of the combustion energy radiated from the flame surface; according to Burgess, Hertzberg [1974], F_s is independent from D between 0.1 – 0.4

m'' = Burning rate at still weather conditions in $kg/(m^2 \cdot s)$

ΔH_c = Heat of combustion in J/kg

L = Average flame height in m

D = Pool diameter in m

The SEP_{max} is greatly reduced by the formation of soot to:

$$SEP_{act} = SEP_{max} \cdot (1 - \zeta) + SEP_{soot} \cdot \zeta \quad (11)$$

with: SEP_{act} = Actual surface emissive power in $J/(m^2 \cdot s)$

SEP_{soot} = Surface emissive power of soot, $\approx 20 \cdot 10^3 J/(m^2 \cdot s)$

ζ = 0.8 (representative figure from the literature for pool fires of oil products)

Step 6: Calculation of atmospheric transmissivity (radiation permeability)

The atmospheric transmissivity τ_a

$$\tau_a = 1 - \alpha_w - \alpha_c \quad (12)$$

$\alpha_w, \alpha_c =$ Absorption factor for water vapour, CO₂ in air

can be read from figure 9 with the partial vapour pressure of water

$$p_w = RH \cdot p_w^o \quad (13)$$

$RH =$ Relative humidity, fraction between 0 and 1

$p_w^o =$ Saturated vapour pressure of water in air, in N/m²

or calculated for $10^4 < p_w \cdot x < 10^5$ to:

$$\tau_a = c_7 \cdot (p_w \cdot x)^{-0.09} \quad (14)$$

with: $x =$ Distance from the surface area of the flame to the object in m

$c_7 = 2.02 (N/m^2)^{0.09} \cdot m^{0.09}$; includes α_c , since the CO₂ concentration in air is constant

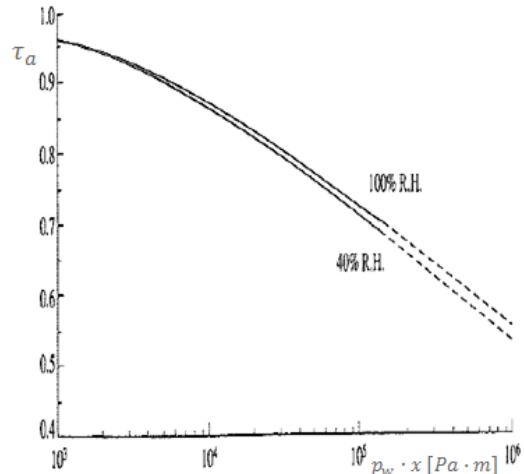


Figure 9: Transmissivity as a function of $p_w \cdot x$ (radiator temperature 1200K)
Source: 'Yellow Book'⁴

Step 7: Calculation of the view factor

When approaching the flame by an inclined cylindrical shape, the maximum view factors F_{max} are calculated from the vertical F_v and horizontal F_h view factors:

$$F_{max} = \sqrt{F_v^2 + F_h^2} \quad (15)$$

with the auxiliary quantities (16)

$$\begin{aligned} a &= L/R; \quad b = X/R \\ A &= \sqrt{a^2 + (b+1)^2 - 2 \cdot a \cdot (b+1) \cdot \sin(\theta)} \\ B &= \sqrt{a^2 + (b-1)^2 - 2 \cdot a \cdot (b-1) \cdot \sin(\theta)} \\ C &= \sqrt{1 + (b^2 - 1) \cdot [\cos(\theta)]^2} \\ D &= \sqrt{(b-1)/(b+1)} \\ E &= [a \cdot \cos(\theta)]/[b - a \cdot \sin(\theta)] \\ F &= \sqrt{b^2 - 1} \\ G &= \sqrt{(a^2 + b^2 + 1)^2 - 4 \cdot (b^2 + a^2 \cdot [\sin(\theta)]^2)} \\ H &= a^2 + (b+1)^2 \\ I &= \sqrt{b^2 - [\sin(\theta)]^2} \end{aligned}$$

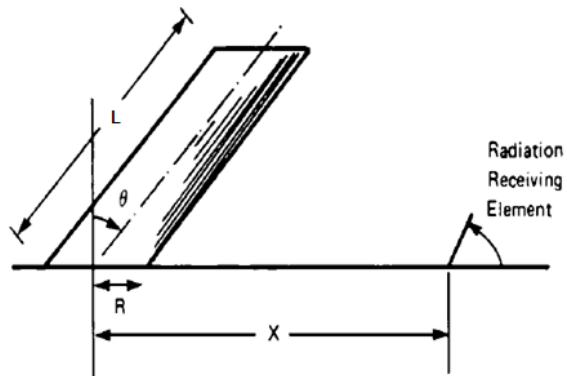


Figure 10: Coordinates of inclined cylindrical flame shape and radiation receiver: Source: 'Yellow Book'⁴

for the calculation of F_v and F_h using the following formulas:

Vertical and horizontal view factor for a radiation receiver in wind direction ($\theta > 0$) respectively against wind direction ($\theta < 0$):

$$\begin{aligned} \pi \cdot F_v &= -E \cdot \tan^{-1}[D] + E \cdot \left[\frac{a^2 + (b+1)^2 - 2 \cdot b \cdot [1 + a \cdot \sin(\theta)]}{A \cdot B} \right] \cdot \tan^{-1} \left[\frac{A \cdot D}{B} \right] + \frac{\cos(\theta)}{C} \\ &\quad \cdot \left\{ \tan^{-1} \left[\frac{a \cdot b - F^2 \cdot \sin(\theta)}{F \cdot C} \right] + \tan^{-1} \left[\frac{F \cdot \sin(\theta)}{C} \right] \right\} \quad (17) \end{aligned}$$

$$\begin{aligned} \pi \cdot F_h &= \tan^{-1} \left[\frac{1}{D} \right] + \frac{\sin(\theta)}{C} \cdot \left\{ \tan^{-1} \left[\frac{a \cdot b - F^2 \cdot \sin(\theta)}{F \cdot C} \right] + \tan^{-1} \left[\frac{F \cdot \sin(\theta)}{C} \right] \right\} \\ &\quad - \left[\frac{a^2 + (b+1)^2 - 2 \cdot [b+1 + a \cdot b \cdot \sin(\theta)]}{A \cdot B} \right] \cdot \tan^{-1} \left[\frac{A \cdot D}{B} \right] \quad (18) \end{aligned}$$

Vertical and horizontal view factor for a radiation receiver perpendicular to the wind direction:

$$2 \cdot \pi \cdot F_v = - \left[\frac{a^2 \cdot \sin(\Theta) \cos(\Theta)}{2 \cdot (a^2 \cdot [\sin(\Theta)]^2 + b^2)} \right] \cdot \ln \left[\frac{a^2 + b^2 - 1 - 2 \cdot a \cdot \left(\frac{F}{b}\right) \cdot \sin(\Theta)}{a^2 + b^2 - 1 + 2 \cdot a \cdot \left(\frac{F}{b}\right) \cdot \sin(\Theta)} \right] + \frac{\cos(\Theta)}{I} \\ \cdot \left\{ \tan^{-1} \left[\frac{\frac{a \cdot b}{F} + \sin(\Theta)}{I} \right] + \tan^{-1} \left[\frac{\frac{a \cdot b}{F} - \sin(\Theta)}{I} \right] \right\} + \left[\frac{a \cdot b \cdot \cos(\Theta)}{b^2 + a^2 \cdot [\sin(\Theta)]^2} \right] \cdot \left[\frac{a^2 + b^2 + 1}{G} \right] \\ \cdot \left\{ \tan^{-1} \left[\frac{H \cdot D - 2 \cdot a \sin(\Theta)}{G} \right] + \tan^{-1} \left[\frac{H \cdot D + 2 \cdot a \sin(\Theta)}{G} \right] \right\} - \left[\frac{2 \cdot a \cdot b \cdot \cos(\Theta)}{b^2 + a^2 \cdot [\sin(\Theta)]^2} \right] \\ \cdot \tan^{-1}(D) \quad (19)$$

$$2\pi \cdot F_h = 2 \cdot \tan^{-1} \left[\frac{1}{D} \right] + F \cdot \frac{\sin(\Theta)}{I} \cdot \left\{ \tan^{-1} \left[\frac{\frac{a \cdot b}{F} + \sin(\Theta)}{I} \right] - \tan^{-1} \left[\frac{\frac{a \cdot b}{F} - \sin(\Theta)}{I} \right] - 2 \cdot \tan^{-1} \left[\frac{\sin(\Theta)}{I} \right] \right\} \\ - \left[\frac{a^2 + b^2 - 1}{G} \right] \cdot \left\{ \tan^{-1} \left[\frac{H \cdot D - 2 \cdot a \sin(\Theta)}{G} \right] + \tan^{-1} \left[\frac{H \cdot D + 2 \cdot a \sin(\Theta)}{G} \right] \right\} \quad (20)$$

Step 8: Calculation of the heat flux

The maximum radiation heat flux q'' from a flame with a pool- \emptyset D onto a radiation receiver at a distance X is calculated to:

$$q'' = SEP_{act} \cdot F_{max} \cdot \tau_a \quad (J/(m^2 \cdot s)) \quad (21)$$

with: SEP_{act} = Actual surface emissive power in $J/(m^2 \cdot s)$
 F_{max} = Maximum geometrical view factor of the radiated object
 τ_a = Atmospheric transmissivity

The maximum pool- \emptyset D corresponds to a leakage rate Λ to:

$$\Lambda = m'' \cdot \pi \cdot D^2 / 4 \quad (kg/s) \quad (22)$$

with: m'' = Burning rate in $kg/(m^2 \cdot s)$

With the respective formulas, dependent on the differential pressure Δp at the leakage, the leak rate can be converted into a leak size expressed as leak- \emptyset .

Results of calculations

The figure 11 shows the calculation results for a typical 30% aluminium alkyl solution in hexane at still weather conditions. The calculated maximum radiant heat of the fire is plotted on the ordinate. The distance to the fire is plotted on the abscissa. Each curve represents a particular pool \emptyset with a certain flame height. The pool \emptyset in turn corresponds to a leakage rate or a leak size, expressed as leak- \emptyset , assuming an internal overpressure of 3 barg at the leak. The effects of the radiation as a function of the radiation intensity are plotted as horizontal lines.

As seen from the diagram (figure 11) a person can only stay for less than 1 min at a distance of 10 m from the fire with a leak size of about 5 mm. At a distance of 10 m from the fire, wood and combustible gases would be ignited with a leak size of about 15 mm. Equipment made of steel would lose their mechanical stability with a leak size of about 25 mm.

Downwind with a wind speed of 2 m/s (figure 12), a significantly higher maximum radiant heat is calculated, compared to still weather conditions. Accordingly the above-mentioned leak sizes are reduced, from 5 mm to 4 mm, from 15 mm to 9 mm and from 25 mm to 15 mm, respectively.

In contrast, upwind at a wind speed of 2 m/s (figure 13) the maximum calculated radiant heat is significantly lower, in comparison to still weather conditions. Perpendicular to the wind direction (Figure 14), the maximum calculated radiation heat approaches to the value at still weather conditions.

In case of another internal overpressure than the here assumed 3 barg, the comparable leak- \emptyset can be roughly estimated, with the approximation formula

$$\text{Leak-}\emptyset_p = \text{Leak-}\emptyset_{3 \text{ barg}} \cdot \sqrt[4]{\frac{3 \text{ barg}}{p}} \quad (23)$$

with: $\text{Leak-}\emptyset_p$ = Leak- \emptyset in mm at an internal overpressure p (barg)
 $\text{Leak-}\emptyset_{3 \text{ barg}}$ = Leak- \emptyset in mm at an internal overpressure of 3 barg
as indicated in the diagrams (figure 11 - 14)

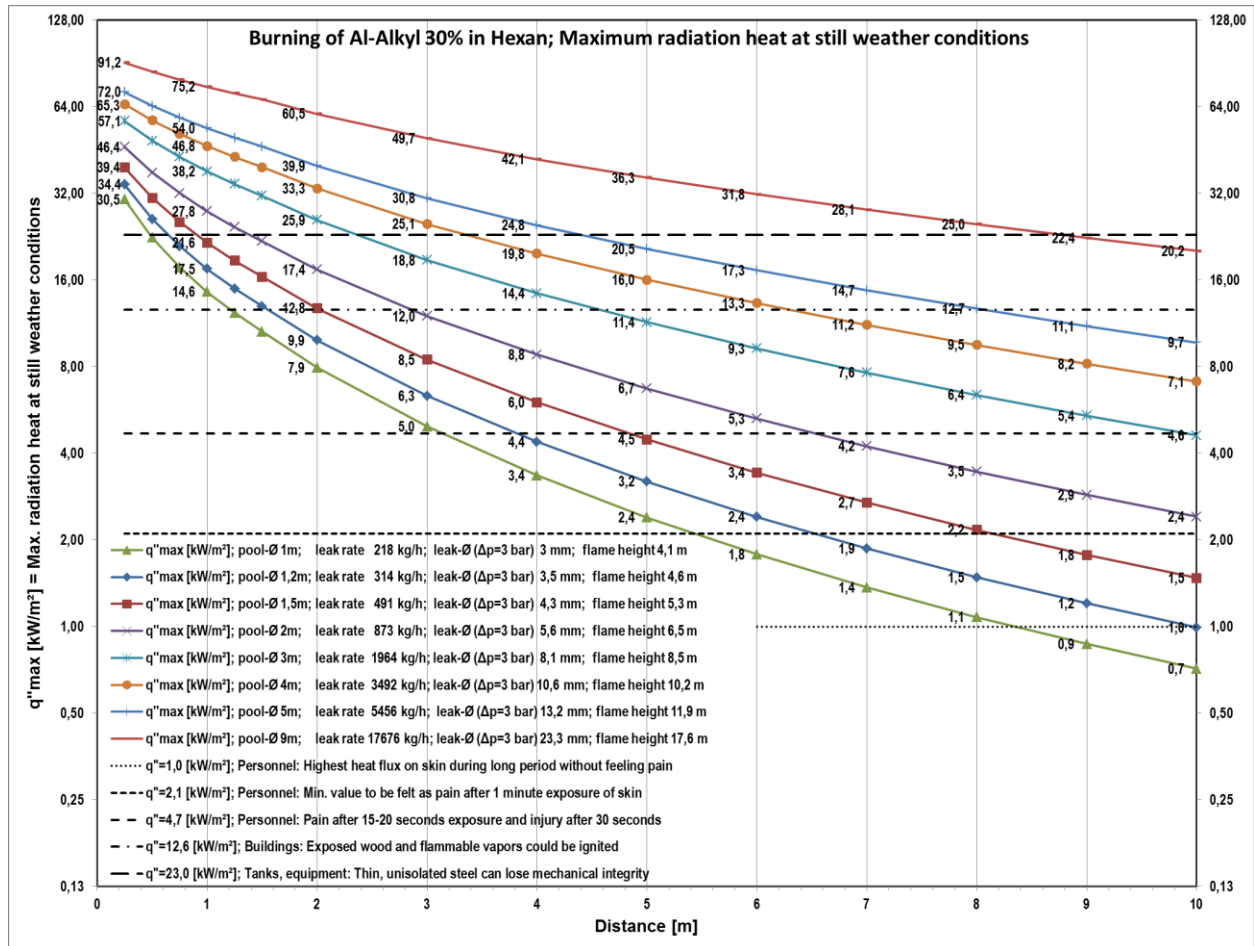


Figure 11: Burning of a 30% Al-alkyl solution in hexane; Calculated maximum radiation heats with still weather conditions as a function of the distance to the fire for different pool-Ø respectively equivalent leak-Ø and leak rates

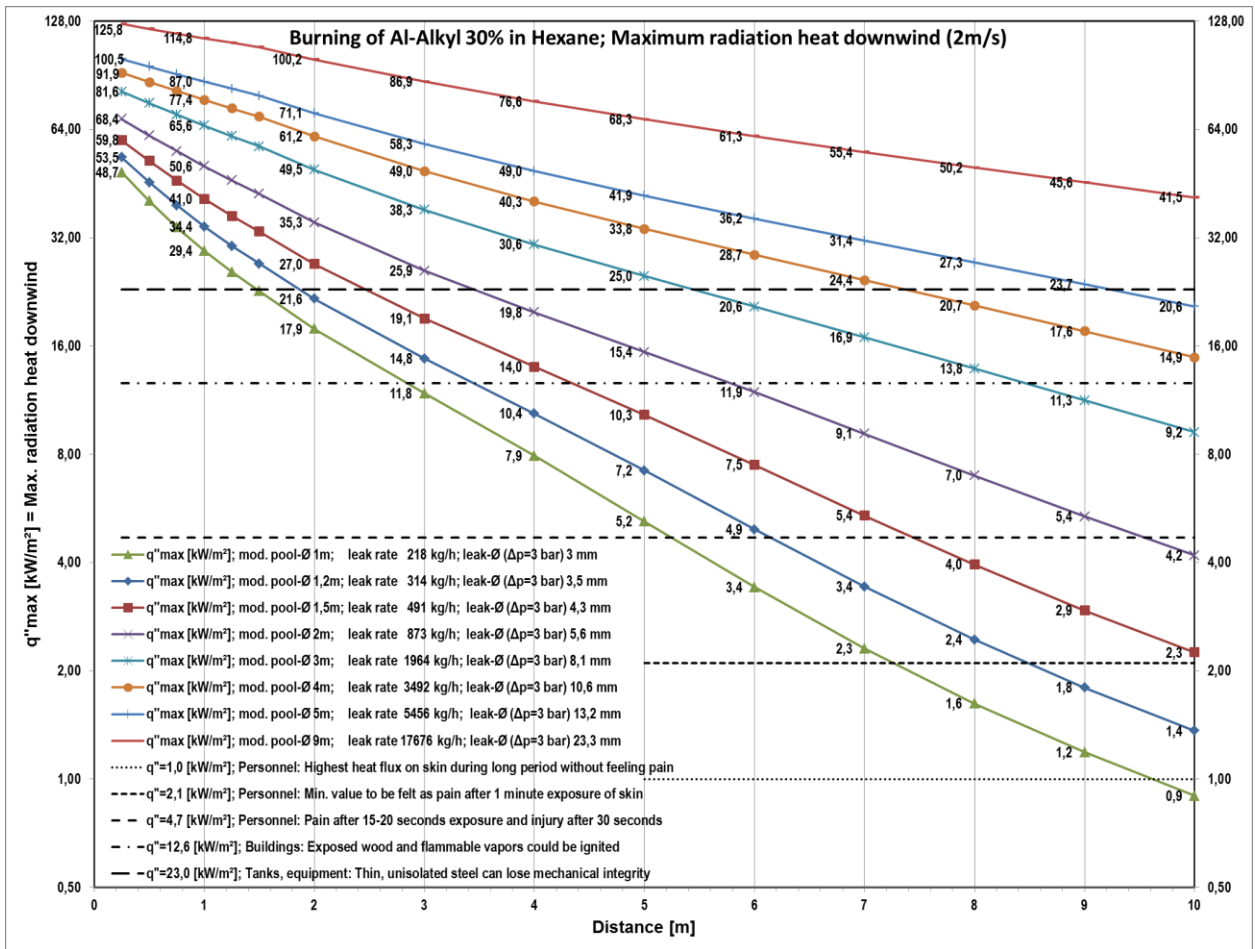


Figure 12: Burning of a 30% Al-alkyl solution in hexane; Calculated maximum radiation heats downwind (2 m/s)

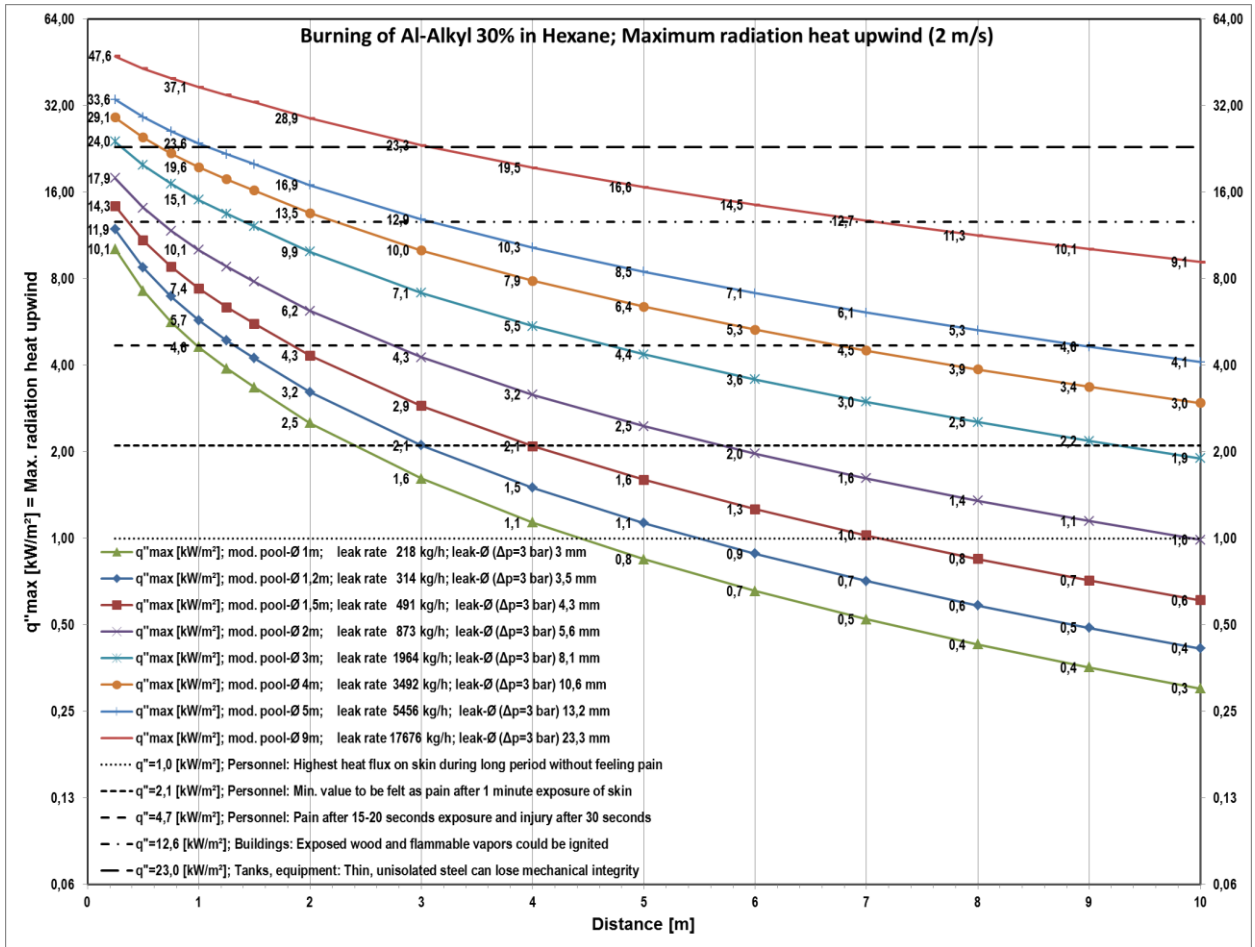


Figure 13: Burning of a 30% Al-alkyl solution in hexane; Calculated maximum radiation heats upwind (2 m/s)

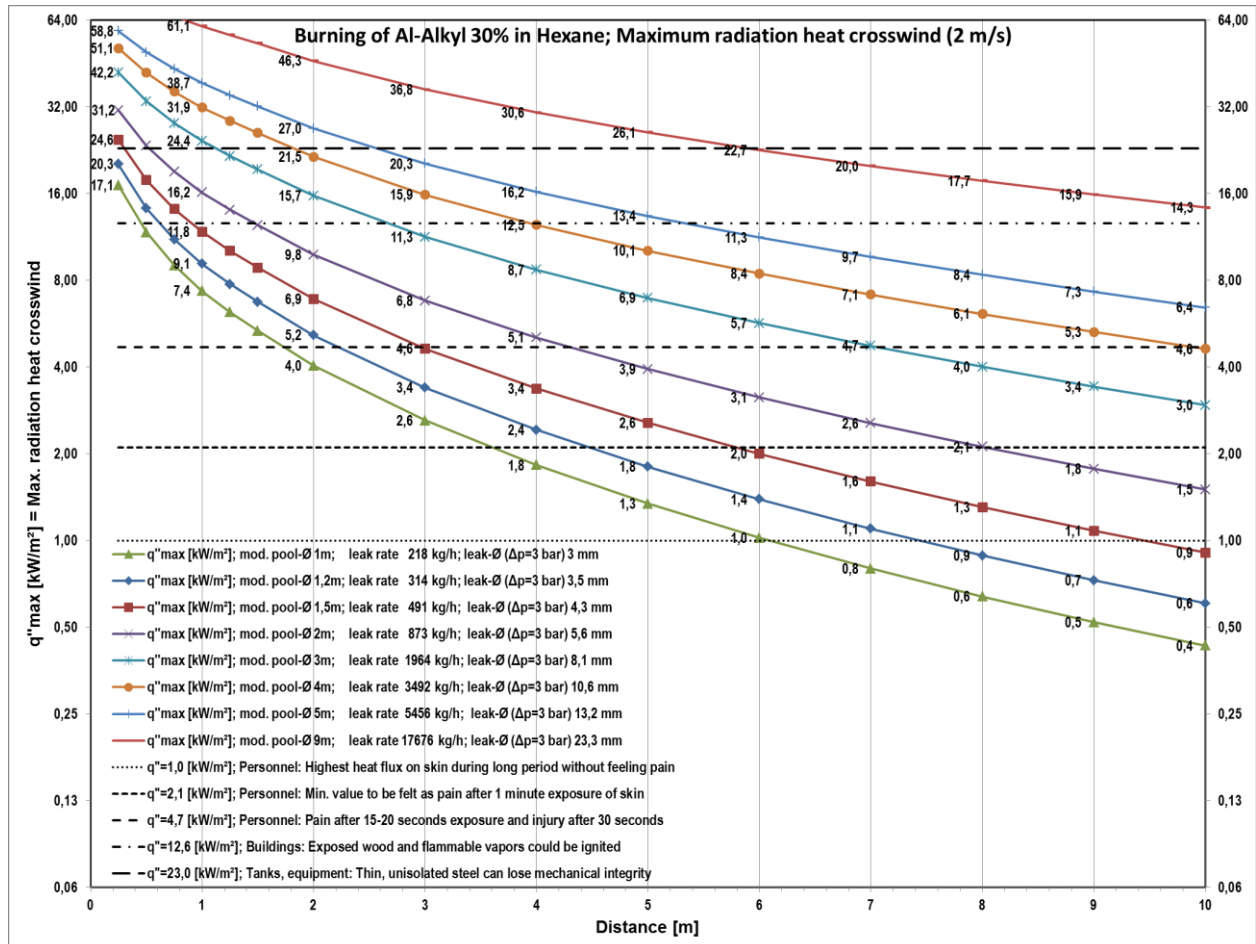


Figure 14: Burning of a 30% Al-alkyl solution in hexane; Calculated maximum radiation heats crosswind (2 m/s)

Realized fire protection concept for the storage of aluminium alkyl solutions

The results of the calculations show, that for larger leakages (and these develop very easily from small leaks under fire conditions) of aluminium alkyl solutions in the tank farm and their accumulation in the dyke area, the required width of the fire protection strip according to the German regulation TRGS 509 (10 m for storage volume from 30 - 200 m³) is not sufficient to protect the neighbouring equipment and buildings from fire exposure, since:

- an aluminium alkyl fire in principle cannot be extinguished because air contact reignites the fire immediately
- the cooling of adjacent areas with a water spray is of only limited use because water aerosols would reinforce the fire due to the extremely violent reaction of aluminium alkyls with water

A fire protection concept for the storage of aluminium alkyl solutions is, therefore, presented below, which can be applied to a large extent on other liquid pyrophoric substance, based on:

- Leakage prevention
- Fire control
- Explosion protection
- Prevention of water contamination / product decomposition

In the layout concept of the tank farm (figure 15 top view, figure 16 side view) some of the following measures are explained below for better understanding.

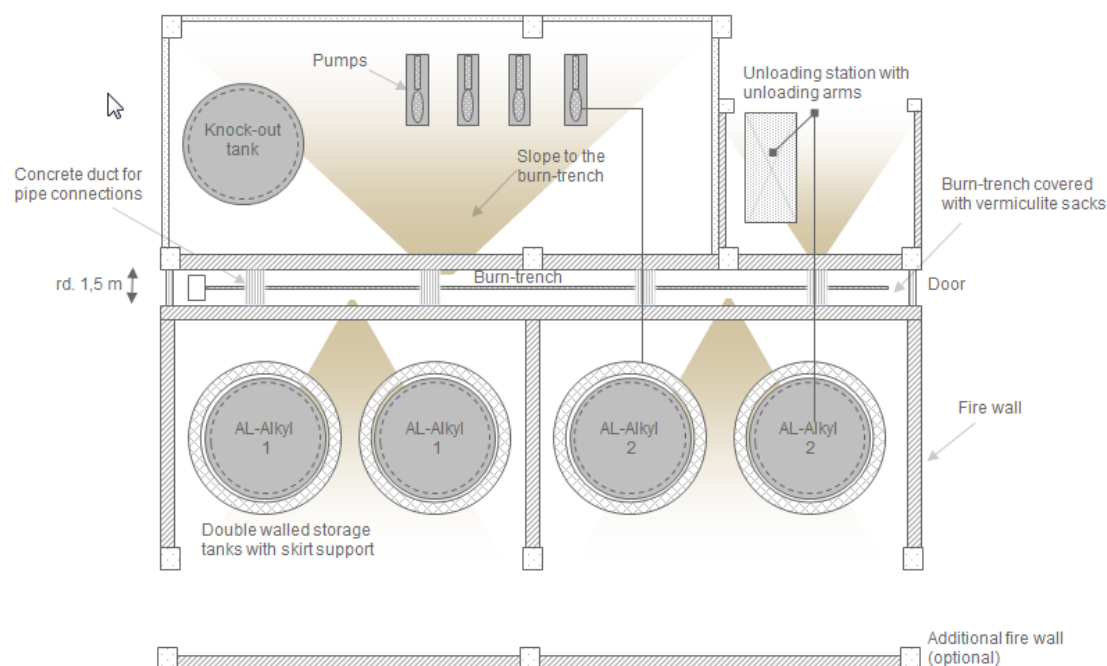


Figure 15: Layout concept (top view) for the storage of aluminum alkyl solutions

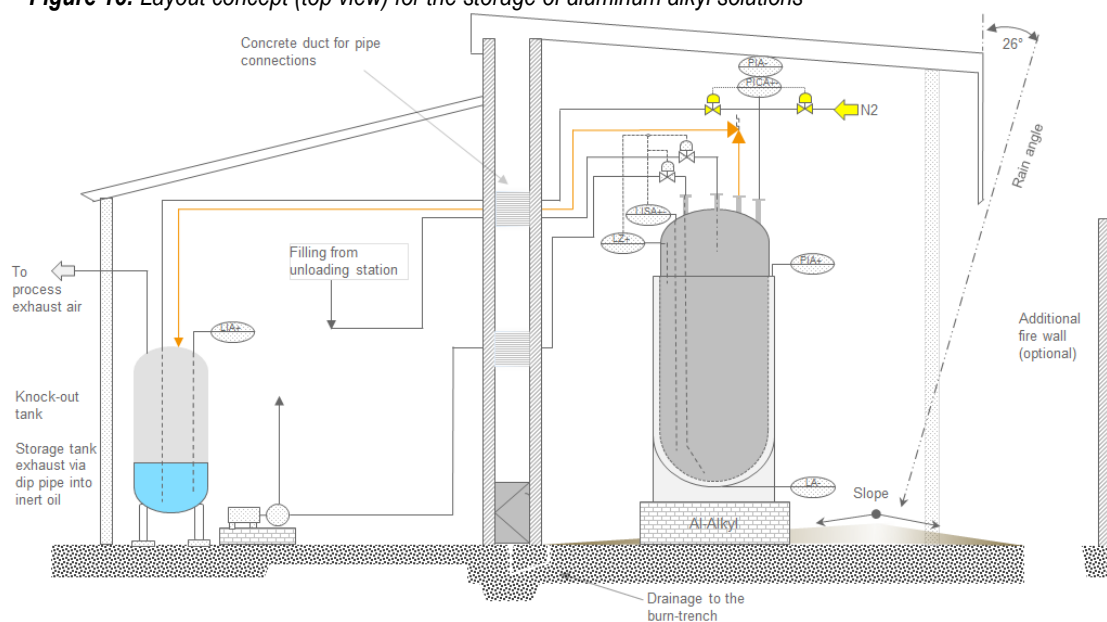


Figure 16: Layout concept (side view) for the storage of aluminum alkyl solutions

Measures for leakage prevention

- Double-walled, leakage-monitored storage tanks made of carbon steel.
- The filling and emptying of the storage tanks occurs only from the top. Thus, a leakage of the tanks is ruled out. Therefore, the assumed leakage is limited to leaks at feed and discharge pipes with their flanges, pumps and valves
- Pipes on pipe-racks are welded at full length with 100% weld inspection. Pipes are supported with stainless steel holders in order to avoid corrosion
- Design and quality of fittings and seals used are according to the recommendation of the metal alkyl manufacturers
- Pipes and fittings easily visible, protected from damage, fittings quick to use.
- Consideration of German regulations respectively follow-up regulations ATV-DVWA-A780, TRbF50, TRR100 for piping over rough terrain
- Hermetically sealed leak-free pumps
- Container unloading only via dip pipe from the top
- Installation of product-carrying unloading arms instead of unloading hoses (connection of the gas pendulum via hose is adequate, since no product would leak in the event of a hose leak)

Measures for fire control

- Since the necessary width of the fire protection strip (greater than required according to the German regulation TRGS 509) is usually not available, a fire wall is built, that also resists fire dynamic loads
- The storage tanks are placed on a drainage surface of concrete. Any product-leakage is drained via drain holes below the fire wall into a burn-trench behind the fire wall, to minimize the heat load of the tanks in case of a fire. The burn-trench is shielded with a second fire wall.
- The highest likelihood of a leakage is in the area of the pumps, where most of the flanges are built-in. Therefore, the dosing pumps are installed in a separate pump room. Any leakage is also drained via a drainage surface into the burn-trench.
- The burn-trench is covered with plastic sacks of suitable extinguishing agents such as dry sand, vermiculite.
- Storage tanks are placed on concrete bases and protected from fire below the tank. If necessary, coating of the tank-feet and the tank with a foam, fire-protection coating
- The use of shut-off valves 'fire resistant' faucets (e.g., self-closing in case of fire by means of plastic tubing for air control).
- Fire walls are built between the tanks at least for the German VCI-storage-classes 4.2 (pyrophoric substances) and 4.3 (substances forming flammable gases in contact with water), to segregate in case of damage.
- The entire tank farm area including the pump room and the burn-trench is protected by a lightweight roof to avoid rain water. Design of the load-bearing parts of the roof out of reinforced concrete
- Fire detection in the storage area, at the container unloading station, in the pump room and at the burn-trench

Measures for explosion protection

- Inertization of the tanks according to level 3 of the German regulation TRGS 509, with alarm and shutdown of the discharge pumps in the overpressure range.
- Inertization of the transfer container during unloading is obtained via gas pendulum to the tank or by pressing with nitrogen.
- Tanks 10 barg pressure-resistant, to ensure explosion pressure shock resistance
- Air monitoring of hexane in the storage area, at the container unloading station, in the pump room and at the burn-trench
- Electrical installation for explosion zone

Measures to prevent water contamination / product decomposition

- Liquid detection in N₂-supply lines.
- Discharge of the storage tank exhausts and the safety valves via a knockout tank into the operating vent system. The knockout tank is required as the vent system could be potentially contaminated with water.
- Exhaust discharge into level-monitored knockout tank via dip pipe into inert oil to prevent rebreathing of moisture.
- Safety valves on the storage tanks designed for the fire case. Their set pressure should consider the decomposition temperature of the aluminium alkyls
- Overfilling protection of the tanks set at a level of about 70% of the total volume, in order to avoid a two-phase flow in case of safety valve activation.

¹ Recommendations on the transport of dangerous goods - Manual of tests and criteria; 2nd rev. Ed. United Nations 2004

² Heitmann, P.: Metal alkyls - safety, properties, behaviour, production, application; Paper Chemtura, September 2007

³ Organometallics – Properties and Handling; Training film, Chemtura 2011

⁴ van den Bosch, C.J.H.; Weterings, R.A.P.M. (Ed.): Methods for the calculation of physical effects - due to releases of hazardous materials (liquids and gases); 'Yellow Book'; Den Haag 1996

⁵ Metal alkyls and their solutions - Burning properties; Technical Bulletin, Amersfoort: AkzoNobel 2008