High Surface Area Oxidation: Can it also happen in my Plant?

Lois van Druten

May 2023.

PSCONGRES

Process Safety Congres

Lois van Druten Speaker Profile

Education

- MSc in Chemical Engineering – Delft University of Technology

Career history: Dow (Terneuzen, The Netherlands)

- Process Engineer
- Improvement Engineer & Process Safety Focal Point
- Reactive Chemicals SME
  - Reactive Chemicals group is a mixed team of chemists and chemical engineer that is chartered to help businesses and functions gain sufficient knowledge to prevent RC incidents and to assist if such an incident would happen

Hobbies and interests

- Working in and around the house; reading; travelling

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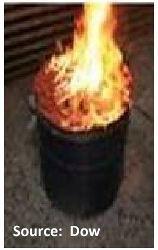
What is High Surface Area Oxidation?

Type of incident caused by **auto-oxidation** of organics on **high surface areas** resulting in smoldering and/or fire.

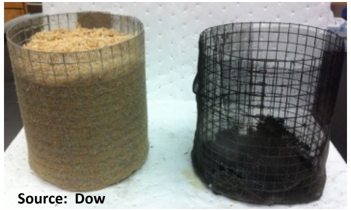
Column packing fires

Carbon/Adsorbent bed fires



Insulation fires

Waste (adsorbent/paper towels) fires



These incidents ALWAYS cost money and can potentially injure/kill people

AUTO-OXIDATION

- Organic and many inorganic materials react with O_2 in the air at all times and at all temperatures.

  "C" + "H" + air (O_2) → CHO → COOH + … (oxidation) → CO_2 + H_2O

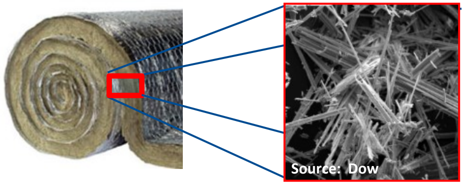
- These oxidation reactions are **very exothermic** (hundreds of kJ/mol)
- Not an issue in most cases because the area where the oxidation occurs is limited to the air-organic interface, which is typically very small
  - ✓ Sufficient heat dissipation to the environment and into the mass of the material
  - ✓ Oxidation rates are usually slow at ambient temperature (e.g. rusting)

→ *Exception: high surface area = high reaction rate*

Influence of Surface Area

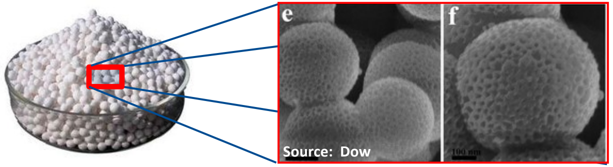
When an oxidizable material is distributed over a large surface area, the access to the O_2 of the surrounding air improves/increases.

Fibrous Insulation



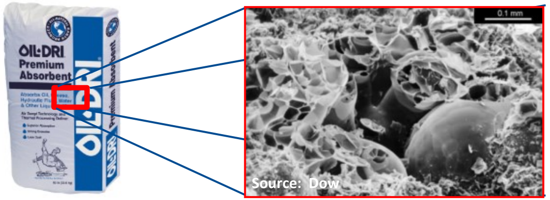
Up to $50 m^2/g$

Alumina Adsorbent



Up to $200 m^2/g$

Spill Adsorbents



Up to $400 m^2/g$

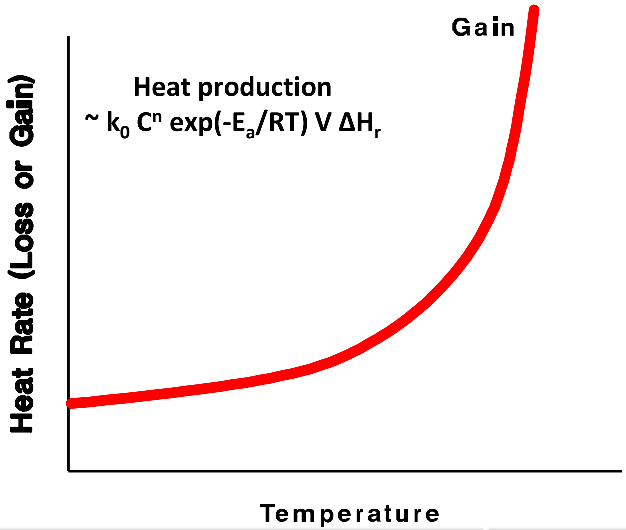
More heat

This increases the <u>quantity</u> of material oxidizing at any given moment.

HEAT GAIN VERSUS HEAT LOSS

Heat Gain

- In general oxidation reaction follow first order Arrhenius kinetics
- Rate of reaction (~ heat generation) increases exponentially with temperature



Heat Gain versus Heat Loss

Heat Gain

- In general oxidation reaction follow first order Arrhenius kinetics
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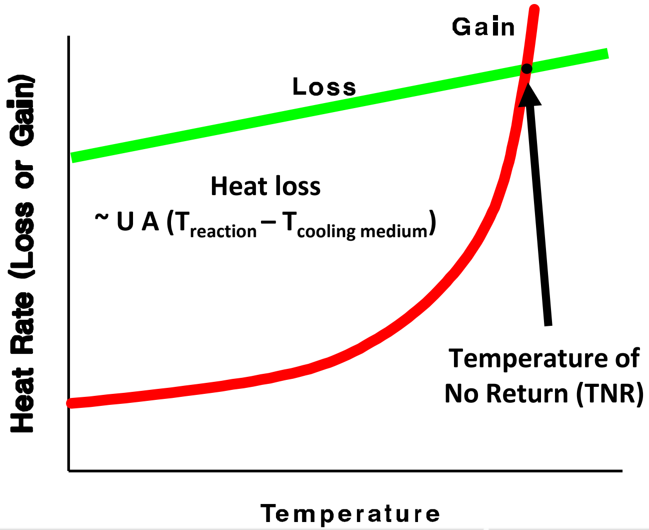
Heat Loss

- Linear proportional to ΔT
- Thermal conductivity significantly reduced for high surface area materials



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Heat Gain

- In general oxidation reaction follow first order Arrhenius kinetics
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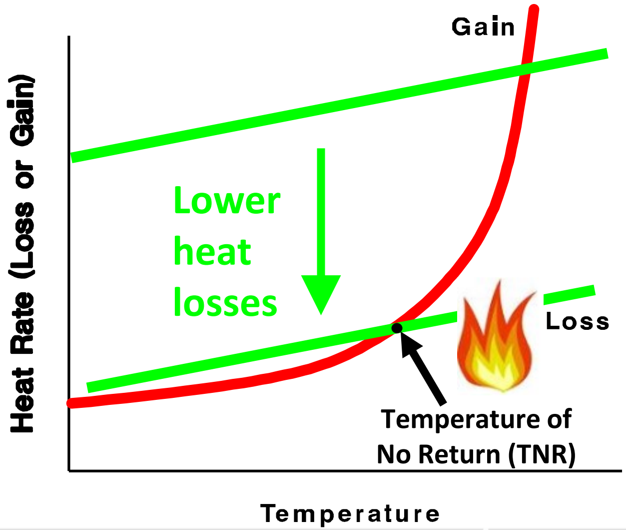
Heat Loss

- Linear proportional to ΔT
- Thermal conductivity significantly reduced for high surface area materials → **reduced heat loss**

Runaway oxidation reaction when heat gains > heat losses, or T > TNR

Also called FIRE!



INFLUENCE OF THE CHEMICAL

High potential for auto-oxidation:

- Highly oxidizable materials e.g. polyols, amines, aldehydes
- Organics with a high boiling point e.g. oils, heat transfer fluids, glycols

Lower potential for auto-oxidation:

- Highly volatile chemicals may evaporate from the surface as they are oxidizing and may not auto-oxidize due to rapid evaporative cooling

  e.g. methanol, acetone, isopropanol

- Exceptions: volatile chemicals that are self-reactive or react with moisture, particularly if they react to make larger, less volatile components

  e.g. ethylene oxide, styrene

Case Study: Column Fire

- Preconditioning a vacuum distillation column for startup at 220 °C, a small leak in the bottom pump seal allowed air to enter the column.
- Organic residues on the structured packing
  - Ignited and initiated metal packing fire (> 1520°C)
  - Column collapsed downward by ~ 1m

The fire burned a hole in the packing.

Root Causes

- ✓ High heat input to the reboiler during preparation.
- ✓ Inadequate follow up on high/low temperature alarms.
- ✓ High surface area packing material (by design).
- ✓ Bottom pump allowed to run dry.
- ✓ Single seal configuration of the bottom pump.

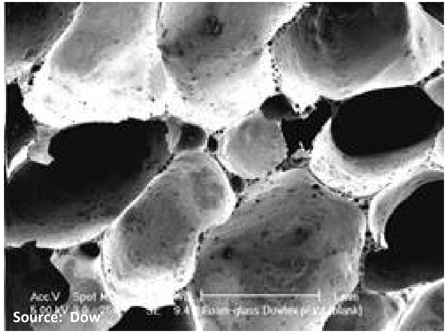
Case Study: Insulation Fire

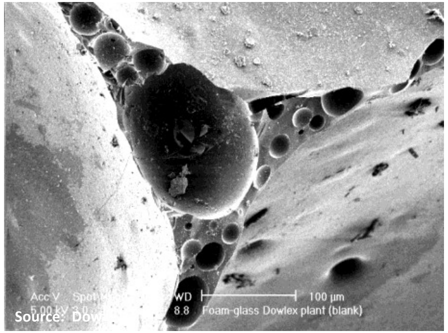
- In 2007, a Dow reactor experienced an insulation fire near an agitator
- Reactor was insulated with Foam glass
  - Foam glass was contaminated with agitator seal oil
  - Foam glass was found to be damaged by wear and tear, weather conditions and probably also stepped on
- Additional tests and modeling indicated incidents can happen at temperatures much lower than the AIT (seal oil >350°C)
- Difference rockwool ↔ closed cell insulation material.

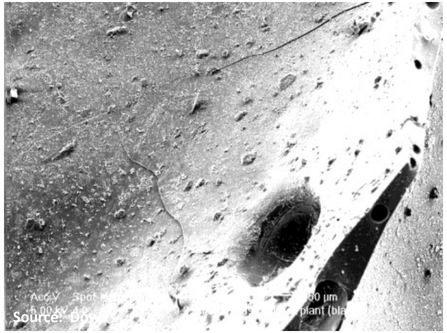
Insulation material	Temperature of No Return (TNR) (°C)	TMR at 125 °C (hrs)
Rockwool 10 cm	109	<1
Foamglass 10 cm (new)	148	16
Foamglass 10 cm (damaged)	<148	<16

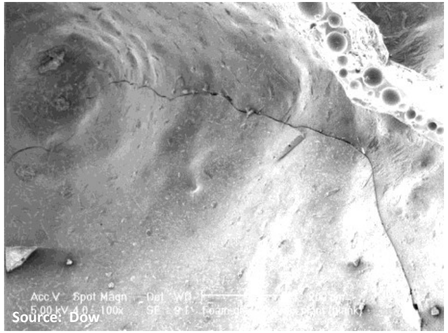
OPEN VERSUS CLOSED CELL INSULATION

- Generally, closed cell insulation (e.g. cellular glass, foam glass) is considered the best insulation choice to reduce auto-oxidation risk
- However, auto-oxidation has been observed in both open cell (e.g. mineral wool, calcium silicate) and closed cell insulation materials.









SEM pictures show partially damaged and porous cellular glass. Such foam glass behaves like "open" insulation material where liquid can penetrate and be oxidized

Closed cell insulation **IS NOT** a miracle cure for insulation fires!

TESTING FOR AUTO-OXIDATION

Method 1: Estimation

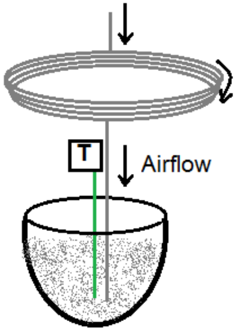
- Simplified techniques available for determining if a chemical poses a high hazard for thermal run-away oxidation
  - ✓ Internal Dow method – estimates heat losses from evaporation and heat gains from oxidation and estimates TNR
  - ✓ Britton method – evaluates the ability of a material to spontaneously combust based on an empirical relationship using flash point and AIT values for a substance
- These tools only evaluate if the material could potentially auto-oxidize, but not for specific scenario-dependent conditions. They should be used as screening tools only

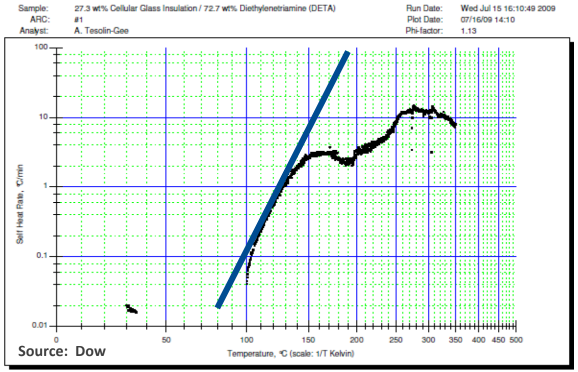
Britton, L. G. (1991). "Spontaneous Fires in Insulation." Plant/Operations Progress 10, 1 (January), 27-44.

TESTING FOR AUTO-OXIDATION

Method 2: ARC testing

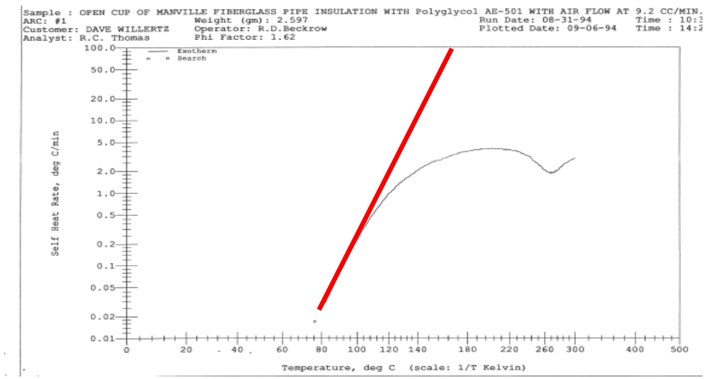
- Accelerating Rate Calorimetry
  - ✓ Adiabatic (no heat loss to environment) reaction calorimeter
  - ✓ Open-cup mode (i.e. no pressure build-up but purge with low flow of preheated air)
- Data input for kinetic modelling
  - ✓ Fit ARC data to Arrhenius model
  - ✓ Use this model in combination with appropriate heat transfer model to predict/estimate time required to reach thermal runaway

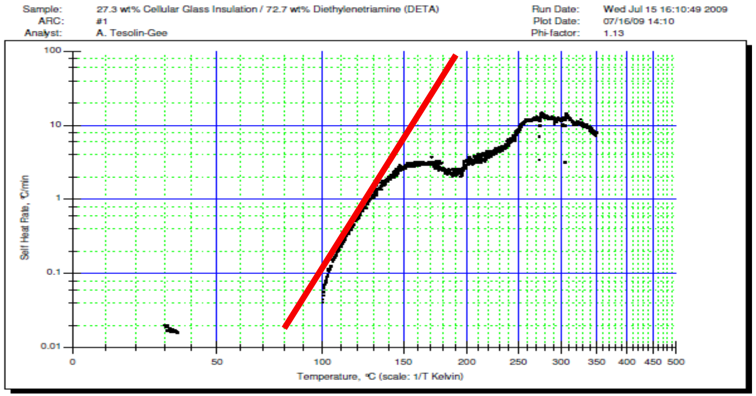




MODELLING OF OPEN-CUP ARC TESTING

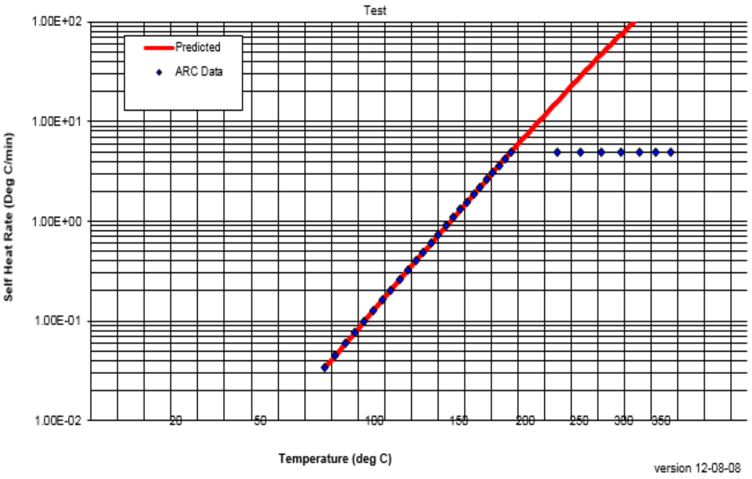
- Due to limited oxygen → peak heat generation rates not known
- Initial kinetics are sufficient for modeling the system under Frank-Kamenetskii type heat transfer
  - TNR in highly insulating environment will likely be toward the start of the detected exotherm (small heat loss)
  - 1st order kinetics is conservative and large HOR ensures sufficient heat generation





Frank-Kamenetskii Critical Diameters

- TNR values are associated with critical diameters of specified geometric shapes
- Usually provided as the diameter at a temperature where heat gains exceed heat losses and a runaway will occur
- Prediction and validation of data



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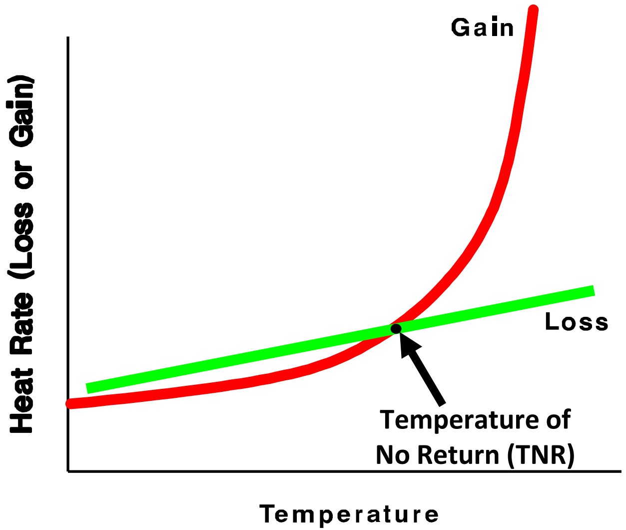

Critical Diameter (in)

$T_{environment}$ (°C)	Inf. Slab	Inf. Cylinder	Sphere
10	29	44	56
20	19	29	37
30	13	19	25
40	9	13	17
50	6	10	12
60	5	7	9
70	3	5	7
80	3	4	5
90	2	3	4
100	2	2	3

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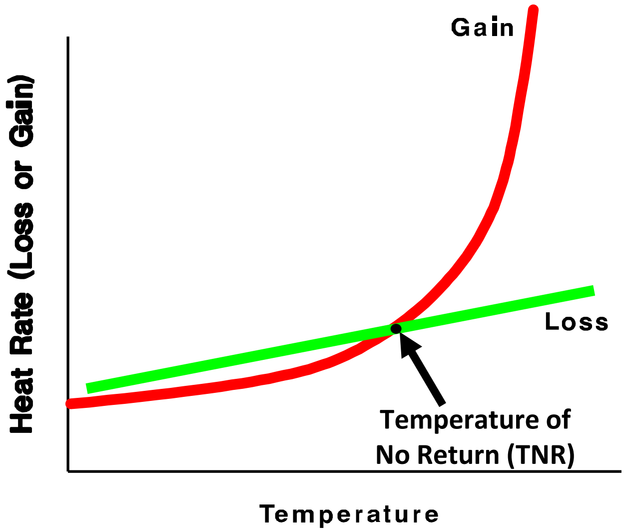

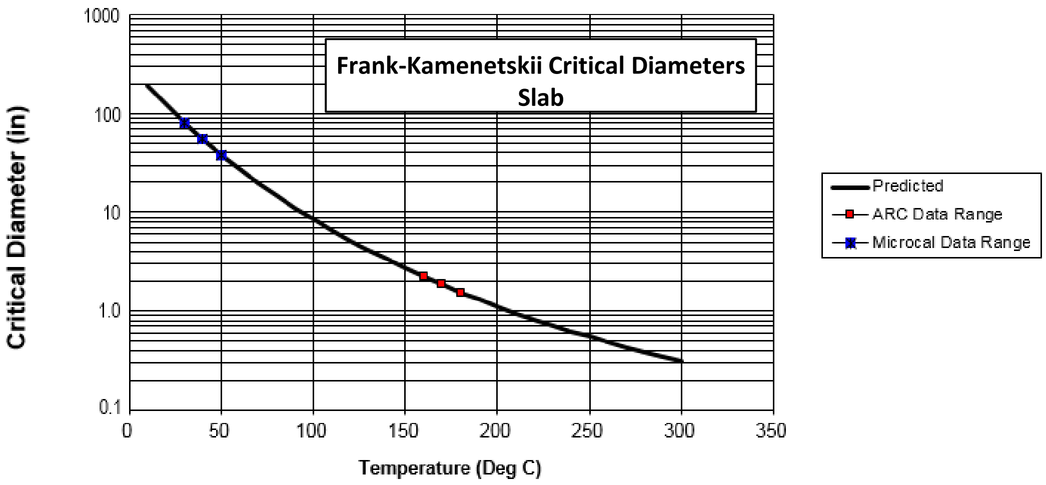

Conclusion

- Access of oxygen to contaminated, high surface area materials always carries the risk of auto-ignition. If ignition sources or elevated temperatures are present the risk increases significantly.
- High surface area oxidation not only happens at Dow but at all chemical facilities worldwide.
  - ✓ Yes, it can also happen at your plant
  - ✓ Multiple examples available in open literature.
- Incidents still happen because hazard awareness is insufficient
- At Dow, we take a scientific-based approach to predict conditions that promote thermal runaway in solid systems.
- Good analytical data and heat-balance calculations are necessary for determining adequate layers of protection, including engineering design and controls

Thank You

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