

HAZARD OF SPONTANEOUS EXPLOSION IN COMPOSITION OF AMMONIUM NITRATE AND DCCNA

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Historical data

- Catastrophic explosion of a warehouse with 300-t off-grade ammonium nitrate at AZF plant in Toulouse, France, took place on September, 21, 2001. The THT equivalent was estimated as 30–40 tons, 30 people were died, ~ 3 000 injured, 600 buildings were destroyed, the losses were estimated as 2.1 billion Euros.

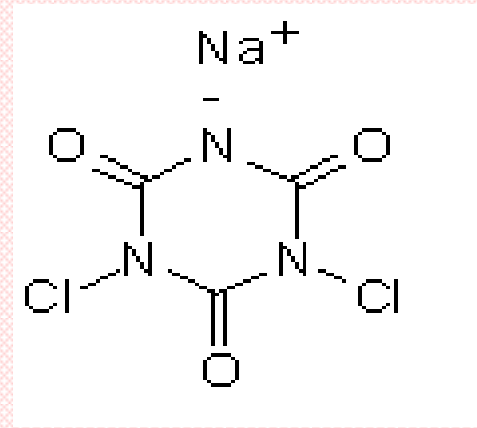


Version of the event

One connects this explosion with dichlorine izocianurate sodium (DCCNa). Some amount of this chemical seems to be brought during regular unloading together with defective portion of ammonium nitrate into the enter section of the warehouse.

Purpose

Dichlorine izocianurate sodium (DCCNa, chemical formula $C_3N_3O_3Cl_2Na$) is a granulated disinfectant of the new generation.



This substance being dissolved in water releases the active chlorine which easily enters into chemical reactions with ammonium nitrate. These reactions have high exothermic effect and produce a real hazard of spontaneous explosion.

- *The purpose of this work* is to get the detailed information on the behavior and consequences of interaction between ammonium nitrate and DCCNa, chemically incompatible organic material, which generates active chlorine in aqua solution.

Contents

- *Material tested and ways of investigation*
- *Investigation results*
 - ✓ *kinetics of chemical interaction*
 - ✓ *shock sensitivity of dry mixture*
 - ✓ *explosions and detonation of confined wetted mixture*
 - ✓ *numerical simulation*
- *Conclusion*

Materials tested

- *French-fabricated industrial ammonium nitrate, $\sim 700 \text{ kg/m}^3$ in loose-packed density, consisting of porous spherical granules 1–2 mm in average diameter, and DCCNa as a polydisperse powder $\sim 0.8 \text{ mm}$ in the particle average size have been studied.*
- ✓ *Chemicals were used as supplied, or sieved after crushing into fractions with particles 0.63–1.25 mm and 0.25–0.63 mm in size*
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- ✓ *Before firings the chemicals were carefully dried up.*
- ✓ *Mixture was prepared at the mass fraction 1:1, that approximately corresponds to stoichiometric mixture*

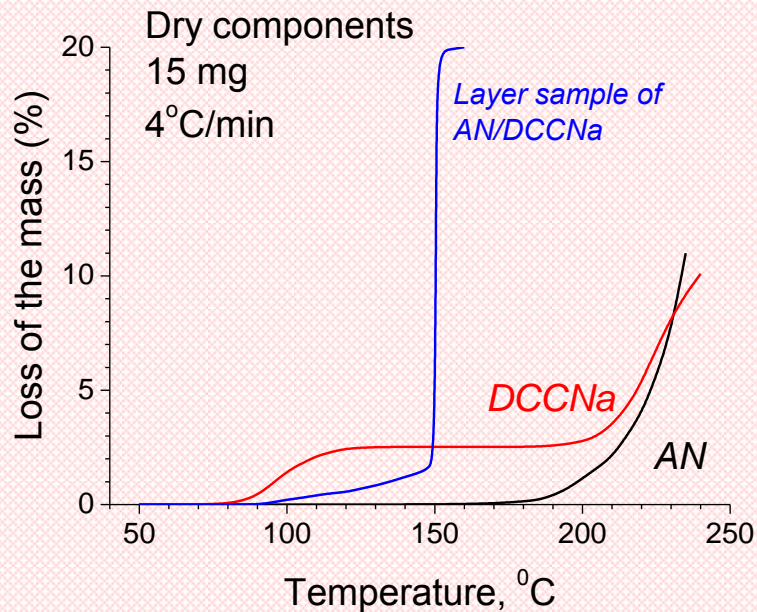
Methods of investigation applied

- **Kinetics of chemical interaction** *was analyzed with use of thermo-gravimetric, calorimetric and manometric devices.*
- **Chemical interaction products** *were determined with use of mass-spectrometry, IR-spectrometry, and release of explosive gases was simply visualized*
- **Explosions, shock sensitivity, detonation:**
 - ✓ *The shock sensitivity was monitored by using the interface deceleration technique with electromagnetic device. Explosion of unconfined charges (up to 25 kg in mass) under standard conditions was studied visually and with use of thermocouples. Explosion and detonation properties of confined charges were studied using the closed-volume bomb, as well as the charge firings in steel and plastic tubes of different diameter equipped with photo, piezo- and contact gauges to monitor the wave propagation Visual observations, monitoring the temperature rise in the unconfined samples up to 25 kg in mass*
- *Mass of the samples: 30 – 300 mg, 1 – 300 g, 1 – 25 kg*
- *Different wetting techniques*

Kinetics of chemical interaction

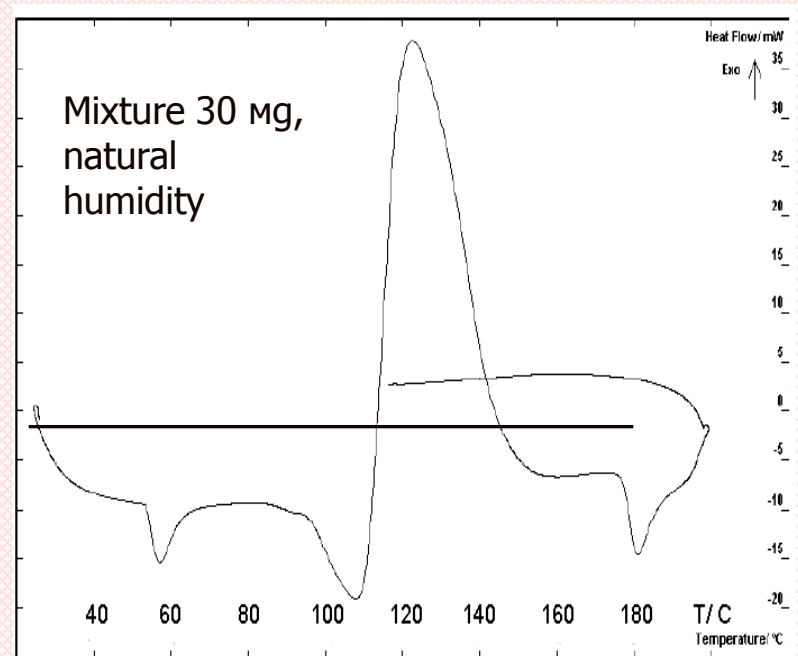
Thermogravimetric analysis:

Electronic device ATB-16M, 6-mm test glasses, air, heating rate 4°C/min



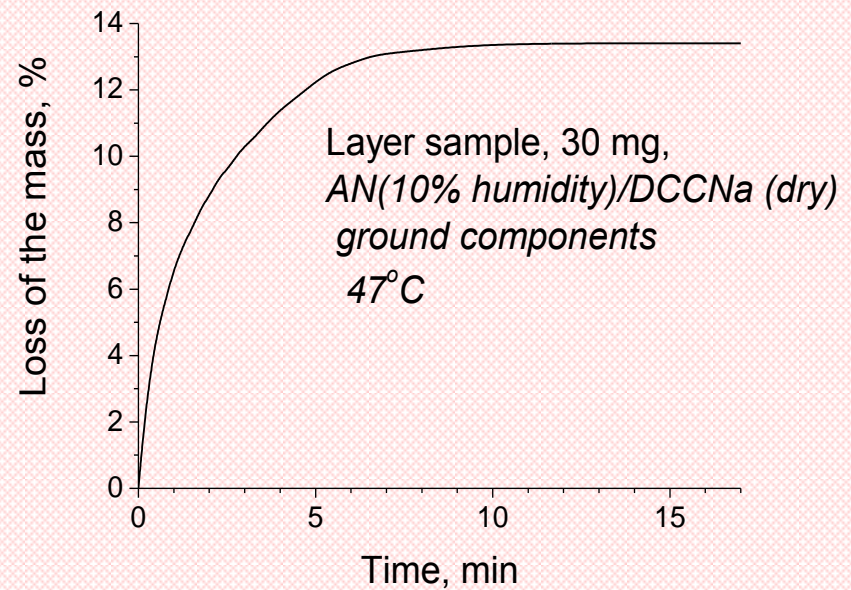
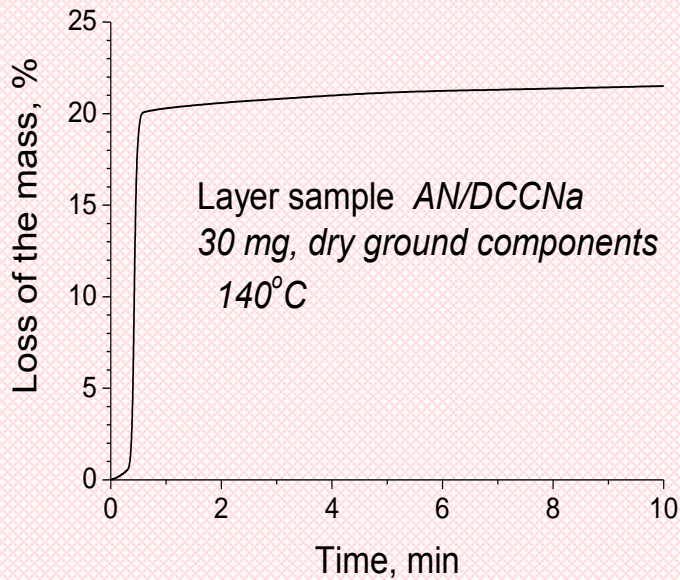
Calorimetric analysis:

DSC 131 "Seteram", Al-pot 0.1 cm³,
20°C/min
Mixture of ground components



Isothermic thermogravimetry

- **Layer samples of dry or slightly wetted (< 2 %) components**
 - ✓ **20–64 °C** : There is no obvious trace of chemical reactions
 - ✓ **140 °C**: Explosion in 25 sec
- **Wetted components**: chemical reactions, starting at room temperature



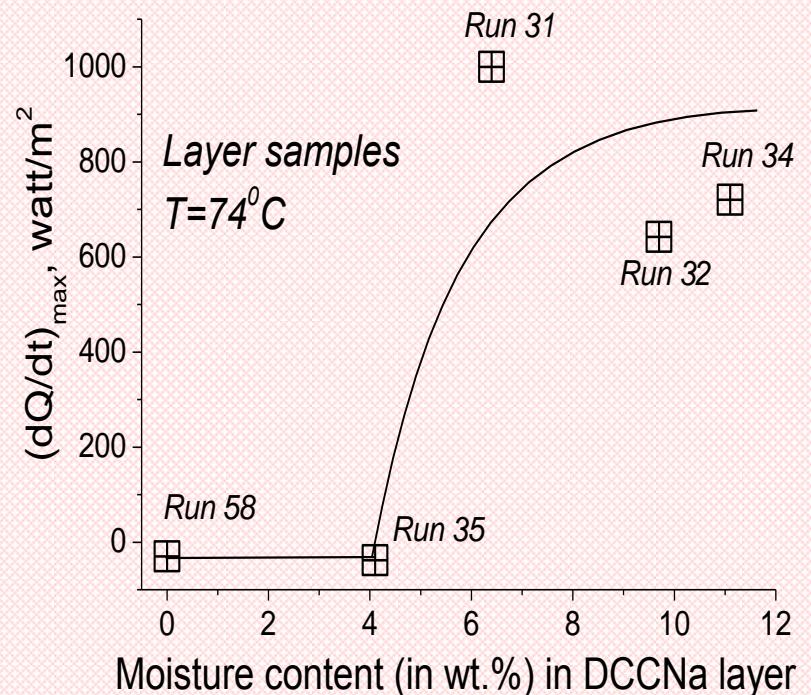
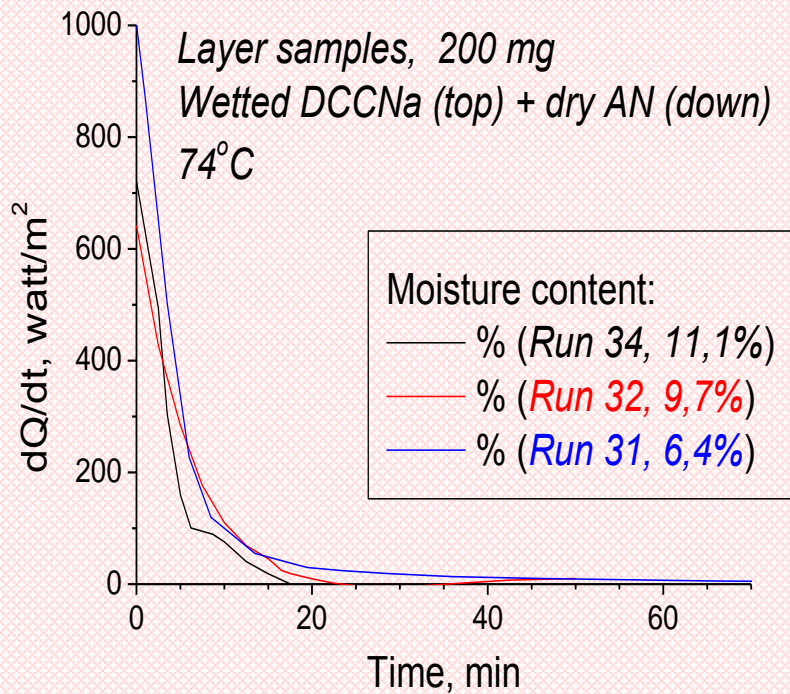
Absorption of the moisture from air

- Absorbability of the components:
 - ✓ natural humidity of materials in closure is 1 – 2 %
 - ✓ in atmosphere of 100%-humidity air, at 35°C,
*30-mg samples demonstrate 25% increase of the mass:
AN for 3–4 hours, and DCCNa for 16–17 hours*
- Chemical reactions developed during the moisture absorption:

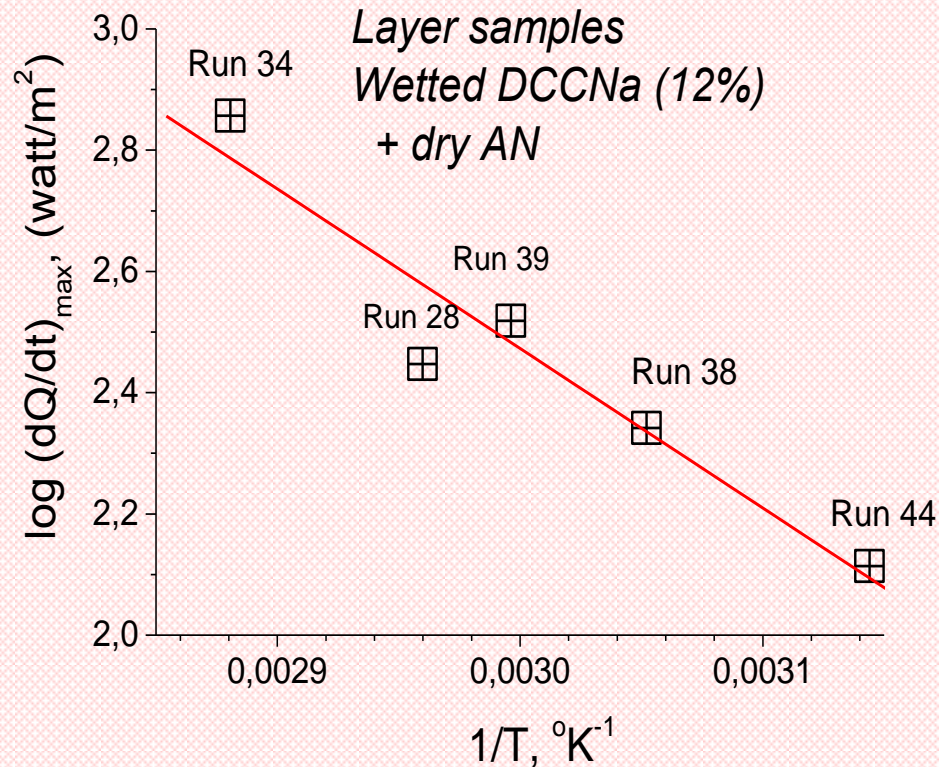
Layer sample, 260 mg, in air of 100% humidity, 32°C	Change of the mass, %		
	For 3 hours	For 6 hours	For 9 hours
AN is the top layer	+ 0.5	- 3.8	+ 21.2
DCCNa is the top layer	+ 1.7	- 1.9	+ 11.3

Isothermic calorimetric analysis

- ДАК-1-1, constant temperature in the range 25–74°C, layer samples 200 mg in mass, one component is wetted, another one is dry



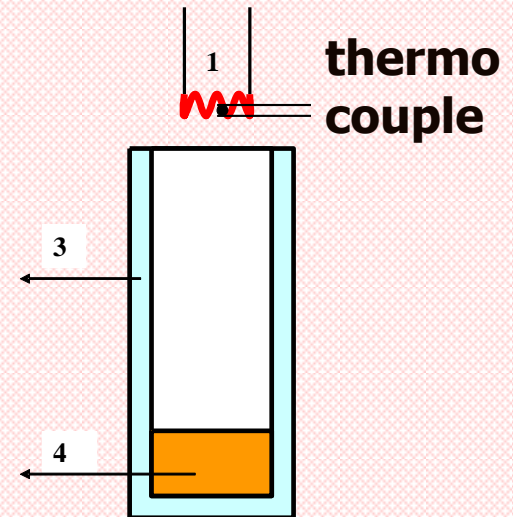
Isothermic calorimetric analysis (2)



- dQ/dt (watt/m²) = $2,33 \times 10^{10} \exp(-50400/RT)$
- For variety of samples studied,
Energy of activation is 30–65 KJ/mole

Composition of reaction products: gas release

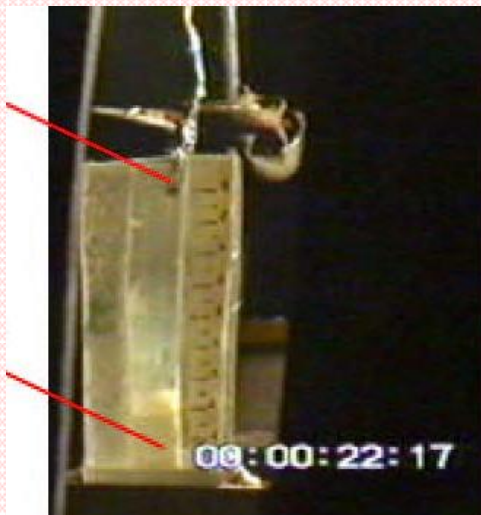
- Consequence of water injection into the sample: foaming, increase of the volume occupied by the sample, gas release
- Gas explosion if the heating coil temperature approaches 115°C (more likely, explosion of trichlorine amine NCl_3)



foam

Heating
Coil
(115°C)

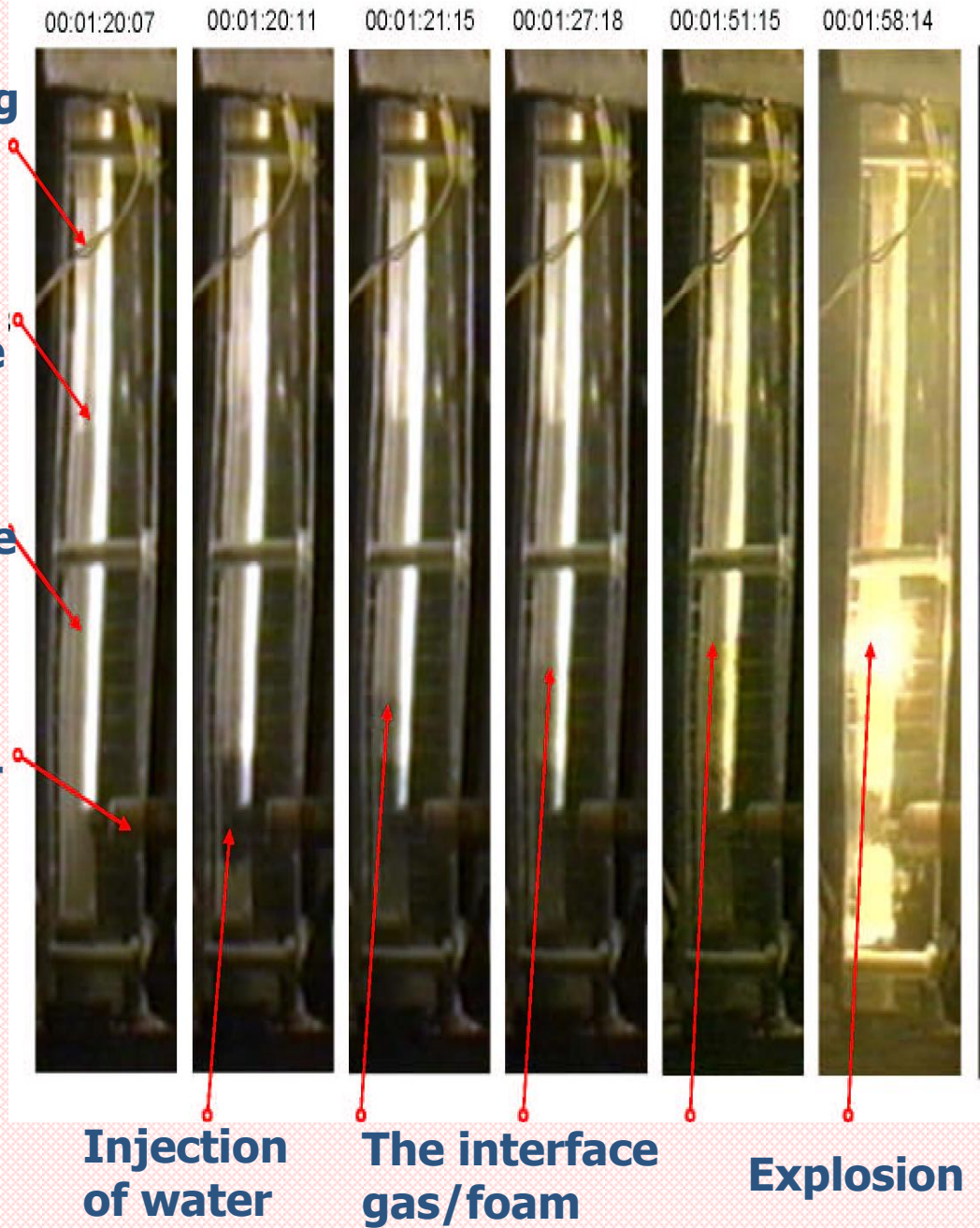
Mixture
tested



Role of the foam

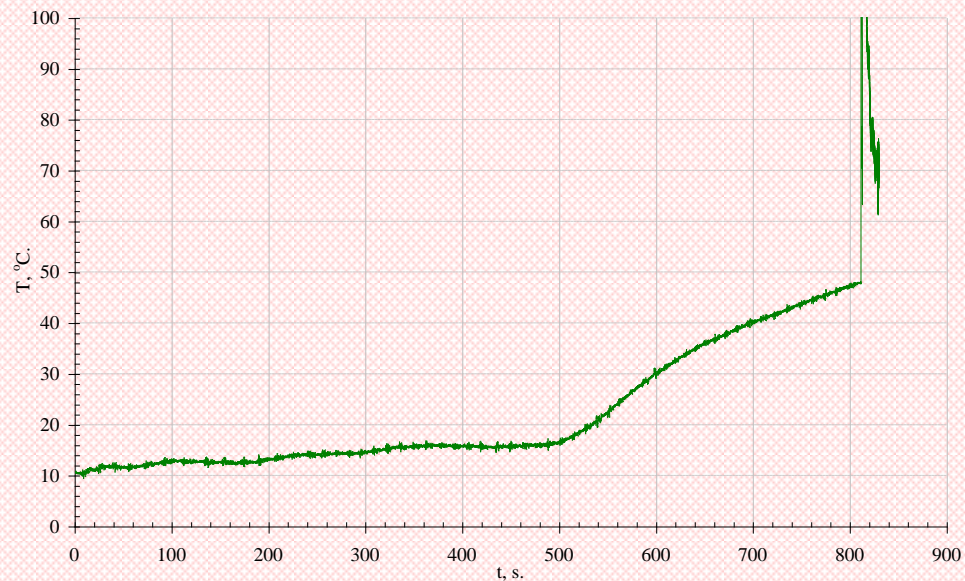
Transparent casing, 15-mm in diameter, mixture of ground components, 22 g, The layer 175 mm high, Heating coil located 50 mm above the layer top, injection of 1.8 g water.

Results of the firing: Explosion, initiated by the heating coil in the gas, produces the bright flash and dent at the steel plate-witness just at the gas/foam interface

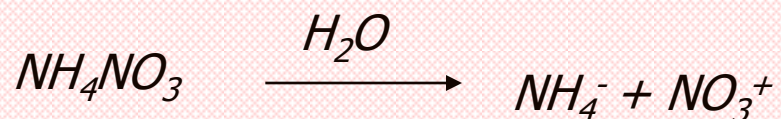
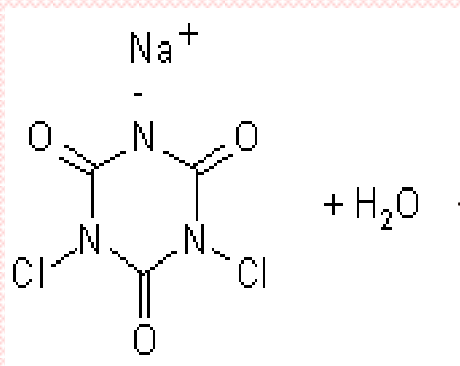


Wave processes

- *Layer samples, confined (300 g in mass) or unconfined (up to 27 kg): after water injection there is temperature rise observed, accompanied with local ejection of material and gas release. For ~ 20 min interval, chemical reaction involves total charge mass. The waves of explosive conversion do not generated.*
- *Mixture samples, unconfined (7 – 15 kg): 3 of 8 firings conducted demonstrate explosive of various intensity, but no normal detonation.*



Some details of chemical mechanism

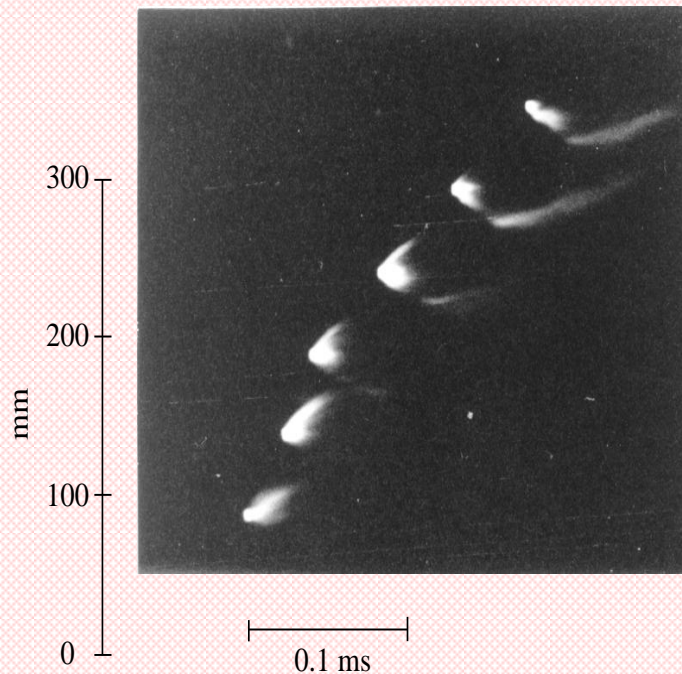


➤ **Confirmation of the mechanism supposed:**

Chemical interaction in the system $\text{NH}_4\text{Cl} + \text{DCCNa} + \text{H}_2\text{O}$

Transition to detonation

- Mixture of grained components AN+DCCNa (1:1), density 810 kg/m³, 280 g, charges confined in steel tubes 32 mm in diameter and 480 mm long, streak photo through orifices in tube wall
- In 25 – 70 sec after injection of water into the charge:
Low velocity detonation, detonation velocity ranged 1.1–1.5 km/s



Role of the explosive gas released

➤ Mixture of ground components AN+DCCNa, sieved fraction 0.25–0.63 mm, charge mass 9 g, the bed 70 mm long, steel tube 15 mm in dia.

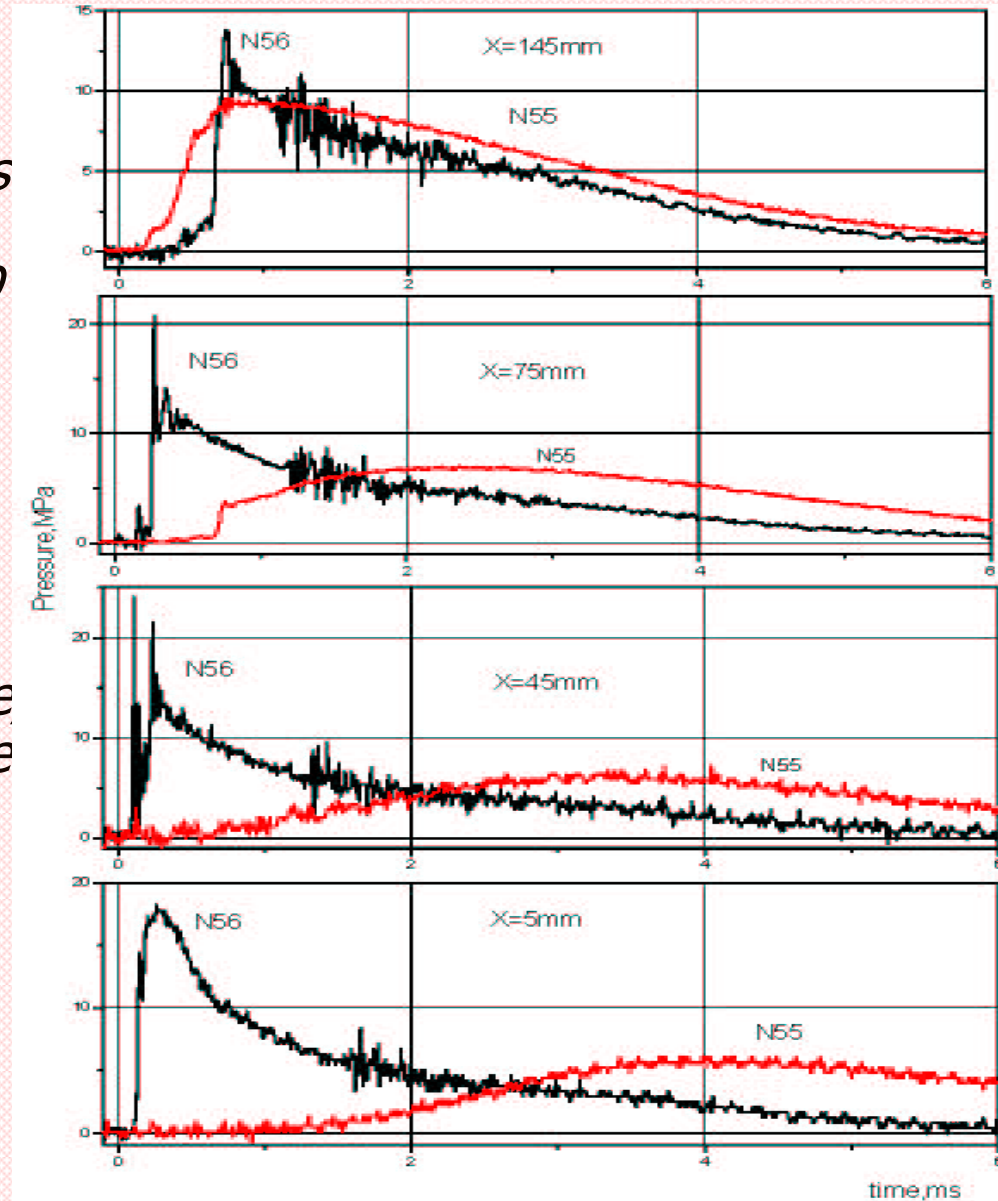
Ignition by cap-igniter:

N^o 55 (red lines) – dry mixture, $W \sim 50$ m/s

N^o 56 (black lines) – wetted mixture ignited by cap in a 30 sec after the water ignition,

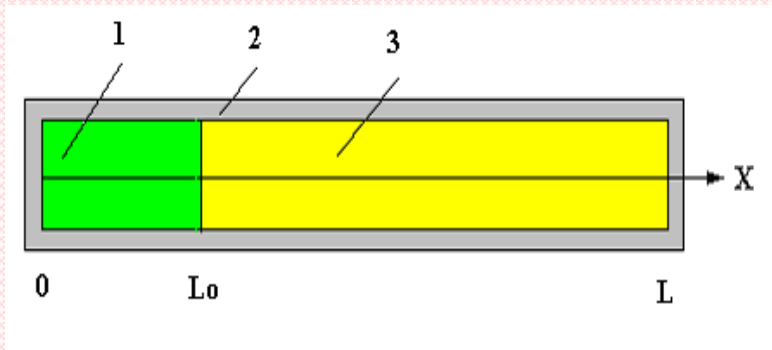
$W \sim 130$ m/c, $P_m \sim 20$ MPa:

Comparison: steep wave front, the higher wave velocity, the quicker pressure rise



Numerical simulation

Experiment shows that the explosion of active gas released does not initiate chemical conversion of AN, however it can initiate the foam. Numerical modeling is used to confirm this conclusion. Quasi-1D computer code developed relying upon two-phase reactive medium approach.



1 – wetted mixture AN/DCCNa

2 – casing

3 - dry mixture AN/DCCNa

Le = 200 mm, K = 800 mm

At $t = 0$ in the wetted mixture begins chemical reaction, resulted in release of active gas (NCl_3) and heating.

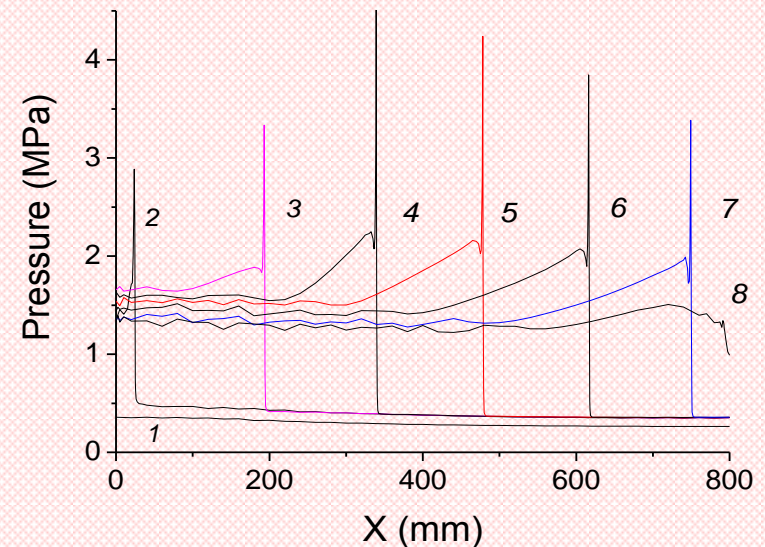
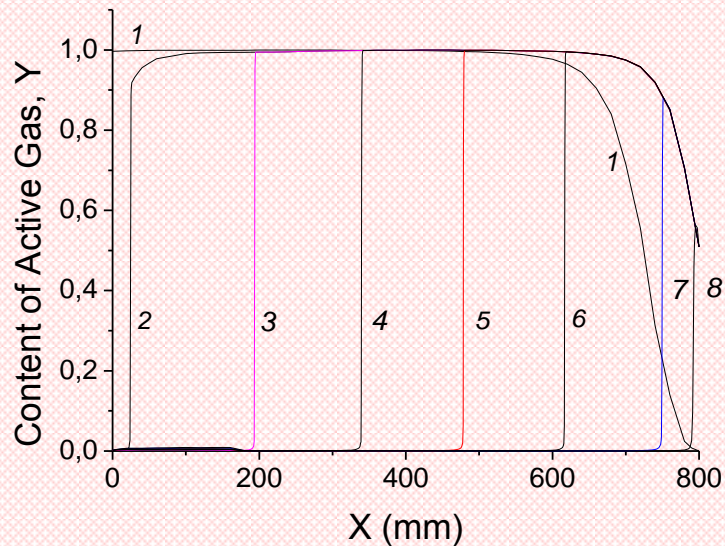
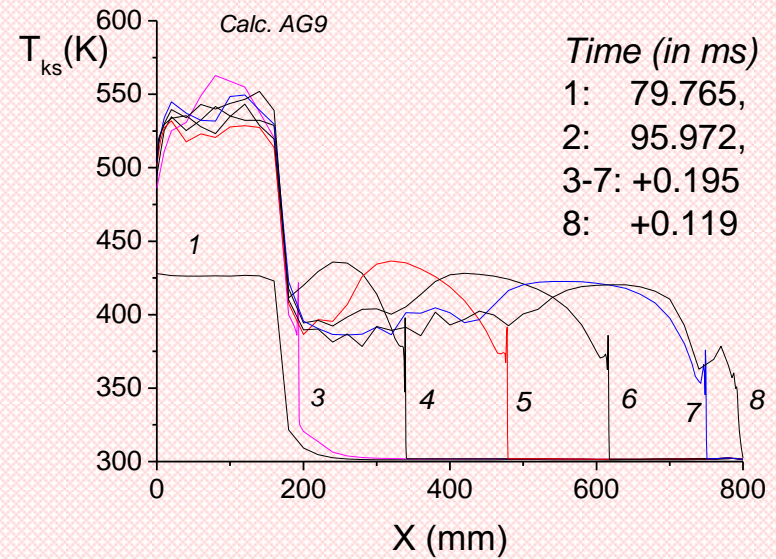
Active gas filtrates into the charge pores and if the temperature approaches 420K it begins to react according the follows equation:

$$\dot{M}_{Arr} = k_{01} \rho_g^2 Y^2 \exp(-E_Y / RT_g)$$

Numerical simulation (2)

Explosion produces reaction wave
with parameters:

$W = 300 \text{ m/c}$, $P = 4 \text{ MPa}$, $T_g = 2300 \text{ K}$



Conclusions

- *Interaction between ammonium ion and active chlorinated chemicals produced in the course of dissolution of AN and DCCNa in water, triggers a chain of chemical reactions resulting in heating, formation of explosive gas NCl_3 and foaming.*
- *Chemical reactions which control the interaction rate, go at a rather low energy of activation, and conversion level is restricted by attaining the temperature at which the gas NCl_3 explodes (115°C). Under the most conditions, there are only local explosives observed which can not involve total mass of the mixture.*
- *So far as there are no conditions providing accumulation of explosive gas in rather large amount, its detonation can not involve AN into chemical conversion. Only the foam which contains solution of active reaction products and has the higher propensity to initiating stimuli in comparison to the pure AN can support the buildup of explosive wave.*