International
Fertilizer Industry
Association

ISMA* Technical Conference

The Hague, The Netherlands
13-16 September 1976

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

International Fertilizer Industry Association - Secretariat: 28 rue Marbeuf - 75008 Paris - France
Tel. +33 1 53 93 05 00 - Fax +33 1 53 93 05 45/47 - ifa@fertilizer.org - www.fertilizer.org

SAFETY IN ROTARY DRYER OPERATION

TA/76/2

G. PERBAL - Unie van Kunstmestfabrieken bv - IJmuiden

INTRODUCTION

In the last decade fertilizers have shown a steady increase in the content of ammonium nitrate. As a consequence a higher ammonium nitrate content means also closer to hazardous products. In the same period competition has led to higher quality standards e.g. the products must be non-dusting and non-caking in bulk transport. To obtain a product of higher quality generally the water content is an important factor. In the production process two points control this water content namely the ammonium nitrate concentrator and the rotary dryer or the spherodizer. Generally the ammonium nitrate concentration plant is rightly considered as hazardous when not operated properly. Changing of the process conditions, temperature and pressure, will only be done after full consideration and additional safety requirements. On the contrary the attitude with respect to safety of the rotary dryer or the spherodizer is not of the same level, especially if the end product is non-hazardous. This type of equipment is operated with flue gas temperatures ranging from 100 - 400°C.
A high temperature of the inlet flue gases will not necessarily result in an accident, but in case of malfunctioning of the equipment this quantity of energy may start off a spontaneous heating of the entire mass in the dryer. Many people are not aware that most of the dryers are being operated in the temperature range of the induction period of the spontaneous heating of the fertilizer. Spontaneous heating may even occur with products with rather low ammonium nitrate contents.
The hazard of such an accident is the development of tons of decomposition fumes within seconds. People working in the same building may not get time to escape and will be poisened by the nitrous fumes.

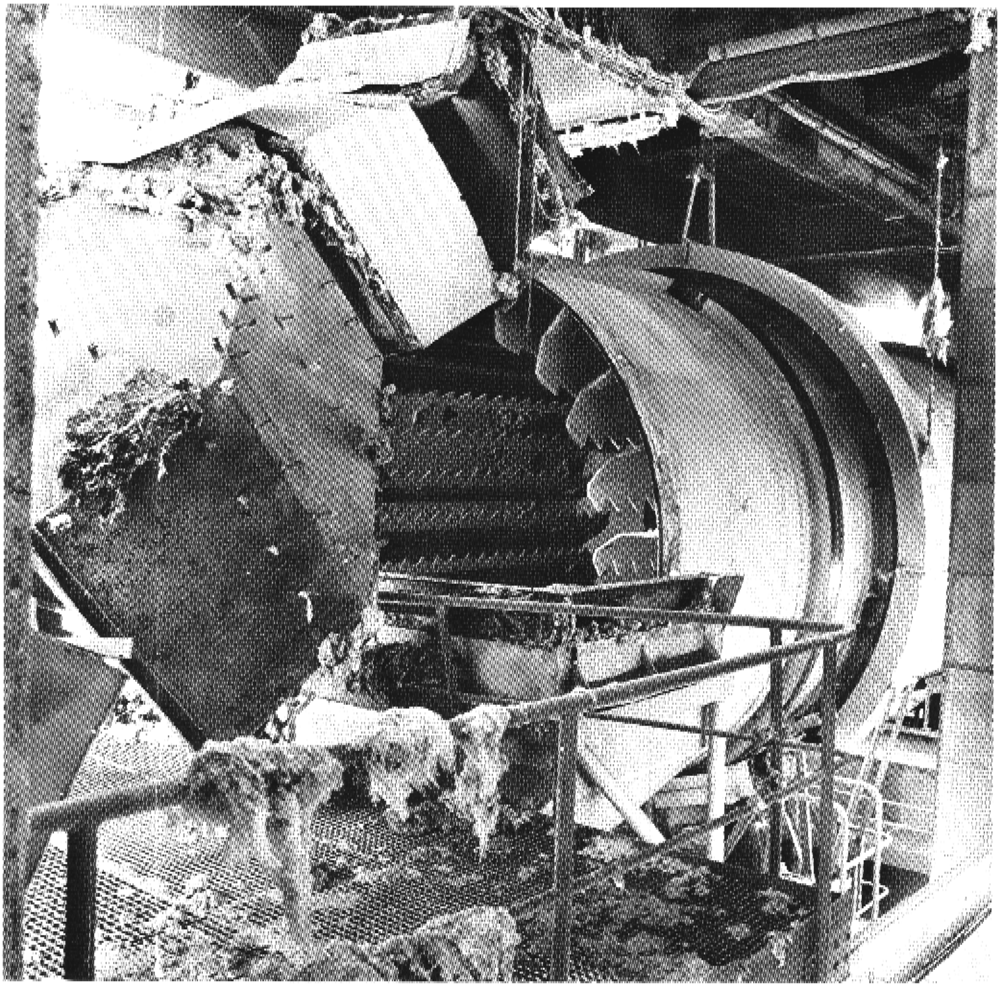


Fig. 1 Spherodizer accident (OSW)

In the past two serious accidents of this type have been taken place, namely at Oesterreichische Stickstoffwerke Linz Austria (1966) and Generale des Engrais SA usine de Nantes Chantenay France (1974), where a number of people have been killed.

A picture of the spherodizer (OSW) after the accident is given above. The situation shows quite clearly the power by which the tons of gases have forced a way out. It can be easily amagined that unwary people don't get time to flee. The amount of decomposition gases developed can be calculated from the hold up of 15 tons of product about 45% of the weight of the product (6,8 tons) is being converted to fumes by the decomposition.

The main part of this paper will be devoted to the analysis of the temperature conditions in relation to spontaneous heating and the measures to be taken to prevent such accidents in rotary dryer or spherodizer operation.

In the past also small decompositions occured in rotary dryers. This is generally caused by the hot flue gases blowing against the fertilizer caked to the vanes or in case of oil firing sparks may occur and start also local decompositions. However both cases can be prevented by a proper design of the equipment and is as a consequence outside the scope of this paper.

THEORY OF SPONTANEOUS HEATING

In an earlier paper (1) spontaneous heating of fertilizers containing ammonium nitrate has been treated in detail. Spontaneous heating takes place when the heat developed by the decomposing product exceeds the heat loss by conductivity through the mass of product. It is obvious that the size and the geometry of the mass determine whether or not a product will be capable of showing spontaneous heating at a certain temperature.

The quantitative conditions under which spontaneous heating may develop have been calculated by Frank-Kamenetsky (2). According to their formulation spontaneous heating is described in a critical radius by the following equation:

$$R_c = \frac{\delta\ R\ \lambda\ T_c^2}{n\ Q\ k\ B}^{\frac{1}{2}}$$

where

R_c	=	critical radius
δ	=	dimensionless constant for a spherical mass 3.32 cilindrical mass 2.00 cubical mass 2.60 slab 0.88
λ	=	coefficient of thermal conductivity
R	=	gas constant
n	=	number of mols/cm^3
Q	=	heat of reaction
k	=	rate of reaction
B	=	activation energy of reaction
T_c	=	initial uniform temperature (Kelvin)

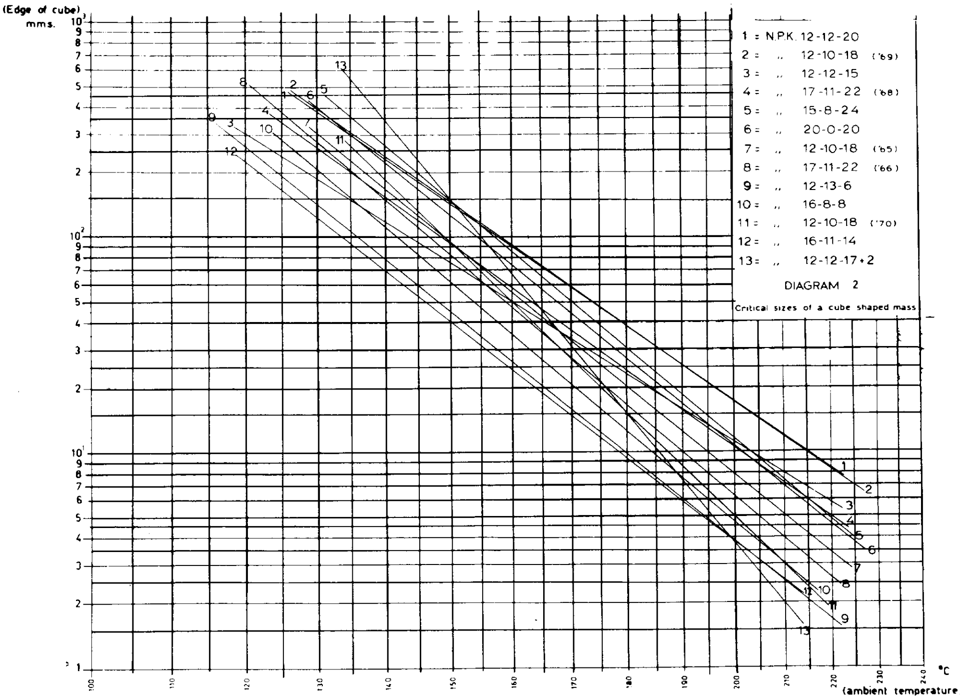
Theoretical treatment of the spontaneous heating with this equation failed (1), because the system was too complex. For example the thermal conductivity showed much variation due to water transport and melting. However the problem was solved by measuring of the critical radius of cube sized masses directly by a method developed by TNO (1).
As known the Frank-Kamenetsky-formula (3) can be simplified to:

$$\ln R_c = C_1 + \frac{C_2}{T_c}$$

where C_1 and C_2 are constants.
It will be clear that if measurements follow the theory a linear function will be obtained when ln R_c is plotted against 1/T.

2 - 5

The results of the measurements (1) of R_c of a number of NPK-fertilizers are plotted accordingly in the diagram below.



Since the way of measuring of these critical diameters was done by trial and error a lot of results concerning the induction time were obtained. When plotting ln t_{ind} against the reciprocal of the ambient temperature (^{o}K) a straight line is obtained. It is obvious that the following relation holds for a certain mass

$$\ln t_{ind} = K_1 + \frac{K_2}{T_a}$$ where T_a = ambient temperature

combining this equation with

$$\ln R_c = C_1 + \frac{C_2}{T_c}$$ and $T_a = T_c + (T_a - T_c)$

$T_a = T_c + \Delta T.$

gives $$\ln t_{ind} = K_1 + \frac{K_2 (\ln R_c - C_1)}{\Delta T (\ln R_c - C_1) + C_2}$$

Since R_c is a constant in this equation, it may be simplified to

$$\ln t_{ind} = K_1 + \frac{K_2 . K_3}{\Delta T . K_3 + C_2}$$

From the definition of the critical diameter it follows

for $\Delta T \rightarrow 0$ $t_{ind} \rightarrow$ infinite

This doesn't follow from the last equation given.
This means that the equation doesn't apply at temperatures very close to the critical temperature.

The chemical analysis of the products of diagram 2 are summarized in the table on next page.

Table chemical analysis of the compound fertilizers under investigation

Product	Total N %	NH_3 -N %	Water soluble P_2O_5 %	Citrate soluble P_2O_5 %	Acid soluble P_2O_5 %	K_2O %	Cl- %	SO_4-- (total) %	CaO (total) %	H_2O (KF) %	pH 1 gr./ 100 gr.	Horizontal decomposition velocity (trought-test 15x15x50 cms.) cms./hr.
12-12-20	11.9	6.5	4.0	11.7	11.7	20.7	1.3	22.9	7.8	0.87	5.90	< 5
12-10-18	13.1	8.0	7.3	10.6	11.0	18.0	10.6	12.5	7.0	0.55	6.00	11.3
12-12-15	12.9	7.1	9.7	10.8	11.2	15.8	3.4	18.3	6.5	0.79	5.80	8
17-11-22	17.5	10.6	10.9	11.4	11.6	22.1	17.7	0.7	< 0.1	0.3	7.09	10
15-8-24	15.2	9.0	6.9	7.2	7.6	25.2	14.1	8.9	2.0	0.49	7.70	10
20-0-20	19.6	11.0	-	-	-	20.4	16.0	9.2	-		6.9	18.2
12-10-18	12.4	7.7	9.0	9.8	10.2	18.2	13.2	14.4	5.8	1.9	4.95	15
17-11-22	16.7	10.2	10.5	10.5	11.2	22.0	17.3	-	-	0.18	7.1	10.6
12-13-6	12.5	7.2	10.1	13.0	13.3	6.6	6.1	17.8	13.9	0.6	5.07	11.9 (trough-test 10x10x50 cms.)
16-8-8(1)	12.6	7.6	8.0	8.9	9.1	9.8	11.1	12.1	6.5	1.1	5.85	10.3
12-10-18	12.1	7.1	8.2	9.8	10.2	18.1	14.5	14.5	7.5	0.49	5.0	20.6
16-11-14	15.4	7.9	4.2	10.7	10.7	15.3	11.8	5.3	6.9	1.1	5.6	32 (trough-test 5x5x50 cms.)
12-12-17-2(2)	12.1	6.5	5.0	11.9	12.2	17.9	8.0	9.4	9.4	0.31	5.77	40 (trough-test 10x10x50 cms.)

(1) MgO = 4.5%
Cu = 0.35%
Co = 0.04%

(2) MgO = 1.7%
B = 0.1%
Mn = 0.1%
Cu = 0.04%
Zu = 0.02%
Co = 0.0005%

RISK ANALYSIS OF A ROTARY DRYER

By the aid of the evidence given in the former chapter an attempt will be made to analyse the risks involved in rotary dryer operation.

The following situations are being analysed:

A - A failure of the electrical supply which causes a standstill of the drum. The inlet flue gases are automatically switched to the open air.
In such a situation a rotary dryer of a diameter of 3 m may contain a layer of product of about 65 cm. To use the critical diameter-diagram it may be assumed that the layer is comparable to a cube with sides of 60 cm.
Line 1 in the diagram may be regarded as the borderline between type B fertilizer and "non-hazardous" product, where as line 12 may be regarded as one of the most hazardous type B products (high decomposition velocity).
Extrapolation of these two lines may be done by using the equation $\ln R_c = K_1 + \frac{K_2}{T}$

- the equation for line 1:

$$\log R_c = - 6,608 + \frac{3706,576}{T_a}$$

$$\text{for } R_c = 600 \text{ mm} \quad T_a = 395^{\circ}K = 122^{\circ}C$$

- the equation for line 12:

$$\log R_c = - 8,140 + \frac{4123,967}{T_a}$$

$$\text{for } R_c = 600 \text{ mm} \quad T_a = 376^{\circ}K = 105^{\circ}C$$

From these figures it may be concluded that it is wise to maintain the product temperature not higher than about 105°C. Otherwise there is a risk of spontaneous heating under the assumed conditions.

B - This case is nearly identical to case A.
In addition to case A it is now assumed that the inlet flue gases will still be fed to the rotary dryer during this standstill. This case will be analysed for flue gas inlet temperatures 160°C and 200°C.
If the product in the dryer is heated to a homogeneous temperature distribution i.e. to the temperature of the flue gases, the following minimum critical diameters are found; partly by extrapolation.

	160°C	200°C	Decomposition velocity through test (15x15x50 cm)
Borderline non-hazardous/type B (NPK 12-12-20)	9 cm	1,7 cm	< 5 cm/hr
Moderate burning type B (NPK 17-11-22)	4,7 cm	0,6 cm	10,6 cm/hr
Violent burning type B (NPK 16-11-14)	2,4 cm	0,4 cm	32 cm/hr (x)

(x) through test dimensions 5 x 5 x 50 cm.

These figures show that the products concerned are now well in the area where spontaneous heating is possible. Also is shown that the critical diameter of 16-11-14 at 200°C approaches the size of a granule. It has to be explained that this 16-11-14 has a high sensitivity to decomposition. It is possible to start off a decomposition in this product by the aid of a burning cigarette!
In the introduction was mentioned the local decompositions e.g. of caked product on the vanes. This phenomenon is easily explained by the figures in the table.

However an important factor in this respect is the induction period; i.e. the time necessary to start off a run away reaction (self-ignition).
Since the figures in the table are critical diameters the induction time becomes infinite.

The lines in diagram 2, giving the critical conditions, were obtained by trial and error. The underlying data of these lines permit to give an impression of the induction periods involved.
The induction period data of cubic shaped masses with sides respectively of 2 cm, 4 cm and 8 cm were, if necessary, extrapolated to inlet flue gas temperatures of 160°C and 200°C. Extrapolation was being done by the aid of the equations given in chapter 2.
As a result the following figures were obtained:

Product	Edge of the cube					
	2 cm		4 cm		8 cm	
	160°C	200°C	160°C	200°C	160°C	200°C
12-12-20	N.D.	N.D.	N.D.	± 75 min.	N.D.	± 180 min.
17-11-22	N.D.	± 60 min.	N.D.	± 6 min.	± 47.5 hrs	± 75 min.
16-11-14	N.D.	± 9 min.	± 6 hrs	± 15 min.	± 10 hrs	± 18 min.

where:

N.D. = No decomposition; the mass is sub-critical.

The extrapolations of the induction times for cube sizes 4 cm and 8 cm to a temperature of 200°C don't seem to be very realistic. The extrapolation to 200°C is too far from the critical conditions where the equation applies. It is easily understood that at such high temperatures as 200°C, the surface layers reach already supercritical conditions before the whole mass is at 200°C. As a consequence burning of the outer layers will occur.

It may be concluded that the actual induction times for the cases of 200°C will more resemble the data of the 2 cm cube.
No attempts have been made to make a full mathematical analysis of non-steady state spontaneous heating. This is far more complicated than the steady state model of Frank-Kamenetsky (2) already mentioned in chapter 2.
Since the situations, as postulated in the rotary dryer, is a non-steady state heating, the induction times may be taken 2 - 3 times the figures given in the table.

According to the postulated conditions of the dryer, with a flue gas inlet temperature of 200°C and filled with product of type 16-11-14, the situation will lead in a rather short period to surface burning (decomposition). The propagation of this decomposition will be high, many times faster than the through test value, because of the product temperature e.g. 110°C.
It is emphasized that the decomposition gases will not develop so fast as in the case of a spontaneous heating of the entire mass.
However it may still be a serious accident.
Products like type 17-11-22 appear to be safer.

However for a safe operation, inlet flue gas temperatures should not be higher than about 160°C.

C - Another risk arises if the temperature control of the flue gases will not work due to a defect and the hot flue gases ($t > 200°C$) are not switched to open air. This may especially be dangerous when starting up the plant and the product is continuously recirculated over the dryer. Obviously this gives a steady increase of the product temperature and results in a decomposition of the entire mass of the rotary dryer in a few seconds. This happened in the two accidents mentioned in the introduction.

Since the product is moving in the rotary dryer the mass of product is not able to build up the self-insulating effect. This means that heating will be continued till the critical diameter is equal to the granular size.

From diagram 2 can be found the following critical conditions

		Line 13	Line 1
R_c = 2 mm	T-critical	210°C	263°C
R_c = 3 mm	T-critical	204°C	250°C

From these figures it may be concluded that an important part of the NPK-fertilizers will be supercritical at temperatures between 205°C and 265°C.
At these temperatures induction periods are very short, generally a matter of minutes.

The temperature at which spontaneous heating of this type in a dryer will occur, can be measured directly at the laboratory by the aid of the ISMA/APEA-test methods (4); namely with the rotating- and stationary-oven test. With these test methods figures have been obtained which are indeed between the limits given above.

SUMMARY

In the foregoing chapters it was shown that a rotary dryer or spherodizer can be operated fairly safe, when the operating conditions are

- product temperature not higher than 105°C

- the inlet flue gas temperature not higher than 160°C

To safeguard these conditions the following provisions have to be present

- temperature control + alarm on the inlèt flue gases

- temperature indicator + alarm on the outlet flue gases

- when the dryer comes to a standstill the flue gases must be switched to open air or the burners must be stopped automatically.
  Note: If the period of standstill is more than half an hour, the temperature of the product in the dryer has to be measured continuously.
  When a steady increase in temperature occurs, the works fire brigade has to be warned and, if necessary, can fight this with water.

- co-current operation seems to be preferable.

It is realized that some existing dryers cannot meet these requirements because of the original design. This will not necessarily lead to an accident if additional precautions have been taken.
The analysis made in this paper, makes clear how close the operation conditions can be to a hazardous situation.
When operating at temperatures of 180°C and higher, hazardous products like 16-11-14 have to be deleted from the production program. In general it is advisable to consider the hazard profile of the product in relation to the inlet flue gas temperature.
Since the induction periods are very short at these high temperatures, the dryer or spherodizer have to be equipped with fixed water-jets.
Automatic operation of these water-jets on the outlet flue gas temperature may be considered.
Easy accessable emergency exits for the operators should be provided. All personnel in the building should have escape respirators.

The aim of this paper is to help people thinking again about the safety in rotary dryer or spherodizer operation. The author hopes that this contribution will prevent new accidents as concerned in the future.
Prevention is better than cure.

LITERATURE

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