EFFECTS OF PROCESS VARIABLES ON THE CAKING TENDENCY OF PRILLED UREA IN THE WAREHOUSE OF UREA PRODUCTION PLANTS

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ABSTRACT

The caking of urea fertilizer is investigated in a warehouse of a large scale petrochemical plant. It is found that the caking tendency below the recommended value of 5 %$_{mass}$ can be achieved if the prill coefficient of variation and the temperature difference between the product and warehouse ambient are kept at 0.07 and 4 °C, respectively. A first order kinetic model is also suggested for description of the urea caking process. The caking tendency is well predicted by the proposed correlation with the overall deviation of ± 3 %$_{mass}$.

Keywords: caking, urea, prilling, warehouse, petrochemical plant.

INTRODUCTION

Urea is in many ways the most convenient form for fixed nitrogen. It has the highest nitrogen content available in a solid fertilizer (46 %). It is easy to produce as prills and easily transported in bulk or bags with no explosive hazard. The change from bagged to bulk handling and the increase in production and handling capacities require that the physical quality of fertilizers should meet higher demands in order to assure customer acceptance. To be assured of good physical quality of prilled urea, the product should have a low caking tendency during storage [1].

In the usual operation of a petrochemical plant, crystalline urea prills with the size range of 1-4 mm are dried to a low moisture content (less than about 0.2 %$_{mass}$), piled up in the warehouse and then packaged in multiply bags. It is always found that the mass of prills tends to set up into a single solid cake when stored in the ordinary manner. In some instances, a hard solid cake is formed in a matter of hours when the bagged urea is subjected to very slight pressure, on the order of 0.5 bar [2]. Thus the caking tendency makes the urea fertilizer quite unsuitable for technical applications and reduces the profitability of the process drastically.

The main cause of caking is the growth of crystal bonds on the contact points of the prills [3]. This process can only take place in the presence of liquid phase, in this case saturated aqueous urea solution. The caking tendency of urea prills is adversely influenced by:

• **The amount of liquid phase**
- ***water (moisture).*** The caking tendency increases with the water content. Difference in the prill water content causes water to migrate through the pile. This too increases the caking tendency.

- *free ammonia.* Excessive amounts of free ammonia increase the amount of the liquid phase in the prills. Ammonia loss in turn leads to the crystallization and essentially to the agglomeration or lumping of prills.

- *prill temperature.* The caking tendency decreases with lower storage temperatures (less liquid phase). What should be avoided are high prill temperatures at the bottom of the prilling tower (higher than 60ºC).

• **Migration of water**

- *migration of water between prills.* This causes crystallization and the formation of crystal bonds resulting in a higher caking tendency. The migration of the water from one prill to another is brought about by differences in the partial vapour pressure of water in the prills resulting from the differences in temperature and the water content. A more uniform prill size distribution is desirable.

- *water absorption from the ambient air and loss back.* It is worth noting that 1 m^3 of urea may contain 1 to 3 kg of water whereas 1 m^3 of air at 40ºC contains only 50 g of water, and that water loss is at least harmful with respect to the caking as is the absorption. Thus the temperature difference between the warehouse ambient and the product could be an important issue.

• **High proportion of unround and small prills, dust and fines**

The caking tendency increases with the number and size of contact points between the prills. Similar to the case of the migration of water between prills, a more uniform prill size distribution may lead to a less caking tendency.

• **Poor mechanical strength**

This is particularly important when the product needs to be stored later, after being subjected to a variety of handling operations. Poor mechanical strength leads to disintegration and dust formation and, thus, as pointed earlier, to increased caking. The problem can be alleviated by proper prilling and seeding so as to prevent subcooling of the prills [4].

The caking tendency of urea prills can be combated by adding specific amount of anticaking agents before (e.g. formaldehyde compounds) or after (e.g. polypropylene glycol or mineral oils) the prilling pro-cess [3,5,6]. Unfortunately the use of anticaking agents may render urea unsuitable for technical applications. Also the recycling part of the treated urea (recovered dust, fines and non-standard prills) lead to the formation of foam in the evaporators and deactivation of the catalyst in the urea synthesis unit [7]. Therefore it is preferred to reduce the rate of urea caking by controlling the process variables rather than using the anticaking agents. In this work we are trying to find the ranges of necessary operating conditions to keep the caking tendency in the urea warehouse below the recommended standard value.

EXPERIMENTAL

The experiments are carried out in an urea warehouse of a 1500 MTPD production plant. The ammonia content of urea melt is kept at the lowest possible value of 50 ppm while the maximum dedusting and fine removal is applied. The average prill moisture content was kept at 0.2 %$_{mass}$ and the crushing strength and impact resistance of urea prills have been kept at the maximum possible values of 25 bar and 82 %, respectively [1]. Considering all these and previously discussed influences, it can be concluded that the rate of caking in the warehouse is mainly affected by prill size distribution expressed as coefficient of variation (CV) and temperature difference between urea bulk and warehouse ambient (ΔT). Effects of these two parameters on the urea caking tendency are rarely discussed in the literature.

The warehouse stack test is used to determine the caking tendency of urea prills because this stack test substantially approaches actual field storage conditions. In these tests, the standard 50 kg bags are employed as in routine commercial production. In a typical experiment, 50 kg of prilled urea entering the warehouse with definite CV and ΔT is quickly transferred to a test bag. These test bags are placed horizontally on a special pallet and are arranged on the pallet in layers of four bags each, one bag along each side of the pallet. Six layers of bags are placed on the pallet. The pallet of test material is then placed in warehouse storage, and weight is added by stacking two full pallets of commercially bagged product (6 x 4 = 24 bags/pallet) on the top of the pallet of the tested material (i.e. 'test pallet'). The tested pallet is stored in this condition for a given

period of time (from 1 to 10 weeks). At the end of the storage period, the bags are carefully removed from the pallet and each is dropped once from a height of about 1 meter to separate any loosely held agglomeration of particles that may have formed during storage. Each bag is opened at one end, and its content is poured onto a 2 mesh U.S. Standard screen which retains any lumps of caked material that may have formed. The lumps are retrieved and weighed. The weight, in kg, of lumps retained on the 2 mesh US Standard screen constitutes a quantitative measure of the urea's caking tendency and, hence of urea's free-flowing characteristics. According to the EFMA Standard [1], urea is substantially free-flowing if, on being subjected to the warehouse stack test, about 5 kg or less lumps (particles which fail to pass a 2 mesh U.S. Standard screen) are produced per 100 kg of urea tested after 6 weeks storage period.

A series of experiments are carried out at different operating covering the ranges of the process variables shown in Table 1.

Modelling of the caking process

In this work a first order kinetic model is used for description of the caking process. It is assumed that the rate of change of non-caked prills into lumps is first order with respect to the mass of non-caked prills. This can be written as:

$$\frac{dm}{dt} = -km, \tag{1}$$

where

m = mass of non-caked prills at time t, kg
t = storage time, weeks
k = caking rate constant, weeks^{-1}.

Eq. (1) can be integrated and written in the following form:

$$-\frac{1}{t}\ln\frac{m}{m_o} = k, \tag{2}$$

where m_o is the initial mass of non-caked urea prills.

Using the experimental data, the values of *k* can be determined by correlating the left side of Eq. (2) in terms of CV and ΔT by the following equation:

$$k = (a + b\Delta T^x) + (c + d\Delta T^y)CV^z \tag{3}$$

where:

    a, b, c, d, x, y, z are parameter in Eq. (3)
    CV = σ/L$_m$ - coefficient of variation [-]
    σ - variance, mm.

The coefficients and exponents in Eq. (3) are estimated by multiple non-linear regression analysis of all experimental data and the results are tabulated in Table 2. The values of the coefficient of determination, R^2, show that a good correlation is obtained. The standard error in parameter estimates is determined at 95 % confidence limits.

Using Eqs. (2, 3) and the parameters, the caking tendency, described as the weight percent of conversion of initial mass of prilled urea into caked lumps, can be determined as follows:

$$\text{caking tendency} = [1 - \exp(-kt)] \times 100 \tag{4}$$

Predicted caking tendencies by using Eq. (4) are compared with experimental data and discussed in the following section.

RESULTS AND DISCUSSION

The measured caking tendencies at a fixed ΔT of 8°C and different prill coefficients of variation are displayed in Fig 1. As shown in this figure, the caking tendency increases from 9.5 %$_{mass}$ to 47.9 %$_{mass}$ after 6 weeks as the CV is increased from 0.07 to 0.28. It is practically impossible to keep the caking tendency below standard recommended value of 5 %$_{mass}$ for the

Table 1. Ranges of run conditions for investigating the caking phenomena.

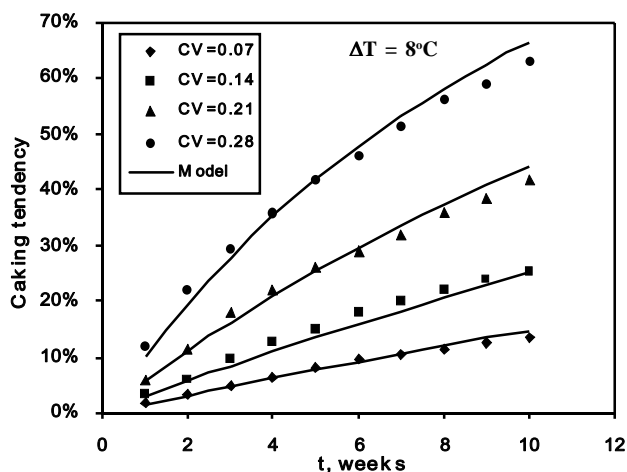| Run number	ΔT (°C)	CV
R1 - R4	0	0.07, 0.14, 0.21, 0.28
R5 - R8	4	0.07, 0.14, 0.21, 0.28
R9 - R12	8	0.07, 0.14, 0.21, 0.28
R13 - R16	12	0.07, 0.14, 0.21, 0.28

Fig. 1. Effect of prill coefficient of variation on the urea caking tendency in the plant warehouse at ΔT of 8°C.
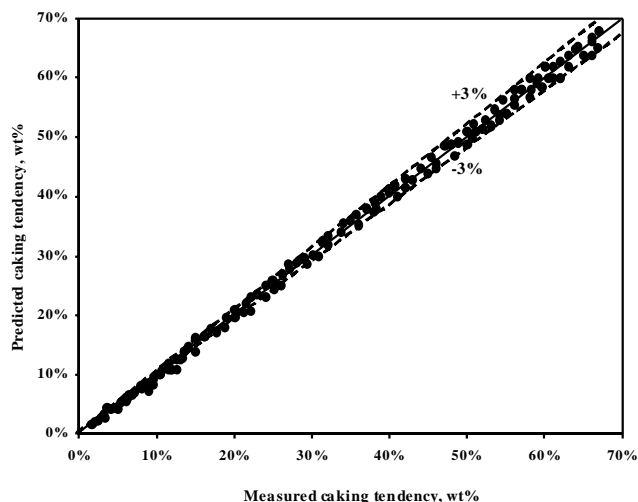

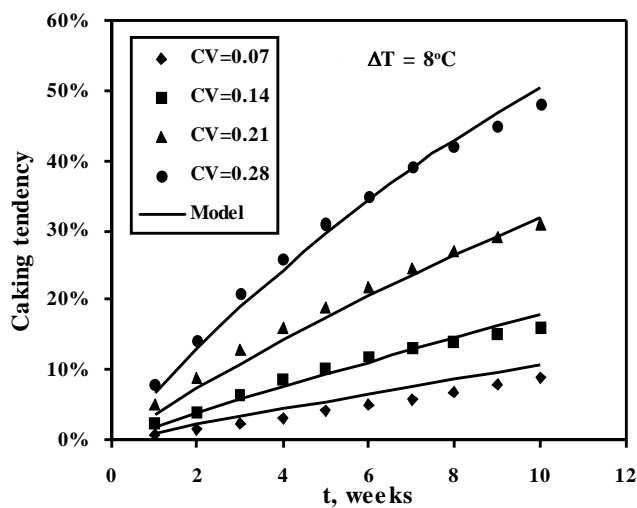Fig. 3. Comparison of predicted and measured urea caking tendency.

Fig. 2. Effect of prill coefficient of variation on the urea caking tendency in the plant warehouse at ΔT of 4°C.

ranges of process variables shown in this figure. According to Fig 1, at higher prill CV, the caking tendency is more severe. An increase in prill CV from 0.07 to 0.14 leads to a 11 $\%_{mass}$ increase in the caking tendency after 10 weeks, while for a further CV increase from 0.14 to 0.21 %, a 19 $\%_{mass}$ increase in caking tendency is observed at the end of the same time period, which is quite significant. This occurs because increasing values for the coefficient of variation result in an increasing abundance of both small and large diameters (relative to mean diameter) in the population of urea prills. This amplifies the rate of moisture migration from large to small prills and speeds up the rate of caking. Also the small prills posses more external surface area and this further increases the rate of agglomeration and caking. Table 3 shows how the < 0.6 and > 3.0 mm size fractions and the < 1.0 mm and > 2.6 mm size fractions decrease as the spread of prills with 1.8 mm mean diameter decreases from 24 % to 10 %. As the coefficient of variation is decreased, the coarse and fine frac-

Table 2. Calculated values of the parameters for Eq. (3).

Constants and exponents for k in Eq. (3)						
a	b	c	d	x	y	z
6.988×10^{-3} ± 0.0002	5.664×10^{-4} ± 0.00007	1.055 ± 0.12	0.08764 ± 0.003	1.1597 ± 0.17	1.3856 ± 0.11	2.6020 ± 0.34
R^2-value = 0.989						

Table 3. Reduction of coarse and fine fractions with decreasing the coefficient of variation.

Coefficient of variation	Standard deviation (mm)	Fraction (%$_{mass}$) < 0.6 mm and > 3.0 mm	Fraction (%$_{mass}$) < 1.0 mm and > 2.6 mm
0.24	0.432	0.27	3.22
0.22	0.396	0.13	2.17
0.20	0.360	0.05	1.32
0.18	0.329	none	0.75
0.16	0.288	none	0.27
0.13	0.234	none	0.03
0.10	0.180	none	none

tions are reduced such that a normal Gaussian distribution is approached and thus caking tendency diminishes as explained before.

In Fig. 2 the caking tendencies at a fixed ΔT of 4°C and different prill coefficient of variations are also compared together. As shown the caking tendency is decreased from 11 to 4.8 %$_{mass}$ as the prill coefficient of variation is decreased from 0.14 to 0.07 after 6 weeks storage. According to this figure, the caking tendency after 6 weeks can be kept below the recommended value of 5 %$_{mass}$, if the ΔT and CV are controlled at 4°C and 0.07, respectively.

The measured and predicted caking tendencies at ΔT of 4 and 8°C and different prill coefficient of variation are compared in Figs. 1 and 2, respectively. Eq. (4) is used to predict the caking tendency of urea prills in the warehouse. As shown in these figures the predicted and measured values are in good agreement at different operating conditions. Predicted results well reproduce the experimental measurements.

The predicted caking tendencies according to Eq. (4) are also compared with experimental data for all runs in Fig. 3 at a relative deviation of $\pm$ 3 %. This figure clearly indicates that the caking process is well described by the proposed model.

CONCLUSIONS

Controlling the caking tendency of urea prills during the storage in the warehouse is of prime importance to keep the product quality at the highest possible level. It is shown that even for an ammonia concentra-

tion of 50 ppm, average prill moisture content of 2 %$_{mass}$, crushing strength of 25 bar and impact resistance of 82 % and maximum dedusting and fine removal, the urea caking tendency could be severe in the warehouse after 6 weeks. It is found that in addition to above process variables it is necessary to keep the ΔT and CV at 4°C and 0.07, respectively, in order to maintain the caking tendency below the maximum permitted value of 5 %$_{mass}$. Thus controlling the temperature difference between prilled product and the warehouse ambient and also the granulometery of the urea prills are essential to minimize the caking tendency of the urea product. The suggested temperature difference can be achieved by warehouse insulation and space heating, while the proposed prill coefficient of variation can be obtained by installation of a vibrating melt spray nozzle at the top of prilling tower. A first order kinetic model is also suggested for description of urea caking process. The effects of temperature difference (ΔT) and prill coefficient of variation (CV) on the product caking tendency are well predicted by the proposed correlation.

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