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UREA CAKING PROBLEMS, HOW TO AVOID THEM (a)

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1. Introduction

To the knowledge of the author there are not enough precise reports explaining the phenomenon of urea general caking stored in bulk (in onshore storage or in hatches of ocean going vessels). In the literature are found many studies and investigations reporting on the effect of various parameters to the caking (CRH, Particle Size and Hardness, Abrasion and Impact Resistance, Treatment and Conditioning, Storage Pressure and Temperature, Urea Moisture, Moisture Absorption, etc.), but only few explaining the <u>mechanism</u> of <u>caking spreading</u> from a relative limited initial area to the whole pile, observed often in stored urea even of very good quality, stored under more or less correct conditions in bulk.

The basic phenomenon governing the spreading of caking in a heap of urea in bulk, where initially a relative thin layer only, has absorbed humidity, (because hatch cover left open during a period of high atmospheric relative humidity), or where a relatively small amount of warm (above 55° C) and of higher residual moisture urea is included into a heap of low residual moisture and relatively cold urea, is the so called <u>humidity migration</u>.

If this water pick-up, or this inclusion happened, and urea is subject to temperature cycling, which usually is the case during storage, or loading - shipping - unloading, then caking of the whole holding of the hatch may result. This caking may be severe resulting in hard to break lumps, or less severe (easy disintegration of lumps), depending on the quality of the urea and the number of cycles.

2. Properties of Urea and the Basics of Caking Theories and Anticaking Actions

2.1 Granular or prilled urea is a single component fertilizer. The produce in modern plants, prilled urea is a pure crystalline non-porous salt of low moisture content (0.15 to 0.25%). Prills are essentially spherical, smooth surfaced and, if produced by modern, efficient prilling devices, they are regularly sized, have a narrow size distribution with only small fraction of small or oversize. (average diameter of about 1.5 to 1.9mm and 90 to 95 % of the prill between 1.2 and 2.2 mm). Prills are less hard and dense and have a lower crushing strength compared to urea granules. To increase the hardness of the prills formaldehyde usually is added to the urea melt before prilling. More details about improved properties of urea are given below.

The humidity of surrounding atmosphere and the temperature of urea has an effect on the storage behaviour, but solid urea can absorb moisture only when the relative humidity of the ambient air is for a given temperature above a specific value, called the Critical Relative Humidity (CRH). For prilled urea this value is 70 % for a temperature of 30°C and 66% for 42°C.

For granular urea produced by the Fluid Bed Granulation (FBG) of Hydro Agri, the CRT, according to Hydro Agri is considerably lower due to the higher formaldehyde content used in the HA FBG process, resulting in:

- higher hygroscopicity of urea-formaldehyde saturated solution,
- extra surface activity in the porous structure of the grain surface.

Due to its crystalline and non porous nature prilled urea is not able to absorb into each individual particle big amounts of moisture (about 3% of urea weight at saturation). When measured in isothermal laboratory tests the rate of penetration of moisture into a sample of urea, when in contact with air of a relative humidity (RH) higher than the specific CRH value, is relatively high due to the nature of urea.

Depending on the movement of air with constant RH over the urea and the easiness of air to diffuse and circulate through, the penetration depth of moisture into the heap, as measured in laboratory tests, can reach 10cm or more within few hours of exposure, especially when the urea temperature is above 35 °C. That means, that the top layer of bulk urea at 40 °C, in a vessel hatch of large free section, or in bulk storage can absorb, within 6 hours of exposure to continuously circulating air at 28°C and 80 % RH above 300 kg of water.

2.2. <u>Caking</u> is a process by which a fertilizer loses its desirable free flowing property. We can consider the caking as the agglomeration among prills or granules with tendency to form more or less hard concrete lumps of large dimension and varying mechanical resistance to disintegration.

If disintegration of lumps is only possible by application of strong mechanical forces and/or impact we have the case of a <u>severe or hard caking</u>. In this case disintegration of lumps is difficult and time consuming and usually results in partial destruction of the particles <u>(formation of fines and dust).</u> Caking is <u>light</u> if lumps disintegrate relatively easily to free-flowing condition again, practically without dust or fines formation.

Caking of urea is caused by formation of crystal bonds between particles: Internal moisture or externally absorbed water is, by capillary or thermal action forces attracted to the contact surface of the particles. Saturated solutions will be then formed at the particle surface attracted by capillary adhesion to the contact area. Due to temperature increase of urea as a result of thermal action, water in the liquid phase can evaporate, and by crystallization process crystals are formed at the contact area of the particles, creating a more or less strong bond between them.

The evaporation due to thermal action will increase the water vapor content of the warmed up air, which can diffuse through the heap. When in contact again with a layer of urea of lower temperature, the vapor is cooled down and moisture content above the CRH is re-condensed and absorbed again at the contact area of the grains.

If we consider the example of bulk urea in a vessel hatch mentioned above, the 300 kg of absorbed water, evaporated due to cycling thermal action, are able to cake initially about 160 to 220 MT of urea. Assuming the evaporated water vapor is entrapped into the pile, it can condense again on a cooler part and so, due to a minimum cycling temperature gradient of about $\pm 8 \, ^\circ C$ (existing within the various parts of the urea mass in bulk in vessel hatch, or in bulk storage), this cycling absorption - reevaporation may result in caking a considerable part of the urea after 5 to 8 such cycles.

This phenomenon is called <u>humidity migration</u> and plays an important role in the caking of urea stored, or shipped in bulk, in the case urea is coming in contact even for short time during loading - unloading with humid air, and temperature cycling within the urea mass can take place. Due to the daily ambient air temperature / RH variations and the temperature difference of the freshly loaded and the urea already in the hatches, a temperature cycling is in most of the cases unavoidable. This phenomenon will be analyzed in detail in Chapter 3.

3.   Main Parameters Minimizing Urea Caking

We will first consider the case of urea produced in hot and humid climates and conveyed immediately to an appropriate bulk storage, without air conditioning or air dehumidification, where ingress of large volume of humid air is restricted by keeping storage doors closed. We also consider   loading from storage into the hatches of an ocean going vessel, as well the unloading at the designation port.

To prevent caking itself, or minimize consequences of caking in a prilled urea bulk storage, where ingress of large volume of humid air is restricted by keeping storage doors closed following main conditions must be satisfied:

- low moisture urea content 0.15 to 0.25%
- sufficiently hard prills by adding formaldehyde, or equivalent HMT content of about 0.2 to 0.3%
- round, possibly uniform size prills, without fines, dust of minimum contact surface, by using appropriate prilling device
- maintaining temperature of the urea going to the bulk storage, as close as possible to the storage ambient air temperature.

3.1 Low moisture urea content 0.15 to 0.25%

Low moisture content, possibly below 0.2% and urea temperature in the storage of around 45° C, which is the bulk storage temperature in hot climates, reduces the water vapor partial pressure level at the surface of the particle and so the effect of water evaporation and humidity migration . Below 0.2% moisture can be easily obtained in a properly operated urea prilling plant of Stamicarbon or other reputable licenser.
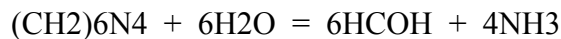
It is impossible urea is picking up humidity from the ambient air in the prilling tower under similar climatic prevailing in South India (35°C, RH = 80 - 90%).This could eventually happen only in cold, foggy climates and during rain storm conditions in hot climates. I am, as many other experts in the industry, very confirmative in stating that for the weather conditions of high RH, the prills do not absorb moisture during their fall in the prilling tower.

3.2 Sufficiently hard prills by adding formaldehyde, or equivalent HMT content of about 0.2 to 0.3%

The crushing strength of prilled urea is relatively low, especially if urea contains large portion of hollow prills, clusters and shells. When subject to increased pressure, at the bottom of pile height above 12 to 13 m, prills of low quality can be deformed and fracture, increasing the

pressure of saturated solution on the surface of urea prills is given. When both air and prill saturated solution vapor pressure are equal no humidity absorption / desorption is taking place. As the air temperature in non air conditioned bulk storage in hot climates is about 40 to 45^0 C, fresh urea from production shall have the same temperature.

The problem is that temperature of prilled urea at the bottom of prilling tower below 70° C is often difficult to be obtained in hot climates during summer days. In order to keep the temperature in the storage around 45^0 C, which is the upper comfort limit for working environment, either air conditioning in the storage, or cooling of urea is required.

If neither air conditioning, nor urea cooling is available, operators keep storage doors open to create air currents in order to lower air temperature in the storage and to accelerate cooling of stored urea as it is shown in Fig. 2. Humid and cooler air is entering and due to the intensity of contact between the urea in the bulk storage and the ambient air with RH above CRT value air humidity is continuously absorbed, until air is dehydrated to the humidity content of CRT. Because there is natural ventilation and ambient air currents, by which the air above the urea is moved and replaced with fresh humid air, the humidity penetration is going deep into the exposed side of the heap.

If the urea temperature at maximum 40-45° C, with bulk storage doors kept shut, air can practically not be renewed and so, even if it has a RH above the CRH, it will cause a small harm only. That means, as recommended by Stamicarbon, storage building with doors kept shut to minimise contact with outside ambient air, air conditioning, or dehumidification of storage is not necessary, provided the urea temperature is low.

In static lab tests at isothermal conditions and by a relatively low rate of penetration of water-vapor by diffusion only, the measured quantity of absorbed moisture at saturation is about 3% by weight. In the case air kinetic is the governing factor for humidity penetration, the average absorption is only a fraction of the saturation value, e.g. the average moisture of the affected layer is 1.0 to 1.5%. In other words the humid air ingress can humidify within 6 hours of exposure at least about 15 cm of the top layer of the one urea heap close to the entering air.

When in the next morning urea at $65-70^{\circ}$ C is poured on the moisturized top layer, the conducted heat makes absorbed moisture to evaporate and to diffuse into the mass of urea. The affected top layer is caked and the evaporated water vapor migrates preferably towards colder parts of the pile. There it can re-condense and initiate caking again, if due to temperature cycling temperature at this part temperature can increase again, by fresh hot urea poured again on the heap.

Similar phenomena are observed in enclosed urea bulk storage, when in the middle of the pile an amount of warm urea (55 to 70^0 C) with slightly elevated moisture is enclosed. The evaporated and recondensed, by migration, moisture in a colder part of the pile, may initiate a spreading of the caking, of variable severity, depending on the urea quality and temperature cycling.

With hot urea even in an air-conditioned storage caking can take place: The heap on which fresh urea in not added will get the storage temperature. When hot urea is now falling on the relatively colder heap, the fresh urea will cool down evaporating some humidity. Evaporated vapours will migrate relatively fast towards colder layers of urea, increasing the RH of air surrounding the prills and humidity will be absorbed. Few hours later, when colder urea gets

warmed by convection, absorbed humidity will evaporate again and caking is the result!

In other words it is possible, to have a generalised caking initiated by a big temperature difference between urea temperature and ambient air storage temperature. This relatively simple mechanism of caking spreading in bulk urea, is, in many cases either not understood or simply overlooked.

4. Means to Reduce Urea Temperature and to Obtain Calibrated Prills

4.1. Fluid Bed Cooler

In Fig. 5 a system is shown to cool urea by a dehumidified air. This dehumidification is necessary to avoid water pickup during sudden climatic changes from dry to humid atmospheric conditions and involves:

- High investment – operating cost
- Complex instrumentation /control (I&C)
- Large layout required
- Long plant shut down required for installation
- Many vendors involved (FBC, Scrubber, blowers, finned coils, I&C, etc.)
- The solution collected in the scrubber needs to be recycled back to the process, increasing the evaporation requirements
- If the dust laden warm air is reintroduced in the prilling tower, this will affect the cooling capacity of the prilling tower and possibly will increase the dust emission.
- On the other hand the introduced dust can act as seeds to modify the prill crystal structure giving to it higher abrasion and impact resistance (see para. 6.1 below).

4.2. Bulk Flow Cooler

In Fig. 6 the diagram of a Bulk Flow Cooler (BFC) is given. The cooling medium is circulating cooling water inside of multiple stainless steel welded plates. Between the plates prilled, or granular urea is moving very slowly by gravity, supported by the vibrating bottom part and cooled to a temperature 10 to 15^0 C, higher than the inlet cooling water temperature.

In hot humid climates, where cooling water temperature is relatively high, it is more advantageous to provide a closed cooling system with a package chiller unit. This helps to reduce length of the BFC and to keep the system fouling and corrosion free.

The main characteristics of a BFC are:

- Less equipment / investment required
- Less operating / maintenance cost
- Easy and simple automatic operation control
- Less lay out requirement, easy installation
- Lower energy consumption
- No ammonia, no steam required
- No interference with process by recycling solution to evaporator

- Low dust content in product recommended!! Look for an improved prilling device, described in para 4.3 below, otherwise maybe a system for periodical washing would be required.
- Avoid in-flow surge. Prilled product has oft a surging flow, due to the rotating scraper discharge. This has to be considered in the design of the BFC.
- 200 m3/h dry air required. An independent cryogenic air dryer, reducing dew point to only +50 C is an economic option.

4.3. High Efficiency Prilling Device (Fig. 7a, 7b, 7c)

In Fig. 7a,b and c, a vibrating prilling device is shown

Depending on the dimensions of the prilling tower and prilled melt properties three types of vibrating granulators are operating at different conditions:

- Static granulator intended for towers with the diameter up to 8 m
- Rotating granulator with the low RPM of the basket of the granulator up to 100 r/min intended for towers with the diameter up to 12 m:
- Rotating granulator with the high RPM of the basket more than 100 r/min intended for towers with the diameter more than 12 m

The extruded melt in form of a cylinder of 1.3 in diameter and 2.8 to 3.1 in length is immediately transformed in a spherical form. The corrugated form of the basket and the varying orientation of the holes, allows an equal distribution of prills in all parts of the prilling tower section, with minimum possible attrition and collisions. The result is almost calibrated in size prills, practically without fines, oversize clusters, without shells and improved cooling.

It is obvious that large, round and narrow size distribution and smooth surface prills have per weight unit a minimum of contact points and consequently a lower tendency of caking.

5. Urea Caking Spreading in Urea Bulk Carriers During Loading / Shipping / Unloading

In a hatch of large opening, shown in Fig. 3 and if air temperature is even by few centigrade lower than the temperature of the urea, then a rather intensive air circulation is established, as visualised in Fig. 3

The ambient air movement (natural ventilation) in a large open hatch, where warm urea is loaded, is rather intensive, due to the *chimney effect* (warm air is moving up replaced by colder air). Due to the same phenomenon penetration of colder-humid air into the warm pile is also accelerated. The bigger the difference of temperature between piled urea and air and the more humid the air is, the more intensive the natural ventilation.

We assume temperature of urea at 42° C and air temperature during night at 28° C 80% RH. Air under these conditions contains 21, 8 g/m3 water. The CRT of urea at 42°C is 66%, corresponding to 17, 9 g/m3. That means, urea absorbs from each m3 of air approx 3 g. Considering the geometry of the hatch, the air circulation configuration shown in Fig. 6 and the buoyancy of the warm air to be around 15 cm/sec for a completely wind still case, the

established natural recirculation is 15x15x0.15x3600 =121 500 m3/h. <u>That means an absorbed per hour water of about 365 kg.</u>

In static lab tests at isothermal conditions and by a relatively low rate of penetration of water-vapour by diffusion only, the measured quantity of absorbed moisture at saturation is about 3% by weight. In the case air kinetic is the governing factor for humidity penetration, the average absorption is only a fraction of the saturation value, e.g. the average moisture of the affected layer is 1.0 to 1.5%. In other words the 365 kg of absorbed water per hour can humidify within 6 hours of exposure in a wind-still night, at least 160 to 220 MT, that is about 35 cm of the top layer of urea.

Let us follow in Fig.4 now what happens, when in the next morning urea at 53 ^{O}C is further loaded into the hatch. Because of the cooling during night of the top layer, moisture has practically not moved, but when new warm urea is covering the moisturized top layer, the conducted heat causes the absorbed moisture to evaporate and diffuse into the mass of urea. The affected top layer is caked and the evaporated water vapour migrates preferably towards colder parts of the pile, where water vapour pressure is low. There it can re-condense and initiate caking again, if due to temperature cycling, temperature at this part can increase again. This temperature cycling is more or less unavoidable, due to the conducted and convected heat of the newly loaded warm urea, due to the daily temperature variations, and also due to the sunlight radiation into the hatch. This humidity migration can be also manifested during daytime, when usually ambient air has a low RH. The re-evaporation of absorbed moisture from an urea layer due to thermal action can locally humidify the air to values above CRT and so this air, moved by convection can humidify colder urea in another location of the pile. The result may be a <u>spreading of the caking</u> in a big part of the pile with only unique moisture absorption from the ambient air, by a relatively thin initial layer, when this moisture is entrapped into the pile.

The theory we have here applied to explain the caking phenomenon, i.e., that absorbed humidity in urea is almost totally re evaporated, and is migrating out of the caked by this re evaporation area, is confirmed by the fact, that quite often, in spite of urea in a hatch is found totally caked, the residual moisture of the urea, as confirmed by analysis of many samples taken during unloading, remained relatively low, below 0.3%.

For instance the air volume in a covered up hatch filled with urea of the size shown in Fig. 1 is approximately 4000 m3. To saturate this air volume of an average temperature of 30°C and RH 70% only 7x4000 = 28,000 g = 28 kg of water needs to be evaporated, i. e., only a small fraction of the initially absorbed water. This saturated air will condense again moisture on only few centigrade colder urea. It is self understood that in case of repeated, cycled evaporation – re-absorption – re-evaporation of moisture on the same location, the crystalline bonds will get stronger and the caking harder.

<u>The mechanical consistence of the formed lump will depend on the cycling frequency and on the quality of the urea: lumps of hard, properly treated for anti-caking and of narrow size distribution prills will disintegrate usually without structural damage.</u>

6. Additional Means to Improve Urea Prill Quality for Harsh Handling Conditions

In case the prilled urea after discharge in the destination port is subject to intensive handling and can be exposed to humidity absorption, then additional means may be required to improve urea quality. We must underline here that it is a wrong decision to compensate high temperature urea going to storage, or improper storage –bulk loading conditions, or bad prill quality (fines, high residual humidity, low strength prills) by external anticaking treatment.

6.1 High abrasion, impact resistance

Abrasion resistance is the resistance of the prills to formation of dust and fines as a result of particle-to-particle and particle-to-equipment contact, and impact resistance is the resistance of particles to breakage upon impact against a hard surface.

When urea melt is introduced into the prilling tower undergoes a sub cooling which makes the final crystalline structure of the prill more fragile to abrasion and impact forces. Stamicarbon claim to have suppressed the sub-cooling by the introduction into the lower part of the prilling tower of a jet stream of powder calcium stearate with certain amount of urea fines. The impact strength of the prills is drastically increased. This together with narrow size distribution and formaldehyde addition makes screening before loading superfluous.

6.2 Anticaking treatment of the final product

In spite the fact, that prilled urea having the physical properties specified above has good handling behavior, it is considered to be inferior to granular urea for bulk shipment in ocean going vessels and loading - unloading operations in humid climates. To improve further the handling properties of prilled urea many producers, whose product is designated for export in bulk, not being sure that urea is properly loaded, hatch covers remain properly closed during voyage, or that improper unloading handling conditions are prevailing at the destination port, are applying, usually in light dosing (300 to 500 ppm), of an anticaking agent for external superficial treatment of the finished product. This agent is often a sophisticated compound of surfactants and soluble polymers.

A very popular agent with references in many urea prilling plants is Uresoft. This is a non toxic decylaldehyde produced by Kao Corporation of Japan. Uresoft is sprayed onto the urea prills at a place where possibly uniform application on the particles of the relatively low dosing can be obtained. When urea is treated with Uresoft, sheaves of fine feather-like crystalline fibers grow on its surface, prohibiting the direct contact of the urea prills. Thus Uresoft prevents urea prills from caking and even caked, the caked lumps are easily fractured. Anti-caking effect is influenced by the moisture content of the urea. Higher moisture can be faced by increasing Uresoft dosing. Because of the low dosing (300 to 500 ppm) drying of treated product is not required.

The effect of the anti-caking treatment is evaluated in lab test, subjecting samples of the product for some days at a certain temperature and pressure. Results are evaluated by determining either the load needed to disintegrate a certain size lump, or the time needed to disintegrate completely on a vibrating screen, or the percentage of product in lump after

having subjected the bagged sample to a certain number of falls.
Here below are some typical results of tests:

Treatment & dose	Disintegration load	Disintegration time	% of caked lumps
None	70	27	37
HCOH 0.3% (internal)	32	14	15
HCOH 0.3%URESOFT 400 ppm (internal plus) test at 0,5 bar pressure	11	8	9

The above tests, although they cannot be generalized, have a certain value in interpreting the expected result a certain treatment may have on the handling behavior of prilled urea. But another important factor affecting dramatically the caking tendency of urea is the caking spreading due to humidity migration, as we have in detail explained in the previous chapters. Humidity migration phenomenon is usually not considered in these tests performed under isothermal conditions.

The mechanical consistence of the formed lump will depend on the cycling frequency and on the quality of the urea: lumps of hard prills, properly treated for anti-caking and of narrow size distribution will disintegrate usually without structural damage.

Fig.1 Water Vapour Pressure of Urea Prills and Air vs. Temperature
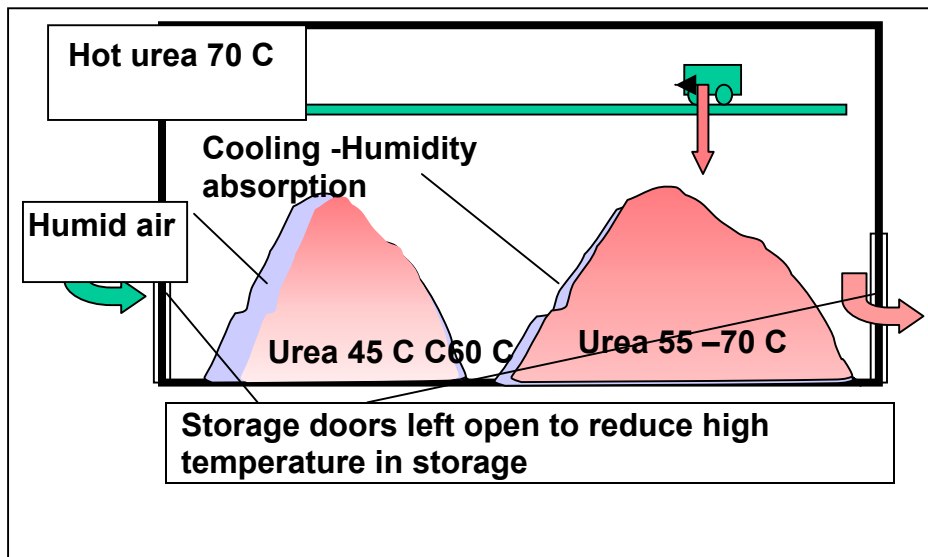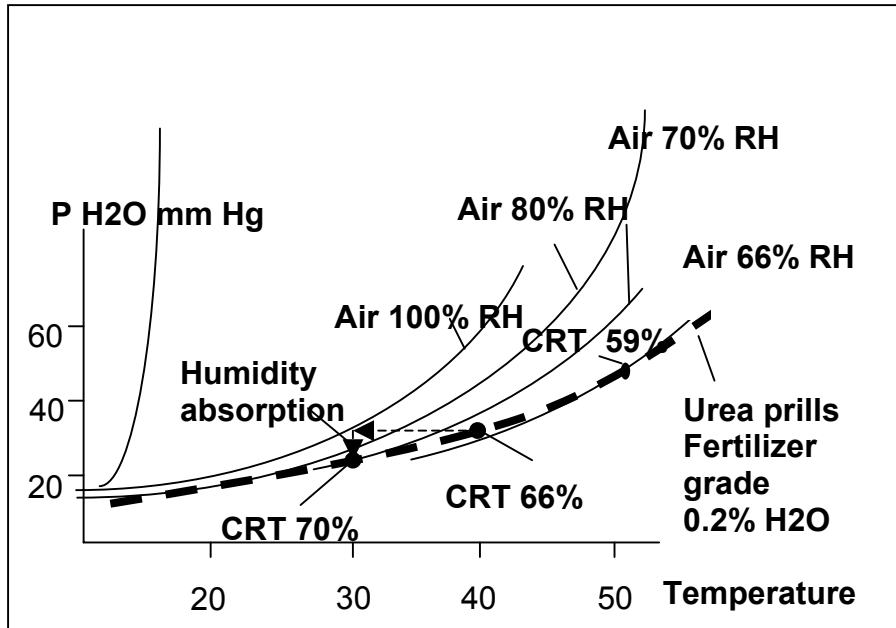
Fig. 2 Hot Urea in bulk storage

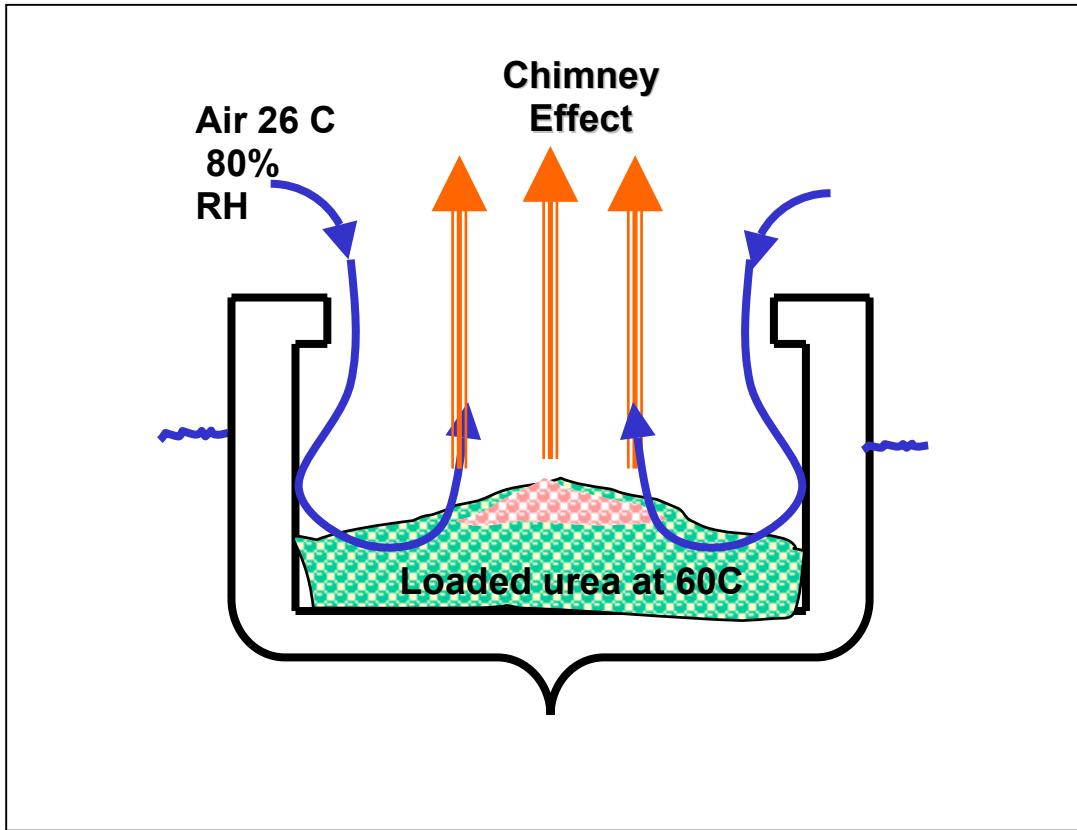**Fig. 3 Loading Hot Urea During Humid Night**

Air 26 C 80% RH

Chimney Effect

Loaded urea at 60C

Fig. 4 Cargo With Hot Urea During Voyage

air temperature during warm day

air temperature during cool night

Fig. 5 Fluid Bed Cooler

Fig. 5 Fluid Bed Cooler

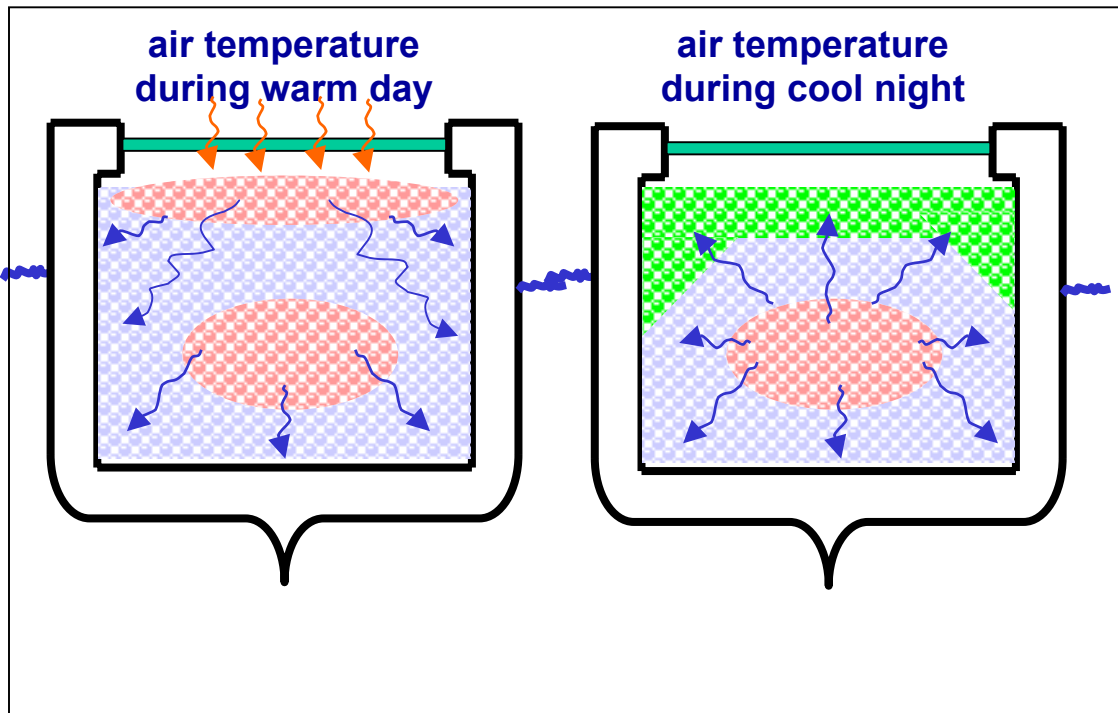## Fig. 6 Fluid Bed Cooler

Fig. 6 Fluid Bed Cooler

Fig. 5 Scheme of Vibrating Gr

1   melt inlet body
2   perforated basket
3   vibrator
4   oil-aerosol generator
5   control panel for vibrator
6   impulse line for melt level measurement

ORHANCO

Vibrating bucket with corrugated surface
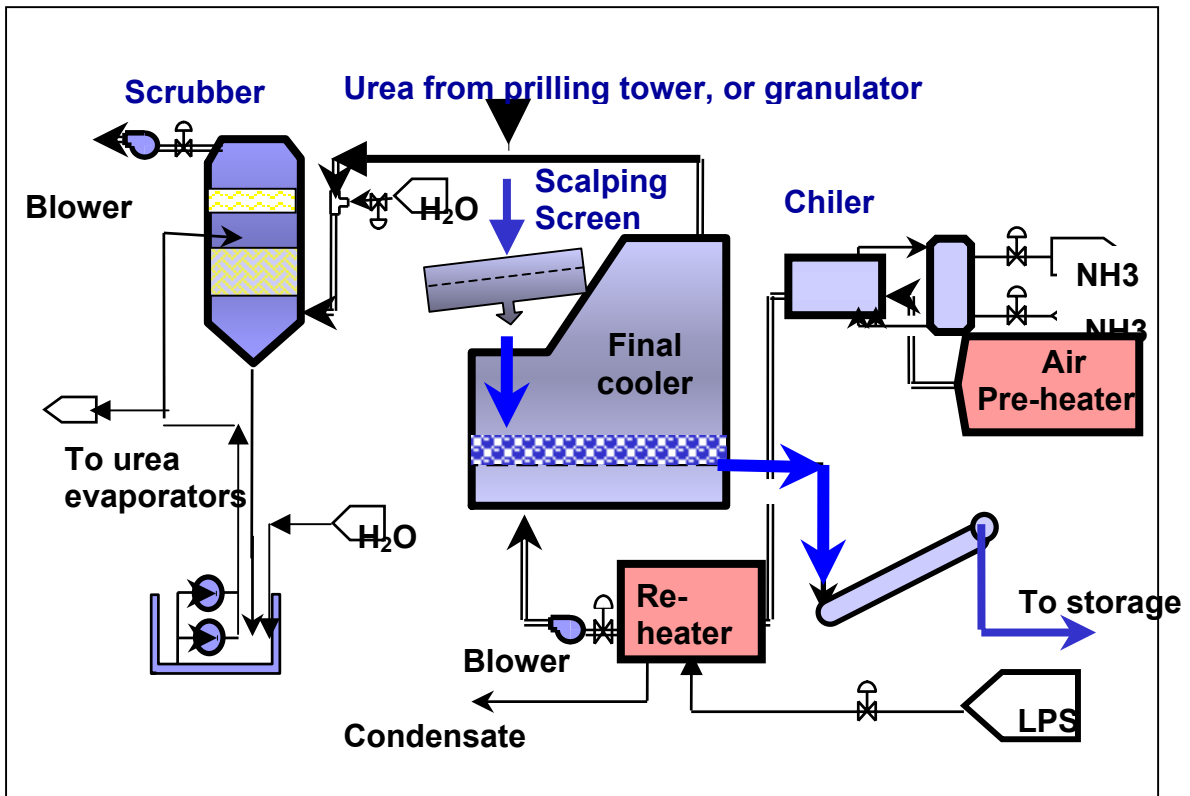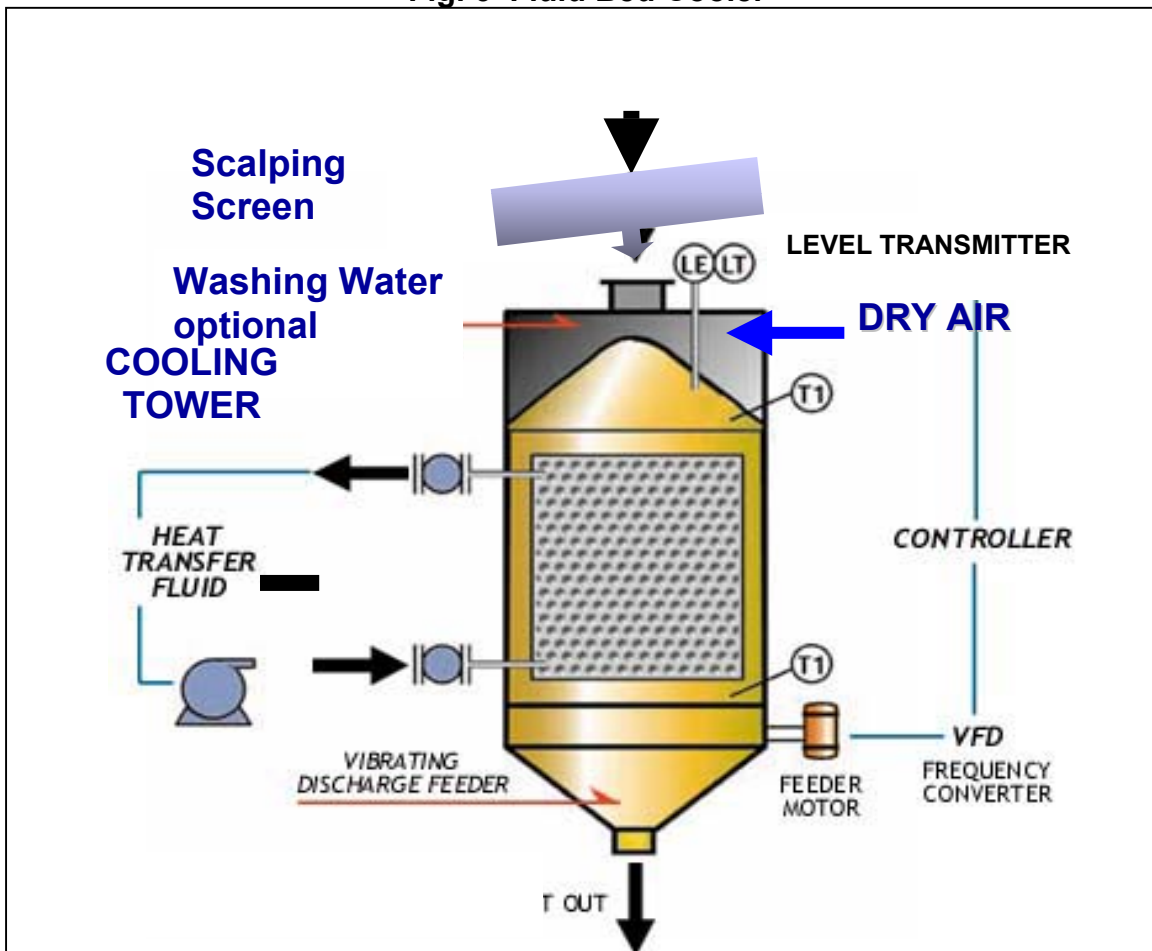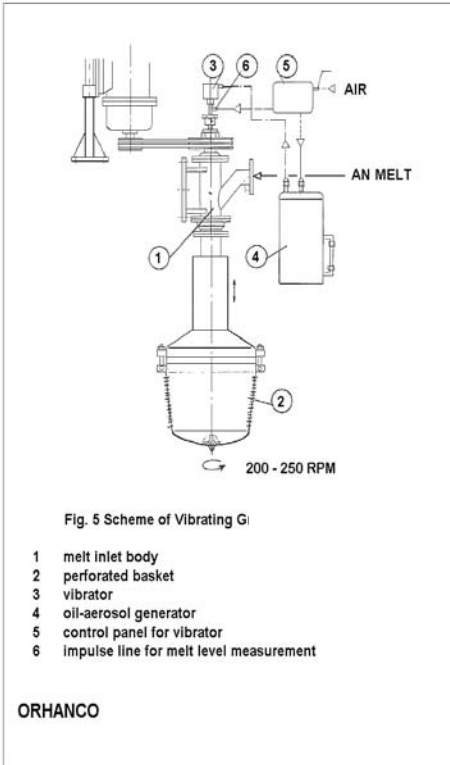

Vibrator

Melt Inlet inlet

• self cleaning
• better product cooling
• no oversize, or clusters
• equal prill distribution
• no fines, no dust
• less emission
• almost calibrated prills