Determination and numerical analysis of moisture content movement for porous urea particle pile

Chen Rugang, Zhao Zhixin, Yuan Xiuling

(*School of Energy and Power Engineering，Xi'an Jiaotong University，Xi'an* 710049，*China*)

Abstract: For the hygroscopic porous urea particle, due to the existence of a lot of interstitial pores and its volatility, thermogravimetric method is inapplicable to determinate its moisture content. The objective of this paper is to construct an experimental apparatus and apply Karl Fischer Titration(KFT) method to determine the real moisture content of a urea particle pile at laboratory. A numerical model for correlating the vapor diffusion and liquid film movement is also presented to simulate moisture migration. Good agreement was demonstrated between the simulation and measured data. It was found that KFT method is a feasible way to determine moisture content of a storage particle pile. The presented model is expected to be a practical tool to predict interior moisture transport within a porous urea particle pile.

Key words: moisture content; porous urea; Karl-Fisher Titration; mass transfer; caking

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1 Introduction

For granular or powdered material, the quantitative analysis of water content has been rapidly expanded to many fields including agriculture engineering, chemical industries and environment science, etc. As one of the most important fertilizers, urea is widely used in agriculture. Urea is often made as granular or prilled forms of approximately spherical shape in diameters from 1 to 4 mm. It contains some impurities such as biuret and small amounts of residual ammonia and carbon dioxide, and it may also be coated with sulphur for anti-caking purposes. Similar to other fertilizers, the agglomeration of urea granules due to moisture accumulation, known as the caking phenomena, is the main problem during its storage and transportation process. Caked urea with strong inter-particle bonds cannot be uniformly distributed by most agricultural machines and decrease the quality of fertilizer. It is important to control and decrease caking potential in

urea storage piles for the fertilizer industry. Caking in urea is a very complex process. The nature of caking is the growth of crystal bridge between urea particles at or near contact points between particles in a bed. These crystal bridges were developed due to continuous internal water interactions and thermal effects, which result in deposition of crystals under certain conditions from the salt solutions presented in granular bed[1-3]. Moisture ingress has been shown to affect granule strength through the study of crush strength of granular NPK fertilizer[4]. Many factors influence the rate and extent of fertilizer caking such as chemical composition, particle size and packing, water content, ambient air humidity, hydrostatic pressure and temperature. Relative humidity variation of the adjacent air and water content included in fertilizer is the most important factor to influence caking[5]. For urea, excessive moisture absorption takes place when surrounding humidity is higher than its critical relative humidity(CRH), 76.5% RH at 25℃. A fluctuating humidity induces a series of successive dissolutions and re-crystallizations, which further bonds adjacent granules. To avoid or decrease caking, it is essential to know how moisture is transferred in a storage urea pile. Therefore, the detailed purpose of this study is: 1) To construct an experimental apparatus and per-

form an experimental analysis of moisture distribution for a urea pile bed by KFT method so that the real moisture content movement can be accurately determined. 2) To present a mathematical model for correlating the vapor diffusion and liquid film movement in a urea pile and investigate how moisture migrates within an isolated urea pile.

2　Particle pile moisture content transport and determination

For urea storage pile, generally the moisture accumulating in urea particle takes place through the air-urea interface. The schematic of a storage urea particle pile for the moisture transport is shown in Fig. 1. Once the water vapor adsorbed and accumulated on the exposed surfaces of urea particle from surrounding air, this process tends to be irreversible. Moisture migrates from the domain with higher water vapor to the domain with lower water vapor or to the interstitial pore. When the layers of water molecules on particle surfaces become sufficiently thick to allow liquid movement relative to the solid particles by surface tension gradients and, perhaps, gravity forces, then capillary movement of the surface liquid occurs. With the development of liquid film, droplets of water condense on the particles and coalesce to form larger droplets on the surface so drainage through the bed occurs.
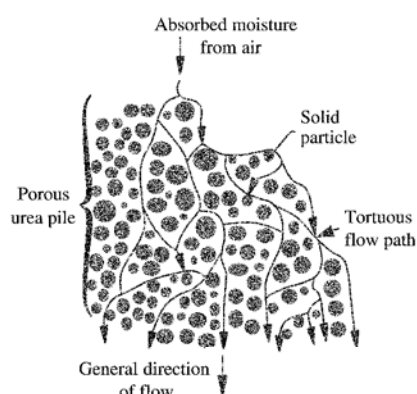

Fig. 1　Schematic of a storage urea pile

The hygroscopic urea particle pile can be described as a mixture of a solid, liquid and gaseous phase as shown in Fig. 2. In a representative average volume, the volumetric fractions of the three phases keep the following constraint. ϵ_σ, ϵ_β, ϵ_γ are the volume fractions of solid, liquid and gas, respectively.

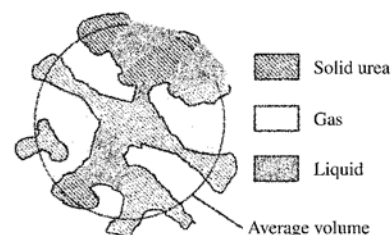$$\epsilon_\sigma + \epsilon_\beta + \epsilon_\gamma = 1 \qquad (1)$$

Fig. 2　Three phases present in hygroscopic urea

The initial value of volume fraction of water can be calculated when the initial moisture content profile ω is known.

$$\epsilon_\beta = \frac{\omega \rho_s (1 - \epsilon)}{\rho_\beta} \qquad (2)$$

Where　ρ_β, ρ_s ——density of water, urea and vapor, kg/m^3.

The most common way to determine water content of sample is thermogravimetry. Chen et al. investigated water content of granular potash by thermogravimetric method and showed that it was possible to model moisture movement once the initial water content of potash was accurately known[6]. Their study also revealed that heating time and temperature is important for the final measurement result of water content. However, due to the internal porous structure of urea, the water existing in interstitial pores may not be easily evaporated completely. Figure 3 shows the Electron Scanning Micrographs of urea(ECM). It can be seen that the connection of pores is very complex.
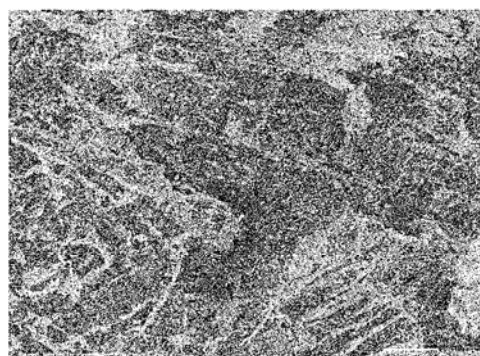

Fig. 3　Cross-sectional ECM of wet urea particle

Unlike potash, urea often contains some impurities such as small amounts of residual ammonia and carbon dioxide. Urea particle is chemically unstable and tends to decompose at moderately high temperatures. Urea hydrolysis may slowly occur to produce ammonium

carbonate at ambient temperatures and that has a high tendency to decompose slowly into ammonia and carbon dioxide at increasing temperatures. The experimental test results for expected water content under different dry and wet conditions were presented in Fig. 4.
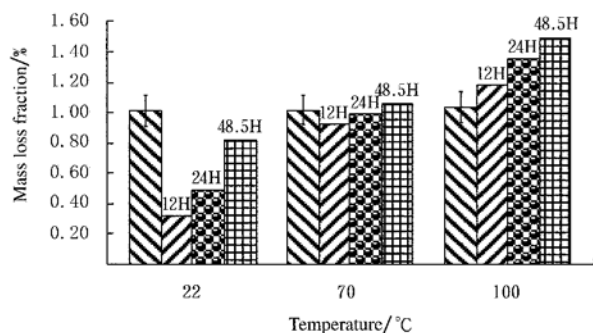

Fig. 4　Urea mass loss fraction versus temperature for various drying time at predicted MC= 1%

It can be shown that drying to a constant weight is difficult due to volatile substances existing and decomposition. The results of a drying method should thus not be called water content, whereas the substitution of the mass loss may come very close or even correspond to the water content. Developing an efficient way to determine moisture content of urea particles and moisture movement is a basic task in this study.

3　Moisture transfer experimental setup

A test apparatus set up for the investigation of one-dimensional redistribution of moisture within urea bed is shown in Fig. 5. It is comprised of three high-density PVC cells stacked vertically as shown. Eight holes are evenly distributed as the sampling position along the circumference for each cell at the center of each cell height. O-rings on either side of each cell and lids on top and bottom are used to prevent moisture loss or gain during moisture transfer process. Rubber plugs fitted holes are used before and after sampling to prevent particles falling on and moisture change due to outside ambient air humidity. Very thin stainless steel sheets, which can be pulled out to start a test, were used to isolate each test cell before each test.

Prior to the start of each test, each cell was packed with urea particle that had been uniformly mixed with a small quantity of moisture. These cells then stacked

together. Stainless steel sheets were carefully removed to start test. The difference of moisture content between three cells will cause moisture migration from one region to the next until the steady state moisture content distribution is achieved. This is a dynamic transport process with no external moisture interactions so that moisture inside the test cells is conserved. After a period of time, sample is taken and the following KFT method is used to determine its moisture content in different cells.
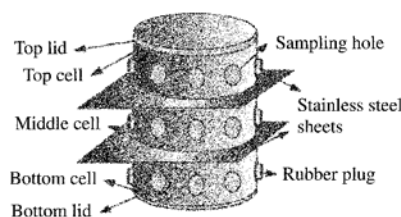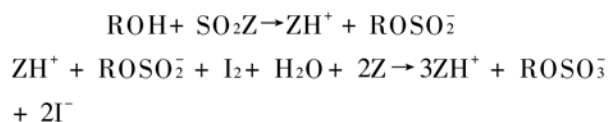

Fig. 5　Schematic of test facility for moisture transfer

4　Water content determination by Karl Fisher Titration

4.1　Principle of Karl Fisher Titration

The Karl Fischer Titration is a well-known analytical technique for quantifying water content in a variety of products[7, 8]. The fundamental principle of KFT is based on a selective chemical reaction:

$$ROH+ SO_2Z \rightarrow ZH^+ + ROSO_2^-$$
$$ZH^+ + ROSO_2^- + I_2 + H_2O + 2Z \rightarrow 3ZH^+ + ROSO_3^- + 2I^-$$

In commercial reagents, ROH is methanol or ethanol and Z is often imidazole. Water and iodine are consumed in a 1 ∶ 1 ratio in the above reaction. The consumption of iodine is monitored during the whole titration process. Once all of the water present is consumed, ion selective electrodes detected the presence of excess iodine. which indicates the end-point of the titration. The high selectivity to water for KFT represents the most important advantage. The exact water equivalent of the measured sample is determined by consumption of known amounts of titrant.

4.2　Experiment of Karl Fisher Titration

1) Apparatus and auxiliary instruments

The titrator is Orion 950. The schematic of KFT apparatus is shown in Fig. 6. The working medium (Solvent) in the titration cell contains sulphur dioxide

and the base dissolved in methanol or ethanol. The titrating solution(Reagent) is a methanolic or ethanolic solution of iodine. Some auxiliary instruments were used including high accuracy electronic balance, syringes, distilled water etc. during experiments. Trinidad urea with mean diameter ranges from 0.8 to 1.3 mm is used as measured sample.

1. Titrator
2. KF reagent
3. Dispensing system
4. Sample pouring hole
5. Desiccant
6. Titration cell
7. Ion selective electrode
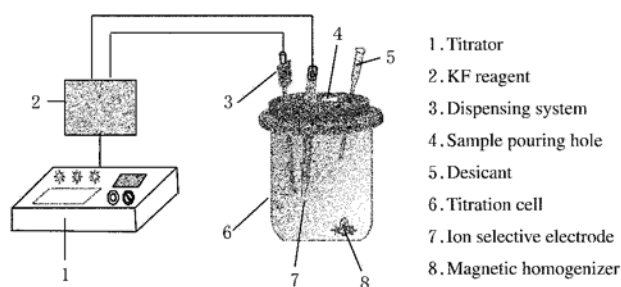8. Magnetic homogenizer

Fig. 6　Schematic of titration apparatus

2) Test procedures

① Pre-titration of blank system to dehydrate water

To keep titration cell dry before determination, a pre-titration of blank system is necessary. The amount of reagent consumption depends on the tightness of the apparatus and humidity of the air in the experimental surrounding and also on the chemicals used because of the previous reasons given, respectively. This important step is performed to eliminate source of error as possible as we can.

② Calibration of the system by distilled water

One of the most important factors to ensure the accuracy of test results is to get the exact water equivalent of the KF reagent, i.e. the titer of KF reagent. Although manufacturer generally gives the titer of the KF reagent, it is still necessary to calibrate system since the titrant concentration may be diluted due to the adsorption or penetration of moist vapor in atmosphere and instability of KF reagent during storage process. The most effective way to calibrate titrant concentration is to determine distilled water to obtain the true titer.

③ Sample handling and successive titration

Before titrate measured sample, the precise sample mass should be known. The weighing procedure represents a critical step during sampling handling. Particular care must be taken while handling the samples to be analyzed. The exact sample weight is determined only after adding the sample into the titration cell. This is achieved by taring the sample in its holder, i.e. syringe, on the electrical balance before adding the sample. Afterwards, the empty holder is weighed again. Then the resulting sample weight actually added in the titration cell can be easily obtained. When adding wet urea sample into titration cell, special care must be taken to avoid the sample sticking to the walls of the titration cell. As the consequence, not the whole sample will be available for titration if sample is stuck on the cell wall. Therefore, the results will be lower, even if the syringe was correctly weighed. To quickly and efficiently dissolve sample, magnetic stirrer is used to accelerate the dissolution and water release from surface and inside of the sample. When sample dissolved almost completely, titration begins. Once obtaining the indicated reading from titrator, the actual result of final water content for measured sample can be gained.

5　Numerical simulation of moisture transport

To study how moisture transports within a urea pile, a mathematical model with physically realistic representation of moisture transport process should be developed to simulate moisture migration. At local low moisture contents the moisture remains immobile. But at high moisture contents, migration of surface moisture due to surface tension and gravity occurs. This migration will become more dominant with the increase of saturation level of the moisture on the particles. Chen et al. experimentally and numerically investigated the moisture movement within potash once accurately known some properties of the particle bed. In terms of whitaker's thery[13, 14], a series of equations are presented for moisture transport via capillarity and gravity, which occur only when continuous liquid films are present on the surfaces of the particles, as well as an equation for water vapor diffusion. Continuous liquid films occur when the bed reaches a saturation level called the irreducible saturation, S_0, $m^3/m^{3[9]}$. Similar to potash, the mathematical treatment of model is based on the following assumptions: 1) One-dimensional moisture transport in the gravitational direction; 2) Urea particle including solid, liquid and gas phases is assumed to be in local thermody-

namic equilibrium; 3) Without displacement or significant dissolution of particles during the moisture transfer process. 4) No chemical reaction occurs during whole transport process. 5) Constant pile temperature. So an unsteady- state transport equation to describe the relationship between saturation and static head can be given by following equations.

$$\frac{\partial S}{\partial t} = \frac{1}{\eta_\beta(1 - \epsilon_\sigma)} \frac{\partial}{\partial x} \left[K_\beta \left(- \frac{\partial(P_c)}{\partial S} \frac{\partial S}{\partial x} + \rho_\beta g \right) \right] - \frac{\dot{m}}{\epsilon \rho_\beta} \quad (3)$$

$$\frac{h}{h_0} = 1 - e^{-a(1-s)} + b(1 - S) + \frac{c}{(S - S_0)^d} \quad (4)$$

$$P_c = \rho_\beta g h \quad (5)$$

An empirical equation based on saturation (S, m^3/m^3) and irreducible saturation (S_0, m^3/m^3) to adjust bed permeability (K_β, m^2) to account for moisture in the bed is

$$K_\beta = K_\beta^0 \left(\frac{S - S_0}{1 - S_0} \right)^n \quad (6)$$

Where P_c is volume average pore pressure, Pa; $\dot{m}$ is phase change rate, $kg/(m^3 \cdot s)$; K_β^0 is permeability for saturated flow, m^2; n is empirical parameter; η_β is viscosity, $Pa \cdot s$; h, h_0 is equivalent and reference static liquid depth, respectively, m; a, b, c, d, n are empirical parameters.

At moisture levels less than the irreducible level, moisture transport occurs only via vapor diffusion through the interstitial air space and that the rate of diffusion depends on an effective diffusivity that is proportional to the porosity of the bed and inversely proportional to the bed tortuosity.

$$\frac{\partial(\epsilon_\gamma \rho_v)}{\partial t} - \dot{m} = \frac{\partial}{\partial x} \left[D_{eff} \frac{\partial \rho_v}{\partial x} \right] \quad (7)$$

Where D_{eff} is effective diffusion coefficient, m^2/s.

To numerically solve the equations above, the discretization equations are derived from the differential governing equations by using control volume method[10], and the fully implicit scheme is employed for the transient terms. The above differential equations can be solved to obtain the transient moisture content distribution. A three layer urea pile bed, which is of wet sample close to 1% moisture content on the top layer and total dry sample on the middle and bottom layer, is illustrated as a case to show in
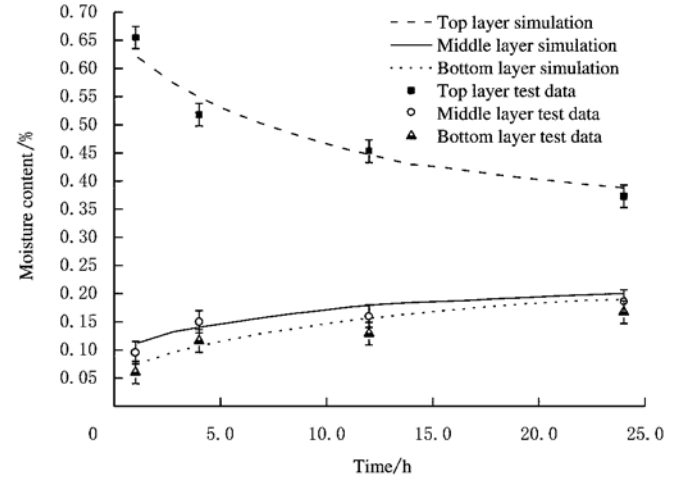
Fig. 7.

Fig. 7　Transient moisture content distribution of urea bed

6　Conclusions

In terms of previous mentioned procedure, the urea particle sample at different layers under different transfer time were taken and titrated, respectively. Comparing numerical simulation results with test data, good agreement was validated. It is demonstrated that moisture content movement versus time for urea pile bed under low moisture content condition can be determined by KFT. It can be used as a way to measure moisture transport within a urea bed for moisture migration caking study. Furthermore, the numerical model has the potential to be used as a predictor to numerically investigate moisture migration and distribution within stored pile. Because moisture content is closely relevant to the level of caking, current study provides a feasible attempt from the view of fluid transfer prospect to study caking.

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多孔尿素颗粒堆中湿分移动的定义和数值分析

陈汝刚, 赵知辛, 袁秀玲

(西安交通大学能源与动力工程学院, 西安 710049)

摘　要: 对于多孔吸湿性的尿素颗粒, 由于其颗粒内部存在大量的孔隙和具有挥发性, 传统的热重力测湿法并不适宜定义其含湿量。该文通过构建一套实验装置并运用卡尔费歇滴定法定义了尿素堆的真实水含量。提出了结合水蒸气扩散和液膜迁移的数值模型并模拟了湿分的迁移。模拟结果和试验测试数据吻合较好。卡尔费歇滴定法是一种可行的定义颗粒堆水含量的方法。所展示的模型有望作为实际的工具预测多孔尿素堆中湿分的传输。

关键词: 含湿量; 多孔尿素; 卡尔费歇滴定法; 传质; 板结