

Measurement of the enthalpy change during potash–moisture interactions

Shi-Wen Peng^a, Robert W. Besant^{a*}, Graeme Strathdee^b

^a Department of Mechanical Engineering, University of Saskatchewan, 57 Campus Drive, Saskatoon, SK S7N 5A9, Canada

^b Potash Corporation of Saskatchewan, Inc., 500–122 1st Ave. S., Saskatoon, SK S7K 7G3, Canada

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Abstract—The enthalpy change, or the thermal energy release during a potash–moisture interaction, is measured using a method previously developed for two typical granular potash fertilizers. The combined enthalpy change (including heat of adsorption, heat of condensation and heat of solution) is found to be a function of the moisture content and trace chemical impurities of potash fertilizer. At low moisture content, the enthalpy change is much larger than the latent heat of condensation, and declines with increasing moisture content toward about 85% of the latent heat of condensation. The uncertainty in this measurement is sensitive to the moisture content, and is estimated to be about $\pm 15\%$. The main reasons for uncertainty are due to the measurement of mass of the adsorbed water and the random sampling error. © 2001 Éditions scientifiques et médicales Elsevier SAS

enthalpy change / potash / water vapor adsorption / condensation / dissolution of potash

Nomenclature

A	area of test section	m^2
c_{pa}	heat capacity of air at constant pressure . .	$J \cdot kg^{-1} \cdot K^{-1}$
c_s	heat capacity of potash	$J \cdot kg^{-1} \cdot K^{-1}$
G	residual average temperature of potash . .	$^{\circ}C$
ΔH	enthalpy change of moisture–potash reaction	$J \cdot kg^{-1}$
$\Delta \bar{H}$	average enthalpy change of moisture–potash reaction for the mass of accumulated water Δm	$J \cdot kg^{-1}$
h_{fg}	heat of vaporization	$J \cdot kg^{-1}$
H	total enthalpy	J
ΔH_{fb}	enthalpy change of fiberglass	J
T	temperature	$^{\circ}C, K$
L	length of sample	m
\dot{m}_a	mass flow rate	$kg \cdot s^{-1}$
Δm	mass of adsorption	kg
S	outlet air temperature signature, equation (8)	$^{\circ}C$
w_p	total mass of dry potash sample	kg
x	axial position within the potash bed	m
X	moisture content	$\%$

Greek symbols

δ	difference	
θ	sensitivity coefficient	
ρ	density	$kg \cdot m^{-3}$
ϕ	relative humidity	

Subscripts

cv	control volume
t	time
γ	air
σ	solid (potash)
0	initial

Superscripts

$-$	average
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1. INTRODUCTION

Potash is an important fertilizer product for plant growth in soils low in potassium. During storage and shipment, potash is often exposed to humid environments and then the initially dry potash will adsorb moisture from the ambient air. In subsequent de-watering processes due to ambient air temperature increases and

* Correspondence and reprints.

humidity decreases, small potash particles will cake into bigger ones, causing problems for typical agricultural fertilizer spreading machines. In this paper, we are only concerned with the heat release associated with adsorption and condensation of water vapor on potash granules. This heat release must be accurately known when experimental and energy analysis studies are done. In practical applications energy and temperature effects are very strongly coupled to moisture accumulation.

Potash is mainly composed by potassium chloride (KCl). After mining and during processing (i.e. a flotation or recrystallation process, followed by a subsequent drying process), the surface of each potash particle is coated by a thin layer of mixed salts comprised of potassium chloride (KCl), sodium chloride (NaCl), and carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) crystals.

The existence of these surface impurities causes the potash–moisture interactions to significantly deviate from that of pure potassium chloride. In a humid environment, potash will first adsorb moisture from the surrounding air to form a monolayer, then, as more water molecules are adsorbed, multilayers, and finally dissolving a part of potash in a layer of aqueous solution on the surface of each particle. The moisture content of the potash by this adsorption and dissolution mechanism is very small, e.g., 0.1 %. However, as soon as this aqueous solution layer is formed, the chemical potential differences of every component in the system become important in determining the final equilibrium moisture content for a given relative humidity in the ambient air.

For the dissolution process of highly soluble salts like KCl, NaCl, and $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$, the dissolution described above is a transport process or diffusion limited process and chemical kinetics are negligible [1–3].

In a recent research work, Peng et al. [4] have analyzed the interaction between potash and moisture at equilibrium. For a system consisting of potassium chloride (KCl), sodium chloride (NaCl), and carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), there is a critical relative humidity around 52 % for a wide range of typical temperatures and this results in the onset of condensation. When very dry potash is exposed to air with a relative humidity lower than this critical humidity, potash can adsorb some moisture, but water vapor condensation will not occur. However, when the relative humidity is higher than this critical one, the chemical potential (partial Gibbs free energy) difference between the water vapor in the air and the water in the surface aqueous solution will provide a diffusion driving force, and the water vapor will condense continuously on the surface until a chemical equilibrium is reached. During this condensation process,

the surface may experience the run-out of carnallite first, and then, with increasing humidity, the sodium chloride. If the potash is exposed to the air with a relative humidity higher than the deliquescent point of potassium chloride (around 85 % relative humidity), the water vapor condensation will continue until all the potash dissolves.

Since this surface aqueous solution layer is usually very thin (e.g., less than 10 μm) on each particle, diffusion within this thin liquid layer does not cause a significant variation in composition within the aqueous solution. This allows us to assume that the surface aqueous solution is uniform in solute concentration and it is in a thermodynamic equilibrium state with potash solid [1–3]. Dissolution in the high humidity range is therefore controlled by mass transfer in the gaseous phase within the pores of a granular potash bed. This gaseous diffusion limited dissolution implies that the enthalpy change associated with moisture–potash interactions is also a physical variable which is due to adsorption for low relative humidity adsorption region, and a combined enthalpy change of water vapor condensation and dissolution for high relative humidity condensation region. A transition region exists between these two limiting cases.

Heat and moisture transfer in granular potash bed is a coupled process. The heat released by adsorption, condensation, and dissolution will change the temperature of both the potash particles and the pore air. When this occurs the local relative humidity decreases, which causes the equilibrium adsorption moisture content of the particles and the rate of the condensation to be altered along with the heat released. To simulate this coupled heat and mass transfer process, it is necessary to characterize the enthalpy change during the potash–moisture interactions.

The enthalpy change of potash–moisture interactions was measured by Pyne et al. [5] and Hansen et al. [6]. For all the different types of potash, they reported a combined enthalpy change around $2090 \pm 165 \text{ kJ} \cdot \text{kg}^{-1}$ regardless of moisture content, which is equal to the latent heat of condensation of water vapor ($44 \text{ kJ} \cdot \text{mol}^{-1}$) minus the heat of solution ($6 \pm 3 \text{ kJ} \cdot \text{mol}^{-1}$). In this paper, we use the method developed by Tao et al. [7] to measure the combined enthalpy change, and compare with the results obtained by Hansen and coworkers.

2. TEST PRINCIPLE

As discussed above, depending on the moisture content and local ambient relative humidity, the potash–moisture interactions may be a monolayer adsorption, a transition multilayer adsorption with some dissolution of

potash, or a water vapor condensation with dissolution of potash.

Monolayer adsorption is a physical process. Moisture accumulation by this monolayer adsorption is icelike in that the water molecules have little or no translational mobility. As the adsorption process continues, a multilayer adsorption is formed. Water molecules in large multilayer adsorption films behaves more like those in free water, which will dissolve the monolayer water and the solid potash to form a layer of electrolytic solution on the surface of each particle. This multilayer adsorption entails the chemical dissolution of potash solid in a coupled physical and chemical process.

Since the chemical dissolution is controlled by a diffusive transport process, the interface between the aqueous solution and solid potash is in a saturated state [1–3]. However, our interest is limited to very low moisture content, and the aqueous solution film is very thin (less than 10 μm); so diffusion in this thin aqueous layer requires only a negligible concentration difference. Thus, the surface aqueous solution film is homogeneous, and is in thermodynamic equilibrium with solid potash phase. This analysis suggests that the enthalpy change in potash–moisture interaction is a function of the particle bed moisture content, temperature, the reacting gas which is water vapor, and the composition and the specific surface area of the potash bed. That is,

$$\Delta H = f(X, T, \text{reacting gas (water vapor), potash (composition and specific surface area)}) \quad (1)$$

where X is the moisture content, T is the temperature of the potash solid. However, if the range of temperature is small, as it is for this experiment, we can ignore the influence of temperature variations on the heat of adsorption [8]. The potash samples tested in this study were typical of those produced throughout the industry.

The test principle is to use a one-dimensional, transient forced convection humid air flow, as shown in the set-up shown in figures 1 and 2. A control volume test section, consisting of a dry granular potash bed, held by a permeable, rigid fiberglass plate within a impermeable insulated channel is shown in figure 2 and, during each test, the potash sample undergoes a transient adsorption/condensation with dissolution reaction. At the initial state of the test section, the temperature of the potash bed is $T_{\sigma,0}$, and the relative humidity is nearly zero. The relative humidity is measured outside the bed where an accurate measurement is possible. At the time 0^+ , a steady moist air flow at temperature T_{∞} , relative humidity ϕ_{∞} ,

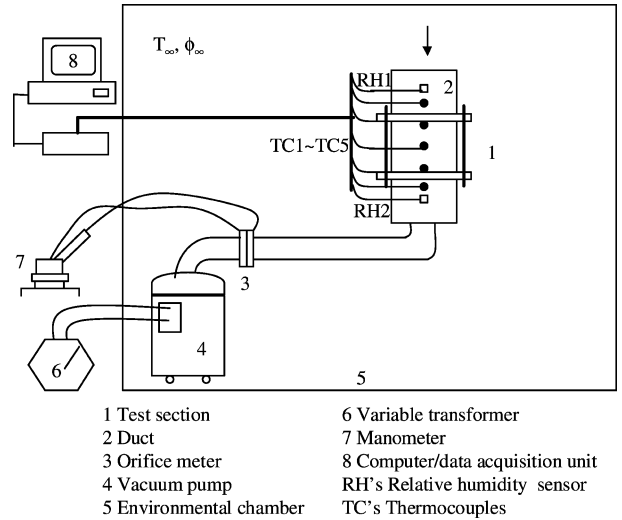


Figure 1. Test facility.

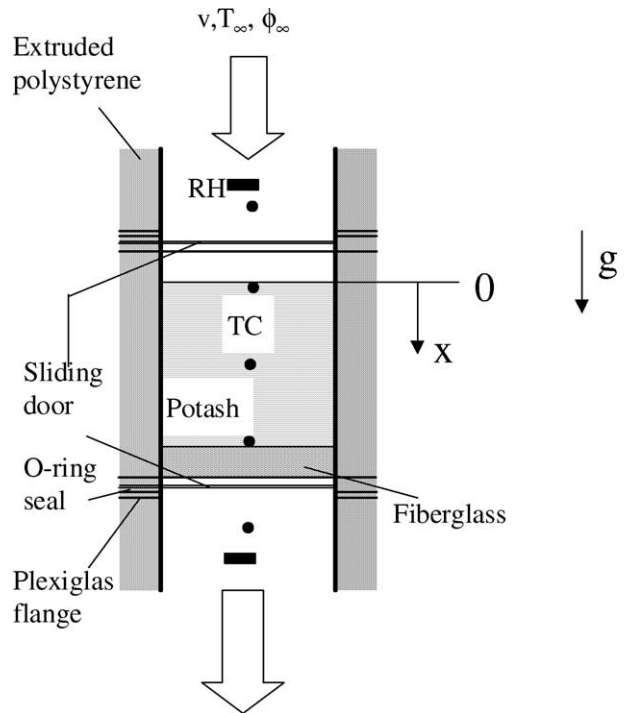


Figure 2. Test section.

and mass flow rate \dot{m}_a passes through the control volume. A fraction of the ambient water vapor is then adsorbed or condensed on the surfaces of granular potash particles. The evolved heat (enthalpy change) is partly carried downstream by the airflow, causing the air temperature first to rise and later to fall on the outlet side. This heat

released is first manifested by a rise in temperature of the solid potash, causing it to rise and later fall. Due to coupling between the air and potash, only small temperature differences are evident between the two at any time.

For the adsorption process, and after a period of time, the control volume is again in thermodynamic equilibrium with the environmental temperature, T_∞ . However, depending on the relative humidity of the supply air, the condensation process may continue for a long time before reaching thermodynamic equilibrium again. After a test period of about one hour, the potash residual temperature will be significantly different from the supply air temperature.

The application of the first law of thermodynamics to the control volume in *figure 2* yields the following:

$$\int_0^t \left[\dot{m}_a c_{pa} (T_{\gamma, \text{out}} - T_\infty) + \left. \frac{\partial H}{\partial t} \right|_{\text{cv}} - \dot{r}_v \Delta H \right] dt = 0 \quad (2)$$

Here the sensible heat due to adsorbed moisture is small because the amount of moisture is very small. In equation (2), \dot{m}_a is the flow rate of air, c_{pa} is the specific heat of air, $T_{\gamma, \text{out}}$ is the outlet air temperature which varies with time, T_∞ is the inlet air temperature (supply air), H_{cv} is the total enthalpy of potash sample and air in test section at any time, \dot{r}_v is the rate of adsorption/condensation, and ΔH is the combined enthalpy change of the adsorption, condensation, and dissolution of potash fertilizer. In equation (2) the change in mass flow of air through the sample due to condensation is negligible except for \dot{r}_v . Applying the mass conservation to the control volume yields the change in mass due to accumulated water

$$\int_0^t \dot{r}_v dt = \Delta m \quad (3)$$

Now we compute $\Delta \bar{H}$ using the other terms in equations (2) and (3) which are established by measurement.

The integration of the enthalpy of the system over the time period t gives

$$\int_0^t \left. \frac{\partial H}{\partial t} \right|_{\text{cv}} dt = H_{\text{cv}, t} - H_{\text{cv}, 0} \quad (4)$$

This total enthalpy change includes the enthalpy of the potash, the enthalpy of the moisture, the enthalpy of the air in the pores of the granular potash bed, and the enthalpy of the fiberglass used to hold the potash particles in a bed. Since the mass of the air in the pores is only about 0.07% of that of potash sample, and the moisture

content in this research is limited to less than about 1.6%, the enthalpy changes of these two components are ignored. The remaining enthalpy changes of the potash and the fiberglass can be estimated by the temperature measurement and from previous experimental data [7].

Assuming the temperature distribution in the potash bed shown in *figure 2* can be described by

$$T_{\sigma, t} = ax^2 + bx + c \quad (5)$$

at any time, the constants $a(t)$, $b(t)$, and $c(t)$ can be determined by the measured temperature in three different locations in the potash bed. If three thermocouples are placed in the inlet, center, and the outlet, the temperatures of which are denoted by $T_{\sigma 1}$, $T_{\sigma 2}$, and $T_{\sigma 3}$, respectively, the three constants can be obtained:

$$\begin{aligned} a &= \frac{2(T_{\sigma 3} - T_{\sigma 1}) - 4(T_{\sigma 2} - T_{\sigma 1})}{L^2} \\ b &= \frac{4(T_{\sigma 2} - T_{\sigma 1}) - (T_{\sigma 3} - T_{\sigma 1})}{L} \\ c &= T_{\sigma 1} \end{aligned}$$

The total enthalpy change of the system is then expressed as

$$\begin{aligned} H_{\text{cv}, t} - H_{\text{cv}, 0} &= \int_0^L \rho_p (1 - \varepsilon) c_s (T_{\sigma, t} - T_{\sigma, 0}) A dx \\ &\quad + w_{\text{fb}} c_{\text{fb}} (T_{\text{fb}, t} - T_{\text{fb}, 0}) \end{aligned} \quad (6)$$

where ρ_p is the density of potash, c_s is the specific heat of potash, ε is the porosity of the granular potash bed, $T_{\sigma, t}$ is the temperature of potash at time t , $T_{\sigma, 0}$ is the initial temperature of potash, w_{fb} is the mass of the fiberglass in the outlet, c_{fb} is the specific heat of fiberglass, $T_{\text{fb}, t}$ is the temperature of fiberglass board at time t , $T_{\text{fb}, 0}$ is the initial temperature of fiberglass board, A is the area of the test section, and L is the length of potash sample. Since the enthalpy change due to adsorption in the fiberglass board is negligible for the tests (which is verified by the repeatability of the experimental results for different initial fiberglass hygroscopic states), it is not included in equation (6).

Substituting the temperature distribution equation (5) into equation (6), and defining the total mass of a potash sample as $w_p = \rho_p (1 - \varepsilon) AL$, where w_p is the total mass of potash sample, one obtains

$$H_{\text{cv}, t} - H_{\text{cv}, 0} = w_p c_s G + \Delta H_{\text{fb}} \quad (7)$$

where the average spatial temperature increase at time t in the potash bed is

$$G = \frac{1}{L} \int_0^L \Delta T_\sigma dx = \frac{1}{L} \int_0^L (T_{\sigma,t} - T_{\sigma,0}) dx$$

$$= \frac{1}{3} aL^2 + \frac{1}{2} bL + c - T_{\sigma,0}$$

and the sensible enthalpy change in the fiberglass board is

$$\Delta H_{fb} = w_{fb} c_{fb} (T_{fb,t} - T_{fb,0})$$

Since the flow rate of air, \dot{m}_a , is constant during the test process and defining time integral of the air temperature difference as

$$S = \int_0^t \Delta T_\gamma dt = \int_0^t (T_{\gamma,out} - T_\infty) dt \quad (8)$$

we can write equation (2) at any time t in the form

$$\Delta \bar{H} = \frac{\dot{m}_a c_{pa} S + w_p c_s G + \Delta H_{fb}}{\Delta m} \quad (9)$$

where $\Delta \bar{H}$ is the average enthalpy change of potash–moisture interactions with respect to the accumulated water Δm . Equation (9) provides a theoretical basis for the measurement of the enthalpy change. The method requires passing a steady moist airflow of constant temperature through porous bed starting at time zero, and measuring the temperature response of the outlet air and the residual temperature distribution in solid potash and fiberglass plate. The moisture mass gain is measured by the before and after weight gain.

The enthalpy change obtained from equation (9) is the average one corresponding to the total moisture adsorbed or condensed, which can be transformed to the thermodynamic one as indicated by Tao et al. [7]. Thus, for a particular type of potash, the thermodynamic heat of adsorption is only a function of moisture content, giving

$$\Delta \bar{H} = f(X) \quad (10)$$

Therefore, for a particular type of potash one can write

$$\Delta H = \frac{\partial X \Delta \bar{H}}{\partial X} = \Delta \bar{H} + X \frac{\partial \Delta \bar{H}}{\partial X} \quad (11)$$

From the measured average enthalpy change, the thermodynamic state enthalpy change can be determined using equation (11).

3. PROPERTIES OF POTASH SAMPLE

The properties of the potash samples used in this experiment include: the density $\rho = 1987 \text{ kg}\cdot\text{m}^{-3}$, and

TABLE I
Properties of the potash bed test samples.

	Average particle size (mm)	Mass surface area ($\text{m}^2\cdot\text{kg}^{-1}$)	Porosity	Permeability (m^2)
Potash A	0.80	1.99	0.448	$4.66\cdot 10^{-9}$
Potash B	2.20	0.57	0.456	$3.88\cdot 10^{-8}$

heat capacity $c_s = 681 \text{ J}\cdot\text{kg}^{-1}$. The estimated average chemical composition of potash A is KCl 98.682 % (mass fraction), NaCl 0.509 %, and $\text{KMgCl}_3\cdot 6\text{H}_2\text{O}$ 0.809 %. The estimated chemical composition of potash B is KCl 98.864 %, NaCl 0.568 %, and $\text{KMgCl}_3\cdot 6\text{H}_2\text{O}$ 0.568 %. Although the uncertainties in ρ and c_s are very small, one should note that there is some uncertainty associated with the chemical composition reported here because it is estimated from the residual brine content and composition after the flotation process. For example, there is typically a 50 % variation in the residual liquid (e.g., 2–4 %) on the potash particles after the centrifuge process and before drying begins during the production of granular potash. This small variation in residual liquid strongly influences the trace fraction of NaCl and $\text{KMgCl}_3\cdot 6\text{H}_2\text{O}$. The other properties are given in *table I*.

The uncertainties in the properties in *table I* are 3–4 % for a typical type of potash product.

4. TEST FACILITY AND PROCEDURE

Schematic diagrams of test section and facility are shown in *figures 1* and *2*, respectively. The test facility consists of an insulated 1 m long $170 \times 170 \text{ mm}$ square duct, test section, vacuum pump, orifice meter, relative humidity sensors, thermocouples and computer data acquisition unit. The test section, which is removable, is 170 mm in length, with a sliding door at each end. The test section and duct are made of extruded polystyrene boards with a thickness of 25.4 mm to ensure an adiabatic boundary condition. The granular potash is held in place by a permeable rigid fiberglass board 15 mm thick.

Three thermocouples ($\pm 0.3 \text{ K}$ potash temperature uncertainty) are mounted in the sample bed, with one close to the inlet, one close to the outlet, and the third one close to the center of the sample. Using several thermocouples in the bed, the uniformity of the temperature in the potash near the outlet was shown to have less than 0.3 K temperature differences. Two additional thermocouples are mounted to measure the

temperatures of the inlet supply air and air leaving the potash samples (± 0.2 K uncertainty), and are about 3–4 mm away from the potash at the top inlet and at the bottom outlet of the fiberglass board in the test section. Two relative humidity sensors ($\pm 2\%$ uncertainty) are used to measure inlet supply and outlet air relative humidities. The computer data acquisition system records temperatures and relative humidities. Downstream of the duct, an orifice meter (diameter 12.5 mm and discharge coefficient 0.6022), designed according to ISO standards, is connected to measure the air flow rate. An air mass flow rate of $3 \cdot 10^{-3} \text{ kg} \cdot \text{s}^{-1}$ was used during the tests, which corresponds to a Darcian velocity of $0.09 \text{ m} \cdot \text{s}^{-1}$ in granular potash bed. An industrial vacuum pump is connected to the downstream end of the tunnel, while the supply air was provided from a 34 m^3 environmental chamber. The inner surfaces of the duct, upstream and downstream, are covered by aluminum foil to minimize thermal radiation coupling with the thermocouples. The whole test facility is placed in an environmental chamber where the temperature is controlled within ± 0.1 K for the temperature range of -20 to 40°C , and the relative humidity is controlled within $\pm 2\%$ from 10 to 95%. An electronic scale, with a resolution of 0.01 g and maximum measurable weight 6.000 g, is used to weigh the mass of the test section before and after each test.

Before starting each experiment, the potash sample is dried in an oven at 100°C for 24 hours to remove any possible surface moisture. After cooling to room temperature (21.5°C), the potash sample of about 1.5 kg is poured into the test section and leveled. Depending on the sample porosity and permeability, the sample length is 40 to 50 mm. The total mass of the test section in a dry state is weighed by the electronic scale. The test section is then placed in the middle part of the duct and bolted to the flanges on the duct (sealed by dry O-rings). To start an experiment, the sliding doors are opened at the entrance and exit to the test section and the vacuum pump for the airflow is turned on at the same time. Meanwhile, the computer records the time variation of the thermocouples and relative humidity sensors, sampling one set of data every 5 s. The test is monitored through the thermocouple and RH sensor outputs on the computer screen and all the data are recorded on disk. After the test continues for about one hour, the experiment is stopped, the sliding doors are once again closed and the air flow is shut off. The test section is carefully disconnected from the duct and weighed again. During this experiment, the pressure drop across the orifice meter is constant.

5. RESULTS AND DISCUSSION

For measured properties to be useful data, their uncertainties must be stated explicitly. Before reporting experimental results, we discuss the uncertainty involved in this experimental method. The overall system bias for $\Delta \bar{H}$ is the sum of the individual measurement error for Δm , \dot{m}_a , S , w_p , G , ΔH_{fg} [9], i.e.

$$\begin{aligned} \delta \Delta \bar{H} = & [(\theta_{\dot{m}_a} \delta \dot{m}_a)^2 + (\theta_{\Delta m} \delta \Delta m)^2 + (\theta_S \delta S)^2 \\ & + (\theta_{w_p} \delta w_p)^2 + (\theta_G \delta G)^2 \\ & + (\theta_{\Delta H_{fg}} \delta \Delta H_{fg})^2]^{1/2} \end{aligned} \quad (12)$$

The total bias is sensitive to the moisture content. For the lowest moisture content case, the bias of the combined enthalpy change is about 5%, where the maximum error contribution is from the measurement of the mass of the adsorbed water. The bias of the measured enthalpy change is about 2% for high moisture content case, where the maximum error contribution is from the measurement of airflow rate. The precision, or the random errors including the sampling error, is implied in the repeatability of the measurement. The repeatability in this measurement is roughly within 15%. This sample variation in the measured responses is thought to be primarily due to small variations in the trace elements, NaCl and $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$, on the surfaces of the particles.

Figure 3 shows a typical adsorption temperature signals, $T_{y,\text{out}}$, as a function of test time. For this test with a low inlet relative humidity for potash sample A (a typical type of potash used as a fertilizer), the final state of the test section is in thermodynamic equilibrium with the environment again, and no residual temperature in potash exists. The same test with potash sample B which has larger particles than A indicated much smaller temperature difference signals, indicating the strong effects of

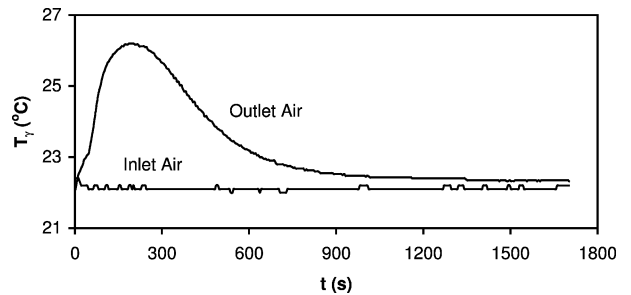


Figure 3. A typical adsorption outlet air temperature signature. $T_\infty = 22.2^\circ\text{C}$, $\phi_\infty = 33\%$, $\dot{m}_a = 3.04 \cdot 10^{-3} \text{ kg} \cdot \text{s}^{-1}$, potash A.

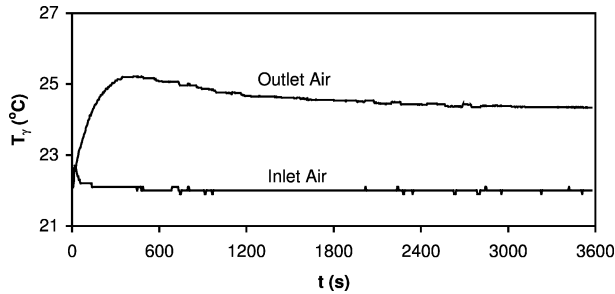


Figure 4. A typical condensation outlet air temperature signature. $T_\infty = 22^\circ\text{C}$, $\phi_\infty = 80\%$, $\dot{m}_a = 3.04 \cdot 10^{-3} \text{ kg} \cdot \text{s}^{-1}$, potash B.

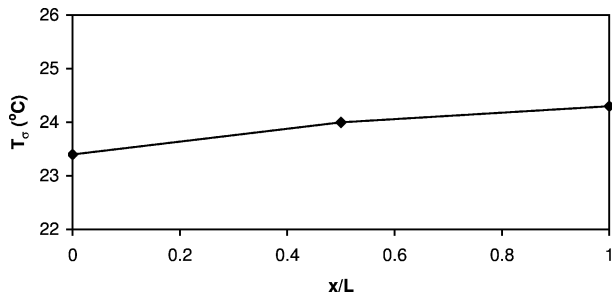


Figure 5. A typical residual solid potash bed temperature at $t = 3600 \text{ s}$. $T_\infty = 22^\circ\text{C}$, $\phi_\infty = 80\%$, $\dot{m}_a = 3.04 \cdot 10^{-3} \text{ kg} \cdot \text{s}^{-1}$, potash B.

small changes in the average chemical composition and specific surface area (i.e. only 38 % of sample A).

Figure 4 shows a typical condensation/dissolution temperature $T_{y,\text{out}}$, signals as a function of test time with a high supply air humidity for potash sample B. The final state of the test section is in a non-equilibrium state because the condensation and dissolution process is on going. The temperature distribution in the potash bed at the final time, $t = 3600 \text{ s}$, is then shown in figure 5. The final fiberglass temperature is assumed to be close to the potash temperature with which it is in contact. Thus, the outlet fiberglass temperature is estimated to be the temperature $T_{\sigma 3}$.

The measured average enthalpy change for two potash samples is shown in figures 6 and 7 where each data point represents a different experiment with the same type of potash and the error bars represent the 95 % root mean square uncertainty. The measured enthalpy change is a function of moisture content. Initially, the enthalpy change is much larger than the latent heat of condensation. As the moisture content increases, the enthalpy change declines toward the latent heat of evaporation with a small offset for the heat of solution. All the experiments were limited to a range the moisture content of less than 1.6%. If the moisture content

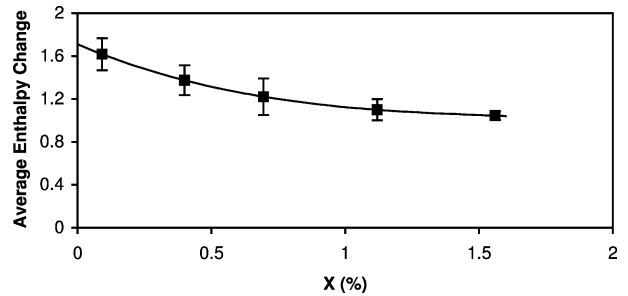


Figure 6. Integral enthalpy change of potash A showing the uncertainty range of the sample data.

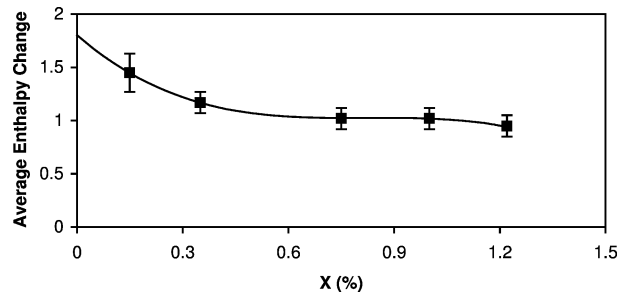


Figure 7. Integral enthalpy change of potash B showing the uncertainty range of the sample data.

is larger than this value, capillary and gravitational effects may cause the surface moisture to drain, and the physical situation will become complicated and beyond the interest of this paper and most practical applications.

Initially, the dry sample of potash will adsorb a monolayer of water. The strong binding force causes the potential energy and local partition function to be different from the water vapor in the gaseous phase. Instead of possessing the normal translational motion of the water molecules in a liquid, they are confined to localized sites on the surfaces of the particles which causes the release of a thermal adsorption energy. Within a monolayer of water vapor adsorption, the three degrees of translational freedom are lost. For the water molecules in this monolayer due to adsorption, the adsorbed molecules may also lose part or all of their freedom to rotate. As the layers of water molecules increase in number these lost freedoms become relaxed.

For the case of adsorption on highly soluble salt particles, the dissolution will result in a concentrated salt solution on the surface. This concentrated salt solution is highly non-idealized, because of the strong interionic force, which will confine the motion of water molecules again.

A least-squares curve fitting gives the following ratios for the time average enthalpy change $\Delta\bar{H}$ and the differential or thermodynamic enthalpy change ΔH .

For potash A:

$$\frac{\Delta\bar{H}}{h_{fg}} = -0.12X^3 + 0.59X^2 - 1.06X + 1.71 \pm U\left(\frac{\Delta\bar{H}}{h_{fg}}\right) \quad (13)$$

where $U(\Delta\bar{H}/h_{fg}) = [-0.07X + 0.15]$ and $X < 1.56\%$;

$$\frac{\Delta H}{h_{fg}} = -0.48X^3 + 1.77X^2 - 2.11X + 1.71 \pm U\left(\frac{\Delta H}{h_{fg}}\right) \quad (14)$$

where

$$U\left(\frac{\Delta H}{h_{fg}}\right) = [(-0.07X + 0.15)^2 + (-0.07X)^2]^{1/2}$$

and $X < 1\%$.

For $X > 1\%$, $\Delta H/h_{fg}$ will remain a constant at 0.89 ± 0.1 where the difference between 1.0 and $\Delta H/h_{fg}$ corresponds to the heat of solution.

For potash B:

$$\frac{\Delta\bar{H}}{h_{fg}} = -1.42X^3 + 3.50X^2 - 2.87X + 1.80 \pm U\left(\frac{\Delta\bar{H}}{h_{fg}}\right) \quad (15)$$

where $U(\Delta\bar{H}/h_{fg}) = [-0.07X + 0.18]$ and $X < 1.22\%$;

$$\frac{\Delta H}{h_{fg}} = -5.68X^3 + 10.51X^2 - 5.74X + 1.80 \pm U\left(\frac{\Delta H}{h_{fg}}\right) \quad (16)$$

where

$$U\left(\frac{\Delta H}{h_{fg}}\right) = [(-0.07X + 0.18)^2 + (-0.07X)^2]^{1/2}$$

and $X < 0.4\%$.

If $X > 0.4\%$, $\Delta H/h_{fg}$ will remain a constant at 0.83 ± 0.15 .

The uncertainty in $\Delta H/h_{fg}$ is estimated using the bias errors discussed above and the precision errors determined by the replication tests. The uncertainty in ΔH is computed from the equation

$$U\left(\frac{\Delta H}{h_{fg}}\right) = \left\{ \left[\delta \left(\frac{\Delta\bar{H}}{h_{fg}} \right) \right]^2 + \left(\frac{\partial \Delta\bar{H}/h_{fg}}{\partial X} \right)^2 (\delta X)^2 + \left[X \delta \left(\frac{\partial \Delta\bar{H}/h_{fg}}{\partial X} \right) \right]^2 \right\}^{1/2} \quad (17)$$

Since the uncertainty of the moisture content δX is in the order of 0.0009%, the second term on the right-hand side of equation (17) is much smaller than the other two terms, and may be ignored in the uncertainty analysis. The uncertainty due to the slope change (the third term on the right-hand side of equation (17)) can be estimated from the uncertainty of average enthalpy change.

The enthalpy change correlation for these two potash samples is different, which implies the surface chemical composition and surface area have important influences on the enthalpy change. Nevertheless, these corrections are sufficiently large that they must be included in any transient energy analysis which includes low moisture content for a potash sample.

These results differ from the measurements of Hansen et al. [6] because they are taken over a range of moisture content from 0.09 to 1.56% starting from a dry sample. This range of moisture content is of considerable practical application. Beyond $X = 1\%$ for potash A and $X = 0.4\%$ for potash B these results agree with Hansen within the experimental uncertainty.

6. SUMMARY AND CONCLUSIONS

The enthalpy change during potash–moisture interactions is measured by passing moist air of constant temperature and constant relative humidity through a dry potash sample. The results show that the enthalpy change is a function of moisture content. This enthalpy change depends on the surface chemical composition and surface area. For a dry potash sample the enthalpy change is much larger than the heat of evaporation at low moisture contents and, as moisture content increases, declines toward a value of about 85% latent heat of evaporation (combined enthalpy change including the latent heat of water vapor condensation and heat of solution). It is concluded that the enthalpy change deviates from the combined heats of condensation and dissolution by a significant fraction at low moisture contents; therefore, this correction must be included for transient energy analysis with potash. This method used to measure the enthalpy change during potash–moisture interactions is expected to be applicable to a wide range of granular fertilizer products.

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