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OPTIMIZATION OF REACTION KINETICS IN GYPSUM CALCINATION

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Abstract: Gypsum (calcium sulphate dihydrate) is of great industrial importance with over 95,000 ktonnes being used in the world per annum. The greatest use of gypsum is in the production of plaster (calcium sulphate hemihydrate) for use as an interior finisher. Plaster is produced by the calcination (thermal decomposition) of gypsum. There are a number of different phenomena occurring within a calciner, including heat transfer, mass transfer, particle and gas mixing, elutriation and the dehydration reaction itself. All these processes interact with each other. Although a lot of research has been carried out in these areas already, the literature has been found to contain significant discrepancies. This study contains experimental work which has been carried out in order to better understand the physical processes occurring within a gypsum calciner. The rate of dehydration of gypsum (35-67μm in diameter) has been studied in a fluidized bed reactor. Experiments were carried out at bed temperatures of 100 to 170°C. The fluidizing gas was air with water vapour pressures of 0.001 to 0.30 atm. The dehydrations were under differential conditions. A study of the fluidisation and elutriation properties of gypsum in batch vessels (cylindrical and conical) has been carried out. The mechanics of elutriation has been investigated and modeled for various freeboards, superficial gas velocities and air humidities. Residence time distributions were elucidated. Finally, the above experimental data and component models have been investigated for their applicability to producing a model of the laboratory scale gypsum calciner.

Keywords: Gypsum, Calcination, Plaster, Fluidization, Modelling, Nucleation

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INTRODUCTION

This paper studies the chemical and physical processes in the industrial production of plaster from gypsum. Gypsum is the common name for calcium sulphate dihydrate, $CaSO_4.2H_2O$. Plaster is the common name for dehydrated gypsum. Plaster is composed of a mixture of the different calcium sulphate phases, including calcium sulphate hemihydrate, $CaSO_4. 1/2H_2O$ and calcium sulphate anhydrite, $CaSO_4$. The aim of the work undertaken in this seminar is to improve the understanding of the processes occurring during the calcination (thermal decomposition) of gypsum to produce plaster in a conical kettle calciner. An experimental study of the dehydration kinetics of gypsum in a fluidised bed reactor;

1.1. Gypsum…?
Gypsum is the common name for calcium sulphate dihydrate, $CaSO_4.2H_2O$. Since the 1980's there has been a large increase in the production and use of synthetic gypsum [Bennet, 1998]. Synthetic gypsum is formed as a by-product of several industrial processes. The main sources are from flue gas desulphurisation (DSG gypsum) and the production of wet phosphoric acid from phosphate rock (phosphogypsum). Greater quantities of phosphogypsum are produced than any other synthetic gypsum; however they are hard to market because of the high levels of impurities, including radioactive elements [Roskill, 1997].

1.3. Gypsum Dehydration Sequence
Plaster is produced from the dehydration of gypsum. The calcium sulphate dehydrate dehydration sequence is shown in Figure 1.1. Calcium sulphate dihydrate (hereafter referred to as dihydrate) dehydrates on heating to calcium sulphate hemihydrate (hereafter referred to as hemihydrate). Hemihydrate can exist as β and αform. The β-hemihydrate is produced by dry calcination and is the main constituent of plaster. The α-hemihydrate is produced by wet calcination at elevated pressures or atmospheric pressure with the addition of acid or aqueous salt solutions. This reaction is reversible in the presence of water. Hemihydrate on heating dehydrates further to calcium sulphate anhydrite (hereafter referred to as anhydrite). At high temperatures dihydrate can be dehydrated directly to anhydrite. Anhydrite exists in 3 forms, AIII, AII and AI depending upon the temperature of reaction. AIII is meta-stable at ambient conditions and will readily rehydrate to hemihydrate in the presence of water vapour. All is stable at ambient conditions and AI is not stable below 1180°C.
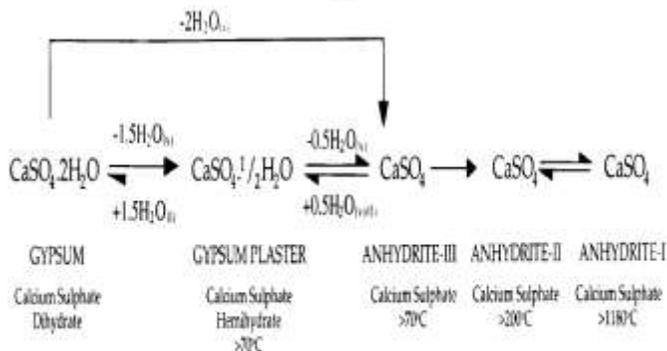

FIGURE 1.1: CaSO₄/H₂O REACTION SYSTEM

1.4. Calcination..?
"Thermal treatment to effect a decomposition, phase transition or removal of a volatile fraction" Calcination is carried out in furnaces or reactors (sometimes referred to as Kiln or calciners) of various design including Shaft Furnaces, Rotary kilns, Multiple hearth furnaces and fluidized bed reactors.

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1.5. Objectives of Calcination

- Maximize rehydratable material to add strength to board core;
- Stabilizing Stucco phases will allow some stabilization of water gauge
- Core Cementitious Gypsum is directly proportional to Bond Strength.

1.6. The Chemistry of the CaSO4-H20 system

The CaSO4-H20 system is characterised by five solid phases, four of which can exist at ambient conditions. The fifth phase, Anhydrite I, exists only at temperatures in excess of 1180°C [Wirsching, 1990]:

1. Calcium Sulphate dihydrate ; $CaSO4.2H_2O$　　: Dihydrate, D
2. Calcium Sulphate hemihydrate : $CaSO4.1/2H_2O$: Hemihydrate, II
3. Calcium Sulphate Anhydrite III : CaSO4: Anhydrite III, AIII
4. Calcium Sulphate Anhydrite II: CaSO4: Anhydrite II, AII

The generation of a model to describe the operation of the conical kettle is an inherently complex task. There are a number of different phenomena occurring within the kettle, namely heat transfer, mass transfer, particle and gas mixing, elutriation and the dehydration reaction itself. The task is further complicated by the fact that all these processes interact with each other. Figure 1.2 shows how the different phenomena interact with the properties within the kettle.
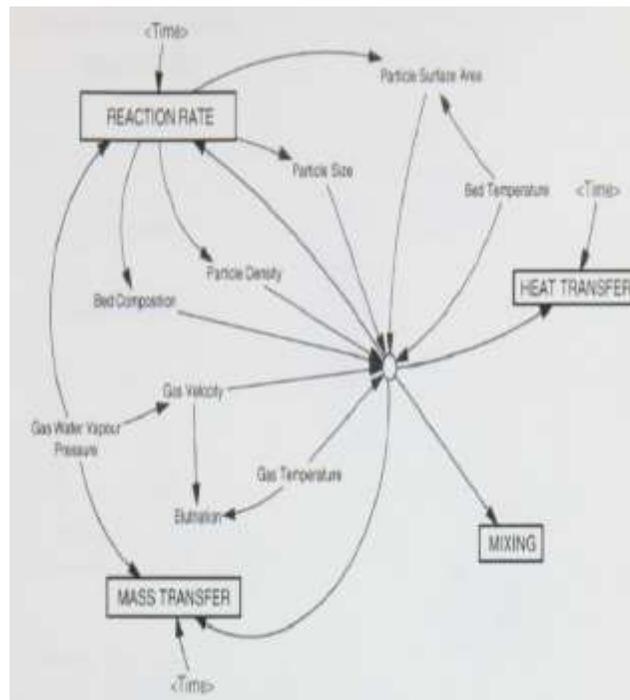

Figure 1.2: Basic influence diagram for the calciner.

1.7. Phase Analysis

Phase analysis allows the differentiation between the dihydrate, hemihydrate and anhydrite forms of calcium sulphate. Analysis techniques must be carried out immediately after sample production as AIII is metastable at ambient conditions. In the presence of water vapour it reverts back to hemihydrate. Also, the hemihydrate phase will readily absorb up to 2% of its own weight of water vapour without transforming to dihydrate. This water can be completely removed by heating at 40°C.

431

The analysis of the separate phases has been attempted by many experimenters. Techniques used include proximate analysis (PA), X-ray diffraction (XRD), infra-red spectroscopy (IRS), microscopy, calorimetry, differential thermal analysis (DTA) and gravimetric thermal analysis (TGA). These techniques have been used qualitatively rather than quantitatively.

1.7.1. Proximate Analysis (PA)

Proximate analysis is a relatively simple technique involving hydrating, heating and weighing samples in order to deduce the phase composition. The results of this technique are quoted to 0.1 %, however it is stressed that this is not the true precision. A sensitivity of 1-5%, depending upon the experience of the analyst, is probably more reasonable. The great advantage of this technique for phase analysis is that a large number of samples can be analyses simultaneously.

The decomposition reactions occur at different temperatures, as shown in Table 2.3:

Reaction	Start	Max	End
$CaSO_4.2H_2O \longrightarrow CaSO_4.\frac{1}{2}H_2O + 1\frac{1}{2}H_2O$ [Fine]	75	240	307
$CaSO_4.2H_2O \longrightarrow CaSO_4.\frac{1}{2}H_2O + 1\frac{1}{2}H_2O$ [Coarse]	83	245	339
$CaSO_4.\frac{1}{2}H_2O \longrightarrow CaSO_4 + \frac{1}{2}H_2O (g)$	111	260	405

Reaction Temperature. °C

Table 1.3: Typical Decomposition reaction temperatures (Wunderlich 1987)

2. METHODOLOGY / CALCULATIONS

2.1. Calculation of Fluidisation Properties

2.1.1. Calculation of Minimum Fluidisation velocity, U_{mf}

The minimum fluidisation velocity, Umf in m/s, can be calculated from the Carman-Kozeny Equation for spherical particles [Coulson & Richardson, 1991]:

$$u_{mf} = 0.0055 \frac{\varepsilon_B^{\ 3}}{(1-\varepsilon_B)} \frac{d_p^2(\rho_s - \rho_g)g}{\mu}$$

... (2.1)

Where Umf= minimum fluidising velocity, m/s

g = 9.81 m/s^2, εB = Bed Voidage

T_B = Bed Temperature (^{0}C),ρg = Gas density (kg/m$^3)$

μ = Gas viscosity (kg/m.s)

dp = Average gypsum particle size (m)

ρs = gypsum density (kg/m^3),ϕs = Shape factor

432

The minimum fluidisation velocity at the conditions described above has been calculated at **0.496 cm/s** (**0.004964916 m/s**). The calciner operates in the region of 0.12 m/s; i.e. around 30 times the estimated u_{mf}

2.1.2 Calculation of Minimum Bubbling Velocity, U_{mb}
The minimum bubbling velocity, U_{mb}, can be calculated from the Abrahamsen-Geldart Correlation [Pell, 1990]:

$$u_{mb}/u_{mf} = \frac{2300 \, \rho^{0.126} \, \mu^{0.523} \, e^{0.716 F}}{d_p^{0.8} \, g^{0.934} \, (\rho_s - \rho)^{0.934}}$$

...... (2.2)

Where Umb = the minimum boiling fluidising velocity (m/s);
F = the fraction of solids which are less than 45 microns
For the conditions above, Umb has been calculated to be approximately twice the minimum fluidising velocity. Therefore the calciner will exist in a `bubbly' region.

2.1.3. Calculation of Terminal Velocity, U*t
For spherical particles with a particle Reynolds number of less than 0.4 it can be assumed that the terminal velocity can be calculated from Stokes law [Pell, 1990]. Therefore:

$$u_t = \frac{d_p^2 \, (\rho_p - \rho) \, g}{18 \, \mu}$$

..... (2.3)

Where Ut = the particle terminal velocity (m/s);

Rep is calculated from:
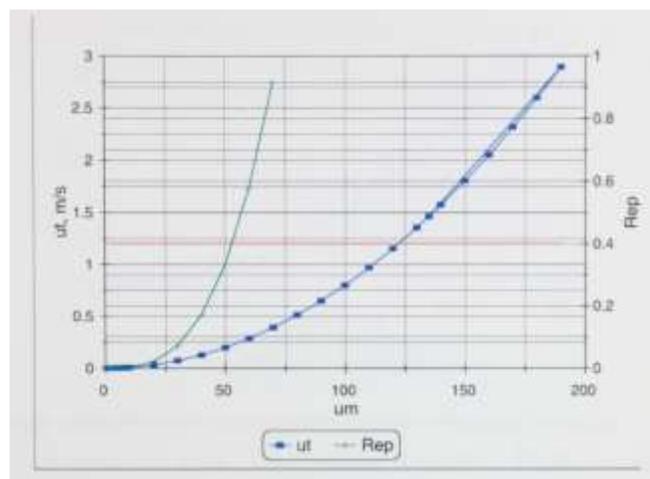
$$Re_p = \frac{d_p \, \rho_g \, u}{\mu}$$

Figure 2.1: Calculation of u_t and r_{ep}

Figure 2.1.Shows the calculation of Ut and Rep for different size particles. As can be seen, the particle Reynolds number is close to the limit of 0.4 for decent accuracy. Therefore a more detailed method for calculating the terminal velocity, which also takes into account the shape factor of the particles. The equation below gives the terminal velocity as [Haider and Levenspiel, 1989]:

$$u_t^* = \left[\frac{18}{(d_p^*)^2} + \frac{2.335 - 1.744\phi_s}{(d_p^*)^{0.5}} \right]^{-1}$$

…. (2.4)

Where dp* = dp[{ρg (ρs- ρg) g}/μ^2]^1/3

2.1.4. Calculation of Superficial gas velocity, u_0 (m/s)
In the simplest sense elutriation occurs when the superficial gas velocity within the bed exceeds a particle terminal velocity. It is measure of the calculation of Dispersion Coefficient (D) and Dispersion Number.
The superficial gas velocity is being calculated by using the below formula as,

$$U0 = \frac{\text{Volumetric flow rate in single chamber } \left(\frac{m3}{hr} \right)}{\text{Area of fluidized bed calciner (m2)} * 3600}$$

………. (2.5)

2.2. Calculation of Heat Transfer Properties
It is apparent that the dehydrations are not limited by heat and mass transfer external to the particles. It is also apparent that the temperature, water vapour pressure and particle size have an effect upon the rate of dehydration. However it is also important to consider whether heat and mass transfer inside the particles is limiting the rate of dehydration. This was investigated by setting up a series of models to describe these transfer processes inside the particles.

2.2.1. Calculations of Internal Heat transfer coefficient
The internal heat transfer coefficient is being calculated by using the following correlation of Nusselt Number as;

$$Nu = 0.027 \, (Re)^{0.8} \, (Pr)^{0.33}$$

……(2.6)

2.2.2. Calculation of Outside Heat transfer coefficient (ho or h_{max})
For the calculation of Outside heat transfer coefficient (h_o) for gas solid system apparent density of the gypsum particle is very important and is being taken into consideration.
The outside heat transfer coefficient for gas solid system in W/m²K will be calculated as,

$$h_{max} = 35.8 \rho_p^{0.2} k_g^{0.6} d_p^{-0.36}$$

….. (2.7)

2.2.3. Calculations of Overall heat transfer coefficient
The Overall heat transfer coefficient (U) for gas solid system in W/m²K will be calculated as

$$\frac{1}{U_c} = \frac{1}{h_o} + \frac{1}{h_i} \frac{d_o}{d_i} + \frac{r_o \ln(r_o/r_i)}{k}$$

…… (2.8)

Where U= overall heat transfer coefficient;

434

2.2.4. Heat Transfer area calculations
Here we have mainly make the calculation of the overall heat transfer coefficient by calculating the internal and external heat transfer coefficient and using the below equation as;

Formula: Q= U*A*ΔT…………… (2.9)

Where,

U= Overall heat transfer coefficient

A= Heat transfer area

ΔT = Log mean temperature difference

Q= Heat supplied to the chamber

Q value is taken from multi-chamber calciner model

Heat supplied to the chamber (Q) = m*Cp*ΔT… (2.10)
Here now we have calculated the Number of tubes required in the given chamber from the above calculated Heat transfer area.

We have check here that from number of tubes whether calculated area is less than the Maximum Possible area. Now the surface area of one tube is calculated as,

Surface area of one tube = 2*π*ro*l…………… (2.11)

Where l = Length of one tube after clearance (m);
ro = Outside radius of one tube (m).

No. of tubes required, N = $\dfrac{Heat\ Transfer\ Area}{Surface\ area\ of\ one\ tube}$… (2.12)

For the diameter of the tube from which we have calculate the required Heat transfer area and number of tubes required, by using the same diameter of the tube we have make calculate the maximum possible area and maximum possible number of tubes required. We have calculate tubes by two sides as

- **Tubes along the length,**
- **Tubes along the width.**

Where

Tubes along length = $\dfrac{(Tube\ pitch-2)}{(Outside\ diameter\ of\ tube-\ Tube\ pitch)}$

Tubes along width = $\dfrac{(Tube\ pitch-1.5)}{(Outside\ diameter\ of\ tube-\ Tube\ pitch)}$

Therefor after getting the tubes on both the sides we have calculate the maximum possible number of tubes in the given chamber by multiplying the tubes along length and tubes along width.

Note: As the maximum possible tubes are more than the required number of tubes, maintaining the temperature is feasible.

2.3. Calculation of Kinetic properties

435

Consider the following reaction as,
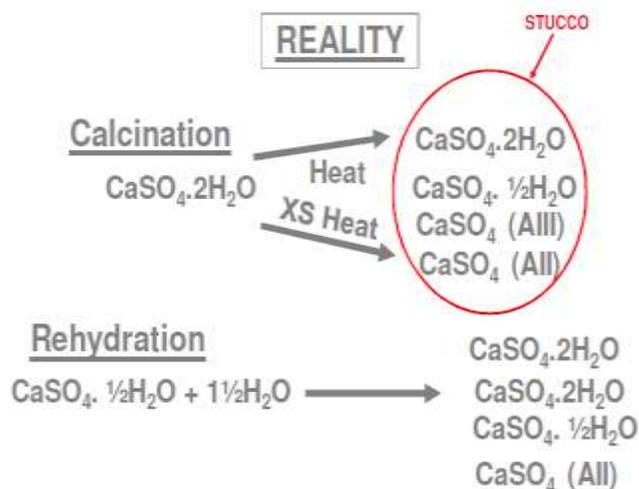
The above reaction is a typical calcination reaction which is carried out in the fluidised bed reactor in which the volatile fraction i.e 1.5 molecules of water are removed from the combined water molecule. In the above reaction we see that there are four phases exist and combinly we called it as STUCCO. Here we analyse the each phase with the help of moisture content which has been determined by the proximate analysis method.

2.3.1. Calculation of Activation Energy and Order of Reaction

Once the mechanism has been decided upon the other kinetic parameters can be calculated. In general the rate constant of a solid state reaction increases with temperature according to an exponential law (Arrhenius equation):

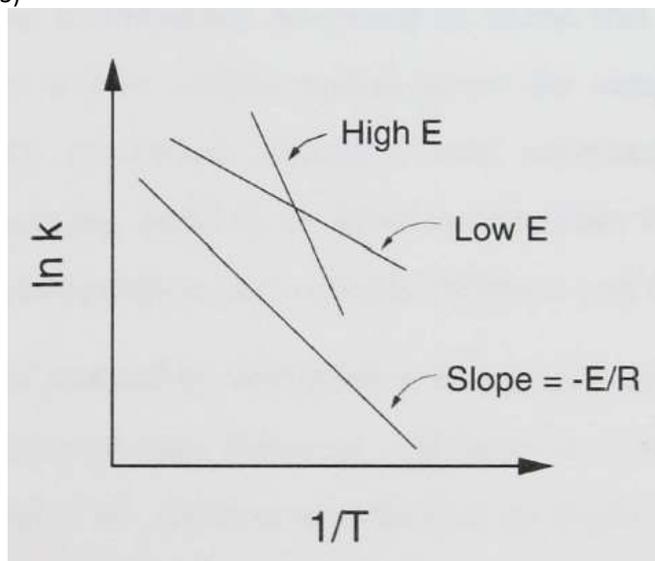**k = A*e $^{-E/RT}$**……………… (2.13)

Figure 2.2: Arrhenius plot

According to **Jim flether-Sion Study thesis,** Arrhenius plots will be drawn and the activation energy, E and frequency factor, A will be calculated for the reaction data. Values of E and A have only been determined for those sets of data with consistent water vapour pressures and with more than three data points. Figure 2.3 gives a typical Arrhenius plot for the 40µm dehydrations of Phosphogypsum. Figure 2.4 demonstrates the difference between the Arrhenius plots for gypsum and hemihydrate. The hemihydrate plot has a lower gradient and a lower intersect than the gypsum plot.
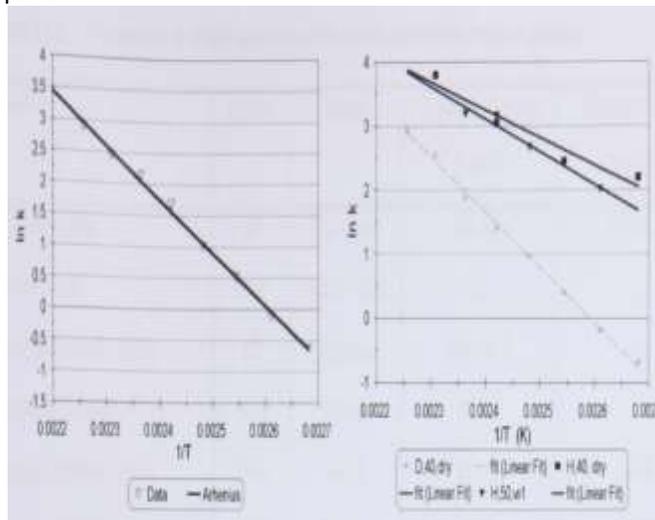

Figure 2.3: typical Arrhenius plot for 40 µm phosphogypsum;
Figure 2.4: comparison of dry Arrhenius plot, hemihydrate and dihydrate;

A series of reactions at different temperatures are carried out with all the remaining experimental conditions constant. Reaction rate constants can then be determined for each temperature. An Arrhenius plot of Ink versus l/T (K) allows the activation energy, E, and frequency factor A, to be calculated from the gradient and intersect as shown in Figure 2.2.

2.3.2. Residence Time Calculations

In order to apply information from kinetic studies of the dehydration of gypsum to the calciner it is necessary to be able to model the residence time distribution of particles in the vessel.

A better understanding of the solids mixing inside the kettle is required in order to develop a model of the calcination system. The extent of mixing within the kettle can be evaluated using a tracer test to elucidate the residence time distribution (RTD) of particles in the system.

Residence time is calculated by knowing the superficial gas velocity and dispersion number, Bed Weight and solid flow rate,

$$t_{mean} \text{ (hr.)} = \frac{\text{Bed weight, W1 (kg)}}{\text{Solid flow rate, F0 (kg/hr)}} \ldots\ldots\ldots (2.14)$$

3. CONCLUSIONS AND FUTURE WORK

Although a lot of research has been carried out on fluidisation, the difference between theoretical models and experimental research has been found to vary by as much as several orders of magnitude. Therefore an experimental study has been carried out into the fluidisation properties of phosphogypsum. Particular emphasis has been placed on the elutriation of phosphogypsum as the superficial velocity in the kettle has been calculated to be greater than the terminal velocity of the majority of the particles in the bed.

437

A model has been developed which give the overall reaction rate under different conditions of water vapor pressure and temperature. It was found that particle size was not a significant factor for the gypsum particles studied. Therefore the local reaction rate in a gypsum calciner can be predicted given the operating conditions.

To summarise, it is recommended that the following **further work** is carried out:

- Studies into the dehydration kinetics of other sources of gypsum (synthetic and mined).
- Investigations into the AIII to HH rehydration reaction at high water vapor pressures.

- Study into the fluidisation properties of gypsum in a system geometrically identical to the laboratory scale kettle.
- Application of the theoretical and experimental work in this thesis to generate a model of the gypsum calciner system.

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