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OXIDATION OF ZINC SULPHIDE CONCENTRATE IN A FLUIDISED BED REACTOR – PART 1: CHARACTERISATION OF THE FLUID DYNAMICS OF THE PARTICLE BED

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Abstract - The oxidation kinetics of a blend of zinc sulphide concentrates in a bench-scale fluidised bed reactor operated in batch regime was studied. This work involves the fluid dynamics characterisation of the bed during the reaction. Its purpose is to determine bed behaviour and to assess the experimental conditions used in the roasting experiments. The characterisation is derived from both fluid dynamics maps and an analysis based on the dynamics of gas bubble growth in the bed. Bed behaviour under any experimental condition is evaluated with the fluid dynamics maps. The transitions fixed/fluidised bed, fluidised bed/pneumatic transport and between several fluidisation regimes are obtained from curves of dimensionless gas velocity versus dimensionless particle diameters. The possibility of fluidisation in the slugging regime is verified by the dynamics of gas bubble growth in the bed.
Keywords: Zinc sulphide oxidation; Fluidised bed; Fluid dynamics.

INTRODUCTION

Considering the growing competitiveness of the world market and the ever more restrictive and specific environmental regulations, the importance of optimising industrial processes and minimising harmful emissions in the environment is paramount.

With the objective of evaluating the oxidising roasting process, unit operation of zinc production, a study of the oxidation kinetics of a blend of zinc sulphide concentrates in a bench-scale fluidised bed reactor operated in batch regime was carried out at DCMM-PUC-Rio.

It is well known that the fluidised bed reactors used in pyrometallurgical processes involving gas-solid reactions are strongly affected by the fluid dynamics of the system. Representative experimental results and mathematical modelling are necessary for scaling up the reactor. Therefore, a detailed characterisation of the fluid dynamics of the particle bed is extremely important.

In this context, the fluid dynamics of the particle bed can be characterised by both the fluid-solid and Geldart diagrams and fluid dynamics maps and an analysis based on the dynamics of gas bubble growth in the bed.

The fluid-solid diagrams show regions where the bed remains fixed or fluidised or when pneumatic

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transport occurs. These diagrams are obtained by setting the boundaries between these states from relationships involving Reynolds and Froude dimensionless numbers. Within these boundaries, the operational conditions, particle diameter and superficial gas velocity, are plotted, which allows establishment of the fluidisation regime.

The Geldart diagram shows the relationships of the difference between the solid and gas densities and the particle diameter. Bed behaviour is obtained according to a practical classification, suggested by Geldart (Abrahamsen and Geldart, 1980). This diagram gives qualitative information about bed behaviour during incipient fluidisation. More details on the theoretical construction of this diagram can be found in Queiroz (1997).

The fluid-solid and Geldart diagrams are practical but insufficient for determining bed behaviour when the superficial gas velocity used is higher than that necessary to obtain the incipient fluidisation of the particles. In this case, several fluidisation regimes occur. These regimes are particulate, bubbling, slugging, turbulent and fast fluidisation. The fluid dynamics maps are useful for determining the fluidisation behaviour under any operational condition. In this diagram, the boundaries between the several fluidisation regimes are established from curves of dimensionless gas velocity as a function of the dimensionless particle diameter. Finally, if the slugging regime is possible, the dynamics of gas bubble growth in the bed should be analysed.

The main objective of this work is to determine the fluid dynamics behaviour of particle beds of a blend of zinc sulphide concentrates using air as reactant gas. The concepts used to plot the fluid dynamics maps are presented and discussed. The dynamics of gas bubble growth in the bed are analysed when there is the possibility of slugging of the bed.

Fluid Dynamics Maps

The fluid dynamics maps consist of diagrams that provide the bed behaviour under any operating condition (Grace, 1990). In these diagrams, the boundaries between the fluid dynamics regimes are obtained from curves of dimensionless gas velocity (U^*) versus dimensionless particle diameter (d_p^*), defined as

$$d_p^* = d_p \left[\frac{\rho_g \left(\rho_s - \rho_g \right) g}{\mu^2} \right]^{1/3} \qquad (1)$$

$$U^* = U \left[\frac{\rho_g^2}{g \left(\rho_s - \rho_g \right) \mu} \right]^{1/3} \qquad (2)$$

where d_p is the mean particle diameter (m), ρ_s is the particle density (kg/m^3), ρ_g is the gas density (kg/m^3), μ is the gas viscosity (Pa.s), g is the acceleration due to gravity (m/s^2) and U is the superficial gas velocity (m/s).

The relationships between U^* and dp^* given below provide the boundaries between the fluid dynamics regimes of the beds.

Fixed/Fluidised Bed Boundary

The expression for the dimensionless minimum fluidisation velocity (U^*_{mf}) in terms of the dimensionless particle diameter gives the fixed/fluidised bed boundary:

$$U^*_{mf} = \left[\left(C_1{}^2 + C_2\, d_p^{*3} \right)^{1/2} - C_1 \right] \frac{1}{d_p^*} \qquad (3)$$

where C_1 and C_2 are the dimensionless empirical constants for particle shape factor and bed porosity, C_1 = 25.7 and C_2 = 0.0365, as suggested by Richardson and Grace (Grace, 1982).

Fluidised Bed/Pneumatic Transport Boundary

The dimensionless terminal velocities (U_t^*) that define the fluidised bed/pneumatic transport boundary are given by

$$U_t^* = \frac{d_p^{*2}}{18} \qquad (\text{Re} < 0.4) \qquad (4)$$

$$U_t^* = \left[\frac{4}{225} \right]^{1/3} d_p^* \qquad (0.4 < \text{Re} < 500) \qquad (5)$$

$$U_t^* = \left[3.1\, d_p^* \right]^{1/2} \qquad (500 < \text{Re} < 200000) \qquad (6)$$

where Re is the Reynolds number (-).

To draw the lines that define the transition between the particulate, bubbling, slugging, turbulent and spouting fluidisation regimes, the following equations were used:

Onset of Bubbles in the Bed

Geldart and Abrahamsen (1978) proposed the following equation for the minimum bubbling velocity in the bed (U_{mb}):

$$U_{mb} = 33\, d_p \left(\frac{\mu_g}{\rho_g} \right)^{-0.1} \tag{7}$$

Onset of Slugs in the Bed

Stewart and Davidson (1967) give the minimum slugging velocity (U_{ms}) according to the following expression:

$$U_{ms} = U_{mf} + 0.07\sqrt{g\,D} \tag{8}$$

where U_{mf} is the minimum fluidisation velocity (m/s) and D is the bed diameter (m).

The conditions necessary for the onset of slugs in the bed are not always satisfied. Furthermore, it should be observed that the location of the slugging regime in the diagram is specific for a particular bed since Equation 8 indicates that the minimum slugging velocity depends on bed diameter.

Turbulent Fluidisation

Yerushalmi and Conkurt (1967) observed that for a certain superficial gas velocity denoted by U_c, the pressure fluctuations that occurred in the slugging bed are reduced and the large voids tend to disappear. Increasing even further the gas velocity to U_{rt}, the pressure fluctuations fall to a value much lower than that corresponding to U_c. The frequency of the pressure oscillations becomes much higher and normally the large voids are no longer observed. For these velocities, the following correlations were obtained:

$$U_c = \left(3.0\,\sqrt{\rho_s\, d_p}\right) - 0.17 \quad \text{and}$$
$$U_{rt} = \left(7.0\,\sqrt{\rho_s\, d_p}\right) - 0.77 \tag{9}$$

Spouting Regime

Geldart (1973) observed that this regime depends only on particle diameter and the difference between the solids and gas densities. The transition is given by

$$\left(\rho_s - \rho_g\right) d_p^2 = 10^{-3}\,(\mathrm{kg/m}) \tag{10}$$

Equations 7 to 11 written in dimensionless form become

$$U_{mb}^* = 33\, d_p^* \left[\frac{\mu^{0.7}\,\rho_g^{1.3}}{g^2 \left(\rho_s - \rho_g\right)^2} \right]^{1/3} \tag{11}$$

$$U_{mp}^* = \left[\left(C_1{}^2 + C_2 \quad d_p^{*3} \right)^{1/2} - C_1 \right]$$
$$\frac{1}{d_p^*} + 0.07 \quad \sqrt{D} \quad \left[\frac{g^{0.5} \quad \rho_s^2}{\left(\rho_s - \rho_g\right) \quad \mu} \right]^{1/3} \tag{12}$$

$$U_c^* = 3.0 \quad \left[\frac{\rho_s \quad \rho_g}{g \quad \left(\rho_s - \rho_g\right)} \quad d_p^* \right]^{1/2} -$$
$$-0.17 \quad \left[\frac{\rho_g^2}{g \quad \left(\rho_s - \rho_g\right) \quad \mu} \right]^{1/3} \tag{13}$$

$$U_{rt}^* = 7.0 \quad \left[\frac{\rho_s \quad \rho_g}{g \quad \left(\rho_s - \rho_g\right)} \quad d_p^* \right]^{1/2} -$$
$$-0.77 \quad \left[\frac{\rho_g^2}{g \quad \left(\rho_s - \rho_g\right) \quad \mu} \right]^{1/3} \tag{14}$$

$$d_p^* = 0.0316 \left[\frac{\rho_g\, g}{\mu^2 \left(\rho_s - \rho_g\right)^{0.5}} \right]^{1/3} \tag{15}$$

For fast fluidisation, there are no equations available. This regime depends on the rate of feeding the solids into the bed.

Dynamics of Gas Bubble Growth in the Bed

The fluid dynamics maps show that slugging of the bed may occur if the superficial gas velocity is higher than the minimum slugging velocity and lower than the value at which the turbulent regime occurs. However, two additional conditions are necessary for the onset of the slugging regime. The maximum stable bubble size for the system must be on the order of or greater than the inside diameter of the bed, and the height-to-diameter ratio of the bed must be large enough that slugs can form (Grace, 1982).

In this context, a study based on the dynamics of gas bubble growth in the bed was conducted, not only to determine the maximum stable bubble size, but also to evaluate the conditions under which these bubbles were stable.

The study of the dynamics of gas bubble growth was based on the upward velocity of the bubbles in the bed. The procedure described by Grace (1982) uses the following equations:

$$U_{b(H/2)} = (U - U_{mf}) + 0.711\sqrt{g\, db_{(H/2)}} \qquad (16)$$

$$db_{(H/2)} = db_m - \left(db_m - db_o\right) \exp\left(\frac{-0.3\ \ (H/2)}{D}\right) \qquad (17)$$

$$db_o = 0.376\,(U - U_{mf})^2 \qquad (18)$$

$$db_m = 1.635\left(\frac{\pi D^2\ (U - U_{mf})}{4}\right)^{0.4} \qquad (19)$$

$$H = \frac{H_{mf}}{1-\delta} \qquad (20)$$

$$H_{mf} = \frac{m_s}{\rho_s\,(1-\varepsilon_{mf})\,\frac{\pi D^2}{4}} \qquad (21)$$

$$\varepsilon_{mf} = (14\,\phi_s)^{-1/3} \qquad (22)$$

where $U_{b(H/2)}$ is the bubble velocity at the midsection of the bed (m/s), $db_{(H/2)}$ is the bubble diameter at the midsection of the bed (m), db_o is the initial bubble diameter (m), db_m is the maximum stable bubble diameter (m), ε_{mf} is the voidage of the bed under minimum fluidisation condition (-), ϕ_s is the particle shape factor or sphericity defined as $\frac{\text{surface area of sphere of equivalent volume}}{\text{actual surface area}}$ (-), δ is the mean volumetric fraction of the bed occupied by bubbles (-), H is the height of the bed (m), H_{mf} is the height of the bed under minimum fluidisation condition (m) and m_s is the mass of solids (kg).

The calculation procedure consists of the following steps:

1. Mean volumetric fraction of the bed occupied by bubbles (δ) is assumed;
2. The height of the bed (H) is calculated;
3. The bubble velocity ($U_{b(H/2)}$) is calculated;
4. The value δ is verified by the equation,

$$\delta = \frac{(U - U_{mf})}{U_{b(H/2)}} \qquad (23)$$

If equation (23) is not satisfied, a new value of δ is assumed and the procedure is repeated until it is satisfied. At this point, the values of δ and H give estimates for the fraction of the bed occupied by bubbles and the expanded bed height, respectively.

RESULTS AND DISCUSSION

Analysis of the Fluid Dynamics Maps

Fluid dynamics maps of ZnS and ZnO particle beds fluidised respectively with air and a gas mixture containing 15% SO_2 and 85% N_2 at 883 and 1213 K were plotted. The temperatures are the extremes used in the kinetics study. The density of the blend of zinc sulphide concentrates is 4130 kg/m^3.

The effect of superficial gas velocity on bed behaviour for 58μm ZnS particles fluidised with air at 883 K is shown in Figure 1. Particulate fluidisation occurs when the superficial gas velocity (U) is equal to the minimum fluidisation velocity (U_{mf}) and bubbling fluidisation takes place for U = 2 U_{mf}. When U = 20 U_{mf}, the possibility of slugging of the bed exists. For U > 80 U_{mf}, the particles enter the pneumatic transport regime.

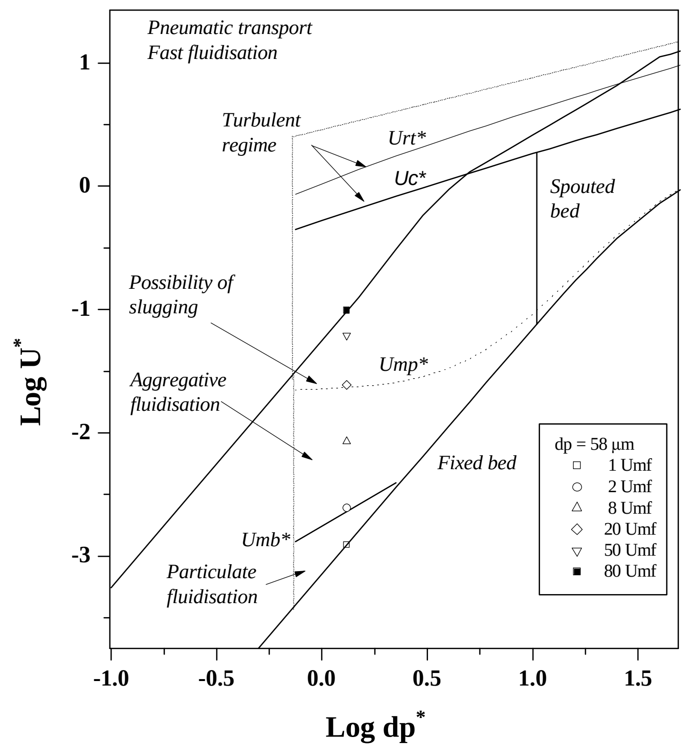

Figure 1: Effect of superficial gas velocity on bed behaviour for concentrate particles fluidised with air at 883 K

The effect of temperature on the behaviour of beds of different particle sizes fluidised at a superficial gas velocity of 0.097 m/s is depicted in Figure 2. With increasing temperature, the positions of the beds shifted downwards and to the left with relation to the fixed/fluidised bed boundary. The same displacement occurs on the lines that define the several fluidisation regimes with the exception of the spouting bed boundary, which is not affected by temperature. It can be observed that the increase in temperature and the possibility of slugging concur, as evidenced by the 272 µm particles. Nevertheless, the influence of temperature is small and is restricted to beds that operate under conditions near those required for slugging flow.

The effects of gas composition and concentrate conversion at 1213 K and a superficial gas velocity of 0.097 m/s are illustrated in Figure 3 for beds of different particle sizes. This figure shows a comparison between the fluid dynamic behaviour of beds consisting of unconverted concentrate, fluidised by air, and fully converted concentrate, fluidised by a gas containing 15% SO_2 and 85% N_2. It is shown that displacement of the positions of the beds in relation to the fixed/fluidised bed boundary is proportional to displacement of the lines that define the fluidisation regimes. This result is justified since the changes in the gas physical properties are followed by the variation in concentrate density during the oxidation reaction. Thus, the modifications in gas and concentrate compositions do not significantly affect bed behaviour.

In order to ensure adequate conditions for mass transfer and good solids mixing, the bed should operate in the bubbling mode and not too far from the boundary with the particulate regime. This will cause the formation of small bubbles that rise in the bed, increasing gas-particle contact and minimising the bypassing of the reactant gas, improving solids mixing and enhancing mass transport. With this in mind, suitable superficial gas velocities and particle diameters for the kinetics study were obtained from the dashed area displayed in Figure 4. This area corresponds to superficial gas velocities between 0.0158 (U_{mf}) and 0.0631 m/s and particle diameters in the 162-324 µm range. For particles smaller than 162 µm fluidised at a gas velocity of 0.0631 m/s, there is the possibility of slugging of the bed. Particles larger than 324 µm remain static (fixed bed).

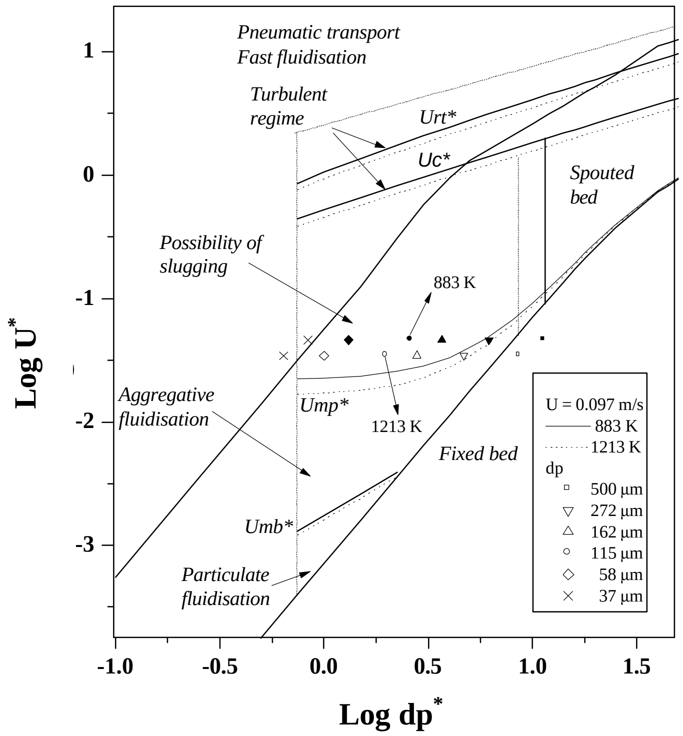

Figure 2: Effect of temperature on bed behaviour for concentrate particles fluidised with air

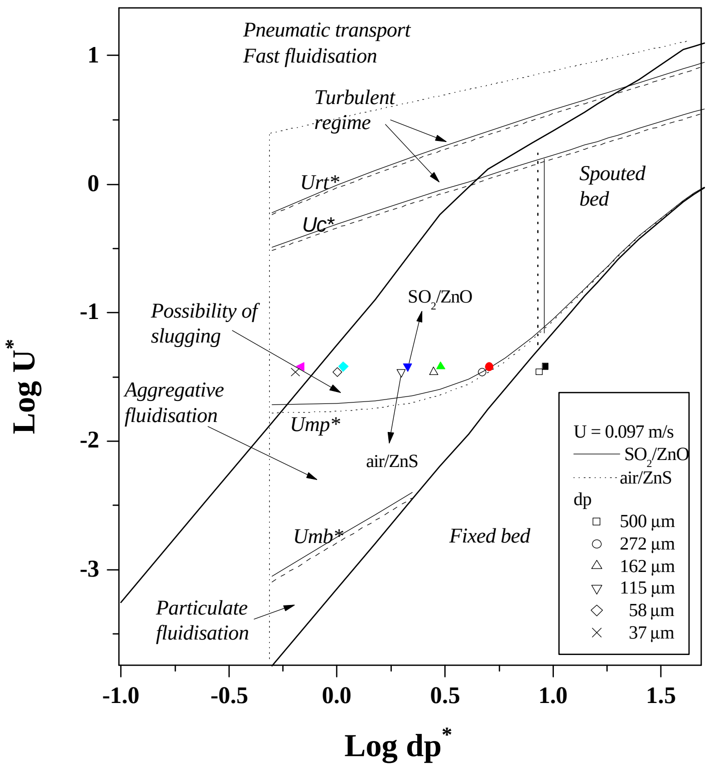

Figure 3: Effects of gas composition and concentrate conversion at 1213 K

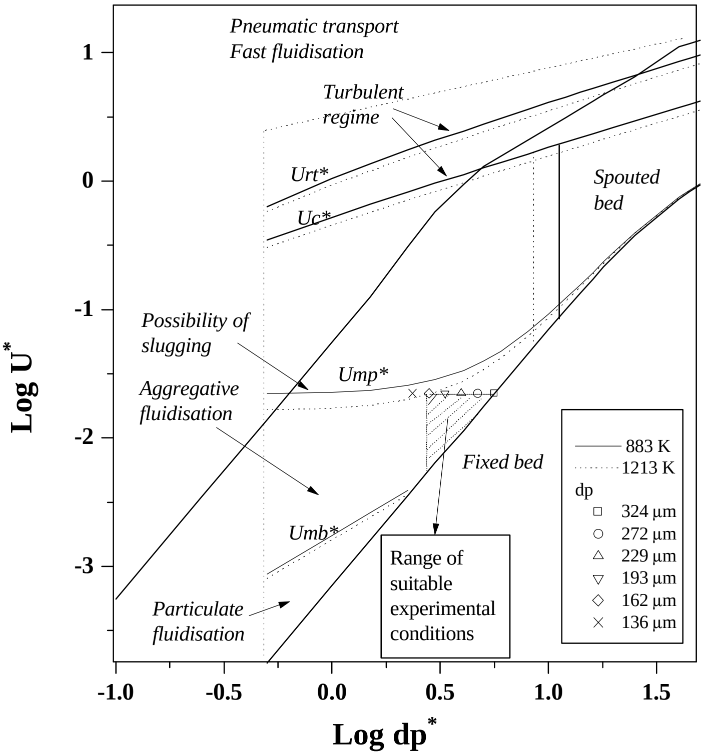

Figure 4: Suitable experimental conditions for the kinetics study based on fluid dynamics maps

Analysis Based on the Dynamics of Gas Bubble Growth in the Bed

The dynamics of gas bubble growth were evaluated for two initial masses of the zinc sulphide concentrate blend and a mean particle diameter of 165 µm. Figure 5 shows the results obtained for initial bubble diameter, bubble diameter at the midsection of the bed, maximum stable bubble diameter and height of the bed as a function of superficial gas velocity.

It can be observed in this figure that initial bubble diameter, bubble diameter at the midsection of the bed and maximum stable bubble diameter increase with increasing superficial gas velocity. The bubble diameters can become greater than the diameter of the bed. It is also observed that the increase in bed height is not proportional to the increase in bubble diameter. It can be seen that for an initial mass of 0.075 kg and a superficial gas velocity of 0.299 m/s there is the possibility of slugging, because the bubble diameter at the midsection of the bed is 0.034 m, while the diameter of the reactor is 0.045 m. For an initial mass of 0.045 kg and a superficial gas velocity of 0.235 m/s, the bubble diameter at the midsection of the bed is 0.020 m. For superficial gas velocities above 0.250 and 0.345 m/s and initial masses of 0.045 and 0.075 kg, respectively, the initial bubble diameter is greater than the bed height, which makes the bubble unstable.

An efficient temperature control and minimal harmful effects, i.e., slugging and/or particle losses produced by the increase in superficial gas velocity, are achieved under conditions where the bubbles are unstable (Grace, 1982). Therefore, initial diameter must be equal to or greater than bed height. Under this condition the bed is strongly agitated, the particles are projected against the wall by the bursting of the bubbles producing a radial gradient and the solids are concentrated around the wall of the reactor. The centre of the column begins to have a relatively small fraction of solids, which causes the breakup of bubbles with smaller initial diameters and higher frequencies. In this case, despite the low superficial velocity the characteristics of the bed are similar to those observed for the turbulent regime. The strong agitation of the bed provides better heat transfer between the solid and the wall of the reactor and mass transport between small and transitory voids, which minimises the bypassing of the gas, enhancing the gas-solid contact. In the present work this condition is achieved for superficial velocities of 0.256 m/s and 0.384 m/s when the initial masses are 0.045 kg and 0.075 kg, respectively.

Figure 6 shows the range of suitable experimental conditions for the kinetics study based on the dynamics of bubble growth in the bed.

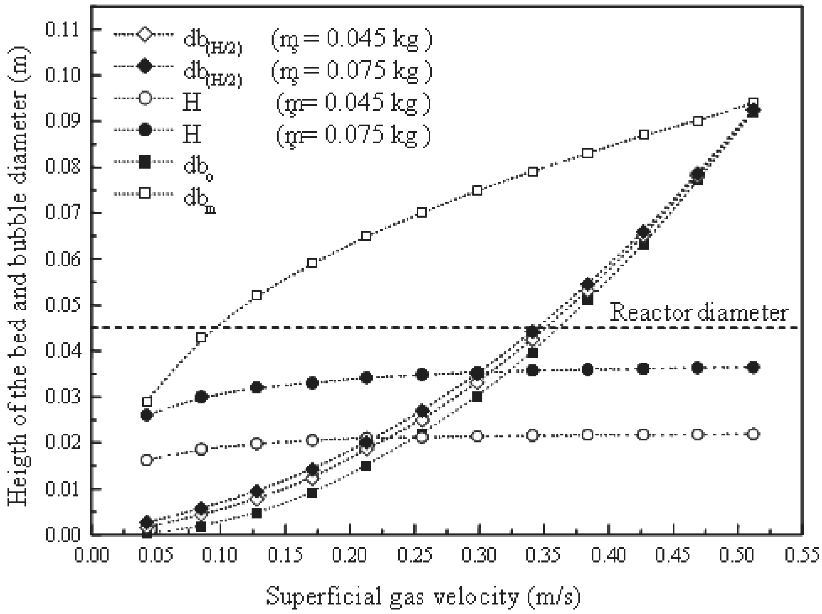

Figure 5: Height of the bed and characteristic gas bubble diameters as a function of superficial gas velocity

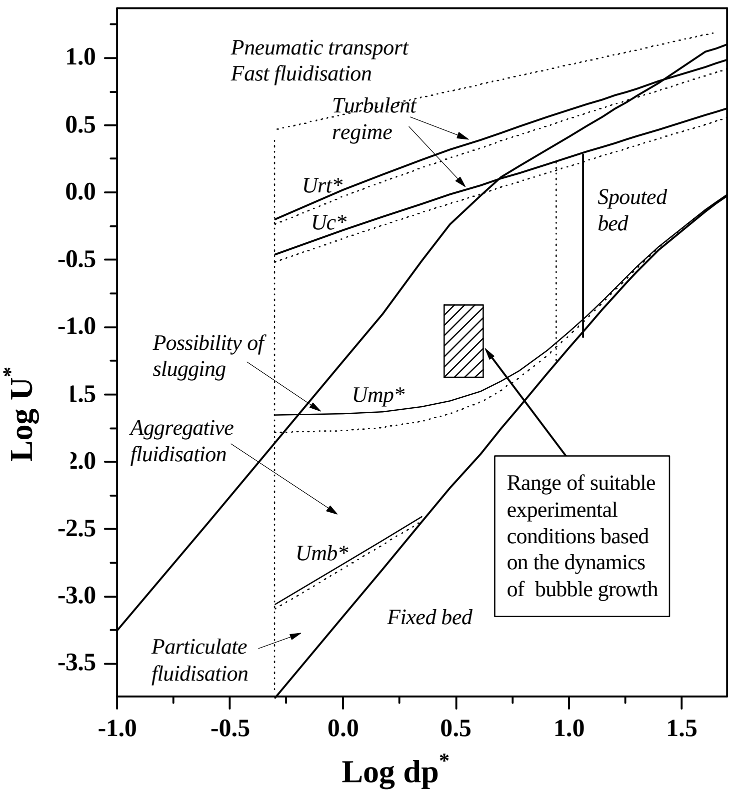

Figure 6: Suitable experimental conditions for the kinetics study based on the dynamics of bubble growth in the bed

CONCLUSIONS

Fluid dynamics maps and analysis of the dynamics of gas bubble growth allowed prediction of the behaviour of particle beds of a blend of zinc sulphide concentrates according to particle size, solid densities, fluidising gas properties and superficial gas velocity.

The fluid dynamics regime of the bed is mainly a function of particle diameter and superficial gas velocity and is subject to modification by an increase in temperature when the bed operates in the vicinity of the boundaries between the different regimes.

Based on the fluid dynamics maps, the ideal experimental condition to carry out the kinetics study was achieved when the bed was operated in the bubbling fluidising regime, close to the particulate/bubbling boundary. This condition corresponds to superficial gas velocities between 0.0158 (U_{mf}) and 0.0631 m/s and particle diameters in the range of 162-324 μm. However, under this condition, agglomeration of the solids and difficulties in controlling the temperature may occur due to the highly exothermic reactions.

The study based on the dynamics of bubble growth allows determination of superficial gas velocities higher than velocities for which conventional studies predict slugging of the bed. For the present project the optimum experimental condition was achieved for superficial gas velocities of 0.256 m/s and 0.384 m/s when the initial masses fed into the reactor were 0.045 kg and 0.075 kg, respectively. These conditions make it possible to control the temperature without preventing gas-solid contact, thereby avoiding excessive particle losses.

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