Forschung, Wissenschaft

Bubbling Gas Fluidised Beds As Chemical Reactors *

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Abstract

This paper is based on a lecture given on 27 April 1977 to the Chemical Society of Zurich. It describes the principal physical features of a bubbling gas fluidised bed and how these affect performance of the system when it is used as a gas/solid chemical reactor. The reasons for gas by-passing are explained and means of minimising this are described. The special case of very fine powders is discussed briefly.

Introduction

If a powder or granular solid is placed in a vessel with a perforated or porous base, a fluid can be caused to flow upwards through it. The pressure drop from bottom to top will increase with increasing fluid velocity and at a critical velocity, U_{mf} this pressure difference multiplied by the cross-sectional area of the vessel will be equal to the gravitational force acting on the whole bed. The powder is then supported by the rising fluid stream and is said to be fluidised. The individual particles are, in a sense, weightless and no longer rest upon each other so that interparticle friction forces are greatly reduced. They can move relative to each other lubricated by the intervening fluid. The whole can be easily stirred and is no longer load bearing. It behaves like a fluid and hence the name, a fluidised bed of powder.

When the supporting fluid is a liquid the particles simply separate more widely as the fluid velocity is increased beyond U_{mf}. Thus, the whole bed expands and allows more fluid to pass whilst maintaining a constant pressure drop. The powder behaves differently when the supporting fluid is a gas and the bed begins to bubble as velocity is increased and in this way the extra flow is accommodated without increasing the pressure drop. Gas fluidised powder looks very like a boiling liquid and is sometimes referred to as a boiling bed.

Fluidised beds are often used to engineer a chemical reaction between a fluid and a granular or powdered solid. The fluid is often a gas and the solid may be one of the reactants or may be a catalyst. The chlorination of alumina with chlorine is an example of the former and the oxidation of benzene to maleic anhydride in the vapour phase over a vanadium pentoxide catalyst is an example of the latter. The most widely known use of fluidised beds is in cat crackers where hydrocarbon vapours fluidised the silica alumina catalyst that cracks the larger molecules.

The gas fluidised bed has many advantages as a chemical reactor. Heat is readily transferred between bed and walls so that reaction heat can be easily added or removed. Temperature is very uniform throughout the bed so that precise reaction conditions can be maintained. The particles are well mixed so there is uniformity of solids composition. Because of its fluid-like nature particles can be added and removed through suitably arranged pipes. This permits continuous processing and, for example, the regeneration of a catalyst that may become fouled in use. Its success as a reactor depends on intimate contact between gas and solid particles and, in appropriate cases, good mixing of different gaseous reactants when these are not premixed. In this respect the fluidised bed is not always a good reactor and to understand why and how it can be improved it is necessary to know something of the hydrodynamics of this interesting gas/solid system.

A bubbling gas fluidised bed looks remarkably like a boiling liquid and at first sight it is difficult to believe that it is a dry powder. The turbulent surface disturbed by bursting bubbles gives an immediate impression of a well mixed system. This led chemical reaction engineers to treat such beds as stirred tank reactors. Several gas phase reactions in the presence of a finely divided catalyst were engineered as fluidised beds with inexplicably disappointing results. The poor gas/solid contacting that occurred in practice provoked research that has led to a much better understanding of this complex hydrodynamic system and has shown the conditions under which serious gas by-passing occurs. The basic features of a gas fluidised bed are best revealed by using fairly uniform spherical particles such as glass Ballotini in the size range around 300 μm. Unlike boiling water, for example, the bubbles within a fluidised bed cannot normally be seen except when they break through the surface. One way of observing them is to make a "two-dimensional" bed which is effectively a vertical slice. The powder is contained between two glass plates about 1 cm apart as illustrated in Fig. 1. With rear illumination the bubbles are seen in silhouette and their size, shape, velocity and number can be readily measured. This technique gives valuable

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[*] Lecture given on April 27, 1977, to the Chemical Society in Zurich

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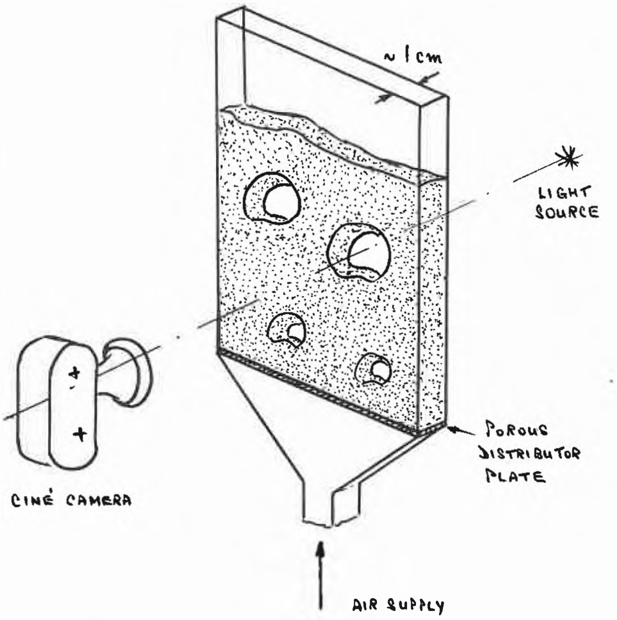

Fig. 1: Diagram of a two-dimensional fluidised bed.

qualitative information about the nature of the bubbles and their motion.

Particle movement caused by bubbles

Fig. 2 is a photograph of an isolated bubble in a two-dimensional bed. It is seen to be roughly circular in shape but with an indented base. The boundaries are very definite and the inside of the bubble is virtually empty of particles. The rise velocity is of order 1 m/s and increases with bubble size (approximately as the square root of diameter). This photograph was taken under frontal lighting with a camera travelling upwards at the bubble velocity. The bubble is therefore stationary relative to the observer. The particles on the other hand are moving relative to the bubble, a distance of a few millimeters during the exposure time of 10^{-2} seconds. Some of the particles therefore appear as streaks in the photograph indicating their direction of motion. The photograph reproduced here may not reveal it very clearly but the original negatives show the particles to be moving in smooth lines around the bubble. They are behaving like elements of a true liquid flowing in stream lines around a circular solid obstruction. This is quite contrary to the impression of turbulence gained by looking at the bed surface.

Fig. 2: An isolated bubble rising through a two-dimensional bed.

The motion appears differently to an observer stationary with respect to the vessel walls. This is shown in Fig. 3 where the bubble looks a little blurred because it has moved during the exposure time. In this experiment the two-dimensional bed was first half filled with black particles and then with white ones so that a horizontal interface was seen between the two colours. The bed was carefully brought to the point of fluidisation without disturbing the colours and then just one bubble allowed to form and rise. Fig. 3 shows the initial disturbance of this pre-arranged colour pattern. The spout of black particles drawn up behind the bubble is a consequence of the pseudo-streamline motion seen in Fig. 2 and is entirely predictable from well established fluid dynamic theory.

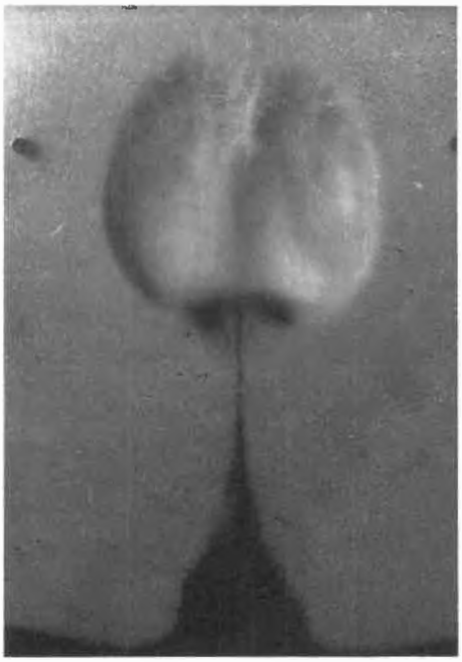

Fig. 3: An isolated bubble rising through a two-colour two-dimensional bed.

In Fig. 3 the bottom part of the bubble is seen to be filled with black particles that are being carried upwards. This explains the indentation of the otherwise circular bubble already seen in Fig. 2. These particles correspond to an attached wake as seen behind a bluff body in a true fluid at a fairly small Reynolds number (of order 10). When a bubble bursts it leaves this wake behind on the surface and Fig. 4 shows the completed pattern after the bubble has gone. This is the basic particle displacement caused by a single bubble and is the fundamental way in which particle mixing occurs in a bubbling gas fluidised bed.

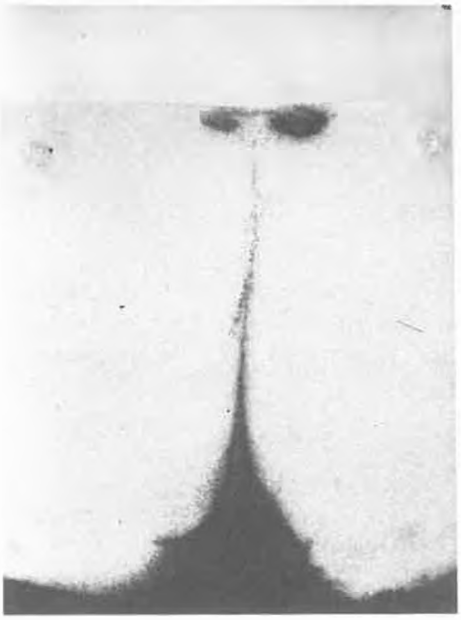

Fig. 4: The particle displacement caused by a single bubble.

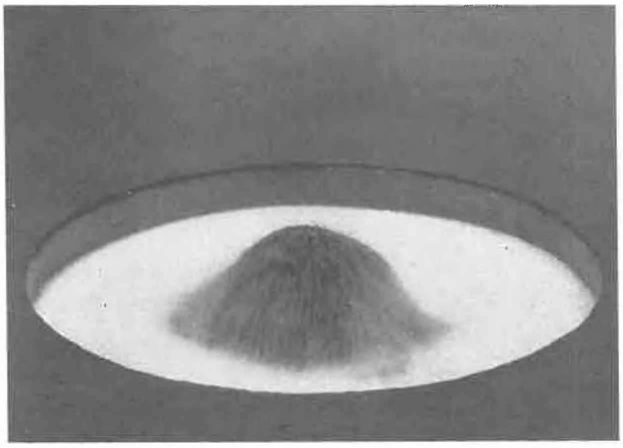

Fig. 5: A bubble wake arriving at the surface.

The evidence presented so far comes from two-dimensional beds which, although very revealing, are a little artificial compared with normal bed geometry. The same phenomena can, however, be confirmed in the more usual cylindrical and other three-dimensional beds. Fig. 5 shows the surface of a cylindrical bed that was initially arranged with black particles at the bottom. The first bubble has just broken the surface and the wake of black particles is splashing over the surface. Fig. 6 shows vertical sections through a diameter of a cylindrical bed of black and white particles. The displacement caused by one bubble is as seen before but also the effect of successive bubbles can be followed.

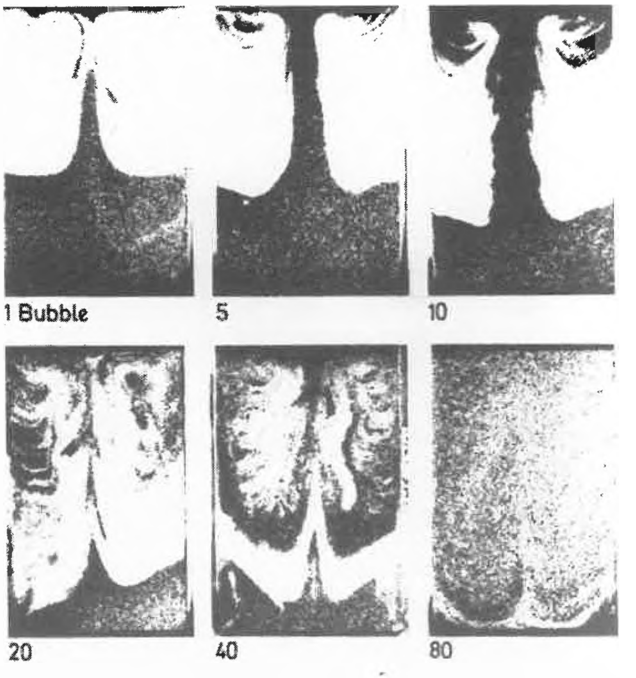

Fig. 6: Bed sections showing progressive particle mixing as bubbles pass through.

In this example the passage of 80 bubbles produces almost perfect mixing but it has been achieved by repetition of the basic displacement seen in the first picture. One conclusion is evident; the degree of particle mixing depends on the number of bubbles that have passed through and the mixing rate depends on the bubbling rate.

Bubbles can be seen in the interior of a fluidised bed by taking X-ray pictures and Fig. 7 shows an example of an isolated bubble. It is seen to be spherical with the indented base that we now know to be a wake. Fig. 8 shows several bubbles revealed by X-rays. As the bubble concentration increases their shapes become distorted as they interfere one with another. The phenomena described above are still observed but with complicated modifications which are easily explained qualitatively but are difficult to follow quantitatively.

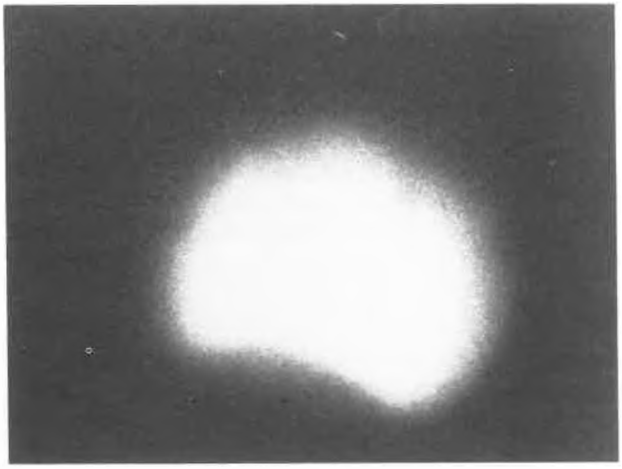

Fig. 7: An X-ray picture of an isolated bubble.

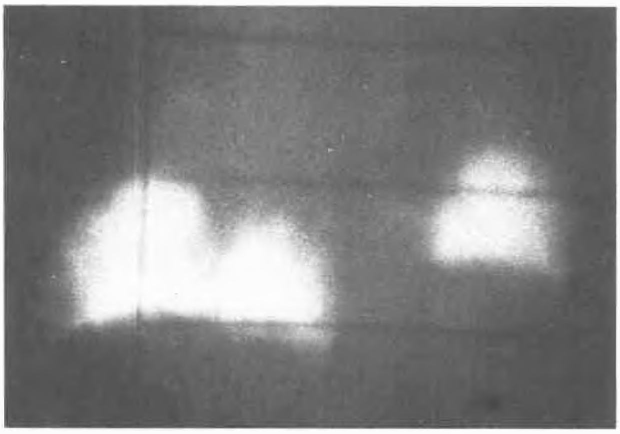

Fig. 8: An X-ray picture of several bubbles.

Gas flow through the bed

The two-dimensional apparatus can also be used to observe gas flow through the bed. Tracer gas can be admitted through a small hole low down in the front face in the same way that Reynolds introduced a fine dye stream to trace the flow of water. The most suitable tracer is NO_2 which, maintained at about 50 °C and with suitable optical filters, gives good contrast on the photographs as Fig. 9 shows.

Many interesting facts are discovered from this simple experiment. The tracer thread retains its identity and does not mix measurably with the fluidising air. This at first appears a remarkable observation and helps to explain why some fluidised beds are very inefficient chemical reactors. In spite of the initial impression of good mixing, gas remains highly segregated and appears to flow in well defined streamlines.

If the tracer gas supply is interrupted and the thread broken then the head or tail can be followed by ciné photography which, with suitable timing, allows the local interstitial gas velocity to be measured. Observations made this way show that the vertical component of interstitial gas velocity remains at the minimum fluidisation value and is independent of the rate at which gas is fed to the bottom of the bed. This leads to the important two-phase theory which can be simply stated as "the excess gas over that required for fluidisation passes through the bed in the form of bubbles". This is subject to modification in certain circumstances but as a first approximation it forms an important basis for chemical reactor models. Minimum fluidisation velocity is given approximately by the simple expression

$$U_{mf} = 6 \times 10^{-4}\, d_p^2\, \varrho_s g / \mu \qquad (1)$$

where d_p is the particle diameter ϱ_s is the solid density and μ the gas viscosity. For a given system it depends on the particle size to which it is quite sensitive.

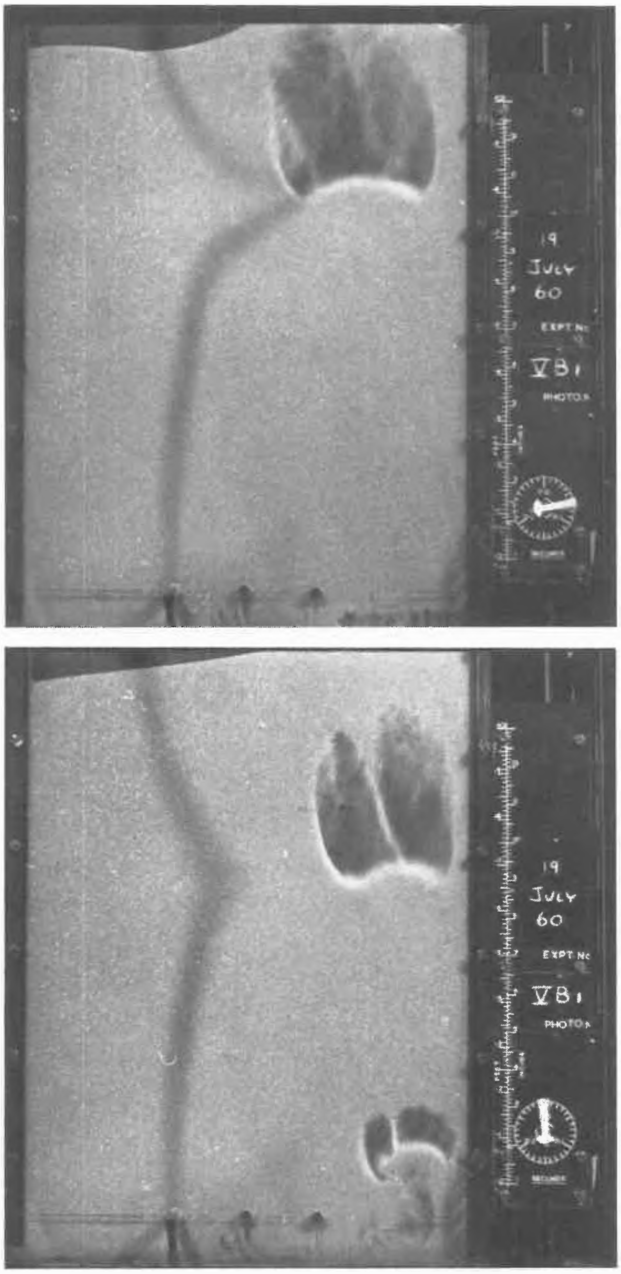

Fig. 9: Gas flow tracing in a two-dimensional bubble.

Returning to Fig. 9, it is not difficult to imagine the bubble-free fluidised bed as a uniformly permeable medium with impermeable vertical boundaries and a uniform pressure over its horizontal surfaces, greater at the bottom so that flow occurs vertically upwards. In the absense of bubbles gas flows upwards in parallel vertical streamlines and this can be observed by gas tracing. When a bubble is present this introduces a region of almost infinite permeability and the streamlines respond. If the bubble were stationary the streamlines would be stationary and their pattern could be predicted by solution of *Laplace*'s equation with appropriate boundary conditions. Fig. 9 gives an indication of how the streamlines converge from below towards the region of high permeability, the bubble. The gas tries to take an easy route from bottom to top by flowing through the empty bubble.

The left hand-half of Fig. 10 shows the kind of pattern the gas streamlines would form if the bubble were stationary. The right-hand half shows the kind of streamline path that the particles follow as they flow around the bubble, as seen in Fig. 2. These two flow fields interact. The particles with their much greater inertia are not materially deflected by the gas but the gas motion is greatly modified by the particles. Consider a point just ahead of the bubble as in Fig. 11. With stationary particles the gas at this point would have a velocity represented by the vector U'_g. A particle at this point has a velocity represented by the vector U_s. The gas is deflected when the bubble is moving and its velocity is closely represented by the resultant vector U_g.

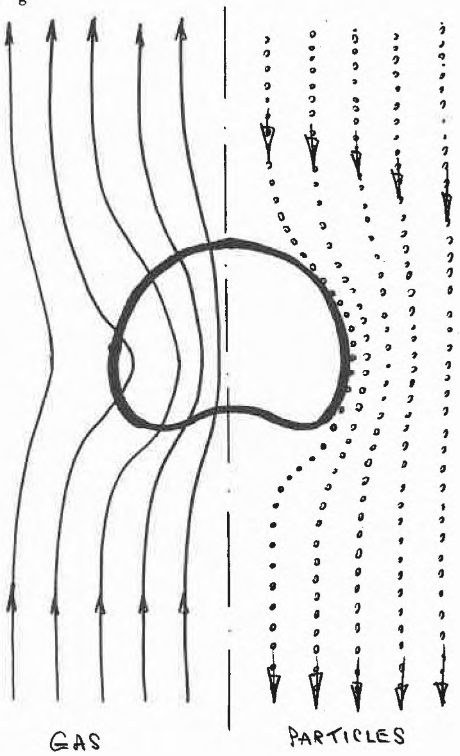

Fig. 10: A diagram of gas and particle streamlines around a bubble.

The angle through which the gas velocity vector is deflected depends upon the ratio of the scalar values of U'_g and U_s. These are in turn proportional to the undisturbed interstitial gas velocity, U_{mf} and the bubble rise velocity, U_B. From equation (1) it is seen that this ratio depends most strongly on the particle diameter, d_p. With small particles U_{mf} is small, U'_g is small everywhere in the field and gas is highly deflected in the neighbourhood of bubbles. With large particles the deflection may be small. The photographs of Fig. 9 refer to moderately large particles where $U_{mf} > U_B$.

A very interesting phenomenon results when $U_{mf} < U_B$. The gas velocity vector is then so greatly deflected in the region illustrated in Fig. 11 that its direction is reversed and it moves down relative to the bubble. As it returns towards the lower part of the bubble the higher gas pressure in that region pushes it back into the bubble. Hence, the gas is captured and remains as a spherical vortex centred on the bubble and rising with it. At a certain radial distance from the bubble the particle velocity is no longer great enough to cause this gas deflection and a surface divides gas flowing interstitially through the bulk of the bed from that captured by the bubble and forced to travel with it.

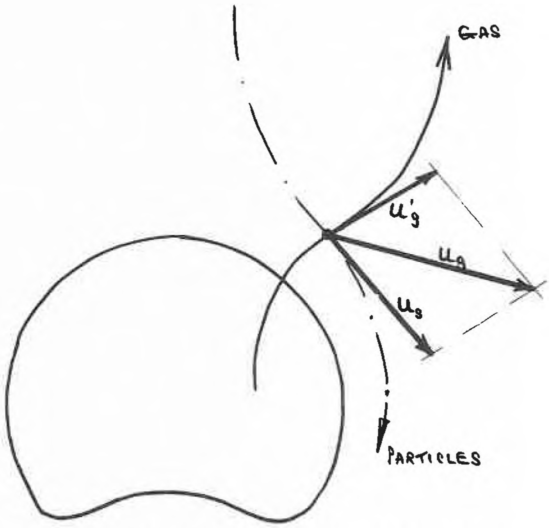

Fig. 11: The way gas is deflected by flowing particles.

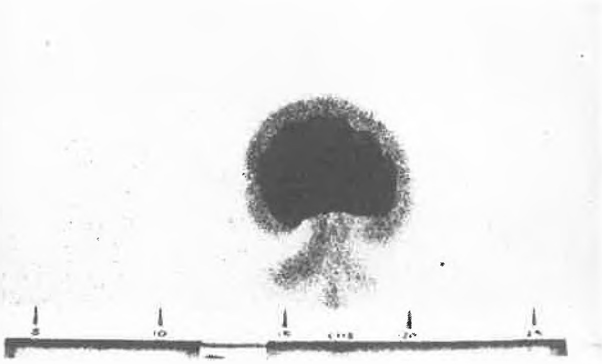

Fig. 12: A bubble with its associated cloud.

This is seen in Fig. 12 where a bubble has been formed in a two-dimensional bed by injecting a rapid "puff" of black NO_2. The inner part is a bubble as normally observed but it is now seen to be surrounded by a "halo" of NO_2 which has extended into the dense phase around the bubble boundary. This is a steady state and the whole cloud (bubble and halo) rises through the bed with little mixing between NO_2 and surrounding air. It is hard to imagine other situations where the interface between two gases not separated by a membrane of any kind could be retained for so long under comparable conditions of motion. It will be noted that there is some leakage of NO_2 from the bottom of the bubble. The annular thickness of the halo depends upon the ratio U_B/U_{mf} and it can be very thin indeed with fine powders that are commonly used, for example, as industrial catalysts.

Fluidised bed chemical reactors

This phenomenon has important implications in chemical reaction engineering. Of the whole volume of NO_2 seen in Fig. 12 only that forming the halo is actually in contact with particles. If this were gas intended to react in the presence of a catalyst powder it would not be a very efficient method of contacting. This situation gets worse as the particle size gets smaller for then proportionately more gas flows as bubbles (the two-phase theory), the halo gets thinner as U_{mf} decreases relative to U_B and the residence time of bubble gas diminishes as U_B increases relative to U_{mf}. It is plain that catalyst powder intended for a fluidised bed chemical reactor should not be ground too finely if this serious contacting limitation is to be avoided. For purely chemical reasons it is advantageous to prepare fine material for then the surface area per unit volume is increased, diffusion path lengths are diminished and the effective rate constant is increased. However, it is of little use to have a very active catalyst if it cannot effectively be brought into contact with reactant gas. Here is an obvious need for compromise, optimisation and a proper understanding of both chemical considerations and the physical means by which the reaction will be engineered.

Recent research with fine powders

It will not surprise the reader to learn that what is written above is a simplification of reality and that the simple models described are subject to second order corrections and that there are exceptions to the general descriptions. In particular, fine powders do not always behave as badly as the foregoing would suggest.

It is a matter of fairly wide experience in industry that the addition of a small proportion of fine material to a fluidised catalyst often has a beneficial effect on the degree of conversion contrary to what would be expected from a shrinking of the halo part of the bubble cloud. The reasons for this are just beginning to be understood. The behaviour of a fluidised powder begins to change as the mean particle size is reduced below about 70 μm. This is quite fine powder (cement dust, fly ash and grass pollens are in this range) but many industrial fluidised catalysts contain an appreciable proportion of smaller particles.

Most powders of mean particle size greater than about 100 μm have a well defined minimum fluidisation velocity and begin to bubble immediately this is exceeded. The voidage or volumetric concentration of particles in the dense phase of the bed remain at or close to its minimum fluidisation value and its permeability remains more or less constant. As the particle size is diminished these statements are no longer true. Fine powders are often difficult to fluidise at gas velocities not much greater than U_{mf} but they usually fluidise well at velocities well in excess. U_{mf} is often imprecise and difficult to measure. Some of these powders will expand uniformly up to several multiples of U_{mf} before they begin to bubble. The voidage and permeability of the dense phase do not remain constant (and may vary with position and time) and in many cases the interstitial gas flow is greater than U_{mf} and sometimes very much greater. The simple two-phase theory breaks down and even though restricting cloud formation occurs the chemical contacting may improve because more gas flows interstitially.

With most powders these effects become noticeable at a mean particle size of about 70 μm but as this size is reduced fluidisation becomes increasingly difficult. The probable reason for this is that the ratio of surface to body forces increases with diminishing size and eventually the orderly hydrodynamic forces are frustrated by such things as particle adhesion, electrostatic forces and the like. The size range in which gas/solid contacting begins to improve with reduced size is a narrow one and does not depend on mean size alone.

This is a difficult region in which to do systematic research experiments because specific fine powders are difficult to prepare and to characterise. The mean particle size is a very crude measure for it can be arrived at by an infinite combination of component sizes. With regard to the behaviour described above it appears that size distribution may be as important as mean size and there is some evidence that a small mass proportion of super fine particles (e.g. $< 10\ \mu$m) is important. The most important thing to measure is the proportion of total gas flowing interstitially and this can be done either by observing the bubble flow or measuring the dense phase voidage. Both of these are difficult and tedious techniques. As information accumulates it will become possible to specify the powder size composition that will maximise the interstitial gas flow and so lead to good fluidised bed chemical reactor performance.

General Reference

"Fluidisation" Edited Davidson & Harrison. Academic Press, London 1971.