FLUIDIZATION

VII

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FLUIDIZATION VII

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PREFACE

Fluidized beds continue to demand closer understanding and improved practice. The emphasis may shift from decade to decade but wherever large-scale processing is under consideration then also fluidized beds are being proposed as a means of meeting modern requirements - not as the only means but as a most important one with many successes to its credit, albeit some failures. Examples are: gasification particularly for combined cycle power generation, steam drying for high moisture brown coals, circulating fluid bed combustors, iron-ore reduction, new catalytic processes - the list could be made very extensive. From around 250 abstracts submitted about 100 papers appear in these Proceedings, covering a wide range of current problems, developments and opportunities.

This is the seventh in a series of international Fluidization Conferences held under the auspices of the Engineering Foundation. Previous conferences have been held in Pacific Grove, USA (1975), Cambridge, England (1978), Henniker, USA (1980), Kashikojima, Japan (1983), Elsinore, Denmark (1986), and Banff, Canada (1989).

Reducing the number of potential papers to a manageable number has been quite a task which has required much cooperation from authors and reviewers, and to both groups gratitude is extended for their forbearance. A perfect balance of papers has not been achieved, but there is broad coverage of work in progress combined with new developments, new processes. Because of the importance of fluidized beds in the energy field, close attention has been paid to heat transfer and drying. New methods of contacting are explored together with an increasing emphasis on fast beds in circulating fluidized beds. Liquid and three-phase fluidization get coverage while much attention is paid to unsolved problems in conventional fluidized beds. New applications deserve and receive attention. Five plenary addresses are included. In order to ensure that the volume is available at the Conference, we have had to adopt a strict schedule but problems have arisen - from the worsening of communications with some countries, to the disappearance in the post of some reviews of papers.

We wish to acknowledge the support of Charles Freiman, Barbara Hickernell, Donna McArdle and Joanne Sforza of the Engineering Foundation in organizing the Conference and publishing the Proceedings. Members of the international working party, Dale Keairns, John Matsen, John Grace, Maurice Bergougnou and also L.S. Fan have assisted in various ways, not least as a sounding board. We are also grateful to fellow members of the Australian organizing committee: P.K. Agarwal, M. Burridge, T. Fane, C. Fryer, C.J. Hamilton, I. Jeffcoat, R.D. La Nauze, V. Rudolph and J. Stubington.

We also called on many referees: R. Abed (USA), P.K. Agarwal (Australia), H. Arastoopour (USA), A.A. Avidan (USA), S.P. Basu (Canada), W. Bauer (Germany), J.M. Beeckmans (Canada), L.A. Behie (Canada), M.A. Bergoygnou (Canada), F. Berruti (Canada), J.S.M. Botterill (UK), C. Brereton (Canada), C. Briens (Canada), D.B. Bukur (USA), M. Burridge (Australia), H.S. Caram (USA), J. Chaouki (Canada), C. Chavarie (Canada), J.C. Chen (USA), S. Chiba (Japan), R. Clift (UK), J.F. Davidson (UK), C.E. Davies (NZ), H.I. deLasa (Canada), R.J. Dry (Australia), M. Dudokovic (USA), S.E. H. Elnashaie (Saudi Arabia), N. Epstein

D.J. Nicklin and O.E. Potter,
Co-Chairmen

Originally L.S. Leung and O.E. Potter were co-chairmen. L.S. Leung died in January 1990 after almost a year's illness, and a memorial note is appended. D.J. Nicklin took over Leung's role.

IN MEMORIAM

LEUNG LEUNG (MING) SUN

B.Sc., Ph.D., F.I.Chem.E., F.I.E.Aust, F.T.S.

Professor Leung was born in Hong Kong on 15th August 1936 and was initially named Leung Ming Sun.

His early education was in Hong Kong. He studied Chemical Engineering at Imperial College, London. He was top graduate in 1958 being awarded the Hinchley Medal. Commencing Ph.D. studies with Peter Danckwerts, he moved to Cambridge when Danckwerts took the Chair there, but responsibility for his supervision was transferred to David Harrison.

Professor Leung's project was simplicity itself. Release two bubbles into an incipiently fluidized bed at times such that bubbles always coalesced, or times such that bubbles never coalesced and reach conclusions about coalescence of bubbles in fluidized beds.

He spent a year or so at Esso's Milford Haven Refinery and three years as Production Manager of the Malay Acid Works (Kuala Lumpur). His first academic post was at the University of Malaya where he taught for one year. He moved to Queensland University in 1967, and was appointed to a personal chair in 1980. He received the Chemeca Medal in 1988. He was elected a Fellow of the Australian Academy of Technological Sciences and Engineering in the same year.

In about 1972 one of us (OEP) was asked to prepare a Fluidizational edition for "Powder Technology". Among the papers elicited was one from John Matsen which I forwarded to Professor Leung for review. His story was that he immediately went to the Ampol Refinery in Brisbane to find out what a stand-pipe was. The rest of the story you know very well.

In 1986, aged 50, he accepted the challenge of leading, as its Chief, the Division of Fossil Fuels of our (Australian) government research organisation CSIRO. His winning style was showing through in 1987 and 1988 but time was running out.

He had made preparations to attention Fluidization VI in Banff, Canada and also to take a holiday in North America with his wife Theresa. He was particularly concerned to have Fluidization VII in Australia. In the event cancer intervened and gave him little respite until his death on January 2nd of 1991. His death was a great loss to Australia and to his many friends both in Australia and throughout the world.

He was a man of many talents in research, teaching and administration where he was supported by his good humour, his charm and his great ability to interact with others.

Ming leaves a wife Theresa whom he married in Cambridge in 1959 and three children - Kam, Ann and Ming. To them we extend our sympathy.

<div align="right">D.J. Nicklin and O.E. Potter</div>

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FLUIDIZED COMBUSTION OF SOLIDS
GASES AND MIXTURES THEREOF

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ABSTRACT

Mechanisms governing combustion of carbon in air-fluidized inert particles at 700° C to 950° C are reviewed. The resulting theory predicts the frequency response of a large pressurised combustor.

With propane in the air supply – to simulate coal volatiles – the carbon may burn faster as bed temperature is decreased, a surprising result.

This lecture marks 25 years of research on fluidized combustion related to burning coal. It began in a way which would be approved by today's generation of bureaucrats who seek to direct our activities towards meaningful objectives. In 1967 the British National Coal Board organised a meeting to promote research in what was then seen as an economical and environmentally friendly way of burning coal. The outcome was programmes of research, some of the findings of which are here reported. What has been their influence on the practical development of fluidized combustion it is not for me to say. Like the research, the industrial development of fluidized coal combustion has been modest, although there are now quite a lot of medium-sized units in factories and a few large demonstration pressurised units for electricity production. What is the future of the process is unpredictable. The fortunes of coal have gone up and down over the last 25 years, inversely with the price of oil. The recent dubious predictions of global warming have reduced the popularity of coal.

FLUIDIZED BED COAL COMBUSTOR: OPERATING CONDITIONS

Figure 1 depicts the conditions in a bubbling fluidized coal combustor. A bed of inert particles, typically sand, is fluidized by air, much of it passing through as bubbles which cause violent agitation of the particles. The bed temperature is 800 to 950° C and the violent agitation of the particles causes rapid heat transfer to immersed tubes not shown in Figure 1: within the tubes there is boiling water to remove the heat of combustion. Coal is fed continuously, either blown in at the bottom or spread over the top surface of the bed. The carbon inventory is usually quite small: typically 0.5% of the particles will be carbon and the question arises, why is the carbon inventory so small? The answer is not straightforward but is helpful in showing the factors that govern the operation of a

bubbling fluidized bed combustor. It is helpful to delineate the steps of a designer working from first principles, as follows.

(1) The primary bed particles are often 0.5 to 1 mm diameter. Smaller particles would be subject to elutriation. Larger particles would give a low heat transfer coefficient to the immersed tubes and hence too much of the bed would be occupied by heat transfer surface: many experiments (1) show that the heat transfer coefficient falls off as particle diameter increases, due to the gas film between the particles and the immersed surface: this film thickness is roughly proportional to particle diameter which must therefore not be too large.

(2) Given that the primary bed particles are about 1mm diameter, simple calculations show that for an air-fluidized bed at 900° C, the free-falling velocity U_t of a sand particle is about 9 m/s for air at 1 bara and about 4 m/s for air at 10 bara. Allowing for the fact that there must be a range of particle sizes and that for these relatively large particles U_t is of order $10U_{mf}$, where U_{mf} is the incipient fluidizing velocity, then the fluidizing velocity of the operating bed has to be about 1 m/s. This gives vigorous fluidization, $U > U_{mf}$, but minimal elutriation, $U < U_t$.

(3) The choice of fluidizing velocity, about 1 m/s, determines the bed heat release. Coal is comprised of carbon and hydrogen whose calorific values are widely different: about 34 MJ/kg for carbon; about 120 MJ/kg for hydrogen (net). For stoichiometric combustion, the heat released per kg of oxygen is similar for the two elements, about 13 MJ when the fuel is carbon and about 15 MJ when the fuel is hydrogen. Hence the heat release per kg of oxygen is almost independent of the fuel. Taking a value of 13 MJ/kg oxygen, then for a bed fluidized by air at a superficial velocity of 1 m/s (1 bar, 900° C), the heat release per square metre of bed is about 0.8 MW; the corresponding figure for a bed at 10 bar is 8 MW on account of the fact that the high pressure bed receives 10 times as much air per m^2 of grate.

(4) The carbon inventory is controlled by the carbon burn-out time. Under representative conditions, see below, the burn-out time for a 1 mm carbon particle is about 200 sec. The above-mentioned air velocity of 1m/s corresponds, at 1 bar pressure, to an oxygen input of about 0.07 kg/m^2s, so that during the burn-out time, 200 sec, the carbon input per m^2 grate must be 0.07 x 200 x 12/32, *i.e.* about 5 kg/m^2. Since the carbon residence time is 200 sec or less, an upper limit to the carbon inventory per m^2 grate is 5 kg. With a bed depth of 1 metre, typical for a large bubbling bed, the inventory of inert material *e.g.* sand will be around 1000kg, so the carbon inventory cannot be more than about 0.5%. With a pressurised unit, the corresponding figure is 5%.

As will be shown below, the carbon inventory is important in considering the unsteady state response and therefore the bed control because the carbon in the bed represents a reservoir of energy. The carbon inventory is of obvious relevance to elutriation.

The above calculations also show the central importance of carbon burn-out time in determining bed behaviour. For this reason and because of its intrinsic interest, the carbon burn-out time has been the subject of much research.

BURN-OUT TIME OF CARBON PARTICLES

The burn-out time of the batch of carbon added to the air-fluidized bed can be measured in several ways as follows.

(1) Early experiments (2) were done by visual observation. The carbon particles in the bed of inerts are red-hot and burn-out can be measured by observing when the bright specks disappear at the surface of the bed. The burn-out is measured with a stop watch.

(2) A subsequent development (3) was to observe the CO_2 concentration in the off-gas. Burn-out was assumed to occur when either (a) the CO_2 concentration fell to zero or (b) when integration of the CO_2-time relation showed that 95% of the injected carbon had burned (4).

(3) Where burn-out of carbon was measured in the presence of a combustible gas, *e.g.* propane (5), neither method (1) nor method (2) will work. Measurement of bed temperature, T_b, was used. The heat generated by the burning carbon causes a rise in bed temperature, but as the carbon burns out the relation between bed temperature and time t reverts to a cooling curve. Figure 2 shows a typical T_b-t relation, with its second derivative. The point of reversion to the cooling curve is the instant of burn-out, assumed (5) to be when $d^2T_b/dt^2 = 0$; arguably it would be better to take the slightly later time when a higher derivative of T_b is zero.

Factors affecting burn-out time

The theoretical equation (3) to predict burn-out time τ for a batch of mass m, containing mono-sized carbon particles of diameter d_i and solid density ρ_p, is

$$\tau = \frac{\rho_p d_i}{24 k_s c_o} + \frac{\rho_p d_i^2}{48 Sh\, D_g\, c_o} + \frac{m}{12 c_o A[U - (U - U_{mf})\, e^{-x}]} \quad (1)$$

$$\underbrace{}_{\begin{array}{c}\text{Chemical}\\\text{kinetics}\end{array}} \qquad \underbrace{}_{\begin{array}{c}\text{Local}\\\text{diffusion}\end{array}} \qquad \underbrace{}_{\begin{array}{c}\text{Bubbles to particulate}\\\text{phase and stoichiometry}\end{array}}$$

Here k_s is the reaction rate constant between carbon and oxygen, c_o is the inlet gas phase oxygen concentration; Sh is the Sherwood number $= k_g d/D_g$ where k_g = particle mass transfer coefficient, d = carbon particle diameter, D_g = gas phase diffusion coefficient. U = superficial gas velocity at bed temperature, $U = U_{mf}$ at incipient fluidization, A = bed cross-section and X = interphase transfer factor. The three terms on the right-hand side of the Eq. (1) represent the factors controlling combustion, as follows.

(i) Chemical rate. For bed temperatures up to at least 900° C, the rate of combustion of carbon to CO at the carbon surface appears to be rate controlling (3): the CO evolved appears to burn close to the carbon surface, forming CO_2 in the presence of excess oxygen and such excess is usually available during burn-out experiments. In earlier work (2) it was assumed that the reduction of CO_2 by carbon was a significant factor. But Patel (6), who reacted pure CO_2 with carbon in a fluidized bed, found that the reaction is slow at temperatures up to 1400° C, see Figure 3: this shows that even at 1400° C the reaction of CO_2 with carbon is partly controlled by chemical rate and partly by diffusion. Therefore at 1000° C and below, as expected in a fluidized combustor, the rate of reaction of CO_2 with carbon should be negligible. This leads to the concentration profiles round the carbon particle postulated (3) in Figure 4. Note the finite concentration of CO_2 adjacent to the particle surface, consistent with the above-mentioned finding that, at the relevant temperature, CO_2 reacts only slowly with carbon. The finite concentration of oxygen adjacent to the particle is consistent with the hypothesis that the rate controlling step is the carbon/oxygen reaction adjacent to the carbon surface of rate constant k_s. The CO generated by this reaction diffuses away from the surface, reacting with incoming oxygen: the large amount of heat generated by this combustion reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$ is generated near the surface of the carbon and contributes to the burning particle heat balance in an equivocal way, see below.

(ii) <u>Local mass transfer around the burning particle</u>. Although the particles in the bubbling bed are violently agitated, the interstitial flow of gas around an individual particle, such as a burning carbon particle, is tranquil. It is easy to show that the local Reynolds number, based on gas density and viscosity, incipient fluidizing velocity and particle diameter, is of order 10. Consequently the particle Sherwood number Sh, which appears in Eq. (1), is of order 2 to 4, not much different from the value of 2 appropriate for a particle in stagnant gas. Indeed the Sherwood number could be less than 2 for a burning particle, because the inert (sand) particles, surrounding the burning particle, reduce the gas volume available for diffusion. Comparing the first and second terms in Eq. (1), the first gives a burn-out time proportional to initial particle diameter d_i whereas the second term gives $\tau \propto d_i^2$; the latter result arises because the Sherwood number is constant, so the local mass transfer coefficient k_g is inversely proportional to particle diameter. This implies that as the particle burns down, chemical reaction will control combustion rate, see below. The effect of pressure P is also of interest: c_o the oxygen concentration is proportional to P but the gas phase diffusion coefficient D_g is inversely proportional to P, so $D_g c_o$ should be independent of P. The chemical rate term in Eq. (1) by contrast is proportional to 1/P because $c_o \propto P$. It follows that as P is increased the chemical rate term becomes faster and at high pressure, combustion should be controlled by the diffusion term which is independent of pressure. This will be discussed below.

(iii) <u>Bubble to particulate phase transfer of oxygen</u>. The last term in Eq. (1) represents diffusion resistance governing mass-transfer of oxygen from the bubble phase to the particulate phase. The interphase transfer term also represents a stoichiometric factor: even if $X \rightarrow \infty$, the burn-out time increases with m because a larger carbon charge implies that more oxygen is needed for combustion.

EXPERIMENTAL RESULTS FOR BURN-OUT TIME

Single particle burn-out time

Figure 5 shows typical results from carbon burn-out time experiments: τ is plotted against carbon charge m; the relation is linear, with a finite intercept at m = 0. This finite intercept has been called the 'single particle burn-out time' τ_s (7): τ_s is the burn-out time for a single carbon particle placed in the bed; assuming m = 0 in the experiment (an assumption which is not quite valid for a large carbon particle), the interphase transfer term is negligible and combustion of the single particle is governed by (a) chemical kinetics and or (b) local diffusion near the particle, the first two terms on the right-hand side of Eq. (1). The relative importance of (a) and (b) depends upon the bed temperature and the nature of the carbon. Campbell (7) plotted τ_s against d_i^2: if there was diffusion control, τ_s would be proportional to d_i^2; in fact the relation is, from Eq. (1), of the form $\tau_s = Bd_i + Ed_i^2$, B and E are constants for given conditions of bed temperature and carbon. Figure 6 shows that this theoretical relation fits the data quite well: evidently chemical rate is the controlling step for small particles. The longer burn-out times for coke as compared with char must be because the latter particles were more reactive.

<u>Effect of pressure</u>. Figure 5 shows the effect of pressure on burn-out time, quite small for coke, Figure 5(a), but very substantial for char derived from a high volatile coal, Illinois no. 5, Figure 5(b). As noted above, increased pressure increases the chemical rate, whereas the mass transfer term is independent of pressure. For the Illinois no. 5 char, chemical rate is evidently important at atmospheric pressure, but at 12 bar and above, the combustion is controlled by mass transfer. Note that the data in Figure 5(b) were for a lower temperature, 850° C, conducive to chemical rate control, as compared