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Experimental reactor development for a gas evolving catalytic decomposition reaction

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Abstract

Previous work on the catalytic decomposition of sodium hypochlorite streams has focussed on high levels of destruction (typically >99.99%), with exit concentrations typically in the 1–50 ppm range. This design requires low space velocities and minimisation of forward mixing, and a multi-bed downflow reactor has been successfully utilised in industry. This paper reports on the development of an alternate reactor for lower conversion levels—in the order of 90%. At the space velocities required to achieve this economically, the downflow bed becomes infeasible due to classic hydraulic limitations. The scenario hare differs from those reported in the literature for upflow packed bubble columns; the gas is evolved through the height of the reactor, and the gas flux therefore varies over the height of the catalyst bed, with implications for gas phase hold-up. The gas phase hold-up is expected to exert considerable influence on reactor performance as the gas will occupy space thereby reducing the residence time of the liquid phase and by blinding the catalyst surface.

The study was based on experimental work in the laboratory, and later on a 0.2 m diameter pilot. In analysing the data, kinetic effects were accounted by the use of intrinsic rate constants from previous work. This allowed decoupling of the kinetic effects from the hydrodynamic effects. The results indicated a strong dependence of the apparent catalyst performance on the liquid and gas superficial velocities, which have been observed in the literature to be the key variables affecting gas phase hold-up in packed bubble columns. The performance data measured on the pilot unit mapped well onto the laboratory data, indicating the process scales simply.

Keywords: Hypochlorite decomposition; Multiphase reactor; Packed bubble column

1. Introduction

In the chlorine manufacturing and chlorine using industry sectors, vent and purge streams containing gaseous chlorine have to processed to avoid the emission of chlorine gas. These streams can be relatively time independent in the case of purge streams, or unsteady state in the case of blowdown and pressure relief incidents. This chlorine containment is commonly achieved through scrubbing with an alkaline solution, normally sodium hydroxide at concentrations up to 20 wt.%. This process, however, results in the generation of sodium hypochlorite stream of up to 15 wt.%. While hypochlorite in pure solutions is an industrially and commercially useful product, notably in water treatment and disinfection, incidental production exceeds demand.

If discharged as a waste stream, it can act as a powerful biotoxin due to its high oxidation potential, can form chlorinated organics when mixed with other

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Nomenclature

a_S	specific surface of packed bed ($m^2\,m^{-3}$)
C_{in}	feed hypochlorite concentration (wt.%)
C_{out}	feed hypochlorite concentration (wt.%)
d_S	hydraulic diameter of solid particles (m)
k_0, k_1, k_2	constants in Eq. (2)
k'	first-order reaction rate constant (h^{-1})
k'_a	apparent first-order rate constant (h^{-1})
LHSV	liquid hourly space velocity (h^{-1})
U_G	gas superficial velocity ($m\,h^{-1}$)
U_L	liquid superficial velocity ($m\,h^{-1}$)
V	reactor volume (m^3)
V_{slip}	bubble slip velocity ($m\,s^{-1}$)
[ ]	concentration of species ($mol\,l^{-1}$)

Greek symbols

ε	fractional voidage of catalyst bed
ϕ	fractional gas hold-up

streams and can release chlorine if the stream becomes acidic. There is thus a need to treat these waste hypochlorite streams.

The abatement of chlorine vents and the subsequent destruction of the resulting sodium hypochlorite has been the subject of many studies. There are a variety of approaches to the destruction of waste hypochlorite, including chemical dosing and homogeneous catalysis as well as heterogeneous catalytic processes using either a slurry and a fixed bed. This paper will focus on reactor development work for a fixed bed heterogeneously catalysed abatement process.

2. Commercial process: chemistry and design

$$2NaOCl_{(aq)} \overset{\text{catalyst}}{\rightarrow} 2NaCl_{(aq)} + O_{2(g)} \qquad (1)$$

The catalytic decomposition of sodium hypochlorite proceeds through reaction (1) in aqueous solution over the heterogeneous catalyst, resulting in the production of gaseous oxygen. A 10 wt.% solution of hypochlorite produces some 30 times its volume of gaseous oxygen during decomposition. The generation of significant gas volumes during the solid–liquid reaction has a major influence on the design and operation of the reactor.

The reaction is strongly exothermic, with a heat of reaction $\Delta H = -59.97\,kJ\,mol^{-1}$, which is equivalent to an adiabatic temperature rise of 1.9–2.5 °C (wt.%)$^{-1}$ sodium hypochlorite in the feed solution.

The catalyst used in this process is iron promoted nickel oxide on a calcium aluminate support [1] manufactured as an extrudate of 3 mm diameter and 3–5 mm length. Because of the highly oxidised state of the nickel, the catalyst is resistant to classic poisons and extended lifetimes have been observed in industrial installations. The global mechanism for the reaction involves the adsorption of the hypochlorite ion onto the nickel oxide, and its decomposition to form a high oxidation state nickel intermediate, probably Ni(IV), with the release of the chloride ion. This Ni(IV) peroxide reduces back, promoted by the iron, to the Ni(II) oxide forming diatomic gaseous oxygen.

2.1. Design for total destruction

The previously published process design [2] was for total destruction of the hypochlorite; down to levels of less than 10 ppm from a feed concentration of 1–10 wt.%. This entails conversions of 99.99% or greater and corresponds to design space velocities in the order of 0.2–1 h^{-1}. For this duty a multi-bed design, to minimise axial mixing effects was developed. Laboratory data, working with extrudates, indicated superior performance of downflow over upflow. This was attributed to the minimisation of forward mixing. The explanation is that forward mixing is promoted by the wakes of the rising bubbles in upflow. This becomes of critical importance when, as noted above, conversions of >99.99% are sought. Under these circumstances even minor forward mixing and bypassing can be critical. The design is documented elsewhere [2], but briefly comprises a series of downflow beds with hydraulic gravity flow between them, controlled by a series of fixed baffles (Fig. 1).

Reactors based on the multi-bed downflow design have been successfully installed and operated at over 20 sites world-wide, all achieving their design exit hypochlorite specification. Units have now been operating for over 6 years and a catalyst life has been demonstrated of 5 years. The success of this

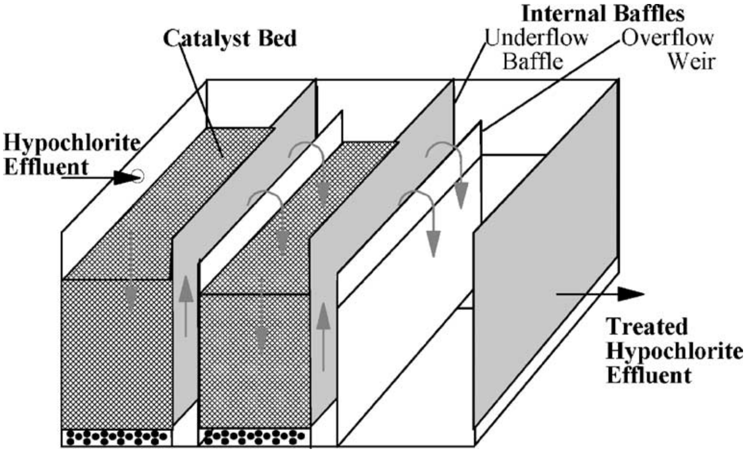

Fig. 1. Multiple downflow bed design for total hypochlorite destruction.

technology, named HYDECAT™, has recently been recognised by a Queen's Award for Environmental Achievement and HYDECAT™ has also has been granted Millennium Product status by the UK Design Council.

2.2. Reaction and reactor modelling

The intrinsic kinetics were described using a Langmuir–Hinschelwood-type expression:

$$V\frac{\mathrm{d[NaOCl]}}{\mathrm{d}x}=\frac{k_0\mathrm{[NaOCl]}}{1+k_1\mathrm{[NaOCl]}+k_2\mathrm{[NaOH]}} \tag{2}$$

The fitting parameters (k_0, k_1, k_2) are all expressed as an Arrhenius-type function of temperature. Sodium hydroxide acts as an inhibitor for the reaction, due to competitive adsorption on the active sites of the hydroxide and hypochlorite ions. At low hydroxide concentrations simple first-order kinetics may be used.

The hydrodynamics were modelled simplistically using an average hold-up and slip velocity type approach:

$$V_{\mathrm{slip}}=\frac{U_{\mathrm{G}}}{\varepsilon\phi}+\frac{U_{\mathrm{L}}}{\varepsilon(1-\phi)}=U_0(1-\phi) \tag{3}$$

where a value for V_{slip} was estimated from experimental observations. For design and rating calculation purposes, the calculated gas hold-up was simply treated as a dead volume and the effective catalyst volume for rate calculations proportionately decreased.

This approach has proved adequate for predicting the performance of the multiple bed downflow reactors. The complication, and a critical difference between this and a bubble column, is that the gas bubbles are formed in situ. The gas flux, and thus gas hold-up, will vary over the bed height. For the downflow beds, a simplified linear gas hold-up profile was inherent in the design models, with no apparent penalty in design accuracy. This is partly because the gas hold-up in all but the first bed is negligible.

While clearly not strictly correct in terms of the observation of churn turbulent bubbles and a bimodal size distribution, discussed further below, the superficial velocities to be used in commercial units were not significantly different from those used at the pilot scale to observe the hydrodynamics and this approach was successful in providing guaranteed performance of installed downflow reactors.

3. Design for partial destruction

Following a number of customer enquiries, it became clear that there was market and technical potential in a version of HYDECAT™ that gave only partial destruction of the hypochlorite: say 90% rather than >99.9%. These cases arise where the operator already has chemical dosing destruction systems installed, but

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™HYDECAT is a trademark of the Johnson Matthey Group of Companies.

where the use of a catalytic reactor for the initial duty would offer significant decrease in operating costs and thus payback on the investment capital. Process design aspects of such applications are presented elsewhere [3].

Preliminary design work, indicated that the space velocities were likely to be 1–2 orders of magnitude greater than those previously encountered; 10–100 rather than 0.2–2 h^{-1}. Further work, using the kinetic and hydraulic model above, indicated that at these space velocities, and at realistic bed aspect ratios, severe hydraulic restrictions would be encountered. Specifically, flooding was predicted, where the volume of gas produced would be such that the liquid would not be able to freely flow downwards. As a consequence, it was necessary to study specifically the reaction and hydraulic behaviour of beds in upflow.

4. Two-phase upflow in packed beds

Of particular interest in the present context are previously unpublished observations regarding bubble dynamics and modelling in the downflow beds. The bubbles were observed qualitatively to be in a bimodal size distribution with very few mobile bubbles observed at intermediate sizes. Very small bubbles, significantly less than 1 mm diameter were assumed to be the natural size expelled from the catalyst pores while the larger bubble size, several mm, appeared to be set by the interstitial voids of the packed bed. The bubble growth appeared to be stationary with a coalescing bubble being held within a given void space until it grew to sufficient size that its buoyancy forced it to rise. Once in motion these large bubbles were observed to rise at a rapid rate (2 cm s^{-1} or greater) despite the hindrance effect of the tortuous path set by the random packed catalyst pellets.

When converting to upflow, essentially the same phenomenon was observed: a strict bimodal bubble size distribution, and in fact qualitative observation indicated that the actual bubble sizes were remarkably similar. The important conclusion here is that the majority of the gas hold-up is present in the form of large bubbles, whose rise velocity is significantly hindered by the column packing. These larger bubbles are clearly in an equivalent of churn turbulence, and deformation of the bubbles was clearly evident.

For the upflow bed development it was initially hoped to derive or obtain a more theoretically sound model than the simple slip velocity relationship of Eq. (3). The expectation was that overall gas hold-up would be higher and thus more critical to reactor design. The time constraints of the development project dictated that unless suitable models were identified in the literature then a simple approach would have to be maintained.

Much of the published work on co-current upflow in bubble columns is focused on empty columns and is thus not relevant to the present study. The key difference between a packed and an empty bubble column is that in the former the bubble coalescence break-up process is dominated by the packing [4]. There are equally many studies on two-phase downflow through packed columns, but relating to trickle flow, which again is not relevant. There are only a limited number of studies reporting work on upward bubbly flow through a packed bed.

In an early paper [5], flow observations plus hold-up and pressure drop measurements are presented. The study uses gas and liquid velocities greater than those in this study. A correlation for liquid phase fraction is proposed:

$$\phi_L = -0.035 + 0.182\left(\frac{U_L}{U_G}\right)^{0.24} \tag{4}$$

The reliance on power law relationships is a retained in later work [6]:

$$\phi_L = 1.47\,Re_G^{0.11}\,Re_L^{-0.19}(a_S d_S)^{-0.41} \tag{5}$$

Two more recent studies [7,8] specifically measure hold-up and interfacial area using chemical techniques. In the latter, Van Gelder and Westerterp [8] also resolve their data using power law type expressions, with the phase superficial velocities as prime independent variables, noting that correlations based on the superficial velocity yield the best results. This paper proposes expressions for the liquid phase fraction of the form:

$$\phi_L = 0.341\frac{U_L^{0.583}}{U_G^{-0.199}} \tag{6a}$$

$$\phi_L = 0.354 + 0.143U_L^{0.405} - 0.206\left(\frac{U_G}{U_L}\right)^{0.125} \tag{6b}$$

where Eq. (6a) has the beauty of simplicity but Eq. (6b) give better confidence intervals. The above implies that understanding is still largely qualitative and correlations are primarily empirical. The equations are not directly applicable due to the basic difference that in HYDECAT^{TM} gas evolution occurs through the bed, and thus the gas superficial and linear velocity will vary through the bed and a more fundamental understanding is required to obtain a predictive model that could be used for design with confidence.

A further complication lies in axial mixing. The influence of axial mixing on downflow design has already been noted. It is well established that axial mixing is more severe in upflow than downflow [9]. Iliuta et al. [9,10] show that axial mixing is promoted by the gas flow and ameliorated at higher liquid rates. They note, however, that this observation, especially with regards to the gas flow, is not consistent with all of the literature. More recently, Belfares et al. [11] have reassessed the data available in the literature and provide support for the general observations of Iliuta et al. regarding the influence of gas and liquid velocities. They note also, however, that the effects of liquid properties (viz. temperature in the present study) and bed characteristics are not yet quantifiable.

As a consequence of the above, it was decided to focus on an experimental development programme, with modelling used primarily as a means to correlate results, with little expectation that it would provide a meaningful representation of the physical system. This naturally implies that experiments needed to be carried out under hydrodynamic conditions that would mimic the future industrial units. Learning from the above literature as well as that pertaining to trickle beds and bubble columns implies that the hydrodynamics are dependent on the superficial or mass velocities whereas the catalysis is a function of space velocity.

5. Laboratory studies

A laboratory programme was commenced to examine the bubble behaviour and to identify the design conditions at which a move from the previously favoured downflow bed to upflow would be required. Experiments confirmed that key values were the liquid velocity and the feed hypochlorite concentration (effectively the gas to liquid ratio).

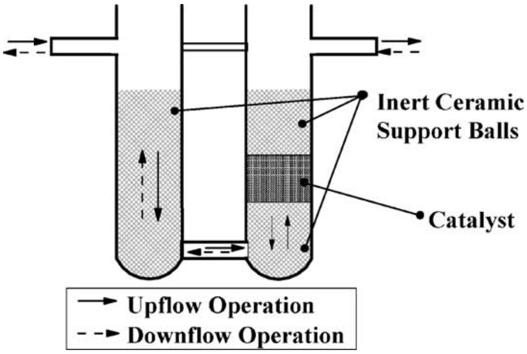


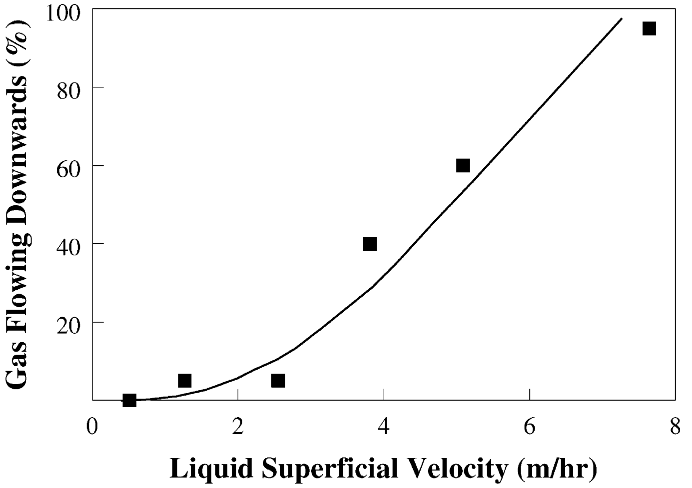
Fig. 2. Experimental reactor configuration.

Three sizes of double tube high flow reactor were used for testing in upflow and downflow (see Fig. 2). The catalyst for these experiments was a smaller version of the commercially available catalyst with 1.6 mm diameter and 2–4 mm length. The catalysts were tested using LHSVs ranging from 5 to 150 h^{-1}. The size of the reactors was varied also. The diameters and catalyst volumes are given in Table 1.

The liquid superficial velocities were thus in the range 0.15–7.6 $m\,h^{-1}$. Sodium hypochlorite concentrations of 0.5, 2, 5 and 10 wt.% and temperatures of 30, 40, 60 and 80 °C were used. The sodium hydroxide concentration was 0.2 wt.%. The measurement of sodium hypochlorite concentrations was performed using a Mettler DL21 auto-titrator and Unicam 8700 UV-Vis spectrophotometer. In addition to monitoring exit concentration, observations were made of the distribution of the gas bubbles between the liquid inlet and outlet. This is a primary indication of entrainment and was used in the first instance to define velocities at which downflow becomes untenable.

Table 1
Experimental reactor dimensions

Reactor internal diameter (mm)	Catalyst volume (ml)
22	25
35	40
50	60 and 80



Reactor Dia. = 25 mm, Temp = 80 C, [NaOCl] in = 2 wt.%, [NaOH] = 0.2 wt.%

Fig. 3. Bubble entrainment in downflow.

6. Results and discussion

6.1. Entrainment observations

Fig. 3 shows the percentage of bubbles in the bottom leg of the reactor in downflow. At superficial velocities of above about 0.2–0.5 m h^{-1} (and these values are confirmed by other data) entrainment of the bubbles by liquid downflow starts to become significant. As the superficial velocity increases further, entrainment increases also in almost monotonic fashion. At these higher velocities the flow became unstable, with evidence of pulsing. This pulsing appeared to be originate both within the catalyst bed and due to gas-locking of the exit tube. Overall reactor performance also deteriorated (as shown below) and at these higher space and superficial velocities, downflow is demonstrably not the correct approach.

6.2. Comparative performance: upflow versus downflow

Fig. 4 shows the percentage hypochlorite conversion as a function of liquid superficial velocity. At all superficial (and also space) velocities used in this study, the upflow arrangement gives better performance.

6.3. Apparent rate constant

Given that the reaction is first order in hypochlorite and that temperature and caustic concentration are all constant, then the reactor design equation can be used in its simplified form. To a first approximation:

$$\ln\left(\frac{C_{\mathrm{in}}}{C_{\mathrm{out}}}\right) = \frac{k'}{\mathrm{LHSV}} \tag{7a}$$

Or rearranging:

$$k' = \ln\left(\frac{C_{\mathrm{in}}}{C_{\mathrm{out}}}\right)\mathrm{LHSV} \tag{7b}$$

where k' is a pseudo-first-order rate constant. It must be remembered that a measured value of k' calculated from Eq. (5) using the raw experimental data will be an apparent rather than intrinsic value. It will include inherently the effects of gas hold-up and axial mixing and will be denoted by k'_{a}. A plot of k'_{a} against superficial velocity (Fig. 5) should therefore give a measure of the apparent activity loss (or dead volume) due to gas hold-up and axial mixing. Unfortunately, the scatter appears considerable. It is, however, apparent that the upflow reactor performs better at all duties. The apparent activity appears to be approximately double that achieved in the downflow configuration. This tends to infer that axial mixing

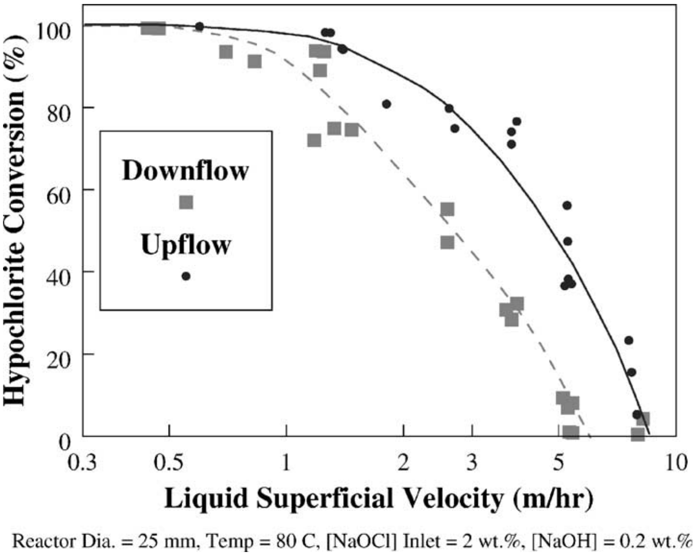


Fig. 4. Comparison of upflow and downflow reactors: effect of feed rate on conversion.

is not a primary effect. If axial mixing were a significant factor then superior performance would be expected from the downflow reactor. As expected, the apparent activity loss increases with increasing space velocity. This does not necessarily indicate a direct dependence on superficial velocity as the average gas to liquid flow ratio will vary with conversion.

The critical issues in designing a fixed bed reactor for a gas evolving reaction are: firstly to minimise the fractional gas hold-up since this contributes simply to dead reactor volume and an effective decrease in

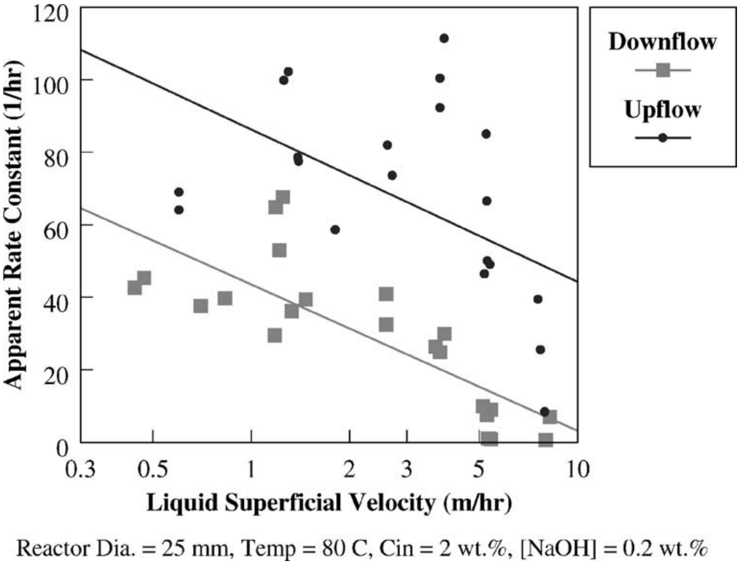


Fig. 5. Comparison of upflow and downflow reactors: apparent rate constant.

the real space time and, secondly, to ensure that, for simplicity of process design, all the gas leaves in a single stream. At the higher superficial velocities the optimum solution becomes upflow.

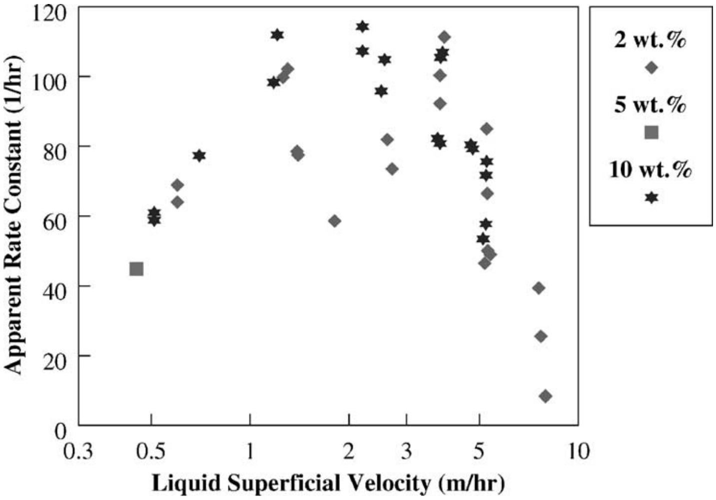
It is not immediately clear whether the apparent scatter on the upflow data is indeed scatter; or a trend. For the downflow case, significant scatter had been noted in previous high space velocity experiments and had been attributed to variations in gas hold-up. Operating with small catalyst bed volumes, single bubbles represent a significant proportion of total gas hold-up and large bubbles had been observed to rest in a same location for significant time periods before dislodging and rising from the bed. This clearly introduces a measure of randomness into the data. For upflow, however, there is a constant kinetic force on the bubble as well as the buoyancy and the distribution of large bubble residence times was expected to be tighter. Thus, while for downflow the scatter is believed to be an experimental artefact, for the upflow case it is more likely to be a direct result of the reaction conditions. When data measured under the same conditions, but with different feed concentrations of NaOCl are plotted then it becomes apparent that there is in fact a maximum (Fig. 6). Note that in this graph, and in later plots, data measured on all three different sizes of laboratory reactor are used.

The presence of this peak in apparent rate constant becomes more apparent when the plotting parameter is temperature rather than feed concentration (Fig. 7). As above, the data are measured on all three laboratory reactors with no apparent effect of diameter or bed depth. This means that space velocity and superficial velocity are no longer inextricably linked. The superficial velocity leading to the maximum apparent rate is dependent on the temperature and becomes less pronounced at the lower temperatures.

Considering the inlet concentration as a parameter at constant temperature, Fig. 8 shows the apparent rate constant as a function again of superficial liquid velocity. The coincidence of the data indicates that liquid superficial velocity is a key parameter in minimising the effects of gas blinding, apparently more important that the variation in gas rate inherent in the differences in feed concentration.

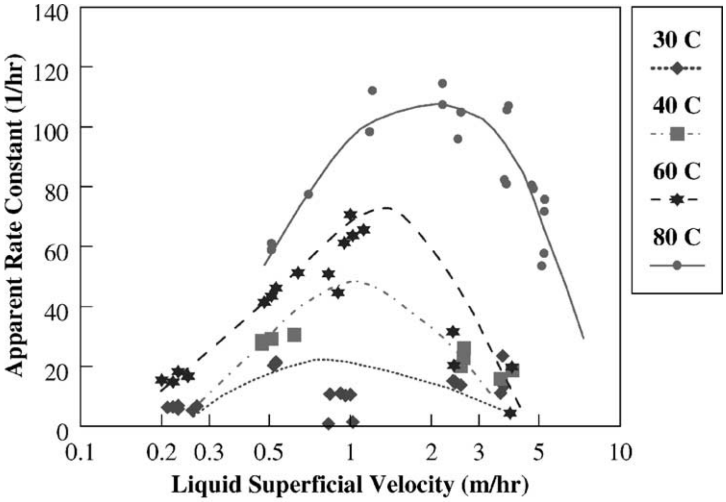
6.4. Activity suppression

In order to try and deconvolute some of the interdependencies it is necessary to normalise the data with respect to at least one variable. Given the clear temperature dependence, it is interesting to try and eradicate the effect of temperature from the data. The value of k'_a incorporates not only the effects of the true first-order rate constant (k') but also the effect of gas hold-up. A



Reactor Dia = 25, 35 & 45 mm, Temperature = 80 C, [NaOH] = 0.2 wt.%

Fig. 6. Effect of feed concentration on the performance of an upflow reactor.



Reactor Dia. = 25, 35 & 45 mm, Cin = 10 wt.%, [NaOH] = 0.2 wt.%

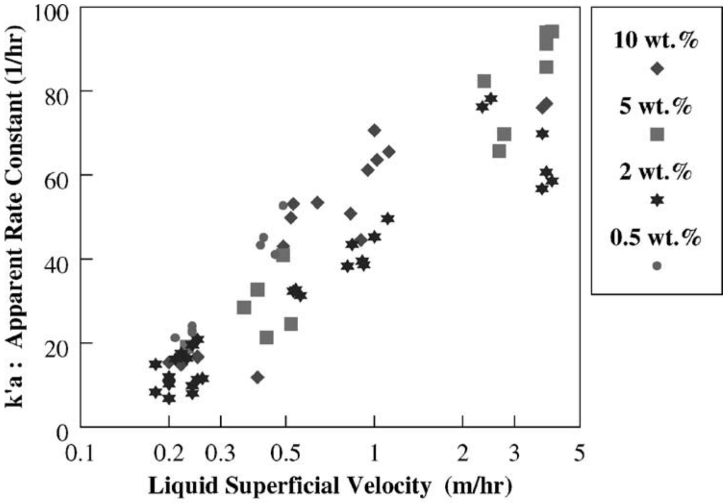
Fig. 7. Optimum superficial velocity for upflow operation.

correlation for k' was available from previous (unpublished, downflow) experiments. The ratio k'_a/k' can be evaluated and will be an activity relative to gas free operation and thus reflect directly the apparent activity suppression caused by gas hold-up and other effects. For simplicity define:

$$A_r = \frac{k'_a}{k'} \qquad (8)$$

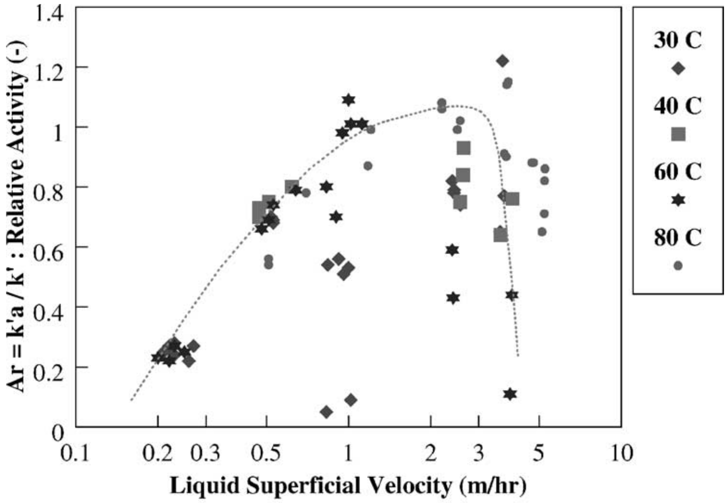
where A_r is in fact a relative activity, where low values indicate high levels of suppression and a value of one infers zero hydrodynamic inhibition. On the basis that the reactor is probably thermally well mixed, k' was calculated at the reactor exit temperature.

Figs. 9 and 10 thus show the value of k'_a/k' as a function of the liquid superficial velocity with feed temperature and feed hypochlorite concentration



Reactor Dia. = 25, 35 & 45 mm ; Temp = 60 C ; [NaOH] = 0.2 wt.%

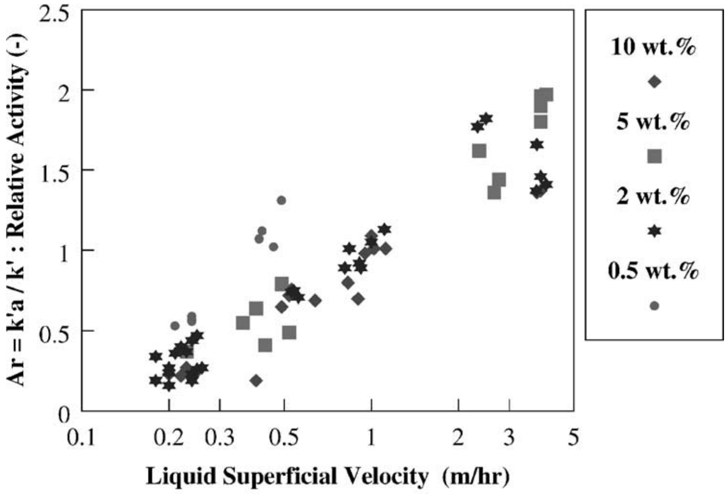
Fig. 8. Apparent rate constant: effect of liquid superficial velocity at constant feed temperature.



Reactor Dia. = 25, 35 & 45 mm, Cin = 10 wt.%, [NaOH] = 0.2 wt.%

Fig. 9. Activity suppression as a function of liquid superficial velocity (parameter: temperature).

as parameters, respectively. Unsurprisingly, Fig. 10 shows little difference from Fig. 8—the equivalent plot on the apparent rate constant. In Fig. 9, the distinct trends for each individual temperature apparent in Fig. 7 appear to have merged into a singular pattern, confirming the importance of temperature. It is interesting to note that values of A_r greater than unity are obtained; that is, an apparent rate constant greater than the previously believed "intrinsic" rate constant. From this it is clear that the values of k' do include a degree of extrinsicity. In the present context, however, there is no reason to believe that the model values of k' do not accurately reflect the effects of temperature on the kinetics.



Reactor Dia. = 25, 35 & 45 mm, Temperature = 60 C, [NaOH] = 0.2 wt.%

Fig. 10. Activity suppression as a function of liquid superficial velocity (parameter: feed concentration).

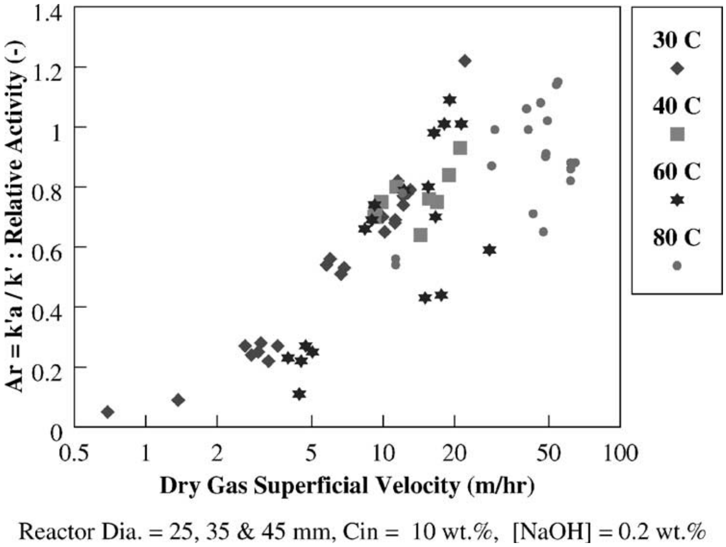


Fig. 11. Activity suppression as a function of dry gas superficial velocity (parameter: temperature).

An additional variable that would be expected to have significance is the gas rate. This, in reality, is a dependent variable, being a function of the feed concentration, apparent activity and temperature. It is possible to calculate the molar gas rate from a mass balance, and to estimate the dry gas velocity using the ideal gas law. A more accurate calculation would include the effects of water vapour but this is a second-order effect, except where the temperature approaches 100 °C.

Figs. 11 and 12 show the relative activity ($A_r = k'_a/k'$) as a function of the calculated superficial exit dry gas velocity. Fig. 11 shows that by plotting against dry gas rate, the effects of temperature are nearly normalised, with all data points lying on a similar trend line. This implies that the key effect of temperature

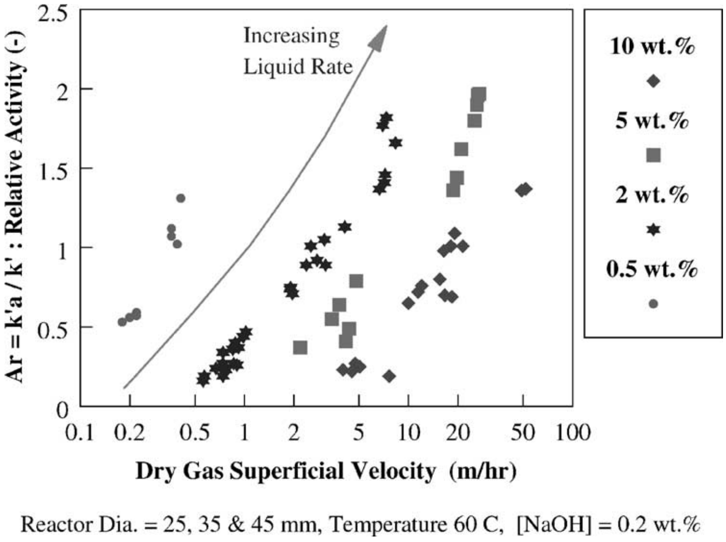


Fig. 12. Activity suppression as a function of dry gas superficial gas velocity (parameter: feed concentration).

on the apparent suppression of catalyst activity is simply its effect on the gas density and thus the gas volume for a given molar reaction or gas evolution rate. By contrast, in Fig. 12, the data for the different concentrations are clearly deconvoluted with each of the four concentrations showing its own distinct trend line. There is a clear pattern, with the relative activity decreasing with increasing concentration; that is, for a given gas rate the suppression is greater at a higher concentration. At higher concentrations more gas will be evolved deep in the bed leading to a proportionately higher hold-up. Further, at the highest rates of decomposition, temperature gradients may persist leading to local evaporation and gas blinding effects, especially at the highest temperatures.

It is also interesting to note that high gas velocity tends to lead to a value of A_r greater than one. This is of course the condition where axial mixing would be expected to be at its worst; and yet the reactor yields its least inhibited performance. This confirms that axial mixing is not a critical effect in the scale up of this reactor. In truth, it appears severely back mixed under most operating conditions.

6.5. Data correlation

The slip velocity approach that had been successful in the downflow beds (Eq. (3)) proved inadequate in modelling the upflow data. It was not possible to fit the data without introducing arbitrary parameters. Given this, a power law approach was taken, in common with approaches in the literature. Examination of the data, specifically the value of $A_r = k'_a/k'$, and in particular the plots presented above, indicated three primary variables that affect the value of A_r: the gas and liquid superficial velocities and the feed concentration. A data correlation of the form shown below was derived:

$$A_r = c_0 U_G^{c_1} U_L^{c_2} C_{in}^{-c_3} \tag{9}$$

Fig. 13 shows the parity plot for data covering a range of exit temperatures (30–100 °C), U_L (0.2–4 m h^{-1}), U_G (0.2–50 m h^{-1}) and concentrations (0.2–10 wt.%) measured over different bed diameters and volumes. The correlation is certainly not perfect, but is successful in grouping the data and is judged adequate for the present purposes of allowing approximate transposition of laboratory data to, initially the pilot unit and

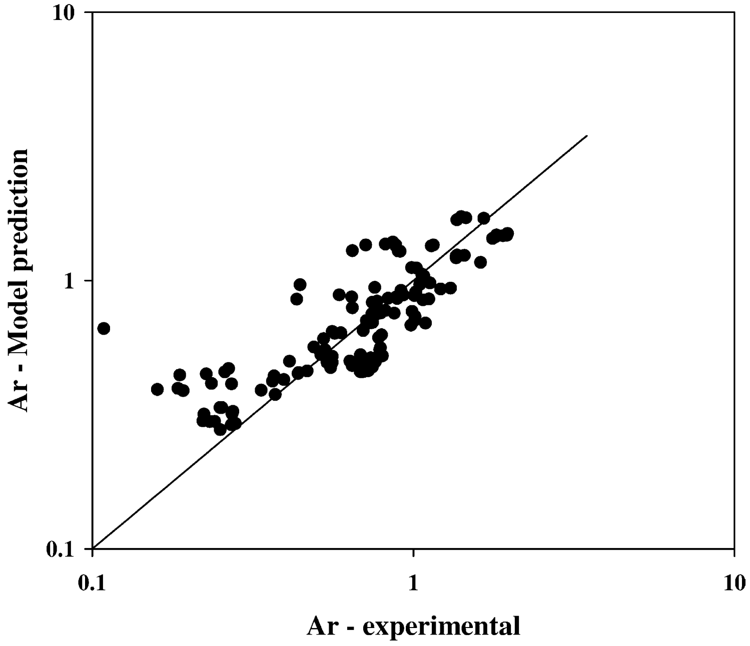


Fig. 13. Quality of fit for A_r correlation (Eq. (9)).

later to the commercial scale. Checks for improvements to the correlation were made, such as including the humidity in the gas flow. These were generally not successful in improving the fit or in reducing apparent systematic error.

7. Scale up and pilot plant studies

The laboratory study described and discussed above clearly shows that the relationship between reactor performance and the variables is complex. Some qualitative understanding has been gained on the effects of the key variables but this is not sufficient to design a commercial unit for installation on an operating plant. It was therefore decided that, in the absence of reliable modelling, pilot scale experiments would be required. The flow conditions of the plant design case were well defined and therefore a pilot unit was designed that allowed the space velocity and superficial velocities to be mimicked directly. The benefit of small catalyst pellets in this particular context, is that wall effects can be eradicated at a relatively low reactor diameter.

The experimental results and empirical modelling were used to design the reactor and experimental programme. The pilot reactor was 200 mm diameter and capable of operating with a bed depth of up to 1.5 m.

On the pilot unit, input temperature, flow rate, hypochlorite and caustic concentration were varied within appropriate ranges. The fit of the simple power law expression including gas and liquid superficial velocities and the feed concentration described above (Eqs. (6a) and (6b)) to the pilot data is shown in Fig. 14. In this case, because of the high caustic concentrations in some runs, the value of k' was calculated as the log mean pseudo-first-order rate constant value from the full Langmuir–Hinschelwood kinetic expression.

The laboratory data are also plotted in Fig. 14, as the smaller points. They demonstrate that the results measured on the 25–45 mm diameter laboratory reactors scale well to the pilot unit (200 mm diameter) and give high confidence in scaling data from the pilot unit to the planned full scale reactor (approximate diameter 2.0 m). Given this ease of data scaling, the inaccuracy of the data correlation is of lower importance, given that it is possible to mimic the design conditions of the full scale units, in terms of feed composition, gas and liquid superficial velocities and space velocity simply by installing the requisite catalyst bed depth on the pilot unit.

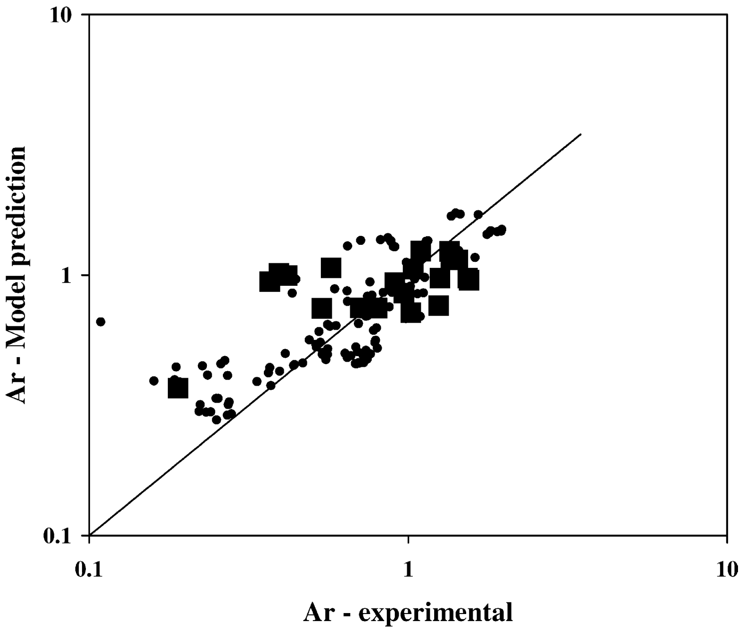


Fig. 14. Data fit plot for pilot plant results.

8. Conclusions

The optimum reactor design for catalytic fixed bed decomposition of sodium hypochlorite streams depends strongly on the degree of destruction required and the resulting space velocity, or more correctly the mass or superficial velocity as well as the gas evolution profile. The important qualitative design criterion is to minimise the fractional gas hold-up. At low space velocities with the gas evolution predominantly in the fixed bed entry region, then downflow is preferred. At higher space and superficial velocities, however, gas evolution extends deep into the bed and disengagement is maximised through an upflow design approach.

Laboratory results, measured on reactors from 25–45 mm diameter indicate a strong dependence of conversion performance on the liquid rate, the temperature and the inlet concentration. Data evaluation shows that the key design variables are in fact the liquid and gas superficial velocities and both have a significant effect on the reactor performance and apparent catalyst activity. Pilot plant experiments, with a 0.2 m diameter, indicate that the data measured in the laboratory reactors scales well, and the two data sets can be mapped onto each other. Therefore, scale up directly from the pilot unit can be used for the design of commercial units; and this has been done successfully.

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