

A STUDY OF HYDRODYNAMICS IN GAS-EVOLVING REACTIONS

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Abstract Three-phase gas-liquid-solid systems in which the gas phase is evolved from the liquid phase by reaction at the solid surface have received little prior attention despite their common occurrence in many industrial processes such as hydrometallurgical leaching or liquid-phase dehydrogenation. This study has examined the effect of reagent concentration and solid loading upon the gas evolution rate, gas-phase hold-up, and solids suspension behaviour for a model reactive system of sodium hypochlorite dissociation over porous nickel catalyst in a laboratory scale stirred vessel equipped with a Rushton Turbine impeller. Gas evolution rate was found to be directly proportional to both nickel loading and hypochlorite concentration. Gas-phase hold-up was found to positively correlate with gas evolution rate, as the gas-phase was fully dispersed at the operating conditions and impeller-driven flow dominated the bubble flow regime. Solid suspension performance was found to be affected severely by gas presence, even though the filling of the catalyst pores with evolved gas reduced the effective particle density.

Keywords: gas-liquid-solid, solid suspension, gas evolution, hold-up

1. Introduction

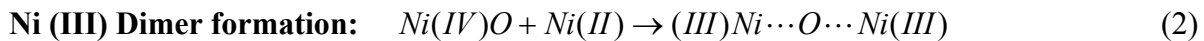
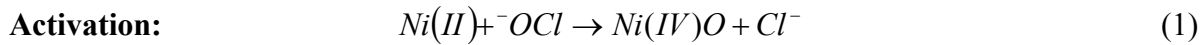
Mixing is a special feature of agitation, which has been established as very important in a vast range of chemical processes. The agitation of multi-component multiphase systems in industry is necessary to enhance mass and heat transfer between phases in systems. Typically, agitation is carried out for three distinct reasons, namely; the production of dynamic uniformity within multi-component multiphase systems, the facilitation of mass or energy transfer within a system not in equilibrium, and the promotion of phase change in multi-component systems with or without a change in composition. Mixing efficiency influences the yield and selectivity of chemical process being considered. Therefore, the design and the operation of mixing devices determine the profitability and acceptability of a given plant.

In this study the interaction between mixing and gas evolving solid-liquid (three phase) reacting systems is investigated for stirred vessels operated under turbulent flow conditions. It is still considered a niche topic, due to the little attention that has been paid to it, despite its common occurrence within the industry. In the available literature of studies on three-phase mixing, previous research has focussed exclusively on systems concerning a pseudo-continuous solid-liquid phase and a sparged/bubbled gas phase. The findings of these studies have benefited processes such as catalytic hydrogenation, wastewater treatment and fermentation. However it cannot be ignored that there is a simplified aspect to them when it comes to gas evolving solid-liquid system.

Examples of gas evolving solid-liquid (three phase) reacting processes in the industry include the leaching and oxidation of ferrous ores, which leads to the production of leach residue (solid particulate matter) and evolved gas, as well as catalytic dehydrogenation reactions such as aromatisation, whereby the six-membered hydrocarbon ring of an alicyclic compound is aromatised in the presence of hydrogenation catalysts, leading to the loss of hydrogen [1].

Gas-sparged systems present a simplification of the hydrodynamic phenomena within processes such as these. This ideal has often been further exaggerated by the use of smooth spherical objects such as glass beads, whereas in real processes the objects could be highly porous. Furthermore, this approach also disregards the influence of trapped bubbles within the solids, which makes them buoyant, hampering solid-gas as well as solid-liquid mass transfer.

This work mimics a leaching process common to many industrial hydrometallurgical processes. Sponge Nickel[®] is used as the solid phase, which catalytically dissociates the liquid phase (sodium hypochlorite), liberating oxygen in the process. The chemical reaction governing this process is given below, as described by Hancock *et al* [2].



The catalytic action on sodium hypochlorite is a simple one, which has been applied previously in the literature by various authors, the main focus of their work being exclusively on the effective abatement and destruction of effluents containing sodium hypochlorite in the chlorine and other related industries [2,3].

Sodium hypochlorite dissociation chemistry is covered in the previous literature presented by Lister *et al.* [4] and Hancock *et al* [2]. Hancock showed that the mechanism behind Ni activity, which is generally considered to involve higher oxidation states of the metal, was true. Lister investigated the catalytic activity of various transition element oxides, including Ni, Cu, Co, Fe and Mn, suggesting that the mechanism of the catalysis is through the oxidation of the metal to a higher oxide, which loses oxygen (4) and is later re-oxidised. During Ni catalytic action, the rate was shown to be proportional to the amount of Ni added with little dependence on hypochlorite concentration. It was thus presumed that since the rate is vaguely dependent on hypochlorite concentration, Ni catalytic reaction to oxygen (4) must be the slow reaction step and the rate-determining step, requiring much the same amount of hypochlorite adsorbed on the catalyst surface over a range of concentration.

Ni catalysis was also found to be a first order reaction. To satisfy this account, the entire Ni surface is required to be covered with adsorbed hypochlorite ions and this happens in concentrated as well as dilute solutions, therefore making the adsorption of hypochlorite proportional to hypochlorite concentration. If the catalyst surface is not completely covered, it is impossible to predict what the reaction kinetics would be without knowing the dependence of adsorption on concentration. They showed that Ni, at the concentrations they used, behaved as though the catalyst were essentially covered with adsorbed ions.

2. Experimental Method

2.1 Materials Characterisation

250g of Sponge Nickel[®] was obtained from Alfa Aesar and characterized to determine the particle size distribution (PSD) using a Mastersizer 2000 particle size analyzer. Diameters of 7.8, 29 and 67.4 μm were obtained for d_{10} , d_{50} and d_{90} respectively. The particles were also characterized for pore size analysis by nitrogen sorption using a Micromeritics 2020 physisorption analyser at 77K. BET surface area value of 55.3 m^2g^{-1} , pore volume of 0.99 (ads) mlg^{-1} and an average pore diameter of 86 \AA were obtained. 2 kg of 14% sodium hypochlorite was purchased from Alfa Aesar. The solution was titrated to confirm the percentage of sodium hypochlorite present within the bulk. The reagents and equipment used for titration were potassium iodide; acetic acid and a Metrohm 857 Titrando equipped with an iPt Titrode, a beaker and stirrer. Titration confirmed that 13.67% w/v sodium hypochlorite was present per unit volume of solution. The specific mass of hypochlorite in the concentrated solution was obtained as 2.231g and its concentration was determined as 0.4464g/ml. In order to minimise experimental hazards, the maximum solution strength used was diluted to 8% w/v sodium hypochlorite and further diluted volumes containing 7%, 6%, 4% and 2% (all w/v) sodium hypochlorite were also studied.

2.2 Gas evolution rate

The gas evolution rates due to the catalytic activity of Sponge Nickel[®] on the diluted volumes were initially investigated using 100ml volume of each dilute solution, subjected to five Sponge Nickel[®] concentration: 0.09, 0.08, 0.07, 0.06 and 0.05 g/cm^3 . The solutions were made-up and their densities were measured. The apparatus for measuring gas evolution rate is shown in Fig 1.

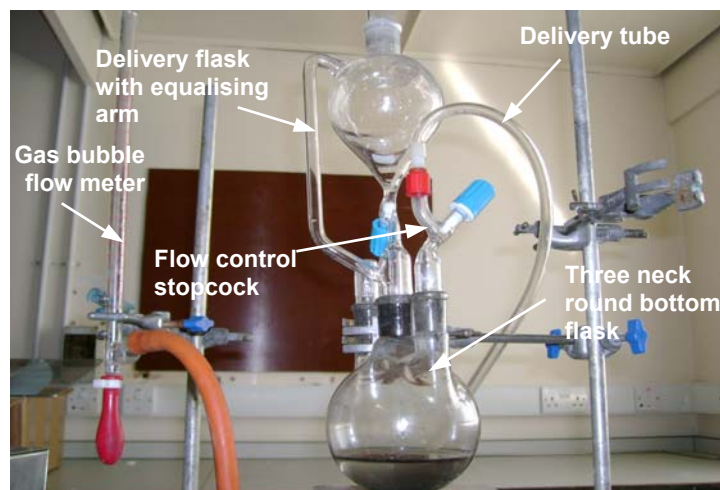


Fig.1 Gas evolution rate measuring apparatus

Sponge Nickel[®] was weighed accordingly and fed to the three-necked flask with the magnetic stirrer in place. 100ml of the solution was transferred into the delivery vessel, which was subsequently stoppered. The fitted valve connected to the delivery tube was closed, and then the valve connected to the delivery vessel was opened, dropping the solution into the flask, and then shut. The rate of gas evolution was obtained by timing the bubble flow through the bubble flow meter. The temperature of reaction was also monitored with time. As per the literature by Lister *et al.* [4], the stirrer was operated at a moderately rapid speed to maintain suspension. The gas

evolution rate obtained for each diluted solution and the corresponding concentration of Sponge Nickel[®] and sodium hypochlorite were plotted to observe behaviour and correlation.

2.3 Vessel Design, Configuration and impeller type

The vessel was a flat base Perspex vessel with internal diameter $T = 0.145\text{m}$; a height 0.33m and 4 equally spaced wall baffles with widths W_b of $14 \times 10^{-3}\text{ m}$ and thickness $2 \times 10^{-3}\text{ m}$. A 6 Blade Rushton Turbine (6BRT) with diameter $T/2.4 = 6 \times 10^{-2}\text{ m}$ and blade widths $W = 1.2 \times 10^{-2}\text{ m}$ was used to stir the medium. A clearance $T/4 = 3.6 \times 10^{-2}\text{ m}$ was maintained between the impeller and the vessel base. The shaft (with impeller) was mounted on an IKA Werke EUROSTAR POWER stirrer motor with a speed range of 0 to 2000rpm, controlled by a Labworldsoft program. The torque meter, IKA Werke VISCOKLICK VK 600, had a full torque range of 0 to 60Ncm. It was connected to the rotor, which had incorporated in it a strain gauge bridge, which was fixed to the shaft, and a stator, which communicated in frequency with the rotor. The output from the torque meter and stirrer motor, fed an amplifier whose output was directed to a computer via a converter. Labworldsoft program displayed the torque, actual and measured rotor speed.

2.4 Just-suspended speed, N_{js}

Different amounts of Sponge Nickel[®]; 0.130, 0.150, 0.190, 0.250 and 0.3 kg, were used to determine the effects of the slurry densities on the suspension of particles in the baffled vessel. In order to determine the effects of the gas phase on solids suspension, a non-gas evolving 2-phase system was evaluated using non-reactive brines of equal density to the various sodium hypochlorite solutions. These data were then compared directly with the equivalent reactive sodium hypochlorite system conditions to determine the effect of gas evolution on solids suspension.

The criterion for quantifying solids suspension was the just-suspended speed, N_{js} , as defined by Zwietering [5]. No characterisation or visualisation equipment was used to observe for N_{js} ; rather a subjective approach of visually observing the vessel base using a see-through Perspex stand and a torch light was used to judge and justify N_{js} . N_{js} was deemed evident when no particle remained at the bottom of the vessel for longer than 1 or 2s. N_{js} values were obtained with an estimated error within $\pm 7\%$. Torque measurements to calculate power draw were also noted at N_{js} . This was carried out to determine the effects of the initial density of the dilute solutions on N_{js} (In actual fact the density of the solutions does change with time due to the loss of O_2 during catalytic dissociation).

3. Results and discussion

Observations and discussions based on 4.22, 4.3, 4.38, 4.55 and 4.74 weight percentages of Sponge Nickel[®] reactions with 2.5L of the varying concentrations of sodium hypochlorite are presented here.

3.1 Gas evolution rate

Gas evolution rate was evaluated on the basis of both Sponge Nickel[®] loading and sodium hypochlorite concentration. As expected, a direct relationship between oxygen evolution rate and concentrations of Sponge Nickel[®] (catalyst) and sodium hypochlorite (reagent) was observed.

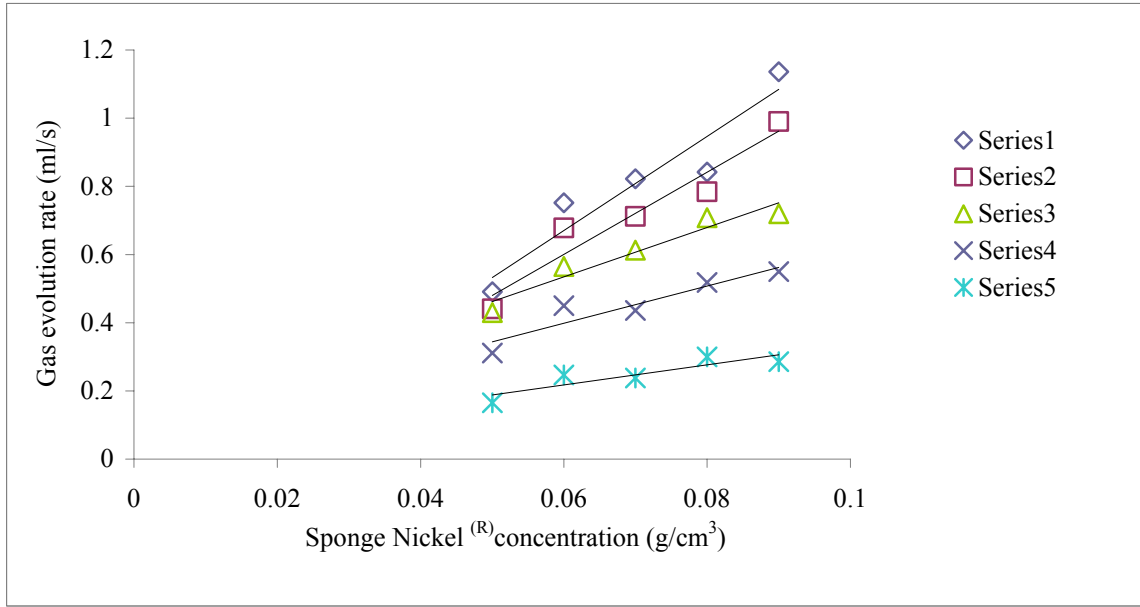


Fig.2 Oxygen evolution rate as a function of nickel loading

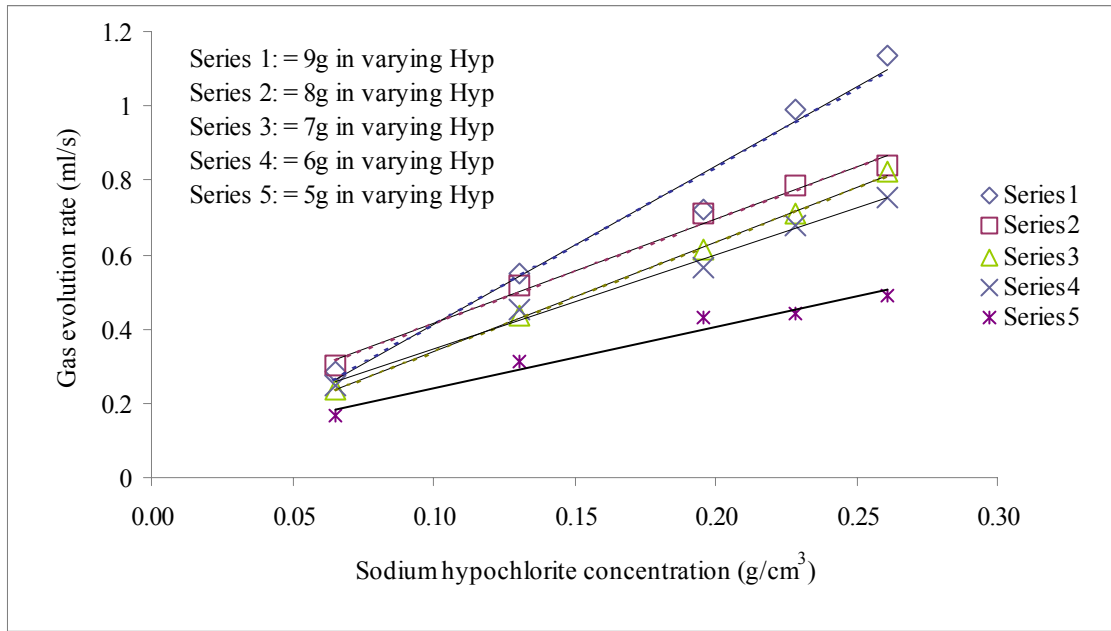


Fig 3. Gas evolution rate as function of hypochlorite ion concentration in solution

3.2 Gas Hold-up (ϕ_g)

Gas holdup was measured by the dynamic disengagement method. For all systems, irrespective of the solvent concentration or amount of Sponge Nickel[®], three liquid levels were observed when the impeller was stopped. ϕ_g was calculated from the gassed and ungassed liquid surface heights using Equation 5. Possible explanations governing these behavioural regimes are detailed below (with reference to the annotations in Fig 4).

$$\phi_g = \frac{H_2 - H_1}{H_2} \quad (5)$$

Regime 1: An initial liquid level (A) associated with the particles settling (H_1). This level was observed to be equal to the level when the solids were just added. At this point, negligible hypochlorite ions are absorbed to the catalyst surface. Sedimented particles were classified into three layers: upper (U), middle (M), and lower (L) particle beds.

Regime 2: Due to particle porosity, the entire Sponge Nickel[®] surface is covered with adsorbed hypochlorite ions. Acknowledging that the rate of reaction is proportional to the amount of Sponge Nickel[®], but independent of hypochlorite concentration, particles (B) beneath the uppermost layer of the particle bed still dissociate adsorbed hypochlorite ions at a rate comparable to particles in the upper layer that are exposed to the bulk hypochlorite solution their until little or zero adsorbed species are left. Over this period, the liquid level due to gas expansion within the bulk liquid reaches a level (C) equal to that noted during impeller motion. This is described as the primary gas hold-up level (H_2).

Regime 3: At little or zero adsorbed hypochlorite ions by particles beneath the upper layer, the liquid level drops to a secondary gas hold-up level (D). This secondary gas hold-up level comes about primarily due to hypochlorite dissociation by particles (E) located at the upper particle bed.

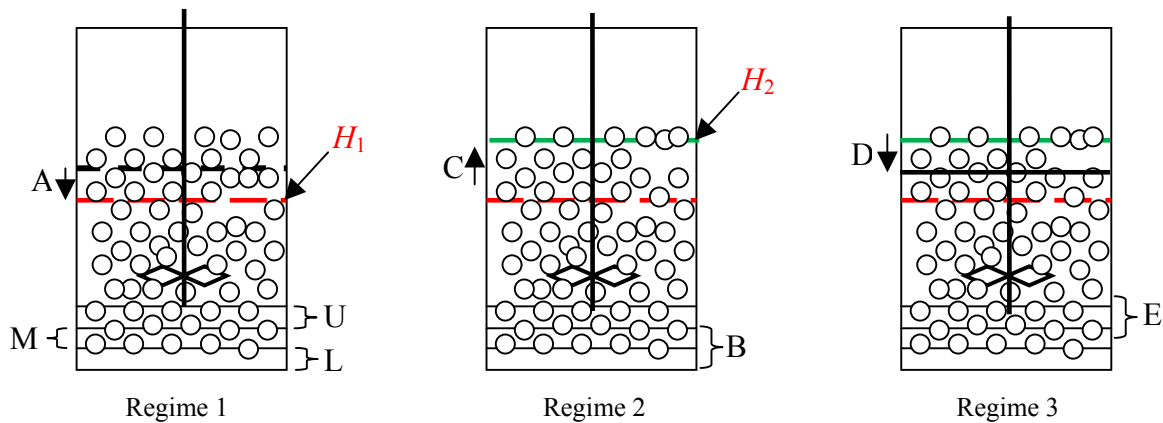


Fig.4 Gas hold-up and liquid levels associated with particle settling, gas expansion and contraction (see main body of text for explanation of annotations).

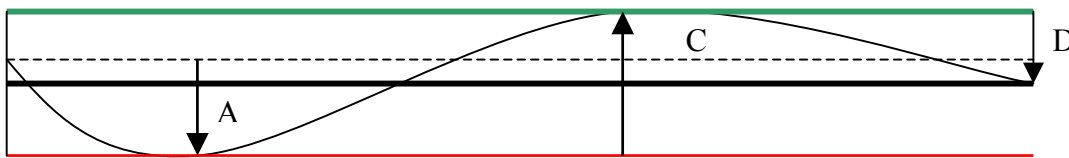


Fig.5 Telemetry of Gas hold-up and liquid levels associated with particle settling, gas expansion and contraction described above.

The change in ϕ_g with respect to gas evolution rate in the vessel is shown in Figure 6. ϕ_g can be seen to increase with gas evolution rate. For the range of gas evolution rates (Q_g), hold-ups (ϕ_g) and operating conditions used in this study the aeration number, N_A , takes values in the range $1.13 - 2.6 \times 10^{-4}$. At these values, the bubble flow regime in a sparged, stirred tank would generally be taken to lie within the fully dispersed regime [6]. Whilst there are undoubtedly differences in the bubble flow behaviour between sparged and gas-evolving two-phase systems, it is proposed that these differences are minimised towards the fully dispersed (low gas flow - high impeller speed) end of the regime spectrum. In the majority of literature covering sparged systems, gas discharge from spargers takes place beneath the turbine, which is classically central

to the vessel. In gas evolving solid-liquid systems, the global gas discharge is spread across the vessel due to gas emission by catalytic action of the well-distributed particles. Furthermore, the high ionic strength of the solution prevents bubble coalescence. Over the full range of operating conditions studied in this work, the bubble flow regime is classified as fully dispersed, and the impeller-driven flow is therefore dominant over the natural bubble convection behaviour. Gas hold-up is therefore a function of gas evolution rate alone.

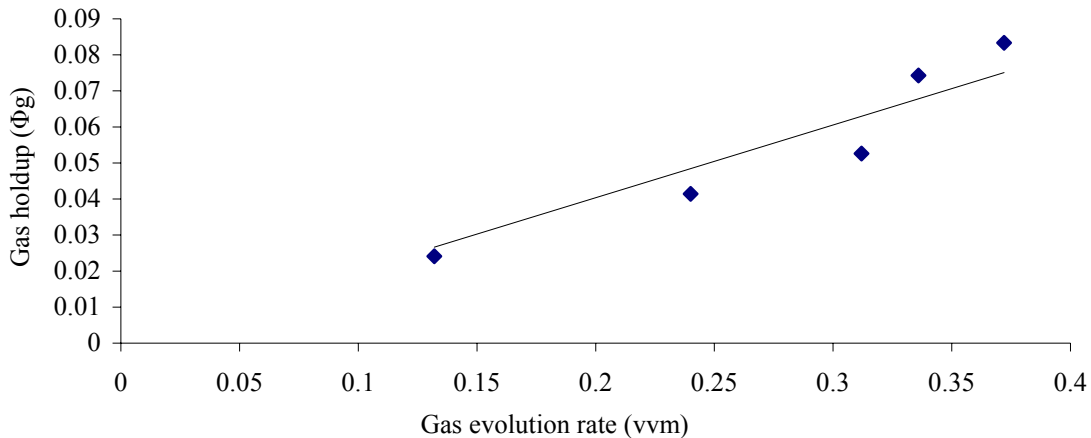


Fig.6 Gas hold-up as a function of gas evolution rate (for 4.22, 4.3, 4.38, 4.55 and 4.74 weight percentages of Sponge Nickel[®] in 8, 7, 6, 4 and 2% sodium hypochlorite solutions)

3.3 Solid phase suspension and settling behaviour

5 out of 25 possible combinations of Sponge Nickel[®] mass–hypochlorite concentrations were studied and the results are given in Table 1, including, N_{js} and power draw at just suspended speed (P_{js}) for the ungasged and gassed system, gas evolution rate (based on experimental trials), and gas hold-up values. From Table 1 it can clearly be seen that the introduction of the gas phase severely reduces the ease of suspension of the nickel particles. The data for the ungasged system were obtained from experiments performed using a non-reactive brine of equal density to the hypochlorite solution. For all operating conditions, the just suspended speed was greater for the three-phase system than for two-phases. This is indicative of high gas phase concentrations surrounding the particles. This gas phase acts as an energy sink via the action of compression and expansion in a fluctuating pressure field around the impeller region. Within incompressible turbulence, energy cascade originates at the largest scale of turbulence (impeller region) where velocity fluctuations in the fluid are spatially correlated (integral scale of turbulence). The energy entering at the integral scale should be successively transferred to scales suitable for particle lift. The absorbance of energy by the bubbles limits this transfer and consequently the available energy in the fluid to lift the particles from the vessel base. This effect is slightly offset by the reduced effective density of the particles once their pores are filled with gas. The terminal falling velocity of a 75 μm diameter particle prior to pore filling (immediately upon addition to the hypochlorite solution and before full adsorption of hypochlorite ions to the nickel surface) was found to be 0.58 cm/s. Once gas generation commenced, the terminal falling velocity of the same particle was found to reduce to 0.40 cm/s. This equates to a reduction in fall velocity by 31% and a pore volume gas filling of 38%.

Table 1. Summary of just suspended speed results for gassed and ungassed systems using various Sponge Nickel[®] amounts

Mass (g)	Percentage Sodium hypochlorite in 2.5L (%)	Gas evolution rate (vvm)	N _{js} (Ungassed system) RPM	N _{js} (Gassed system) RPM	P_g/P_u (Ratio of gassed to ungassed power draw)	Gas hold-up (%)
250	8	0.70	430	670	2.34	7.36
250	4	0.36	430	550	2.98	3.21
190	6	0.378	410	604	4.05	3.82
130	8	0.372	400	665	4.24	9.04
130	4	0.24	380	570	4.55	3.21

4. Conclusions

Gas evolution rate was characterised for a model nickel-sodium hypochlorite system over a range of operating conditions. Gas evolution rate was found to exhibit dependence on both parameters. Gas phase hold-up was found to lie in the range 3 – 7%, and was not dependent upon agitation speed over the range of operating conditions studied here, as the gas evolution rate was low enough to let impeller flow dominate the bubble flow regime. The solids suspension performance for 2-phase liquid-solid and 3-phase gas-liquid-solid systems was quantified using Zwietering’s just-suspended impeller speed condition. Although the presence of gas was found to markedly increase the impeller speed required to fulfil this criterion, a coherent pattern to the relationship between $N_{js}(u)$ and $N_{js}(g)$ could not be readily ascertained with respect to the concentrations of nickel and hypochlorite. An additional experimental programme is required to evaluate the significance of each variable and provide insight to which parameter controls solids suspension performance in gas-evolving systems.

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