Pulsed electrogeneration of bubbles for electroflotation

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Fine bubbles of the size required for many processes such as electroflotation can be generated by electrolysis. A large number of factors such as electrode material, electrode surface/morphological properties, pH and current density affect the gas bubble size distribution. This work is aimed at studies on the effect of interrupted current (pulsed) electrolysis on the generation of gas bubbles. A microcomputer-controlled current source designed to generate the required pulses is described along with typical results obtained with this system. It was observed that a decrease in duty cycle at a given pH and average current density causes an increase in fine sized bubbles and concomitant increase in bubble flux. A mechanism based on local potential gradients is proposed to explain this phenomenon.

1. Introduction

Much of the experimental work addressing the generation of bubbles has been concerned with nucleate boiling, gas generation during electrolytic processing of materials as well as mass transfer/hydrodynamic aspects [1, 2]. A special consideration however for electro-flotation of mineral fines is the need to generate fine (< 50 µm) dispersed gas bubbles. Fine particle flotation which is limited due to the diminishing probability of bubble-particle collisions, can be improved by increasing the number of fine sized bubbles [3]. Thus, the present work is addressed towards the generation of small sized bubbles. An important outcome of smaller bubble size is an increase in bubble flux (the number of bubbles traversing unit cross-section per unit time) as well as the number of bubbles per unit volume for a given volume of gas evolved. These two factors have been shown to have a strong influence in fine particle flotation [3].

A primary concern in processes such as electro-flotation is the generation of fine bubbles of known size at a known bubble flux [3-7]. Various investigators [3, 4-16] have studied electrolytic generation of gas bubbles and the physical parameters governing the bubble size. The occurrence of increased hydrogen bubble size in the acidic pH region and that of oxygen in the alkaline region is well known. Bubble contact angle [9-13], electrode condition (for example, surface roughness) [3, 16, 17], hydrogen overvoltage [3], current density [3, 9-11, 17], polarization potential [3] and bubble charge [15, 18] have been suggested by many workers to be among the factors governing the bubble departure diameter. For a given set of system parameters such as pH, temperature, reagent concentration and electrode material, the bubble properties are fixed and it becomes impractical to adjust these parameters to obtain efficient generation of the desired fine sized bubbles. Thus, there is need for a technique to generate bubbles of desired bubble size distribution largely independent of the solution conditions. Pulsed electrolysis can be carried out by using a waveform generator along with a potentiostat capable of fast slew rates. PC programmable power supplies usually have low slew rates and may not prove suitable as a pulsed current source for a capacitive load such as an electrolytic cell in the frequency range discussed in this work. In this work an IBM/PC controlled pulsed current source having a high voltage slew rate has been described. The pulsed source can be controlled by appropriate software which can be tailored to an individual application.

2. Literature review

The physical process of gas evolution can be divided into three stages: nucleation, growth and detachment. Bubbles nucleate at electrode surfaces from solutions highly supersaturated with product gas and grow by diffusion of dissolved gas to the bubble surface or by coalescence at the electrode with other bubbles [19]. They detach from the electrode when buoyancy or liquid shearing forces pulling the bubbles away overcome the forces binding them.

Surface inhomogeneities such as cracks are generally considered high energy nucleation sites due to the availability of atomic ledges as high energy anchorage points. This phenomenon has been a subject of detailed investigation in nucleate boiling [13], crystallization and solidification [20, 21]. For bubble generation in vacuum or pressure release flotation (analogous to precipitation) the above phenomenon is important. During the electrolysis it is generally agreed that the preferred nucleation sites are at surface inhomogen-
cities such as fissures, cracks and scratches [13, 17] as well as local inhomogeneities resulting in donor-acceptor [3] and low overpotential sites [3, 17]. The dependence of the voltage gradient at the tip of a needle electrode upon its curvature is a well known phenomenon. Occurrence of such sharp points on an electrode and the consequent presence of high local potential gradient sites can be ruled out. The importance of the role of voltage gradients towards nucleation is clear from the observation that on wire and mesh electrodes bubble size depends largely on electrode curvature (and thus potential gradient) almost independent of the current density [3, 13]. However, bubble growth rates are not strongly dependent on the diameter of wire electrodes [17].

Various mechanisms have been proposed to determine the bubble departure diameter. Coehn [8] proposed that electrostatic attraction between the bubble and the electrode is instrumental in determining the departure diameter. Stronger attraction requires a larger buoyant force for detachment necessitating larger bubble diameters. Bubble charge studies [18] conducted on platinum anodes at 10-40 kA m$^{-2}$ tend to support this mechanism. However, electrostatic forces are predominant at current densities ($10^4$ A m$^{-2}$), larger than those encountered in electroflotation [9-11, 14, 16]. Using high speed photography, Glas and Westwater [17] observed that contact angle is not as significant a factor as surface roughness or electrode material in determining the growth rate of bubbles.

A relation between the hydrogen overvoltage and the bubble size has been observed [4].

Increasing bubble size

Pb Sn Cu Ag Fe Ni W Pd

Increasing overvoltage

It was also observed that under clean conditions contact angle is dependent on the overvoltage [4].

Thus bubble size and flux in aqueous electrolysis seems to depend upon (a) surface morphological factors including donor acceptor and low overpotential sites and (b) the inherent overvoltage property of the electrode material.

3. Experimental details

The pulsed d.c. source was designed as a circuit board to be interfaced to a microcomputer giving the system flexibility in its configuration as a constant current/voltage source (Fig. 1). User interface is more versatile due to software control of the equipment. The circuit is mapped on the I/O bus of the microcomputer using the switch S-1 and address decoder (DEC). The microcomputer sends data to the digital to analog converter (DA) through buffers (BUF). The timer (TIM) is programmed to generate timing pulses to update DA under the direct memory access (DMA) mode of the microcomputer. Thus, the requisite waveform is generated by the computer in the background while the computer is simultaneously available for computational and other control work. The DA output is fed to the power amplifier (PA). The high current supply (PS) is capable of providing a peak current of 5 A. The use of a 12-bit DA operating under direct memory access of an IBM/PC operating at 8 MHz offers a resolution of 0.024% for current (maximum current of 4 A) and minimum pulse cycle time of 3.2 ms with 0.5% resolution.

Software was developed for the generation of pulses (Fig. 2) of variable duty cycle at a selected average current. The average current ($i_a = id/100$) was computed from the area under the curve (shaded) and the duty cycle ($d$) as the percentage of cycle time ($t_{cy}$) during which the current flows through the cell. Thus, for a square wave, the duty cycle is 50%. The software was designed to generate a high peak current nucleation pulse at the start of each cycle. The contribution of the nucleation pulse to the total energy was negligible ($<0.2\%$).

Electrolysis was carried out in a quartz cell mounted
on a stand backlit with a bright light source. A shuttered video camera (1/1000 shutter speed) fitted with microscope objective 50X to 300X) was used to record bubble dimensions on a video recorder. A videographic printer was used to print the picture frames for subsequent bubble size measurement. The quartz cell was designed to circulate the electrolyte (1 M Na₃SO₄). The electrolyte (pH 10.0) was circulated by means of peristaltic pump and a large external reservoir of the electrolyte was maintained to ensure minimal pH change. Electrolyte circulation also facilitated removal of the generated gases.

The platinum plate cathode (1 cm²) was carefully polished and thoroughly degreased. Care was taken to exclude surface active contaminants. The external glass reservoir for the electrolyte was always kept covered to prevent air-borne contamination. The bubbles were observed between 2 to 2.5 mm vertically above the electrode.

Experiments were carried out for the electrogene-
ation of hydrogen bubbles with a pulsed current having a step waveform (Fig. 2). The solutions were electrolysed with an average current density ranging from 0.5 to 2.0 A m⁻² and duty cycle ranging from 5 to 100%. A cycle time of 30 ms was used and a recording period of 5 min was used at each experimental condition. Bubble size distribution was computed by examining at least 150-200 bubbles in sharp focus.

4. Results

Initial experimental work on electrolysis with rectangular waveform having a leading high energy nucleation pulse, showed no significant difference from the electrolysis carried out without the leading nucleation pulse. Thus all subsequent work was conducted without a leading nucleation pulse.

The results obtained for bubble size distribution as a function of current density and duty cycle are presented in Figs 3–6. Bubble diameters were computed from the video prints by taking the average of bubbles found in sharp focus. It can be seen from Figs 3–6 that at a given average current density, a decrease in duty cycle results in an increase of bubbles of smaller diameter. This is expected to significantly increase the bubble flux.

5. Discussion

The chief effect of pulsing observed during electrolysis is the occurrence of an increased number of small sized (<10–15μm) bubbles (Figs 3–5). Thus at low duty cycle, higher current during the 'on' time forces a larger number of bubbles to nucleate and grow resulting in an increased bubble flux. The requirement of high current density for nucleation and growth has been observed by Brandon [18] to be due to diffusion.
Pulsed Electrogeneration of Bubbles for Electroflotation

Potential nucleation sites on the electrode surface, such as scratch edges and cavities, possess a wide variation in energy. The higher voltage required for higher instantaneous currents under pulsed conditions largely offsets the effect of local potential gradients and also results in a high degree of local gas supersaturation, thus resulting in homogeneous nucleation. At short times i.e. \( t < 10 \) ms, bubbles grow by acting as sinks for the previously generated dissolved gas in the supersaturated solution adjacent to the electrode [18]. Such growth is hydrodynamically controlled by liquid inertia.

5.2. Growth and detachment

Growth is driven by the high internal excess pressure inside the bubble which is related to the surface of liquid-vapour interface. From 10 ms onwards, diffusion of dissolved gas to the bubble contact perimeter becomes rate controlling [22]. Under pulsed conditions of low duty cycle, growth is either entirely inertial or inertial and diffusion controlled. Under conditions of low current density (high duty cycle), while most nuclei may grow in a similar manner during the inertial phase, only nuclei at the lowest overpotential sites grow during the diffusion control phase due to concentration polarization. Frequent interruptions in current during pulsed electrolysis also promote bubble detachment. Bubble size increase by coalescence at the electrode [1, 19], as well as by coalescence in bulk, results in further increase in bubble diameter.

6. Conclusions

1. Pulsed electrolysis can be used to regulate bubble size independent of the average current density and other such parameters.
2. During water electrolysis, increase in current density results in finer bubbles which may find application in processes such as electroflotation.

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