Electrogenerated Gas Bubbles in Flotation

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Electrolytic gas evolution plays a very significant part in a number of electrochemical processes. In the electrowinning of metals the evolution of gases at the electrodes is a very important phenomenon. Gas evolution is common in chlorine and water electrolysis and in a number of other processes. Electrogenerated gas bubbles have been used in the treatment of waste water and considerable amount of work has been done on the electroflotation of mineral fines which are unsuited for treatment by conventional flotation techniques. The physical process of gas evolution viz nucleation, growth and detachment are discussed. The dynamic process of electrogeneration of gas bubbles as affected by the interaction amongst a large number of process variables has been dealt with in detail. Flotation of mineral fines as affected by the size and charge of the bubbles is also discussed.

INTRODUCTION

In many electrochemical processes, electrolytic gas evolution plays a very important role. In the fused salt electrowinning of aluminium by the Hall process, the oxygen evolving at the carbon anode leads to the so called "Anode effect" which has been studied in considerable detail. Also, in the aqueous electrowinning of metals, gas evolution at the electrode is important. The oxygen evolving at the nonconsumable anode contributes mostly to the highly energy intensive nature of the electrowinning process. Gas evolution is not restricted to the anodes. In the electrowinning of zinc hydrogen evolution at the cathodes affects the deposition of zinc. Electrolytically evolved gas bubbles have been shown to enhance the transport of heat and mass at gas evolving electrodes.

THE PHYSICAL PROCESS OF GAS EVOLUTION

The first step in the gas evolution is nucleation. With regard to electrogenerated gas bubbles, we have to discuss the influence of current or rather the current density at the electrodes. If the current density is very low, the dissolved gas is removed from the electrode in the direction of liquid bulk by molecular diffusion and convection and no gas phase is formed. Even at high current densities this may happen

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if the dissolved gas reacts homogeneously and quickly like chlorine. If the current density is sufficiently high, gas bubbles form at predetermined nucleation sites located at the electrode surface. Adjacent to the electrode, sufficient supersaturation of the liquid would have occurred prior to nucleation[1].

Real surfaces contain pits, scratches and grooves of various sizes which act as nucleation sites. Westerheide and Westwater[2] have reported that nucleation on their micro electrodes occurred at preferred sites. Janssen and Hoogland[3] observed that bubbles nucleated on a rotating platinum wire at specific sites that depended on the pre treatment as well as current density.

After nucleation, bubble growth takes place. A bubble adhering to the surface grows by the supply of dissolved gas from the surrounding liquid and due to the high internal pressure. It must be noted here only that the bubbles of a critical radius and larger grow while bubbles having radii less than this dimension tend to decay[4]. Scriven[5] has presented a general analysis of a diffusion controlled growth of a bubble. The growth rate is given by $R = 2\beta(Dt)^{1/2}$, where R is the radius, D the diffusivity, t the time and β is a coefficient characteristic of the degree of supersaturation. Westerheide and Westwater[2] photographed individual hydrogen bubbles and quantitatively compared their growth data to the diffusion square root of time growth dependence. Good agreement was found for a single bubble. The importance of mass transfer of dissolved gas to the bubble surface as the asymptotic mechanism by which the bubbles grow before and between coalescence has been established. This work has been extended to oxygen, chlorine and carbon dioxide[6].

The validity of the growth law is restricted to gases where the adhering bubbles do not mutually interfere at moderate current densities. At current densities above ~ 1000 A/m^2 various anomalies occur[2]. A very important anomaly is the coalescence of bubbles on the electrode surface. While growing, two single bubbles may touch each other and coalesce[2]. Bubbles of a moderate size (40 microns) establish themselves as central collectors and receive the smaller bubbles nucleating and growing around them. This has been termed as radial specific coalescence[7]. A third mode of coalescence called a scavenging mechanism, that is, bubbles sliding along the electrode and consuming other smaller bubbles has also been noted[8,9]. Hydrogen bubbles produced in acid have been shown to grow by such a mechanism. Coalescence has been shown to occur with in short times. ($\sim 10^{-4}$ seconds)[2]. Sides and Tobias[7] have proposed a cyclic mechanism of oxygen bubble growth in basic medium. The sequence of events, namely nucleation, growth by diffusion, coalescence of small bubbles, coalescence by radial motion and scavenging coalescence has been termed as the cyclic process of the bubble growth. The period of the cycle, at a current density of 100 mA/cm^2, was approximately 0.1 second. However, this is not a general phenomena and need not occur on different electrodes evolving other gases. In particular, it may be noted that coalescence seems unimportant in hydrogen evolution from basic solution because the bubbles evolved are quite small. This is discussed in the latter section. Further, it may be noted that larger bubbles formed by the coalescence need not detach from the electrode but at least under certain conditions adhere to the electrode while smaller bubbles depart.

The last stage of the process of gas evolution is the detachment of bubbles. Frumkin and Kabanov[10] have found that the buoyant gas bubbles detach when

surface adhesive forces, related to bubble contact angles, can no longer restrain them. Without present knowledge, we are not in a position to predict the departure diameter of the bubbles. The positioning of the electrodes horizontally or vertically has also been shown to affect the bubble size. The mobility of the bubbles on the electrode surfaces is related to detachment. The relation between hysteresis angle, the contact angle and the volume of the largest bubble that sticks to a surface facing downward and inclined to the horizontal has been studied[11].

TREATMENT OF MINERAL FINES BY ELECTROFLOTATION

The unsuitability of conventional flotation techniques for the treatment of mineral fines has been attributed mainly to the large bubble size which reduces the probability of collision with fine particles, thereby decreasing collection efficiency. Because of small mass and low inertia, fine particles are carried along the stream lines the stream lines of the bubbles and do not collide with the bubbles. To increase the collision probability fine bubbles can be used which may be generated in a number of ways. One of the methods to produce fine bubbles and carry out the flotation is known as electroflotation, that is, flotation using electrogenerated gas bubbles.

The gas bubbles produced in conventional flotation machines of mechanical type are 0.8 to 0.9 mm, about 2 mm in pneumatic machines and about 0.1 to 0.5 mm in vacuum flotation. Electroflotation permits the formation of extremely finely dispersed gas bubbles in the range of 10-100 microns depending upon the conditions of electrolysis[12]. In view of the importance of bubble size in flotation, this feature of electroflotation offers a great advantage over conventional flotation. In addition to the bubble size, the bubble flux and bubble density are also important. Bubble flux may be defined as the number of bubbles per unit area per unit time and bubble density as the number of bubbles per unit volume. Continuous adjustment of the bubble size, bubble flux and bubble density is possible in electroflotation. It is also possible to use hydrogen and oxygen gases separately or in combination. The electrogenerated bubbles can be used along with air which could ensure that the bigger particles are floated by the bigger air bubbles and the finer ones by the

The advantage of electroflotation over conventional flotation lies not only in the smaller bubble size produced but the ability of hydrogen and oxygen bubbles generated by electrolysis to alter the flotation properties to a great extent than the molecular gases. This is because the nascent gases are most effective. The thin film of water between the mineral and the gas can be easily removed by the smaller bubbles because of the high capillary pressure inside them[13]. The mineral surfaces can be either activated or passivated by the electrolytic gases. This can give rise to an improvement or deterioration in the flotation properties of the mineral. The oxidation–reduction changes that can occur on the surfaces of some minerals with electrolytic gases is very striking. It has been shown that with certain minerals, flotation could be achieved in the absence of collector also. Chalcopyrite and pyrite have been shown to float with electrolytic oxygen even in the absence of a collector[14]. Increased recovery and grade of tin ore (cassiterite) with electrolytic

hydrogen bubbles has also been reported.[15,16] In the former case, oxidation by electrolytic oxygen and in the latter case, reduction by electrolytic hydrogen is responsible for the activation of the surface[14,15,16]. At this stage it must be emphasized that not all sulphide surfaces behave similar to chalcopyrite and pyrite. In the case of chalcocite the use of electrolytic oxygen has not been found to be beneficial.

EFFECT OF PROCESS VARIABLES ON BUBBLE SIZE

The size of the bubbles produced by electrolysis is dependent upon several variables. Figure 1 shown various parameters affecting the bubble diameter. Some of the important variables are discussed below.

Pulp pH

In flotation systems, the pH of the pulp plays a vital role. pH affects the charge on the mineral. In the case of oxide minerals H^+ and OH^- ions modify the electrical double layer and hence the zeta potential. pH may have an effect on the collector also. Further, OH^- ions act as depressants in a number of flotation systems. The critical pH value beyond which flotation does not occur depends on the nature of mineral, the collector and its concentration. In addition to its effect on the mineral and the collector it has been shown that the pH of the pulp is a very important variable determining the bubble diameter.

In electroflotation if both the gases hydrogen and oxygen are used for the flotation then the pH of the pulp is not expected to change. However if a diaphragm separates the anolyte and catholyte and either hydrogen or oxygen alone is used for flotation
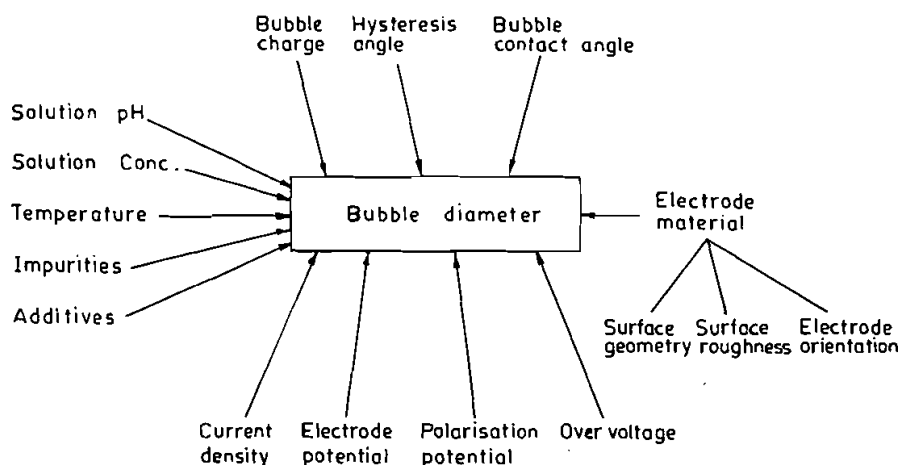
FIGURE 1.   Parameters Affecting Bubble Size

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