

Acid mist formation in the electrowinning of copper

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Abstract

The formation of acid mist in electrowinning plants results in a hazardous environment for the operators as sulphuric acid is classified as a carcinogen. This study found that small bubbles ($d < 1$ mm) give rise to the largest acid mist flux while large bubbles ($d > 10$ mm) resulted in reduction of acid mist flux by a magnitude. The acid mist flux was found to vary inversely with the bubble diameter and this provides a simple means of estimating the bubble size necessary to reduce the acid mist flux to safe levels for operation of electrowinning plants. However, some means to coalesce the fine bubbles produced during the process must be provided to ensure that only large bubbles burst at the free surface of the electrolyte.

1. INTRODUCTION

In the hydrometallurgical recovery of copper from ores, sulphuric acid is used to leach the copper out to form a weak solution of copper sulphate which is then electrowon to recover the copper metal (Habashi, 1993). The solution for electrowinning normally contains 25 to 60 g/l of copper sulphate and 50 to 180 g/l sulphuric acid kept at 50 to 60°C. A lead anode and stainless steel cathode are immersed in an electrolyte bath containing the copper sulphate/sulphuric acid solution. An electrical current passes from the anode to the cathode, giving rise to an electrochemical reaction whereby metallic copper is deposited onto the cathode. Simultaneously, oxygen is released at the anode surface. The oxygen forms bubbles that detach from the anode and rise through the electrolyte. At the free surface of the electrolyte, the bubbles burst and give rise to acid mist which is a fine spray of acid droplets suspended in the air space above the electrolyte bath. Acid mist poses a significant health hazard to operators and this paper looks at the source of the acid mist and possible means of controlling the extent of acid mist formation.

1.1. This study

Although the formation of acid mist is reasonably well understood, the quantity of acid mist formed as a function of bubble size is not well documented. This study aimed to investigate the relationship between bubble sizes in electrowinning cells and to quantify the acid mist concentrations generated.

1.2. Health hazard related to sulphuric acid mist

The acid mists, generated in electrowinning plants, contain both sulphuric acid and copper sulphate, both of which can pose significant health risks. Exposure to sulphuric acid mists includes inhalation, ingestion, and dermal contact. Acid mists, containing particles with a diameter of up to a few micrometers, tend to deposit in both the upper and lower airways (IARC, 1992). These particles are irritating to the mucous epithelia, cause dental erosion, and produce acute effects in the lungs (symptoms and changes in pulmonary function).

Asthmatics are more vulnerable to such risks. Based on human data, the IARC concluded that there was sufficient evidence that occupational exposure to strong inorganic acid mists containing sulphuric acid is carcinogenic to humans (IARC, 1992) and classified sulphuric acid in Group 1 (carcinogenic to humans).

A study undertaken by the US National Institute for Occupational Safety and Health (NIOSH) (Beaumont *et al.*, 1987), investigated the mortality patterns of 1,165 male steelworkers exposed to sulphuric acid and other acid mists in three steel-pickling operations. Of those workers, 722 had been exposed only to sulphuric acid. The investigators found that these workers had a highly significant excess risk for laryngeal and lung cancer.

A nested case-control study of workers in a US petrochemical plant showed an elevated risk for laryngeal cancer among workers exposed to sulphuric acid. Of two population-based case-control studies in Canada, one of laryngeal cancer showed an increased risk for exposure to sulphuric acid, and one of lung cancer suggested an excess risk; the latter also suggested a risk associated with exposure to mixed inorganic acids. In all these studies, sulphuric acid mists were the most common exposure, and positive exposure-response relationships were seen in two of the studies (Soskolne *et al.*, 1992).

Griffiths (1996) discussed how acid concentration and droplet size affected the irritant responses of humans. Studies conducted at concentrations of 0.1–1 mg/m³ for a short period of time, approximately 15 minutes, indicated that droplets with a diameter of less than 1 µm will not result in respiratory effects. The study also monitored a group of 15 healthy and 15 asthmatic volunteers subjected to a concentration of 0.1 mg/m³ of sulphuric acid aerosols in a chamber for one-hour periods. No effects on their respiratory systems were noted. Asthmatics exposed to sulphuric acid aerosols at concentrations of 0.1 mg/m³ via a mouthpiece also showed no effect at this concentration. It is possible that those trials were of too short a duration as carcinogens usually act over long periods.

The study by the IARC (1992) indicates that people working with exposure to sulphuric acid mist are affected by the size of particles. It is believed that the particle size of the acid mist is a defining factor in the site of cancer and mode of action. The acid mist particles that are inhaled cause local reactions; therefore, if the acid mist particle is too large to reach the lungs, cancer will not occur. The primary response is believed to be in the upper respiratory tract with particles of diameter 5–30 µm, and in the tracheal, bronchial and bronchiolar regions with 1–5 µm diameter particles (IARC, 1992). Soskolne *et al.* (1989) reviewed pH as a modulator of mitotic activity and cell differentiation by sulphuric acid mist exposure and suggested that a decrease of pH in the extra-cellular matrix might cause structural/functional alterations in the mitotic apparatus, thus resulting in spindle damage and non-disjunction. This, in turn, may affect gene expression and alter cell differentiation. Swenberg and Beauchamp (1997) support the carcinogenicity mechanism where inorganic acid mist reduces pH and thereby affecting chromosomal integrity.

The concerns of sulphuric acid mist have led to the implementation of a National Exposure Standards for Atmospheric Contaminants in the Occupational Environment (National Occupational Health and Safety Commission, NOHSC: 1003, 1995) for sulphuric acid mist. The time-weighted average is currently set at 1 mg/m³. Exposure standards are based on an eight-hour work period of normal intensity, under normal climatic conditions and where a sixteen-hour break between shifts exists to enable the body to eliminate absorbed contaminants. There are calls for the standard to be more stringent at 0.1 mg/m³ (Hery *et al.* 1992).

1.3. Health hazard related to copper sulphate mist

Copper sulphate is not specifically listed in the NOHSC guidelines (NOHSC: 1003, 1995), instead the guidelines state that a time weighted average of less than 1 mg/m³ for copper dusts/ mists (same as sulphuric acid mist) must be maintained and 0.2 mg/m³ for copper fumes. Copper has not yet been listed as a known carcinogen, though inhalation of copper and copper compounds has been reported to cause lung and liver damage in animals. There is a dearth of studies on the health effects of copper sulphate mist.

1.4. Mechanism of mist formation

In the electrowinning of copper, metallic copper deposits on the cathodes. At the anode, water is decomposed

and the hydrogen combines with the sulphate to form sulphuric acid and oxygen is evolved as a by-product. The oxygen gas bubbles formed at the anode surface coalesce. When the buoyancy force on the bubble overcomes the surface tension forces holding it to the anode surface, the gas bubble detaches and rises through the electrolyte and bursts at the free surface. The bursting of bubble is the main mechanism that results in the formation of fine droplets of liquid that constitute the acid mist. Early work by Newitt *et al.* (1954), with the aid of a high speed cine camera, showed the bursting mechanism of the bubble as illustrated in Figure 1.

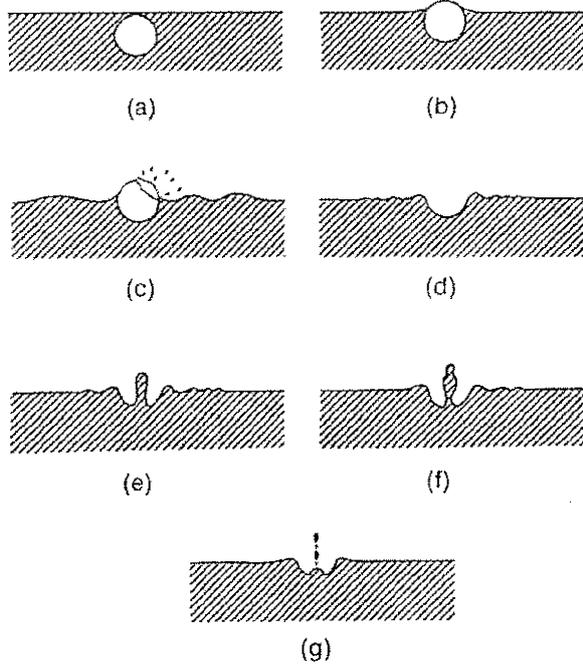


Figure 1 Mechanism of bubble bursting at a free surface (Newitt *et al.*, 1954).

to its minimal area resulting in cavity collapse. The collapse of the cavity may or may not give rise to a central jet emanating from the cavity (Van Dusen *et al.* 1988). Laboratory studies show that the bursting of air bubbles of diameters between 0.3 mm and 4 mm at the surface of sea water produces small numbers of rather large drops (diameters 50–500 μm), the majority of which would fall back quickly into the sea. The large salt nuclei found in the atmosphere are probably the residues of smaller drops produced by disintegration of the bubble caps (Moore and Mason, 2006).

A study of bursting air bubble in water of diameter between 5 and 20 mm (equivalent spherical diameter) was carried out by Morton and Liow (1999). They found that bubbles arriving at the free surface with diameters less than 5 mm were ellipsoidal in shape while bubbles with diameters larger than 10 mm arrive as spherical caps. The study showed that the rupture of the gas bubble film is the dominant mechanism for the formation of fine droplets. For bubbles with diameters less than 5 mm, the central jet formed during the collapse of the bubble cavity usually broke up to form one or more drops. The total volume splashed rapidly decreased when bubble diameters became larger than 4 mm. For bubbles with diameters larger than 10 mm, the rising bubble formed a dome which collapse resulting in plunging behaviour on its edges. The plunging resulted in liquid drops being ejected (Liow *et al.*, 1996).

1.5. Control of mist formation

Several techniques have been used in the past to control acid mist concentration in electrowinning tank houses; they include surfactants, mechanical methods, hooding, forced coalescence and improved ventilation.

Surfactants, such as Pluronic F67 (Sigley *et al.*, 2003), detergents, and saponins, have been used to produce a

When a bubble approaches a free surface, the liquid above does not drain away immediately. It forms a film that progressively thins out with time. The gas bubble on reaching the free surface is trapped until the liquid film thins sufficiently for weak spots to be formed due to small irregularities in the draining process. When a weak spot collapses to form a hole, the surface tension forces act to minimize the surface area of the liquid film resulting in a rapid folding back into the bulk liquid. The speed of the rupture is fast, up to 10 m/s (Pandit and Davidson, 1990). When the film ruptures, the film forms finger that break up into tiny streams of liquid that are unstable. These tiny streams of liquid break up into small droplets due to Rayleigh instabilities where the drop size is of the order of the asymmetric wave given by a radius of 2 to 2.7 times that of the diameter of the tiny liquid stream (Rayleigh, 1897).

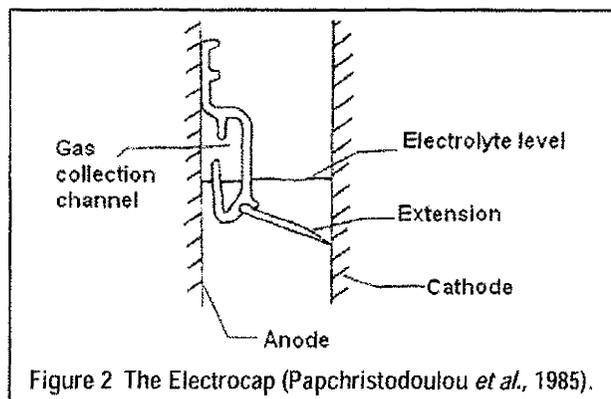
After the film has ruptured, a crater is left behind from the gas bubble. Prior to rupture, the crater shape is held in equilibrium by the gas pressure in the bubble. After rupture, the gravitational and surface tension forces will act to restore the surface

foam layer. The foam layer promotes coalescence and reduces the rate of bubble bursting but it interferes with the quality of the copper deposit due to its solubility (usually quite low) and the tendency to coat the electrodes during removing and replacement through the foam layer. High concentrations of surfactants can also reduce current efficiency (Van Dusen and Smith, 1989). Keeping a uniform and not excessively thick layer of foam on the electrolyte surface can be difficult.

Mechanical interfaces are created by adding floating objects to suppress the acid mist. Floating beads, spheres, and cylinders are effective interfaces that are usually used. They cover the free surface of the electrolyte and reduce the area for bubbles to burst. However, they are a nuisance when they adhere to the cathodes as copper growth occurs. The beads often spread throughout the tank house creating a messy and hazardous environment. They are also relatively expensive (Papachristodoulou *et al.*, 1985).

Hooding of the cells is the most efficient method of controlling acid mist above electrowinning cells as it completely isolates the system from the environment (Van Dusen and Smith, 1988). However this approach may not be practical in cells where it is necessary to remove electrodes for frequent harvesting as well as being a very costly and inconvenient solution to the acid mist problem.

In forced coalescence, larger bubbles are formed to reduce aerosol emissions (Van Dusen *et al.*, 1988). A representative device is the Electrocap (Van Dusen and Smith 1989) seen in Figure 2. The gas collection channel attached to the anode collects the gas from the bubbles as they rupture, and then removes the gas. A seal is provided by long, flexible extensions that protrude to the cathode. The Electrocap reduced acid mist emissions by up to 90% but had some disadvantages. The flexible extensions that met at the cathode were difficult to seal onto the cathode, causing acid mist to escape. The sealing edge of the Electrocap on the anode tended to warp and allow acid mist to escape. Often, as the copper began to be refined, the cathode end of the Electrocap would become trapped in the plated copper and break off as the cathode was harvested (Papachristodoulou *et al.* 1985).



Ventilation acts by displacing the mist before it gets into the breathing zone of the workers. This system is used as a secondary control measure, by diluting the aerosols instead of preventing them. Several types of ventilation systems are used in electrowinning plants, such as natural drafts, mechanical drafts and also gravity ventilation. Large volumes of air are required for general ventilation, where operational power requirements can approach 20% of the electrowinning power. The volume of re-entrained vented air can be a concern. Often ventilation is used as a secondary system or in combination with an

effective acid mist suppression system.

2. EXPERIMENTAL

A Hull cell of dimensions 210×80×75 mm, capable of holding approximately 1 litre of electrolyte was used. An adjustable heater that was molded into the cell base, with an adjustable thermostat fixed to the cell rear allowed a constant temperature of 45°C to be maintained throughout the cell. The cathode was a 61×151×3 mm flat piece of stainless steel and the anode was a 72×83×1.92 mm lead strip. A synthetic electrolyte made of 170 g/L sulphuric acid, 45 g/L copper as hydrated copper sulphate, and 40 ppm chlorides as sodium chloride, was used in all the experiments. Samples of the electrolyte were analysed at Xstrata Laboratories to ensure that the concentrations were correct. A Redlake HG-100K high speed video was used to film the bubbles for size distribution analysis.

A second set of experiments were performed using different air nozzles to produce a range of bubble size to study its effect on the amount of splashing and hence, acid mist, being produced. Wooden and stone diffusers as well as pipe nozzles were used to enable a dispersion of bubbles to be produced for generating a reasonable amount of acid mist. Gas was injected into the diffusers and nozzles from an air tank through a

rotameter and needle valve. The setup is shown in Figure 3.



Figure 3 Left: The Hull cell and electrodes used in the study. The cathode is on the left while the anode is on the right. Right: The glass tank used to house the second set of experiments where different diffusers were tested for their acid mist production capability.

3. RESULTS

3.1. Hull cell results



Figure 4 The fine mist of acid from the bubbles in a Hull cell near the anode.

The bubble sizes were determined by analyzing the high speed video images. The thickness of the anode (1.92 mm) was used as the reference dimension and the pixel resolution was about 12 μm . The bubble sizes generated in the Hull cell were between 0.08–0.10 mm in diameter (3 standard deviations). Images of the acid mist generated, similar to that shown above in Figure 4, were also analysed. The largest droplets were of the order of 30 μm which as close to the resolution of the camera. As the bubbles are smaller than those of Moore and Mason (2003), the corresponding droplets were also smaller. Visual observation showed that the fine acid mist droplets were small enough to remain air borne above the electrolyte free surface for a long enough period of time to be carried away with the smallest drafts of air above electrolyte free surface. Using Stokes law for the settling of the acid mist droplets, the terminal velocity of a 30 μm drop is about 3 cm/s. The terminal velocity scales to the diameter d^2 , and one needs to double the drop size to increase the terminal velocity by a factor of 4. Even then, the terminal velocities still small and hence there is always the possibility that the acid mist droplets generated will be carried away into the tankhouse workers' breathing environment when a light breeze is blowing.

3.2. Diffuser and nozzle results

Six arrangements of the diffusers and nozzles were used. They were 1) three wooden air diffusers connected in parallel, 2) two wooden air diffusers connected in parallel, 3) one wooden air diffuser, 4) four cylindrical sintered stone air diffusers connected in parallel, 5) one long rectangular sintered stone air diffuser, and 6) four nozzles connected in parallel. The pore size was the finest for the wooden air diffusers, larger for the sintered stone diffuser and 4 mm tubing and fittings for the nozzles. The bubble size ranges obtained from high speed video measurements are shown in Table 1.

Table 1. Range of bubble diameters from the six different injection arrangements used with different air flow rates.

Device	Bubble diameter (mm) [3 standard deviations]		
	0.5 l/m	1.0 l/m	2.0 l/m
Three wooden air diffusers	0.26 – 0.30	0.34 – 0.38	0.41 – 0.550
Two wooden air diffusers	0.31 – 0.36	0.34 – 0.38	0.49 – 0.61
One wooden air diffuser	0.34 – 0.39	0.48 – 0.63	0.51 – 0.64
Four blue sintered stone air diffuser	1.64 – 1.88	1.89 – 2.19	2.10 – 2.39
Long blue sintered stone	3.42 – 3.69	2.70 – 4.05	3.75 – 4.30
Four open nozzles	6.75 – 6.99	9.72 – 10.21	13.99 – 14.22

The results show that the bubble size increases with pore size and gas flow rate indicating that the bubble formation is inertia controlled.

The acid mist formed was measured by collecting it with filter paper of 56 mm diameter, stacked to a 5 mm thickness, and located 150 mm above the free surface of the electrolyte. The filters were then soaked in water and the complete mixture of filter paper and acid solution titrated with 0.1M KOH with phenolphthalein as indicator. The results in Figure 5 show considerable scatter in the data for the finer bubble sizes obtained with wooden blocks as diffusers and more consistent results with larger bubbles. The trend shows that larger bubbles produce less fine acid mist as any large droplets formed from the breakup of the central jet will fall back into the electrolyte bath. The flux of acid mist is not increased with increasing gas flow rate and this can be attributed to the fact that the bubbles tend to form a plume that spreads to even out the flux of bubbles passing through the free surface.

The slopes of the lines show that the acid mist flux is inversely proportional to the bubble diameter and increasing the bubble diameter will reduce the acid mist formed. This power law relationship has also been found with the splash height in gas injected pyrometallurgical baths (Liow and Gray, 1996).

4. DISCUSSION

The results of this study have confirmed that the acid mist is formed predominantly from small bubbles bursting at the free surface. The flux of acid mist is quite high, reaching up to 12-13 mg/(m²s) which will require an upward air velocity of at least 10 m/s to ensure that the air is diluted to the NOSH requirements. With the larger bubbles, the upward air velocity can be reduced to less than 1 m/s. The inverse relationship between acid mist flux and bubble diameter has not been reported before and this provides a means of reducing the acid mist, which is to ensure that bubbles bursting at the electrolyte free surface are at least 10 mm or larger. Unfortunately, the coalescence of fine bubbles formed during electrolysis is governed by surface impurities and will require a larger number of fine bubbles to coalesce to form such large bubbles. It is likely that artificial aids, such as mechanical devices or surfactants, will be needed to promote such coalescence.

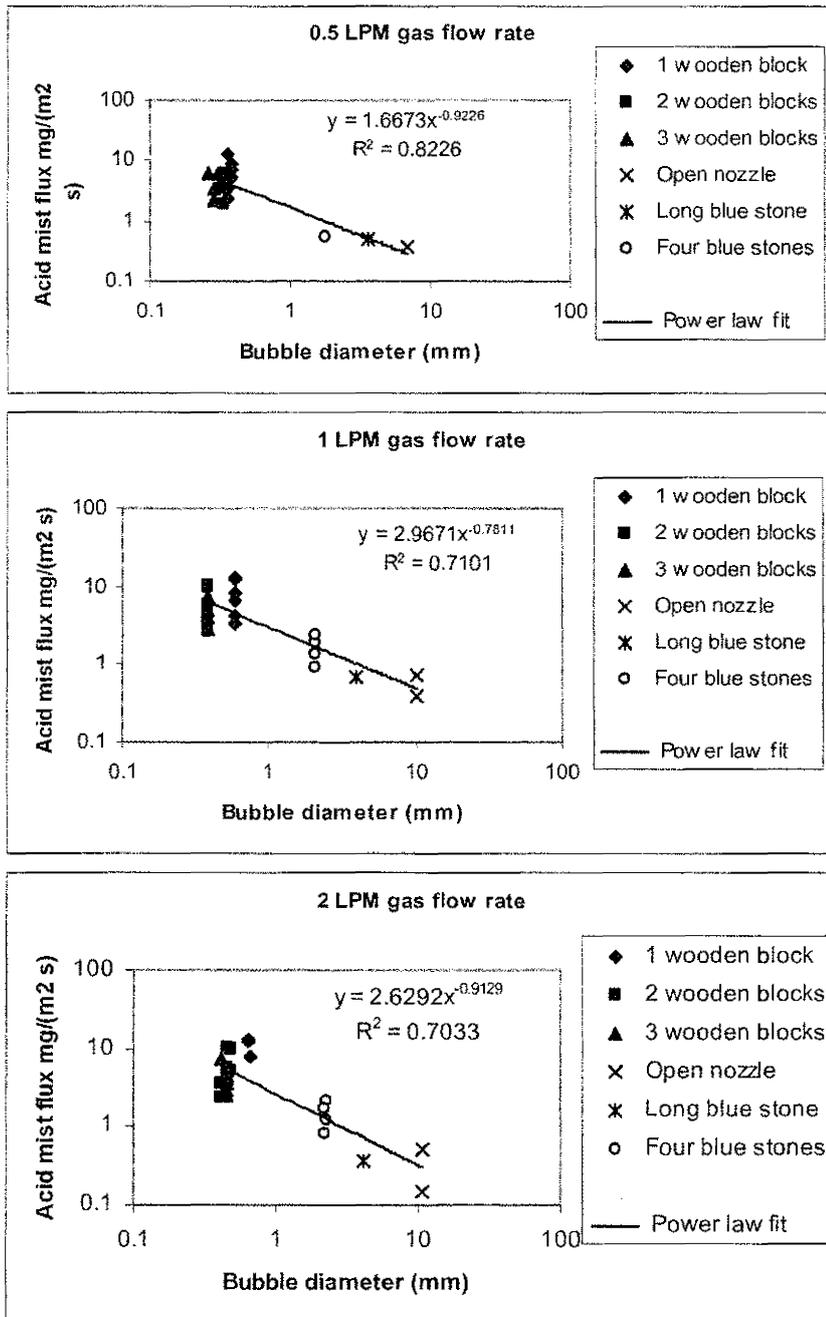


Figure 5 The acid mist flux for different gas flow rates as a function of the bubble size.

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5. CONCLUSION

The formation of acid mist in electrowinning plants results in a hazardous environment for operators. This study has shown that small bubbles, less than 1 mm in diameter, give rise to the largest acid mist flux while bubbles greater than 10 mm in diameter resulted in a factor of 10 less in acid mist flux. The inverse relationship between acid mist flux and bubble diameter provides a simple means of estimating the bubble size necessary to reduce the acid mist flux to safe levels for operation of electrowinning plants. However, some means of coalescing the fine bubbles produced during the process must be provided to ensure that only large bubbles burst at the electrolyte free surface.

6. ACKNOWLEDGMENTS

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