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MASS TRANSFER OF HYDROGEN BETWEEN LIQUID
ALUMINUM AND BUBBLES OF ARGON GAS

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October, 1961

IP-538

ACKNOWLEDGEMENT

The authors gratefully acknowledge the encouragement of the Research Division of Federal Mogal Corporation who supplied some of the materials used in this investigation.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENT.....	ii
LIST OF FIGURES.....	iv
INTRODUCTION.....	1
DERIVATION OF THE MODEL.....	1
Mass Transport Control.....	3
Thermal Expansion of the Bubble.....	4
Expansion Caused by Reduced Pressure Head.....	5
APPARATUS AND EXPERIMENTAL PROCEDURES.....	6
EXPERIMENTAL RESULTS AND DISCUSSION.....	6
Equilibrium Degassing.....	9
Loss of Hydrogen from the Melt Surface.....	9
Influence of Bubble Size.....	9
Influence of Flow Rate.....	9
SUMMARY.....	14
BIBLIOGRAPHY.....	15

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Experimental System.....	7
2	Comparison of Equilibrium Degassing With Experimental Result.....	10
3	Loss of Hydrogen From Melt in Absence of Argon Flushing.....	11
4	Influence of Bubble Size on Removal of Hydrogen by Argon Flushing.....	12
5	Influence of Flushing Rate on Hydrogen Removal for Bubble Radius of 0.5 cm.....	13

INTRODUCTION

The presence of hydrogen in liquid metals in amounts which exceed the solid solubility at one atmosphere hydrogen pressure is highly undesirable, causing unsound ingots or castings, or resulting in difficulties during further fabrication. The removal of hydrogen from liquid metals can be accomplished by several methods, the principal two being vacuum treating and inert flush degassing. The design of a process involving either of these techniques is based on the mass transfer coefficient for hydrogen between the liquid metal and a hydrogen-dilute gas phase. In an effort to extend our knowledge in this area, an investigation of the rate of removal of hydrogen from liquid metals by inert gas flushing was undertaken. In view of the difficulties encountered with gas porosity in the casting of aluminum and aluminum alloys, and because of certain experimental advantages, liquid aluminum was selected for the study.

The removal of gases from liquid metals has received considerable attention in recent years. Sims⁽¹⁾ has reported on the removal of hydrogen from liquid steel by flushing with argon, and Vallet⁽²⁾ has considered the degassing of an open-hearth bath by carbon monoxide bubbles during the boil. Pehlke and Elliott⁽³⁾ have studied the kinetics of nitrogen liquid-iron reactions. Machlin⁽⁴⁾ has presented an analytical treatment of vacuum induction refining. Considerable work has also been reported on aqueous and organic liquid-gas systems, and an excellent summary prepared by Hovis.⁽⁵⁾

The treatment of liquid aluminum by a flushing gas has been an established practice for several years.⁽⁶⁾ A number of gases have been used for this purpose, including nitrogen, argon, and chlorine, or mixtures of these gases. Tikkanen and Erko⁽⁷⁾ have studied the relative density changes of aluminum castings poured from melts degassed with chlorine, nitrogen, and mixtures of the two gases. Their results show that in the case of chlorine, chemical reactions play an important and sometimes detrimental part in the degassing operation. Unfortunately, much of the data reported for the degassing of aluminum melts are not in sufficient detail or in proper form for quantitatively evaluating the mechanism of hydrogen removal.

DERIVATION OF THE MODEL

Equilibrium Degassing - In view of the high diffusion coefficients for hydrogen in liquid metals, some consideration was given to the possibility that the equilibrium pressure of hydrogen in the inert

flush gas bubble might be reached during the rise of the bubble in the liquid metal. In the case where equilibrium is assumed, the following mass balance may be written expressing the hydrogen removed:

$$dN_g = (dN_g + dN_f) P_g / (P_g + P_f) \quad (1)$$

where N_g and N_f are the liters of diatomic hydrogen and flushing gas, respectively, and P_g and P_f are their partial pressures. If it is assumed that the purging gas leaves the melt at one atmosphere pressure and is in equilibrium with the residual hydrogen content of the liquid metal, and noting that the inert flush gas enters at the same rate that it leaves, then:

$$dN_f = -dN_g ((1 + P_g)/P_g) \quad (2)$$

Converting to concentrations:

$$dC_g = \frac{-99.0 M dN_f}{((1 + P_g)/P_g)W} \quad (3)$$

where M is the molecular weight of the diatomic gas (2 in the case to be considered), W is the weight of the metal bath in pounds, and C_g is the concentration of dissolved gas in parts per million by weight. From Sieverts' Law:

$$C_g = K_g \sqrt{P_g} \quad (4)$$

where K_g is the equilibrium constant for the solution of hydrogen in the liquid metal under consideration. Combining Equations (3) and (4) and integrating:

$$\int_{C_0}^C \left[\frac{dC_g}{C_g^2} + \frac{dC_g}{K_g^2} \right] = \frac{99.0 M}{K_g^2 W} \int_0^{V_g} dN_f \quad (5)$$

and

$$V_g = \frac{1.01 W}{M} (C_0 - C)(K_g^2 + C C_0) / C C_0 \quad (6)$$

where V_g is the volume of flushing gas in liters required to reduce the dissolved hydrogen content from C_0 to C .

Mass Transport Control - Assuming that mass transfer is limited by the transport of hydrogen through the liquid metal phase, the removal of hydrogen by a single bubble may be described by the relation:

$$dn_g/dt = - k_L a_b (C_B - C_M) \quad (7)$$

where n_g is the moles of hydrogen being removed, k_L is the mass transfer coefficient in cm/sec, a_b is the area of the bubble-metal interface in cm^2 , and C_B and C_M are the concentrations of hydrogen in the metal at the bubble interface and in the bulk metal, respectively, in moles/cm³.

For a system consisting of a crucible of liquid metal exposed to a hydrogen-free atmosphere in which an inert flush gas bubble generator is immersed, mass transfer across the free surface of the melt must also be considered. This portion of the mass transfer can be described by Fick's first law:

$$dn_g/dt = DA_s \frac{dC_g}{dx} \quad (8)$$

where D is the diffusion coefficient of hydrogen dissolved in the liquid phase and A_s is the surface area of the melt. Assuming that the hydrogen content of the atmosphere is negligibly small, the concentration gradient can be replaced by C_M/δ where δ is the boundary layer thickness.

In Equation (7) the term C_B is approximately zero if the rate of transfer to the bubble is small, since it represents the concentration in equilibrium with the partial pressure of hydrogen in the bubble. Noting also that n_g can be converted to concentration units by dividing by the volume of the melt, Equations (7) and (8) can be combined to give:

$$\frac{dC_g}{C_g} = - \frac{1}{V_M} \left[\frac{D}{\delta} A_s + k_L a_b n \right] dt \quad (9)$$

where n is the number of bubbles in the melt at any instant, and is given by the relationship:

$$n = F\tau_r/v_b \quad (10)$$

where F is the flow rate of the flush gas, τ_r is the time required for a bubble to rise through the melt, and v_b is the volume of a single bubble. The total instantaneous bubble area, $n a_b$, is given by the relation:

$$A_b = \frac{3}{r_b} F \quad (11)$$

where f_b is the bubble radius. Combining Equations (9) and (11) and integrating:

$$\int_{C_0}^C \frac{dC_g}{C_g} = - \frac{1}{V_m} \int_0^t \left[\frac{D}{\delta} A_s + \frac{3k_L F \tau_r}{r_b} \right] dt \quad (12)$$

or:

$$C = C_0 \exp \left[- \frac{DA_s t}{\delta V_m} - \frac{3k_L F}{V_m} \int_0^t \frac{\tau_r}{r_b} dt \right] \quad (13)$$

Equation (13) now expresses the instantaneous concentration of the melt in terms of the original concentration, several geometry factors, the diffusion coefficient and boundary layer thickness at the exposed melt surface, and the mass transfer coefficient for the rising bubbles.

Further simplification of Equation (13) requires a closer examination of the nature of bubble generation and rise in the melt. After a bubble of flush gas is released into the liquid metal environment, it can change dimensions due to the following effects:

- (1) Thermal expansion, if the gas is not at the melt temperature upon release.
- (2) Expansion caused by reduced pressure head as the bubble rises.
- (3) Expansion due to hydrogen diffusion into the bubble.
- (4) Contraction due to argon diffusion out of the bubble.

Statements (3) and (4) are neglected, assuming that the volume of hydrogen removed is extremely small compared to the volume of flush gas, and assuming that the flush gas is completely insoluble in the liquid metal. Statements (1) and (2), however, require further consideration.

Thermal Expansion of the Bubble - Before the bubble is released into the liquid metal, it may be preheated depending upon whether or not the delivery mechanism is immersed in the melt. Under the experimental conditions of this investigation, the gas was preheated while flowing down a vycor tube with an immersed length of approximately 25 cm. Hence, for the case under consideration, heat transfer can be based on forced convection in a heated tube. The Reynolds number for the flow rates used in this investigation, assuming a mean gas temperature of 350°C in the tube, indicate that the gas stream in the delivery tubes was in the region of streamline flow. Assuming a parabolic velocity distribution and a uniform

Wall temperature, the exit gas temperature may be shown to be essentially equal to the wall temperature of the tube.⁽⁸⁾ Examination of the thermal resistances involved in heat transfer from the melt to the gas flowing in the delivery tube revealed that transfer of heat to the gas is rate limiting compared to conduction through the tube wall. Hence, it was concluded that the gas reached the melt temperature prior to release from the delivery tube.

Expansion Caused by Reduced Pressure Head - When the diameter of the bubble becomes much larger than the outside diameter of the delivery tube, it becomes unstable and breaks off.⁽⁹⁾ Hence, in the present study, the initial bubble diameter will be assumed to be equal to twice the diameter of the tube opening. Calculations of the change in bubble diameter during rise to the surface through 20 cm of liquid aluminum showed that the small changes in bubble size caused by a reduced pressure head can be neglected, and that the rise velocity of the bubble can be considered approximately constant.

The rise time for the bubble can be calculated from the terminal rise velocity, V_t , which is given by the expression:

$$V_t = \left[\frac{4(\rho_l - \rho_b)gd_b}{3\rho_l f} \right] \quad (14)$$

where ρ_l is the liquid density, ρ_b is the gas density in the bubble, d_b is the bubble diameter, and f is a friction factor which is defined in terms of the Reynolds number.⁽¹⁰⁾ The rise time of the bubble through the melt is then given by the relationship:

$$r = h/V_t \quad (15)$$

where h is the height of the melt above the exit of the delivery mechanism. This expression neglects the time of formation of the bubble and its initial acceleration to the terminal velocity. The time of formation would be extremely short under the flow conditions used in the experiments to be considered below. The period of initial acceleration can also be shown to be very short relative to the rise time.

In view of the considerations presented above, Equation (13) reduces to:

$$\ln\left[\frac{C}{C_0}\right] = - \left[\frac{DA_s}{\delta V_m} + \frac{3k_L F r}{r_b V_m} \right] t \quad (16)$$

APPARATUS AND EXPERIMENTAL PROCEDURES

The experimental system employed in this investigation is shown in Figure 1. The melt consisted of 18 kg of commercially pure aluminum held in a 23 cm diameter, clay-graphite refractory crucible which was heated inductively. Moist wooden sticks were placed in the melt at 800°C to introduce hydrogen. The temperature of the metal, measured with an immersion thermocouple, was lowered to approximately 700°C, and maintained at that level throughout the degassing experiment.

Argon gas, which was dried by passing it through an anhydron tower, was delivered at a constant flow rate into the liquid metal through a straight section of vycor tubing. In an effort to demonstrate that traces of oxygen in the argon flush gas had no influence on the results, separate experiments were run in which the argon was passed over heated copper gauze and heated titanium chips in addition to the drying compound.

Samples of the liquid metal were taken periodically for hydrogen analysis by drawing molten aluminum up against copper gauze in a small-diameter vycor tube and immediately quenching the tube in liquid nitrogen. The sample was then trimmed, wrapped in aluminum foil, and stored in liquid nitrogen.

The hydrogen content of the aluminum samples was determined by hot-vacuum extraction at 500°C using a standard NRC Vacuum Fusion apparatus. A period of approximately 40 minutes was found sufficient to collect the evolved gases which were found to be 95 percent or more hydrogen. A ten-minute circulation period, during which the hydrogen was frozen out of the sample as reacted water vapor, was employed.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results of this investigation are presented in Table I. Vycor delivery tubes with inside diameters of 5, 3.5 and 2 millimeters were used to evaluate the effects of bubble size. The depth of immersion was 20 cm for all of the experiments. The initial hydrogen content varies considerably for the 8 experiments due to the uncontrolled technique of charging hydrogen with wet sticks. The data of Ransley and Neufeld⁽¹¹⁾ indicate that the equilibrium solubility of hydrogen in aluminum at 700°C and one atmosphere hydrogen pressure is 0.8 parts per million by weight, and at 800°C and one atmosphere hydrogen pressure is 1.5 ppm. These data indicate that the charged hydrogen contents in the present experiments approached or exceeded these saturation values.

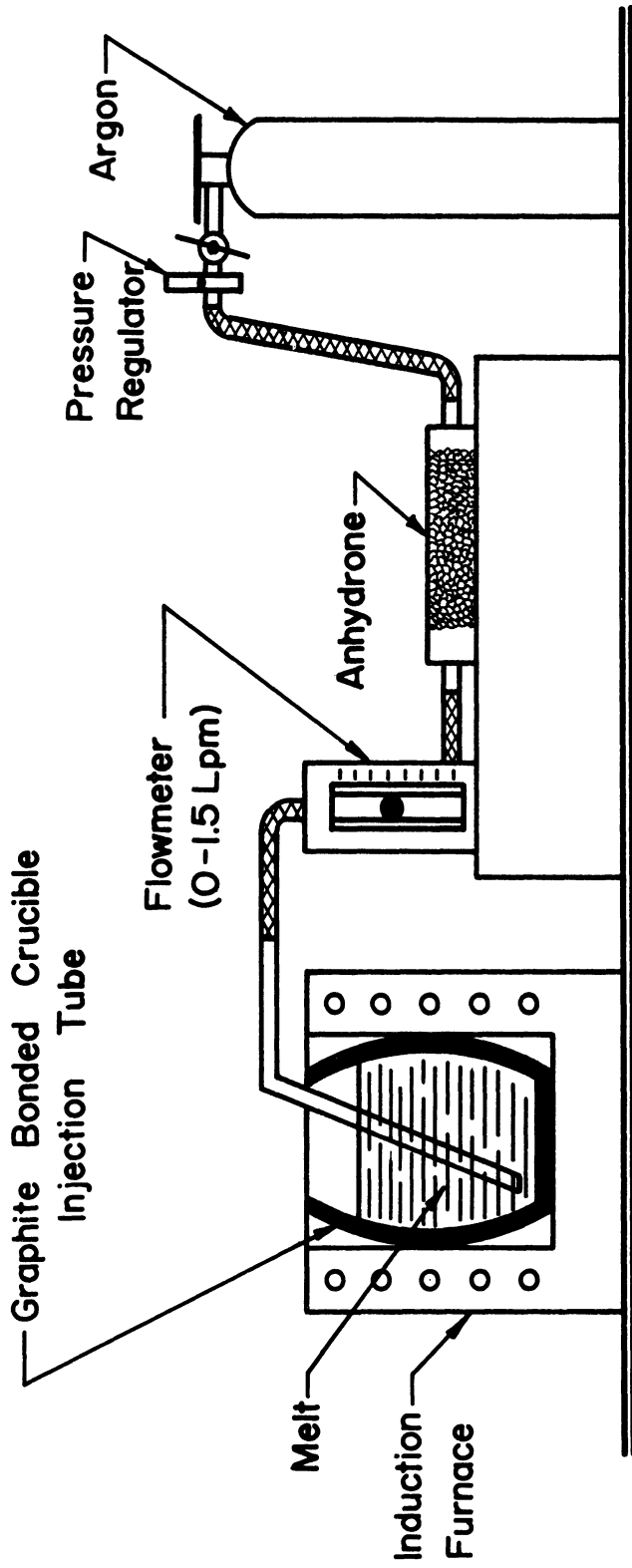


Figure 1. Experimental System.

TABLE I

HYDROGEN CONCENTRATION OF LIQUID
ALUMINUM DURING ARGON DEGASSING

Run	Tube Opening (mm)	Flow Rate (liters/min)	Degassing Time (minutes)	Concentration Hydrogen (ppm)
1	none	0	0	1.53
			8	1.45
2	none	0	0	1.605
			9	1.50
3	5	0.8	0	0.775
			3	0.72
			6	0.735
			12	0.645
4	5	1.6	0	1.03
			3	0.855
			6	0.83
			9	0.695
			16	0.555
5	3.5	0.8	0	1.225
			6	1.045
*6	3.5	0.8	0	0.965
			6	0.825
*7	3.5	0.8	0	1.535
			24	0.82
8	2	0.8	0	0.975
			6	0.86
			12	0.60

* These degassing runs were carried out using argon which had been deoxidized by passing over heated copper gauze and heated titanium chips.

Equilibrium Degassing - Equation (6) was derived for the case in which equilibrium is established between the hydrogen dissolved in the melt and the rising gas bubbles before the bubbles leave the melt. A calculation of the fraction of hydrogen remaining in the melt as a function of flushing gas volume under equilibrium conditions is plotted in Figure 2, assuming a melt saturated with hydrogen at 700°C and neglecting loss of hydrogen from the melt surface. The experimental data for a flow rate of 0.8 liters per minute and an intermediate bubble size are also shown in Figure 2 and reveal that much less hydrogen is removed per unit volume of flushing gas than predicted for equilibrium conditions. Hence, the equilibrium approach defined by Equation (6) does not describe the experimental data. Mass transport control, as defined by Equation (16), can be considered to better represent the removal of hydrogen from the liquid metal phase, as shown below.

Loss of Hydrogen From the Melt Surface - Hydrogen is removed from the melt during the experiment by direct evolution into the atmosphere at the exposed melt surface as well as by mass transfer to the argon bubble stream. In order to separate the two paths for hydrogen evolution, Runs 1 and 2 were carried out in a standard manner except that no argon was bubbled through the melt. The results of these two experiments are shown graphically in Figure 3. Applying Equation (16), where F (the flow rate of argon) is zero, the slope of a plot of $\ln C/C_0$ versus time will be $-DA_S/\delta V_M$. The mass transfer coefficient at the melt surface, D/δ , can be calculated from the melt geometry and the mean slope of Figure 3, and is found to be 1.6×10^{-3} cm/sec. This value appears to be low, but may be accounted for by the presence of a thin oxide crust which appeared on the melt surface during the experiments.

Influence of Bubble Size - The results of Runs 3, 5, 6, 7, and 8 are presented on a semi-log plot in Figure 4. The slopes of the straight lines drawn through these data points are given in Table II, which also lists the calculated mass transfer coefficients between the melt and the argon bubbles. The mass transfer coefficient is independent of bubble size, at least within the experimental accuracy which is estimated to be 25 percent. An average value for the mass transfer coefficient, k_L , at 700°C at a flow rate of 13.3 cm³/sec is 3.9×10^{-2} cm/sec. This result is in agreement with the correlation of Sherwood and Pigford⁽¹²⁾ which predicts a transfer coefficient of about 4×10^{-2} cm/sec for mass transfer in flow past single spheres.

Influence of Flow Rate - Flow rates of 0.8 and 1.6 liters per minute were investigated using a 5-mm ID delivery tube. The results of these experiments, Runs 3 and 4, are shown in Figure 5, and the mass transfer coefficients are given in Table II. The mass transfer coefficient was

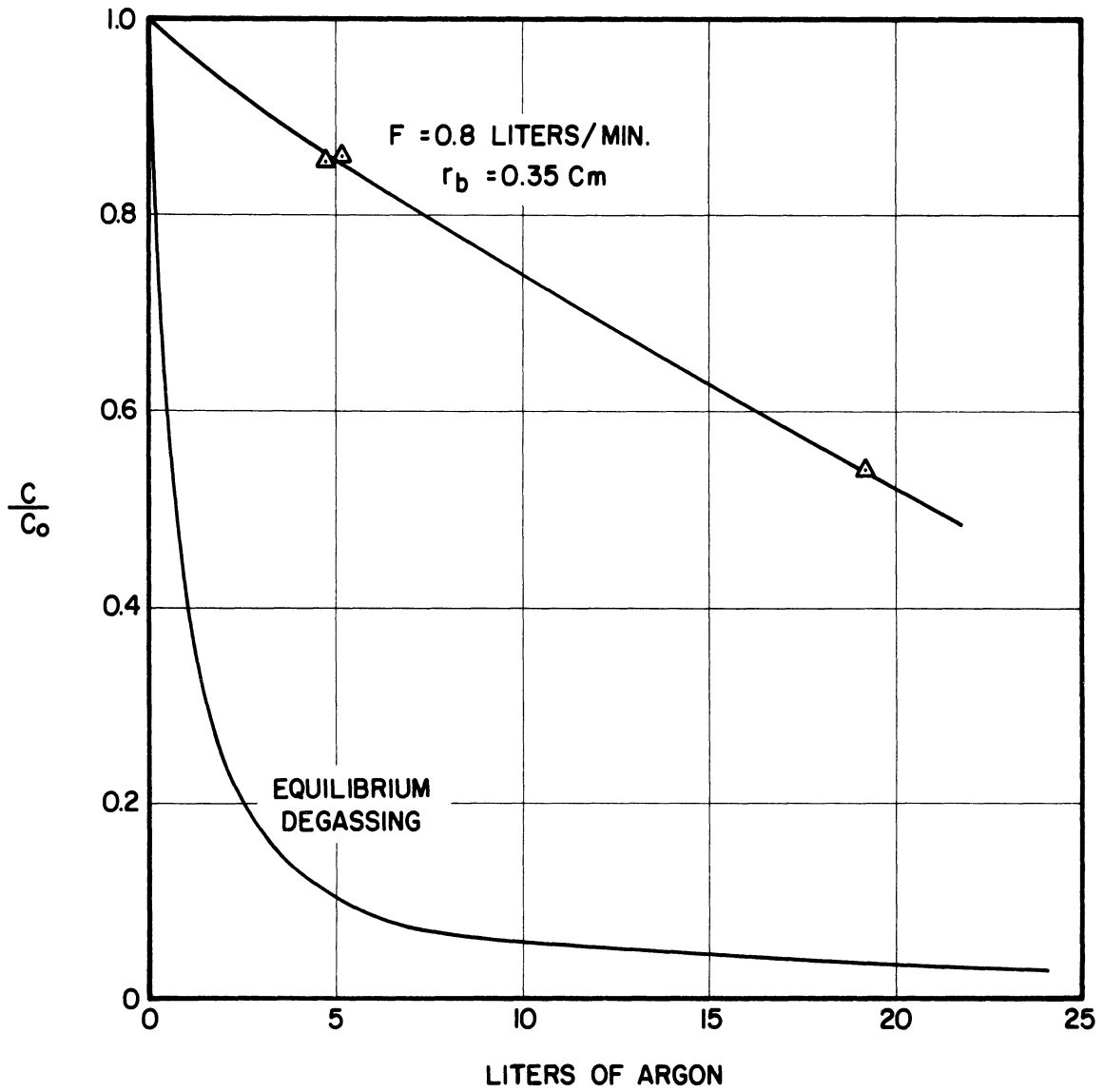


Figure 2. Comparison of Equilibrium Degassing With Experimental Result. (Surface losses neglected in calculating equilibrium degassing line.)

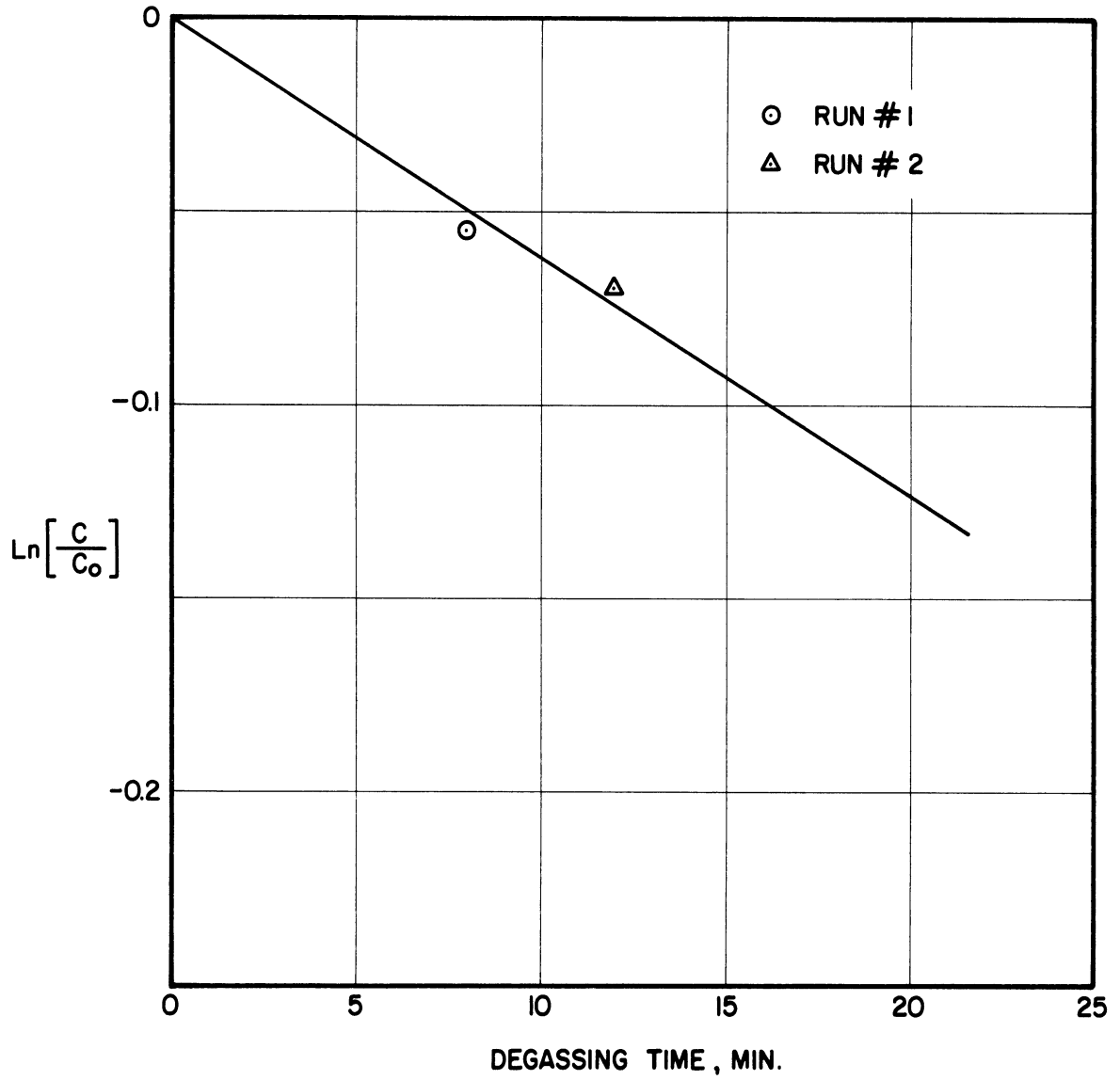


Figure 3. Loss of Hydrogen From Melt in Absence of Argon Flushing.

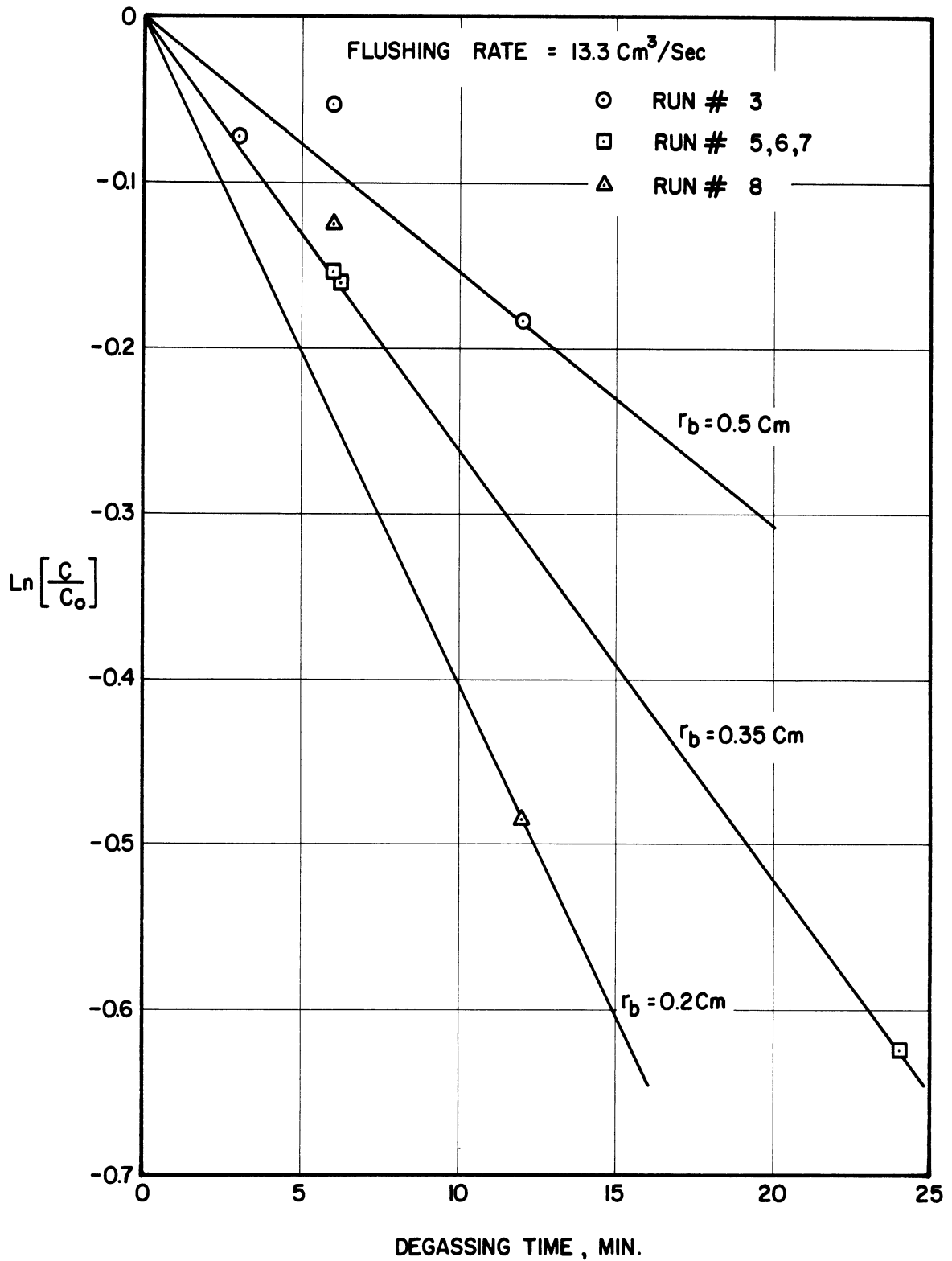


Figure 4. Influence of Bubble Size on Removal of Hydrogen by Argon Flushing.

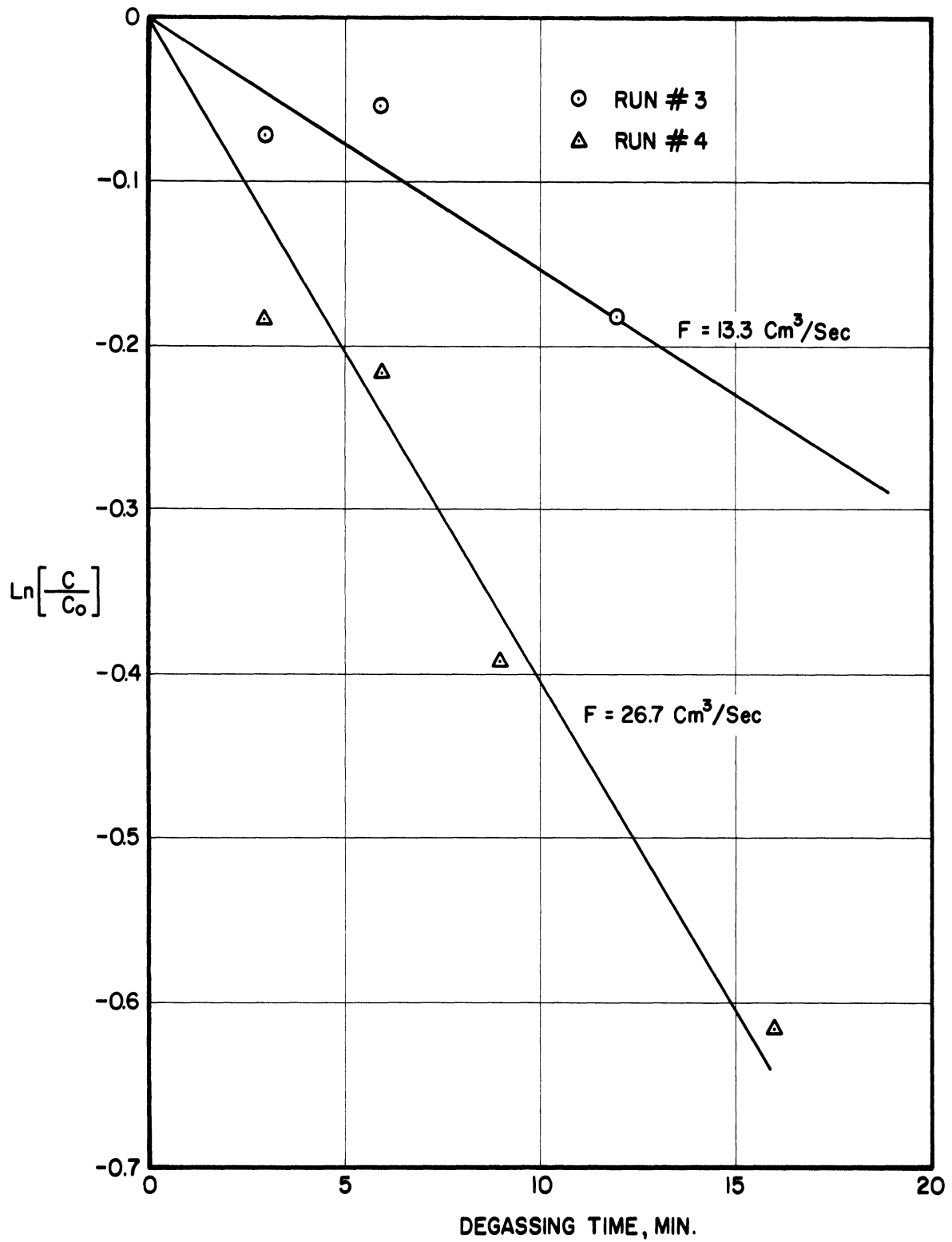


Figure 5. Influence of Flushing Rate on Hydrogen Removal for Bubble Radius of 0.5 cm.

larger for the higher flow rate, which may be due to turbulence in the melt. Such turbulence, which becomes noticeable at flow rates above 1 liter/min, undoubtedly increases the loss of hydrogen at the melt surface. Also, increasing the flow rate may result in physical conditions which are not accurately described by the individual-sphere model.

TABLE II
CALCULATION OF MASS TRANSFER COEFFICIENTS

Bubble Radius cm	cm ³ /sec	Bubble Residence time sec	Slope sec ⁻¹	k _L cm/sec	D/δ cm/sec
-	None	-	-1.03 x 10 ⁻⁴		1.64 x 10 ⁻³
0.5	13.3	0.356	-2.56 x 10 ⁻⁴	3.7 x 10 ⁻²	
0.35	13.3	0.425	-4.35 x 10 ⁻⁴	4.5 x 10 ⁻²	
0.2	13.3	0.563	-6.79 x 10 ⁻⁴	3.5 x 10 ⁻²	
0.5	26.7	0.356	-6.72 x 10 ⁻⁴	6.8 x 10 ⁻²	

SUMMARY

1. The removal of hydrogen from liquid aluminum by inert flush degassing has been shown to be a non-equilibrium process, and to be described in terms of mass transport control in the liquid phase.
2. The mass transfer coefficient for the removal of hydrogen from liquid aluminum at 700°C is 3.9 x 10⁻² cm/sec, as determined for bubbles from 0.4 to 1.0 cm in diameter at a flow rate of 13.3 cm³/sec (0.8 liters/min).
3. The rate of removal of hydrogen is increased by decreasing bubble size, and by increasing the flow rate.

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