Technical Notes

Surface Activity and Preferential Ablation

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Introduction

ALTHOUGH the relationship between viscosity and liquid ablation has been thoroughly explored,[1-4] the influence of surface phenomena on ablation has received little attention Since ablation is in many instances the transport of material through surfaces or interfaces, ablation characteristics are controlled to a large degree by the physicochemical constitution of the surface The relative importance of surface effects such as surface tension, surface activity, and wettability will increase as the surface-volume ratio increases Thus, surface effects will become more pronounced with a decrease in liquid film thickness or an enlargement of the surface area by the formation of gas bubbles

In liquid ablation, material may be lost by two different mechanisms: flow and evaporation Loss by spattering is neglected The ablation efficiency is determined by the ratio of the loss rates, and the efficiency is high when evaporation is high and the flow rate to the back is small When the ablating material consists—as in most practical cases—of different chemical constituents, it is possible that one of these components ablates with a faster rate than the rest This phenomenon may be called preferential ablation, and it will be shown that it is closely related to surface phenomena Preferential ablation could, of course, occur by distillation of the more volatile component But even if all the components have a similar vapor pressure, preferential ablation may still be noticeable, if one of the components is surface active If this component is also the more volatile one, substantial losses of this ingredient are possible

Under equilibrium conditions, surface-active agents are more concentrated in the surface layer than in the bulk of the liquid In an ablating liquid, this equilibrium distribution will be more or less disturbed, but there is the tendency to replenish the surface layers steadily by diffusion The transport of the active agent to the surface may be vastly increased when gas bubbles are generated during the ablation process For glassy ablation materials, where diffusion is small because of the high viscosity, the latter process may be far more pronounced than transport by diffusion

Despite small bulk concentrations, the surface-active agent can have a decisive influence on the evaporation rate because of its high concentration in the surface layer Under certain conditions, this phenomenon may be used to improve ablation efficiency Phase systems in which the partial vapor pressure of one constituent is enhanced by the presence of the other constituents would be favorable for this purpose, provided that in such a system surface activity occurs Fortunately there is a strong relationship between this type of phase systems and the phenomenon of surface activity The vapor pressure of a solution will increase above the ideal value the more the molecules of the solvent and the solute repel each other Such heterophobic behavior, however, is also responsible for the occurrence of surface activity when one type of molecule is pushed out of the solution into the surface The occurrence of surface activity and phase systems with increased vapor pressure is therefore in many cases a parallel phenomenon, and this may be used to improve ablation performance [5]

Diffusion in Laminar Flow

A liquid that contains a surface-active ingredient of concentration c_0 in the bulk of the liquid will have an equilibrium surface concentration Γ Under ideal conditions, Γ is expressed by Gibb's law as

$$\Gamma = -(c_0/RT)(\partial\gamma/\partial c) \tag{1}$$

where γ is the surface tension and R the gas constant The more negative the value of $\partial\gamma/\partial c$, i e , the more rapidly the surface tension decreases with increasing concentration, the larger will be the value of Γ For liquid inorganic melts like slags and glasses, which are of greatest interest for liquid ablation, Gibbs' relationship may be assumed to be true

In the ablation process the enriched surface layers are continuously removed, and the equilibrium saturation concentration Γ, as determined by Gibbs' law, is disturbed With a steady rate of ablation there will be an even, diffusion-controlled flow of surface-active substance to the surface If the liquid film is turbulent, the diffusion flow is vastly intensified by convective transport For the present purposes, it will be assumed that the liquid film has the laminar flow structure that is characteristic of thin, viscous films Since only an introductory survey of the phenomenon is intended, it is also assumed, for the sake of simplicity, that the mass transport of liquid under the influence of the shear stress along the body is negligible in comparison with the mass transport perpendicular to the body walls by evaporation, so that ablation will occur almost exclusively by evaporation In other words, only ablation materials of high efficiency will be considered as desirable in practical application Simple considerations of continuity of mass and chemical species lead immediately to an expression for the degree of preferential ablation Π, which is the ratio of the diffusion flow of the surface-active substance to the total loss rate:

$$\Pi = \rho[(c_w - c_0)v/(e^{-v/D\delta} - 1)] \tag{2}$$

where ρ is the density of the liquid, v the ablation velocity, δ the thickness of the liquid layer, D the diffusion coefficient, and c_w the concentration in the surface layer Preferential ablation will become pronounced when the denominator becomes very small, i e , when the exponent $v/D\delta$ approaches zero This will occur for large D and small δ values The case where v tends to zero is of no interest from an ablation standpoint c_w is always smaller than or equal to Γ, and its true value can only be obtained by considering the aerodynamic stream conditions This can be done by relating the concentration of the injected substance in the gas boundary layer to the concentration of the surface active agent in the liquid surface The necessary thermodynamic relations will be given in the next section, where the practically more important case of gas-bubble transportation is described However, the same method may be used to interpret the parameters in Eq (2) by the heat- and mass-transfer relations of given aerodynamic flight conditions

Convection by Gas Bubbles

For most practical applications, the viscosity of the liquid should be large, and the diffusion coefficient is therefore small

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In the light of Eq (2), preferential ablation cannot be very pronounced under these conditions Most ablation materials develop gases by either boiling, decomposition, or degassing The gas bubbles collect the surface-active agent as they rise to the surface If the gas volume is sufficiently large, this type of transport can far offset the diffusion flow, especially in highly viscous liquids

The number of bubbles n generated per second per unit area depends upon the gas volume $\dot{G}$ developed per second per unit area and the average radius of the bubbles, so that

$$n = 3\dot{G}/4r^2\pi \tag{3}$$

The size of the bubbles is assumed to be smaller than the thickness of the liquid layer The rate of surface area production is then

$$\dot{S} = n4\pi r^2 = 3\dot{G}/r \tag{4}$$

Because of the shear force in the liquid layer, the bubbles will attain an elliptical shape, and the actual surface area will be larger by a certain factor f than the value indicated by Eq (4) Our own experiments show that this factor is not much larger than 2, even for high shear forces Under the assumed conditions, the surface layer of the gas bubbles will attain the equilibrium concentration of the surface-active compound as given by Gibbs' law Regardless of the viscosity and the thickness of the film, the amount of the active compound transported per unit time per unit area will be, under steady-state conditions,

$$\alpha\Gamma\dot{S} = -(3c_0\dot{G}/rRT)(\partial\gamma/\partial c) \tag{5}$$

α is a conversion factor to change molar surface percent to weight percent

Under certain conditions the rate of convection of a surface-active agent by gas bubbles to the film surface may be so large that oversaturation will occur, and part of the agent will diffuse back into the liquid When the ablation rate is large, it can be assumed that the total convected quantity is evaporated without back diffusion, and the factor for preferential ablation will then attain its maximum value:

$$\Pi_{\max} = -(3c_0\dot{G}/rRT\dot{m})(\partial\gamma/\partial c) \tag{6}$$

With this formula, an estimate can be made of how large and how pronounced the effect may become under extreme conditions The value of $\dot{G}/\dot{m}$ is determined by the choice of the ablation material and the proportion of volatile compounds A $\dot{G}/\dot{m}$ value of about 5000 is a realistic estimate for the plastic Fiberglas-reinforced ablation materials The value of $\partial\gamma/\partial c$ determines the degree of surface activity A value of 1000–10,000 dyne/cm² is a reasonable assumption The size of the gas bubbles is determined by the pore structure of the charred sublayer A high porosity with small pore diameters will enhance preferential ablation A realistic value for r is in the order of 0 005 cm With a surface temperature of 2000°K, $\Pi_{\max}$ is in the order of a few percent If the surface-active agent has a concentration of a few percent, it will therefore be removed about twice as fast as the neutral constituents This shows that preferential ablation rates are not abnormally high, and suitable surface-active agents may therefore be used to improve ablation performance effectively Preferential ablation rates of this order of magnitude were actually observed[6] However, in order to obtain quantitative results for a given flight condition, the properties and concentrations of the liquid must be coupled to the properties and concentrations of the gas boundary layer We indicate the gas and the liquid phase by the subscripts g and L, respectively The subscript 2 refers to the neutral components, and 1 refers to the surface-active component The relation between the mole fractions on the liquid and gaseous side of the interface are

$$x_{1g} = x_{1L}\gamma_1 e^{-\lambda_1} \tag{7a}$$

$$x_{2g} = x_{2L}\gamma_2 e^{-\lambda_2} \tag{7b}$$

γ_1 and γ_2 are the activity coefficients in the liquid, and λ_1 and λ_2 are defined by

$$\lambda_1 = \frac{L_{v1}}{R}\left(\frac{1}{T} - \frac{1}{T_{1b}}\right) \tag{8a}$$

$$\lambda_2 = \frac{L_{v2}}{R}\left(\frac{1}{T} - \frac{1}{T_{2b}}\right) \tag{8b}$$

$L_{\ i}$ are the heats of evaporation, and T_{ib} are the boiling points of the corresponding components

In boiling liquids or with ablation materials of the plastic-glass type, the developed gas volume is very large, and, therefore, large amounts of the surface-active substance are transported to the surface It may therefore be assumed that the equilibrium concentration Γ is attained in the surface of the liquid layer

The factor for preferential ablation Π may be defined as the ratio of loss of the active agent to the total weight loss referred to the gas phase:

$$\Pi = w_{1g}/(w_{1g} + w_{2g}) \tag{9}$$

The transformation of weight percent into mole percent is $w_j = (M_j/\overline{M})x_j$, where M_j is the molecular weight of component j, and $\overline{M}$ is the average molecular weight of the mixture This yields, under the described conditions,

$$\Pi = \alpha M_1\Gamma\gamma_1 e^{-\lambda_1}/[\alpha M_1\gamma_1\Gamma e^{-\lambda_1} + \alpha M_2(1 - \Gamma)\gamma_2 e^{-\lambda_2}] \tag{10}$$

The total concentration of ablated foreign gas $w_g = w_{1g} + w_{2g}$ at the liquid gas interface near the stagnation point is[8]

$$w_g = \frac{N_{Sc,w}{}^{0\ 6}[\dot{m}/(\rho_w\mu_w K)^{1/2}]}{(N_{Nu\ w}/R_w{}^{1/2}) + \frac{1}{3}[\dot{m}/(\rho_w\mu_w K)^{1/2}]} \tag{11}$$

where $N_{S\ \ w}$ is the Schmidt number at the wall, K is defined by $u_\infty = Kx$, where x is the coordinate in the stream direction along the surface of the body, $N_{Nu\ w}$ is the Nusselt number at the wall, and R_w is the Reynolds number at the wall

Inserting Eqs (10) and (11) into Eq (9) yields

$$\Pi = \alpha\,\frac{M_1\gamma_1 e^{-\lambda_1}\,(N_{Nu,w}/R_w{}^{1/2}) + \frac{1}{3}[\dot{m}/(\rho_w\mu_w K)^{1/2}]}{N_{S\ \ w}[\dot{m}/(\rho_w\mu_w K)^{1/2}]} \tag{12}$$

Inserting the well-known expressions for $N_{Nu\ w}/R_w{}^{1/2}$ (Ref 7) and $\dot{m}$ (Ref 8) determines Π as a function of the wall temperature and several material parameters In order to simplify the result somewhat, it may be assumed that the Schmidt and Prandtl numbers are unity One obtains, then, for axisymmetric flow near the stagnation point

$$\Pi = \alpha M_1\Gamma\gamma_1 e^{-L\ _1/R(1/T-1/T_{b1})} \times$$
$$\left\{K^{0\ 4}\left[\left(\frac{c_{p1}}{c_{p2}}\,\frac{T_w - T_c}{T\ - T\ } + \frac{1}{2}\right) + \frac{1}{6}\right] + \frac{1}{3}\right\} \tag{13}$$

K and the stagnation temperature T are given by the flight condition

Because of their high viscosity, liquid glasses are most attractive for liquid ablation The substances that will increase the surface activity of liquid glasses are foreign molecules, which are not easily incorporated into the molecular network of the glass and, therefore, concentrate on free surfaces One example is boron oxide, which is rejected by the SiO_4 network because its glass structure differs from that of the silica glasses As a consequence, this substance becomes surface active The addition of boron oxide to silica glasses for ablation purposes has, therefore, definite advantages

For the case that spattering cannot be neglected, a quite different loss mechanism might be initiated[9]

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Conversion of Coordinates: Latitude-Longitude to Cislunar

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THE problem of navigation of a space vehicle from Earth to the moon and back again is complicated by the fact that different coordinates are more convenient to use at different phases of the voyage Close to Earth, an Earth-centered latitude-longitude coordinate system or another of the same general type would be most applicable Close to the moon, a moon-centered system would be most applicable In the region between the Earth and the moon, a different set of coordinates might be more applicable such that the X axis is directed along the line of centers of mass of both the Earth and the moon, the Y axis is directed along a line parallel to the plane of the ecliptic, and the Z axis is perpendicular to each of the other axes The origin for this particular coordinate system may be taken as the center of mass of the Earth In further discussions of this particular coordinate system, it will be referred to as the cislunar coordinate system, and a subscript c will be used with the X, Y, Z of this system

It is important that a relation between the various coordinate systems be shown such that a smooth transition between the various coordinate systems can be made As an example, the relationships between an Earth-centered latitude-longitude system of coordinates and the cislunar set of coordinates will be shown with the realization that a transition from the cislunar set of coordinates to an Earth-centered latitude-longitude coordinate system would be made in a similar manner as would transitions involving a moon-centered coordinate system and a cislunar set of coordinates

The Earth-centered latitude-longitude system that will be used will be the one used by Isakson[1] relating a vehicle to inertial space The position of a vehicle is related to inertial space first by a rotation of the coordinate system about a Z axis through a longitude angle Λ and then through a latitude angle λ about the Y axis The X axis will then pass through the centroid of the vehicle A subscript g will be used with quantities referring to this particular coordinate system

In order to relate the position of the moon to the coordinate system involving X , Y , and Z , information regarding the moon's orbit must be known The moon's orbit about the Earth will be inclined at some angle i to the plane of the ecliptic In Fig 1 the plane of the moon's orbit and the plane of the ecliptic intersect in a line N-N' called the line of nodes The angle between the line of nodes and a line extended from the center of Earth through the position of the moon when it is at perigee and measured in the plane of the orbit is denoted as ω In Fig 1 this is indicated by the arc NA_1 The angle in the plane of the ecliptic measured between a line extended from Earth to the first point of Aries and the line of nodes is called the longitude of the ascending node θ In Fig 1 this is indicated by the arc ♈N The longitude of the moon when it is at perigee is defined as $\bar{\omega} = \theta + \omega$ The angular position of the moon at any instant would be given by $\bar{\omega} + v$, where v is the true anomaly In the figure v is increasing; consequently, the arc measured from N refers to the ascending node The true anomaly v would be the angle subtended by a line extending from Earth to perigee of the moon and a line extending from Earth to the position of the moon (arc A_1P_1 of Fig 1)

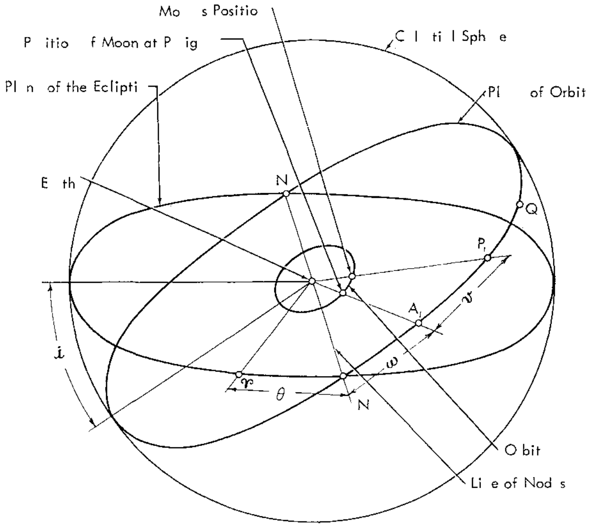

Fig 1 Orbital elements of the moon in its orbit about the Earth

The eccentricity of the moon's orbit is small; the position of the moon as a function of time will be adequately described by use of mean anomaly rather than true anomaly The mean anomaly is defined by the equation $\bar{v} = \sigma(T - T_0)$, where T_0 is the time that the moon is at perigee and T is the time under consideration such that $(T - T_0)$ is the time that it takes the moon to go from perigee position to its present position In Fig 1 the mean anomaly would correspond to the arc A_1Q Actually, the arcs A_1P_1 and A_1Q are very nearly equal Use of mean anomaly rather than true anomaly simplifies the required calculations considerably with little degradation in accuracy

Having defined the orbital elements, it is now necessary to define the navigational elements The celestial equator is the great circle formed on the celestial sphere by extension of the plane of the equator of the Earth Declination, δ, is measured northward or southward from the celestial equator The sideral hour angle, SHA, is measured westward from the hour circle of the vernal equinox, the first point of Aries (an hour circle being a great circle related to a point on the celestial sphere) The right ascension, RA, is measured eastward from the vernal equinox and is such that RA $= 24^h -$ SHA Figure 2 shows the relationships of these angles as well as their directional sense The Greenwich hour angle, GHA, and local hour angle, LHA, are measured westward from 0° to 360° with the Greenwich or local celestial meridian, respectively, used as a reference Because of the apparent daily rotation of the celestial sphere, the hour

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