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GRAVITY-DEPENDENT TRANSPORT IN INDUSTRIAL PROCESSES

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ABSTRACT

Gravity-dependent transport phenomena in various industrial processes is investigated in order to address a broader range of microgravity phenomena and to develop new applications of microgravity. A number of important topics are identified and analyzed in detail. The present article describes the results of some of topics which are: coating flow, zeolite growth and rotating electrochemical system.

INTRODUCTION

New directions for microgravity research that will also enhance commercial successes for the space program were indicated by Ostrach (1987). In particular, it was noted that microgravity research is dispersed over a number of disciplines but the underlying and unifying basis for new and unusual aspects in microgravity is gravitationally modified biophysicochemical transport phenomena. This means that the effects of fluid flow and heat and mass transfer on physical transport and biological and chemical reactions and, inversely, the transport associated with such processes will be different in a low-gravity environment. When it is realized that such phenomena are vital elements in the chemical, pharmaceutical, food-processing, and biotech industries as well as in material processing it is evident that commercialization possibilities will be increased by consideration of such topics and the scope of the microgravity research program will be broadened if it is directed to understand such phenomena in order to develop a knowledge base for the applications.

On this basis, grants jointly supported by NASA Code SN and C were granted, and as a result of the research efforts, a number of topics were identified that were important and which were of particular interest to us. These are: coating flows, rotating electrochemical systems, transport phenomena in zeolite growth, two-phase flows (bubble generation in liquid flow), and effect of g-jitter on liquid-gas interface. All of the topics, in the first phase of the research, were carefully reviewed and, thereafter, were thoroughly investigated in the second phase. Both scaling and numerical analysis of coating flows was performed by Kizito et al. (1991) for the applications both on earth and in space. In addition, experiments were carried out to verify some of their results (Ostrach et al., 1994; Kamotani et al., 1994). Kim (1992) completed a theoretical analysis of bubble formation in flowing continuous liquid phases under both terrestrial and microgravity environments. Lateral g-jitter (both regular and random modes) effects with and without thermocapillary convection on liquid motion in an open container under weightless conditions were studied numerically and analytically (Chao et al., 1991; Kamotani et al., 1994). Gulic et al. (1991) performed both scaling and experimental studied on natural convection in fluids contained in a flat, shallow, rapidly rotating annulus exposed to an axial stable temperature gradient. A detailed scaling analysis of natural convection in dilute electrochemical systems with multiple species was completed by Jiang et al. (1992, 1994) in which temperature gradients exist. An experimental study of transport phenomena in zeolite growth has been recently finished by Zhang et al. (1992, 1993, and 1994).

Based on these works, additional ground-based research and definitive low-gravity experiments have been identified. Due to the limited space, the information on three topics, coating flow, zeolite growth, and rotating electrochemical system, will be described individually in the following sections.

COATING FLOW

In industrial coating processes, surfaces are covered with one or more uniform liquid layers that are, subsequently cured or dried. Recently, new advanced technologies have emerged that use coating operation such as in the manufacture of semiconductor components, magnetic information storage systems and photoresist microelectronics. In these processes, the final film thickness can be very thin and must be highly accurate. The liquid layer may not be smooth and, in which case, waves or ribs or streaks may occur. In most coating configurations, the gravitational force acts parallel to the flow thereby creating shear stresses in the film making it more prone to shear instability. The instabilities tend to be three dimensional, making numerical simulation difficult and inaccurate thus requiring a careful experimental study. The present experiment investigates in details the nature and conditions under which an interfacial film instability occurs in coating flow.

Since the primary objective of the experiment is to determine the conditions under which the interfacial instability occurs for a coating film, the experimental apparatus was designed to minimize vibrations from the motor, building and other undesired movements of the coating belt and pulley. The major components of the experiment are sub-divided as follows; coating applicator, the working fluid and flow visualization; recording and analysis equipment. Fig. 1 shows the schematic experimental setup. The dip coating applicator was a rectangular open container constructed from clear scratch-proof LEXAN. Silicone oil (polydimethylsiloxane polymer) was the primary test fluid.

Coating flows have very small characteristic dimensions with a free surface. To enhance the image of the meniscus profile, a method called laser induced fluorescence was used. The two-dimensional flow field was viewed and recorded by a CCD camera placed perpendicular to the laser sheet. The camera was found to be very suitable because it was able to penetrate into the flow field past any edge effects at the same time giving good resolution. Finally, the position and shape of the free surfaces were accurately measured by pixel analysis of digitized images.

When the belt is steadily withdrawn from the applicator, a thin liquid film adheres to it because of the no slip condition at the belt wall and fluid viscosity. The free interface deforms at the meniscus creating capillary pressure because of its curvature. Also, the downstream film size and its stability depend on the withdrawal rate, physico-chemical properties of the fluid and the balance of viscous and body forces.

The inverse Stokes number St^{-1} can be defined as a ratio of gravitational force to viscous force, in which $St^{-1} = \rho g h_o^2/\mu U_o$, h_o and U_o represent the characteristic film thickness and the velocity of the belt, respectively. The experimental data of the final film thickness is plotted in Fig. 2 together with the theoretical results (Levich, 1962; Kizito et al., 1991) showing $St^{-1/2} = 0.93\ Ca^{1/6}$ when Ca number is small (where $Ca=\mu U/\sigma$). From this figure, for all the fluids tested, the non-dimensional final thickness ($St^{-1/2}$) was no longer a function of Ca number beyond a certain Ca number. In the cases of this study, $St^{-1/2}$ was about 0.65 for high capillary number flow whereas for high Reynolds number flow $St^{-1/2}$ was about 0.69. However, we have not included values of $St^{-1/2}$ greater than 0.69 because the film interface had already become wavy. The existence of a maximum $St^{-1/2}$ has also been shown theoretically by Kamotani et al. (1994) for low Re number flow (where Re is Reynolds number = $h_o \rho U_o/\mu$). When the non-dimensional final thickness exceeded a certain critical value, the film interface became wavy. That St^{-1} number attains a maximum is a necessary condition for the wave motion to exist at the interface of the coating film. This condition implies that the appearance of waves is somehow related to the diminishing importance of surface tension forces relative to gravity and viscous forces in the meniscus region. The waves on the interface are constantly maintained by gravity. (Ostrach et al., 1994; Levich, 1962).

The techniques described above were suitable for the first phase of the coating instability study. Capillary forces are the restoring force which causes the damping of the waviness of the interface. That, the effect of surface tension is relatively small when Ca number is large and when the film becomes wavy seems to suggest the following. Any small disturbances generated in the meniscus region are no longer damped and thus propagated downstream to trigger the wavy motion there. The conclusion from this experiment that gravity significantly influences the stability of the coating film is important in the design and implementation of industrial coating processes.

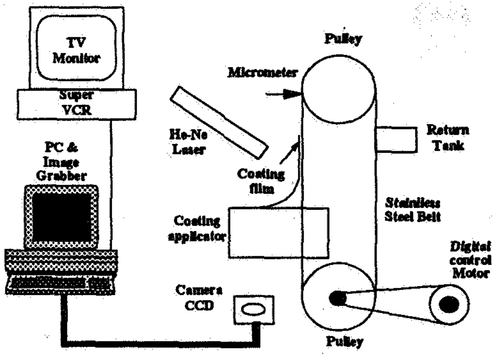


Figure 1. Schematic experimental setup.

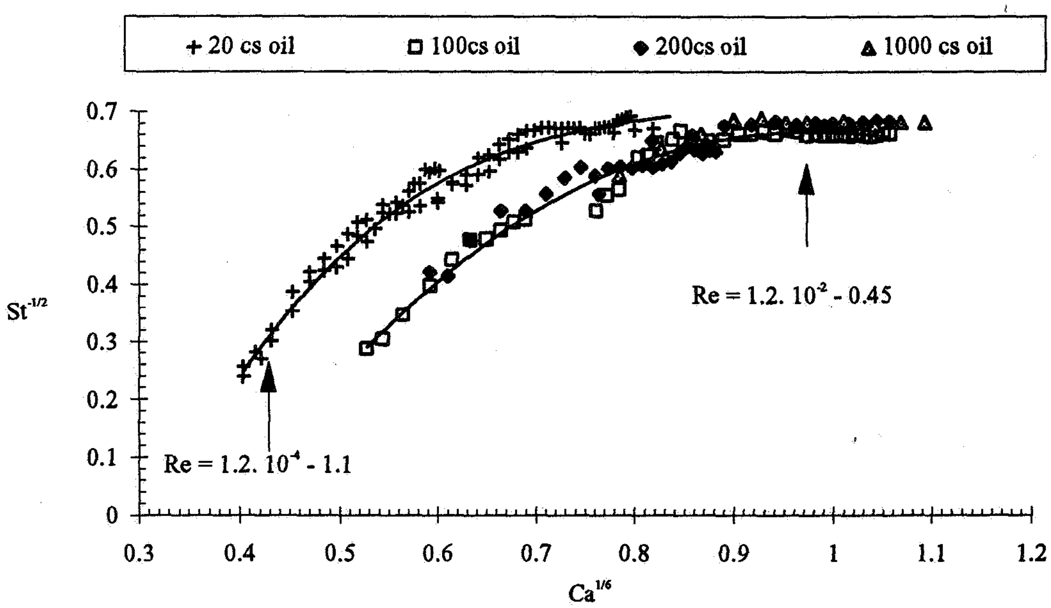


Figure 2. Non-dimensional final thickness ($St^{-1/2}$) vs. non-dimensional velocity ($Ca^{1/6}$) at low and high Reynolds number.

ZEOLITE GROWTH

Aluminosilicate crystals, commonly referred to as zeolites, have been extensively used in the petroleum, chemical and environmental industries because of their unique microporous structures. Considerable research efforts have been devoted to the field of zeolite synthesis, aimed mainly at creating new structures and, thus, finding new commercial applications. In recent years potential applications of zeolites in chemical sensor technology, electronics and optics are being examined. Therefore, zeolite crystals of considerably large size are expected in order to have characterization studies that would help open up their uses in such novel technologies.

However, under terrestrial conditions, there is no available technology to grow large zeolite crystals, which was believed to be the consequence of crystal particles sedimentation through their mother liquid where they nucleate and crystallize (Sand et al., 1987). Orbiting spacecraft seems to offer an attractive environment to researchers for seeking a new approach to accomplish the task since the sedimentation is significantly reduced under microgravity conditions. There have been a number of attempts to grow zeolites in space, but with no quantitative study whatsoever regarding the gravity-dependent transport phenomena in zeolite growth. Zhang *et al.* (1992) investigated gravitational effects on zeolite growth, first considered by Sand et al. (1987), and found that gravity-induced secondary nucleation (GSN) is the only possible detrimental effect. GSN means as follows: after an induction period some primary nuclei are formed within the reaction mixture. These nuclei shortly become crystals of certain sizes and then, due to gravity, settle down to the bottom of the reactor to form a close-packed layer where growth terminates. After that, some nuclei are formed again (i.e. secondary nucleation) at the top part of the reaction mixture, and they would follow the same course as their predecessors. This process continues until the concentration of nutrients in this part goes below a threshold value. In this manner, the total number of crystals increases for a fixed amount of nutrients, therefore, the average crystal size decreases. In reality, the phenomenon of GSN is more complicated than that described as above. Usually, zeolites grow within cavities of the porous gel network formed by gel particles of the colloidal size due to London-van der Waals forces. The gel particles serve as a source for nutrients, dissolving and then transferring to growing crystal surfaces through the solution. Under normal gravity, a discrete boundary is seen separating the clear solution at the top from the opaque white column called the gel portion. As the growth process proceeds, this boundary moves downward. Figure 1 shows this phenomenon, which is called the gel shrinkage, giving a microscopic view of the opaque white gel portion. We modeled the growth-in-gel crystallization and found that the gel shrinkage, a gravity-dependent phenomenon, can be used as a parameter to identify different stages of a growth process, nucleation and crystallization (Zhang et al., 1993). A method of increasing the crystal size by adding nutrients after the onset of crystallization was subsequently developed.

Additionally, a non-dimensional parameter was derived as a criterion for the occurrence of GSN, based on the modeling of growth-in-gel crystallization. Thereby, the benefit of microgravity concerning the increment of the crystal size is discussed in terms of whether or not GSN (detrimental) will occur on earth. Our theory was found to be consistent with the results of STS-40 (SLS-1 mission) and STS-50 (USML-1 mission) experiments (Zhang et al., 1994), systematic space experimental studies performed by Sacco et al. (1993).

As mentioned above, adding nutrients at some moment after the onset of crystallization can increase the crystal size. However, for a system designed to grow large crystals (e.g. 30 mm), this method did not work because gravity caused large crystals to settle out the added nutrients. Consequently, microgravity seems to provide an ideal environment to grow much larger zeolite crystals. However, there will be no discrete boundary seen at μ-g. In order to define an appropriate parameter for space growth, corresponding to the gel shrinkage for 1-g growth, to determine the moment of adding nutrients (after the onset of crystallization), zeolite crystallization at μ-g was modeled (Zhang et al., 1994). Unlike the growth process at 1-g, the porosity of the gel portion will increase under microgravity, because cavities of the porous gel network, within which crystals grow, will enlarge due to continuous dissolution of gel particles and to the lack of a packing effect resulting from gravity (Fig. 3 a). Hence, the overall porosity change was defined as the parameter to determine the moment of adding nutrients for μ-g growth. It was found that this parameter is proportional to the mass transfer rate at crystal growing surfaces, which will eventually approach zero. Hence, this moment can be easily identified and therefore is proposed to be the moment at which to add nutrients at μ-g. Nevertheless, how to measure the overall porosity change needs to be investigated, so that the method of nutrient addition can be applied to the growth process in space (which is aimed at growing large crystals), thus further increasing the crystal size.

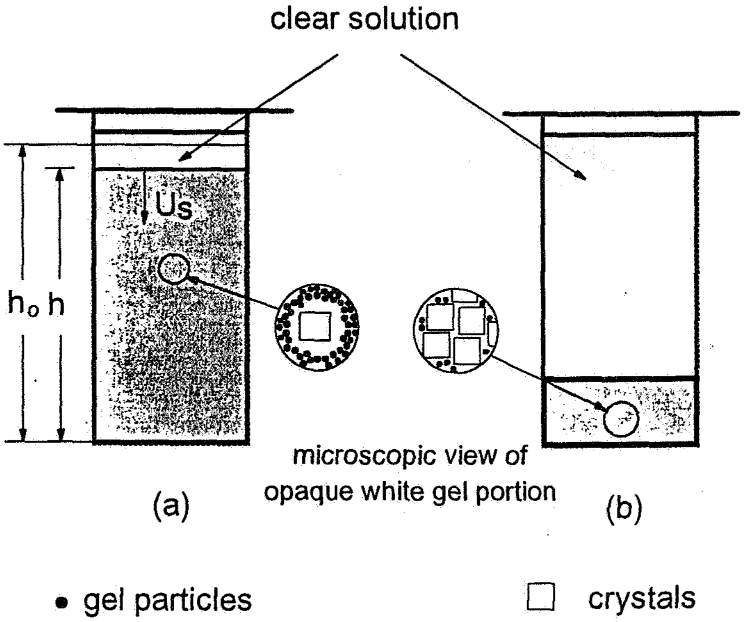


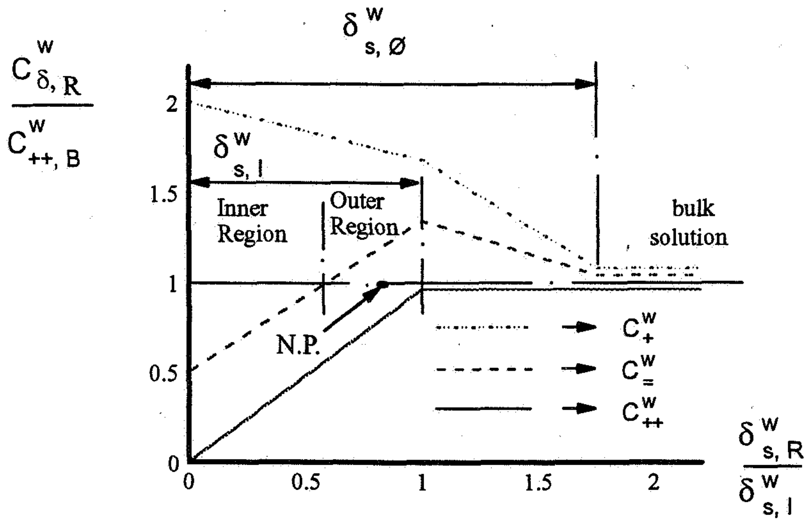
Figure 3. The observation of growth-in-gel zeolite crystallization.

ROTATING ELECTROCHEMICAL SYSTEM

The present research was motivated by a recent discovery of a rotating nickel-zinc battery system that has considerable advantages over conventional ones. A nickel-zinc battery provides very high energy density and power density, and low toxicity at a comparatively low cost. Therefore, the advanced rechargeable Ni-Zn battery is one of leading candidates for large-scale energy storage technologies, such as, electric vehicles and electric utility load leveling. The battery system can also find its space applications in life support systems and in energy storage and power generation. The major problem for the stationary Ni-Zn batteries is the limited cycle life of the Zn electrode during multiple recharge cycles, which has been traced to: first, formation and propagation of Zn dentrites that leads to cell shorting, and second, Zn electrode instability that causes gradual capacity loss (Mclarnon and Cairns, 1991). By rotating battery, the following effects were noticed: (i) at the rotation corresponding to 50 g (earth's gravitation) the dentrite growth was nearly eliminated, (ii) the discharge current density was increased by a factor of five over non-rotating battery performance, and (iii) the electrochemical by-products were continuously removed due to a strong centrifugal force.

The rotating Ni-Zn battery system can be considered as a rotating electrolyte inside shallow cylinders subjected to axial concentration and temperature gradients. The lack of knowledge of transport phenomena in such configurations not only hinders the commercialization of Ni-Zn battery, but could also lead to erroneous conclusion with regard to the practicability of the battery. To understand the transport processes in the system, Gulic et al. (1991) and Ostrach et al. (1992) performed both scaling analysis and experiments on heat transfer in a rotating cylinder heated from above for the cases with large Prandtl number and small Ekman number. In the experiment a photochromic technique was used to visualize the flow field. When $(\Pr \beta_T \Delta T)^{1/4} > 1$, the flow field is dominated by thermal buoyancy force in the radial direction and Nusselt number, Nu, is characterized by the one-fourth power of $\Pr \beta_T \Delta T E^{-2}$, while for $\Pr \beta_T \Delta T < 1$, the vertical Ekman suction dominates the heat transfer process and Nu is proportional to $\Pr \beta_T \Delta T E^{-1/2}$. Good agreement between the scaling results and the experimental data have been demonstrated. It is believed that successful control of dentrite growth at the higher rotation rates in the rotating battery can be attributed to well-behaved solutal convection. The conclusions drawn from the experiment appeared to support this argument.

In general, transport phenomena in an electrochemical system is different from that in a nonelectrolytic system. It is known that under the limiting current condition mass transfer process in the electrochemical system is controlled by solutal diffusion and convection, which by no means indicates that the transport phenomena in the system become the same as that in the nonelectrolytic system. First, the electrochemical system must satisfy the electroneutrality condition in the bulk solution except in the so-called double layer. Secondly, the migration contribution to mass transfer does not occur for the nonelectrolytic system. Most of the theoretical work on transport phenomena in electrochemical systems is highly idealized and inadequate for practical applications. In order to obtain meaningful models a detailed scaling analysis was performed by Jiang et al. (1992, 1994) for multiple-component electrochemical systems. Both binary and well-supported ternary systems were considered in which convection along a vertical flat plate is generated by both horizontal temperature and concentration gradients. For the ternary system, such as cupric-sulphate-acid solution, the hydrogen and sulphate ions must share a common solutal boundary layer to satisfy electroneutrality. Therefore only two solutal layers, the inner and outer layers can be defined. Concentration profiles of the sulphate, hydrogen, and cupric ions were estimated in both layers respectively. In the inner layer, the bulk concentration of both sulphate and hydrogen ions increase toward the values at the interface between the inner and outer layers, while that of cupric ion remains constant. The concentration of the sulphate ions reaches a maximum at the interface as shown in Fig. 4. As a result, near the cathode surface the solutal buoyancy force is upward in the inner portion of the entire solutal layer, and downward in the rest of the layer. A new approach which considers the effects of heat and mass transfer simultaneously with the momentum transport is developed to study transport correlation for the thermosolutal convection. It is found that the ratio of thermal to solutal boundary layers as well as the ratio of the dimensionless mass transfer number, Sherwood number, to Nusselt number, are proportional to the two-fifth power of Lewis Number. The Scaling results were compared with both analytical and experimental data, and satisfactory agreement was demonstrated (Fig. 5).



S electrode surface, B bulk solution
i interface of inner and outer solutal layers
N.P. neutral point

Figure 4. Estimated concentration profiles of all ions in a cupric-sulphate-acid electrolyte

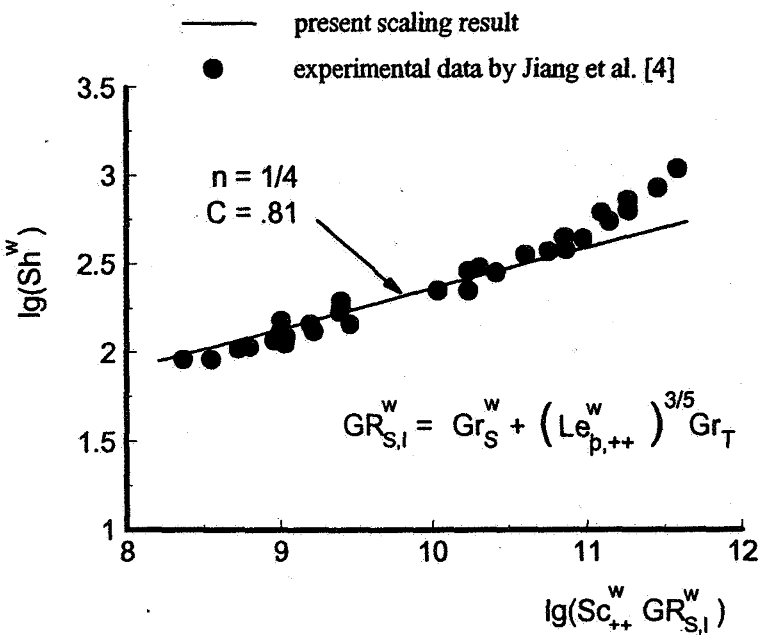


Figure 5. Comparison between the experimental data and the present scaling result

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