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MODELING OF MACROSCOPIC/MICROSCOPIC TRANSPORT PHENOMENA IN ZEOLITE CRYSTAL SOLUTIONS UNDER MICROGRAVITY CONDITIONS

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Summary

Crystals grown from special liquid solutions find important industrial applications. Most often the physics and chemistry of the growth processes are not well understood due to complex microscopic chemical and thermo-fluid phenomena. Microgravity could help elucidate these phenomena and allow the control of defect concentration and crystal size. We are proposing to study zeolites grown in silica solutions as a typical crystal growth system. By using macroscopic fluid dynamics, coupled with first-principle microscopic fluid physics and advanced particle simulations, we will study: (a) the effect of transport phenomena and nutrient flow under microgravity conditions along with (b) the nucleation process and (b) the microscopic crystal growth dynamics. The macroscopic model will account for the bulk fluid-crystal motions. The microscopic model will include multiple nutrient species and growth sites, and microscopic interactions during the nucleation and crystallization processes. The numerical results will be compared with data we obtained from terrestrial and space experiments.

Project Description

In general, crystals grown from solutions are relatively inexpensive and find extensive use in many industrial applications. Many of the phenomena associated with crystal growth processes are not well understood due to complex microscopic and macroscopic

interactions. Since many physical parameters are simultaneously involved in the process, experiments are difficult to interpret, and cannot be easily used to derive empirical or other laws. At the same time, there is increased urgency in the development of such an understanding in order to more accurately quantify the process.

In the past, extensive efforts have been made to characterize zeolite structures and to understand their nucleation and growth mechanisms so as to be able to custom-make crystals for a desired application. To date, for most solution systems both the nucleation mechanics and chemistry are as yet still unknown. Furthermore, the effects of the transport phenomena in the growth process are effectively unknown. The problem is compounded by a "gel" phase that forms upon mixing which controls the degree of supersaturation. The gel undegoes a continuous "polymerization" type reaction during nucleation and growth.

It was hypothesized that the microgravity levels achieved in an orbiting spacecraft could help isolate the effects of natural convection and minimize sedimentation so crystals would stay suspended in the nutrient pool under diffusion-limited growth conditions. Microgravity is expected to promote larger crystals by allowing growing crystals a longer residence time in a high-concentration nutrient field. It is hoped that larger, more defect-free zeolite crystals in high yield would result. Zeolite crystallizations performed in space resulted in mixed results. Earlier experiments (STS-50, STS-57) indicated an enhancement in size in the range of 10 to 50 percent compared to ground based controls with a corresponding reduction in lattice defects. However, the knowledge gained from the first space flight experiments has resulted in ground samples being grown to approximately the same size as those grown in these initial space flights. More recent space samples (STS-73) indicate an additional 10 to 50 increase in size. Again, when compared to the ground-based results, there appears to be a reduction in lattice defect concentration (although less than seen previusouly) , as well as a substantial difference in the OH concentration. Currently, the results from these space experiments are still being analyzed.

Modeling Plan

There have been no substantive studies on the fluid physics and mass transport associated with crystallization of zeolites to help quantify the experimental observations. Our computational model will attempt to elucidate some of the parameters that influence the growth process and to provide the framework for future extensions. Despite the idealized nature of the model, it will include the essential features of the real process.

At the macroscopic level, upon mixing the solution undergoes instantaneous ``polymerization" resulting in the formation of a gel phase with liquid pockets. The crystals then grow suspended in the liquid phase while the gel continuously dissolves by releasing nutrients into the liquid. Gel dynamics and dissolution then, coupled with diffusion in the liquid, control the growth of the crystals. As nucleation and growth proceeds the gel phase finally disappears. In the early stages of the growth, the dynamics are dominated by diffusion-limited processes. However, as the crystals increase in size, gravity and particle migration become important. Along with the gel-liquid dynamics, there is coupling between crystal-crystal and liquid-crystal interactions which induce macroscopic fluid motions. The macroscopic motions, and the growth dynamics are then coupled to the concentration fields affecting the rates of growth. Bulk mass and flow transport, along with gravity, can force the crystals to the bottom of the reactor resulting in a sedimentation layer where the growth rate of the crystals slows down as the crystals compete for limited nutrients.

At the microscopic level there are normally two different but parallel stages during the crystal growth of zeolites, nucleation and growth The number of nuclei is proportional to the amount of gel that is formed. If this number decreases, the average crystal size in the final distribution increases. Therefore, among other factors, the crystal size distribution is a function of the nucleation rate and growth.

At the early stages of our study we are proposing a parallel modeling effort in order to develop separately the macroscopic and microscopic models. Eventually, the two models will be combined to yield a complete analysis.

<u>Macroscopic Model:</u> The macroscopic model will be built on our experience with the dynamics of suspension flows and phase change phenomena in complex flows [Ahmed and Alexandrou 1994, Alexandrou and Papanastasiou 1990]. As a prototype flow geometry, we will consider a 3-D cubic container, with randomly distributed nuclei sites and uniform concentration fields. At this level we will consider the solution as a continuun mixture of solid crystals in a matrix of gel and liquid phases. Mass conservation for each is given by

$$\frac{\partial \rho_s f_s}{\partial t} + \nabla \cdot (\rho_s f_s \mathbf{v}_s) = \dot{r}_s$$

$$\frac{\partial \rho_l f_l}{\partial t} + \nabla \cdot (\rho_l f_l \mathbf{v}_l) = \dot{r}_g - \dot{r}_s$$

$$\frac{\partial \rho_g f_g}{\partial t} + \nabla \cdot (\rho_g f_g \mathbf{v}_g) = -\dot{r}_g$$

where subscripts l, s and g, refer to the liquid, solid and gel phases. Here ρ is the density and $\mathbf{v}$ the velocity field. f is the volume fraction. The term $\dot{r}_s$ is the rate of growth of the crystals and depends on the local concentration field in the liquid and the local microscopic growth dynamics. Similarly $\dot{r}_g$ represents the rate at which the gel dissolves into liquid. At first, these parameters will be estimated using empirical and experimental data. However, eventually, they will be provided by the microscopic model. Therefore, $\dot{r}_s$ and $\dot{r}_g$ represent the coupling between the macroscopic and microscopic models. To keep track of the nutrient species, for simplicity we will introduce the concentration field for a single component. At a later stage the number of species will be increased.

The momentum equation introduced for each phase provides the dynamic evolution of the three phases i.e.

$$\frac{\partial \rho_s f_s \mathbf{v}_s}{\partial t} + \nabla \cdot (\rho_s f_s \mathbf{v}_s \mathbf{v}_s) = F + \rho_s f_s g$$

$$\frac{\partial \rho_l f_l \mathbf{v}_l}{\partial t} + \nabla \cdot (\rho_l f_l \mathbf{v}_l \mathbf{v}_l) = -\nabla \cdot ((1-f_g)\nabla P) - F + \nabla \cdot ((1-f_g)\tau_l) + \rho_l f_l g$$

$$\frac{\partial \rho_g f_g \mathbf{v}_g}{\partial t} + \nabla \cdot (\rho_g f_g \mathbf{v}_g \mathbf{v}_g) = -\nabla \cdot (f_g \nabla P) + \nabla \cdot (f_g \tau_g) + \rho_g f_g g$$

where P is the pressure. The force per unit volume F, represents the interaction between the solid and liquid phases. At the dilute limit, the interaction is due to the drag force on the solid particles. However, as the concentration of the crystals increases the force will be modified accordingly. The liquid stress tensor will be described as a Newtonian fluid and the gel stress tensor as a non-Newtonian power-law type of fluid. The numerical solution to the macroscopic theory will be obtained using the Finite Element method. The solution procedure will be formulated and solved using an iterative solver.

Microscopic Model: The microscopic model will be based on our experience in hybrid Monte Carlo/particle-in-cell methods in the areas of dust particle interactions in space plasmas [*Gatsonis et al.*, 1994a] and hybrid fluid/particle-in-cell methods in plasma flows [*Gatsonis et al.*; 1994b; *Roy et al.*, 1994].

The model will include both the nutrients and the growing crystals in a liquid solution. At this stage we will not model the dissolution of the gel into liquid at the microscopic level. The theory and model will be developed for a domain with dimensions much larger than the typical crystal size. The cell structure will be non-uniform to allow for the macroscopic

variation of the flow parameters. Nutrients p with mass m_p in the system will be treated as separate species, following a prescribed velocity distribution with mean velocity $U(r,t)$ which will be obtained form the mean flow equations. The random motion will determine the diffusive fluxes of nutrients. At this level, the model will be able to reproduce previous DLA results. The macroscopic fluid parameters will be varied and the effects on crystal growth will be examined. The nutrients will be moved under the action of gravity force or liquid drag. A discussion of the treatment of forces within the concept of particle simulations can be found in *Gatsonis et al.* [1994a]. In addition to their motion, nutrients will undergo collisions which in a real system can be elastic, inelastic or chemically reacting. These types of collision processes can be modeled with the Direct Simulation Monte Carlo technique. The elastic collisions between the nutrients will be modeled using the No-Time-Counter model of *Bird* [1994]. In addition, those nutrients that are attached to the crystal will be removed from the domain, thus allowing the study of the nutrient depletion process [*Gatsonis et al.*, 1994a]. Since the DSMC is particularly suited for chemical reactions, such possible reactions could be introduced in the model as well [*Bird*, 1994].

The nucleation will be introduced with a Monte Carlo based model that resembles closely the actual process. In a zeolite solution nucleation and growth overlap and interact with each other. The nucleation sites will be created in random with a probability based on a model that describes the nucleation as a function of local thermodynamic and macroscopic variables. Another alternative is to introduce nucleation via a chemically reacting process based on a rate coefficient that depends on thermodynamic parameters. Ultimately, this issue must be resolved using experimental data. Once a nucleation site is established, the growing crystal will move under the influence of forces such as gravity and collisional drag. The inclusion of this effect is a significant departure from all previous crystal growth models which consider only stationary sites on a lattice. The nucleation sites will eventually grow to crystals of finite size. At this level we will introduce the dynamic interactions with the fluid. The motion of nucleation sites will also affect the crystallization process since subsequent crystal growth will depend on whether the sites are in rich or poor nutrient areas. The motion of the crystals is, therefore, expected to be very important in determining the crystal size distribution in the system.

The details of modeling of the growth however, is dictated by the computational requirements. Our approach is to describe the key physical processes with a model which will be refined through successive iterations with data comparisons. For this reason, we

will initially concentrate our efforts in the determination of the size distribution of the crystals under the influence of microgravity. As such, the crystals will be considered as spherical particles that grow after their attraction and attachment of nutrients. An attachment probability will be evaluated in those cells in which nucleation sites or crystals exist. This probability will be calculated on concentrations or surface kinetics based on impingement rates. At first, the model will not examine morphological characteristics of the crystals but we will instead develop appropriate crystallization models. At a later stage this additional complexity will be addressed with the introduction of a fine grid structure around each one of the growing sites.

As a first approximation, we will assume a stationary liquid in which the motion of the crystals will be determined by gravity and drag forces based on the local crystal velocity. This procedure will allow the parametrization of the sedimentation process under variable gravity conditions. At a later stage we will introduce the effect of the mean flow and copule the microscopic with the previously described macroscopic model.

Experimental Verification

The computational results will be verified using our extensive database of experimental results. This long term ongoing experimental program on zeolite growth includes various solution systems under different growth conditions. Some of these experiments have been performed under microgravity conditions and are helpful in understanding the effects of crystal settling and nutrient flow/depletion. As part of our work we will use the theoretical/ computational model to evaluate and analyze existing data. The model will also be used in the design of future terrestrial or space based experiments.

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