

MODELING OF COMBUSTION PROCESSES IN A SOLID FUEL PARTICLE

by

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ABSTRACT

During the production of granules of uranium oxide, granules of ion exchange resin, loaded with uranium ions, are burned to remove the resin matrix and leave a uranium oxide "ash". Under some conditions of combustion, the oxide granules are produced in a highly fractured, porous state, while other conditions result in hard, dense, solid granules. ABAQUS, a commercial finite-element code, run on an IBM 3090, was used to model the physical processes occurring during combustion: heat transfer with a very nonlinear temperature-dependent rate of heat generation, diffusion of reactants and products, and stress/strain resulting from the differential temperatures and from the phase changes during the combustion. The ABAQUS simulation successfully explained the differences in morphology of the granules under different conditions, and lead to control strategies to produce the desired morphology.

INTRODUCTION

The Savannah River Laboratory in Aiken, South Carolina, has been developing a process to convert uranium ions in a dilute aqueous solution into uranium oxide powder. The uranium ions are removed from solution by sorbing onto ion exchange resin, which concentrates the uranium to about 140 gm U per liter of resin. The uranium-loaded resin is dried to a free-flowing powder, and then calcined (burned) to remove the resin framework and leave the uranium as U_3O_8 . The ion exchange resin is a copolymer of styrene and di-vinylbenzene, as shown in Figure 1, with sulfonic acid groups attached to many of the nonbridging benzene rings.

Specifications require that all oxide particles be between 45 and 150 microns. Past experience has shown that there is a reproducible shrinkage in size of particles as the loaded resin is calcined to uranium oxide. Consequently, starting with resin particles of 150 to 300 microns will lead to oxide particles with the desired size distribution.

CHEMICAL PROCESSES DURING CALCINATION

During calcination of the loaded resin two chemical processes occur: pyrolysis and oxidation. When the ion exchange resin is heated to high temperatures in the absence of oxygen, pyrolysis breaks the polymer structure down into fragments of varying size, which are vaporized and driven off. If the heating occurs in the presence of oxygen, oxidation of the resin causes a more aggressive attack on the structure and ruptures additional chemical bonds that were resistant to pyrolysis alone.

Pyrolysis alone is not sufficient to convert the loaded resin into uranium oxide. There is an appreciable weight difference between the residue remaining after the resin is heated under

pyrolyzing or oxidizing conditions. The difference is material (mainly carbon) that must be removed by oxidation. Consequently, the calcination is performed under oxidizing conditions.

PHYSICAL PROCESSES DURING CALCINATION

The physical processes of heat transfer and diffusion play important roles in the calcination behavior of the resin, as do volume changes (shrinkage) and the associated stress/strain relationships. The calcination process necessarily involves heating the resin to high temperature, which requires heat transfer. The resin starts out at room temperature, is dropped through the hot (850°C) exhaust gases leaving the calciner, and lands on the heated calciner tube surface. Heat is also radiated from other portions of the calciner tube to the surface of the resin particles. Because the resin is basically an organic polymer, it has a relatively poor thermal conductivity. During the initial heat-up of the resin, the input of heat at the surface of the particle and the low thermal conductivity cause the center of the particle to be much cooler than the outer surface.

When the temperature of the resin reaches the point where the oxidation rate becomes appreciable, the temperature gradient reverses. Oxidation is a very exothermic reaction, and the heat of reaction must be transferred out of the resin to the surroundings. The heat generation within a resin particle and the low thermal conductivity cause the thermal gradient to reverse, with the center of the particle much hotter than the outer surface. Because of the increasing rate of oxidation at higher temperatures, this can lead to an autocatalytic or "runaway" reaction. The oxidation in the center of the particle generates heat faster than the low thermal conductivity can transfer it to the outer surface. This causes the center of the particle to increase in temperature, which speeds up the oxidation reaction, generating heat even faster. This runaway reaction will be limited only by the supply of reactants: oxygen and resin. The runaway temperature increase will cease either when the resin has been totally consumed or when the rate at which oxygen can diffuse into the center of the resin particle becomes the rate-limiting step in the reaction.

During the calcination process, there is a large shrinkage in the volume (by about a factor of 15) of the material as the resin matrix is burned away, leaving behind uranium oxide. Even before the matrix is removed, pyrolysis and oxidation collapse the macroporous structure, decreasing the ease of gas diffusion through the particle. The volume shrinkage during conversion of the loaded resin to uranium oxide occurs first at the outer surface of particle, and the skin of dense oxide formed will be more difficult for the oxygen to diffuse through. This shrinkage occurs individually and independently in each resin particle. Each resin particle retains its general shape as it shrinks and converts.

During the initial development of the process, oxide produced in batch calcinations consisted of hard, dense, solid particles with only occasional cracks or fissures in the particles. Figure 2 shows a Scanning Electron Microscope (SEM) image of a high density oxide particle. During scale-up of the process, oxide produced in a continuous rotary calciner consisted of particles that were porous, and heavily cracked and fissured. This cracking and fissuring extends throughout the particle. Figure 3 shows a similar image for a low density oxide particle, and Figure 4 shows an image of the interior of a particle that has been sectioned.

ABAQUS MODELING

Computer simulation has been an important tool in improving the resin calcination process. ABAQUS, a commercial finite element code, has been used to simulate the heat transfer, chemical reaction, and thermal expansion/contraction processes that occur during calcination. The ABAQUS simulation reveals the nature of events occurring within the interior of the particles during calcination that are inaccessible to actual observation, and reveals events that are occurring too rapidly for observation.

The ABAQUS simulation has focused on a single resin particle since each resin particle retains its identity during calcination, and the calcination of bulk resin is the collective behavior of all the individual resin particles. Because of some limitations of the ABAQUS code discussed below, and limitations of current experimental measurements, the simulation of the processes is not exact, and agreement with the experimental observations is only qualitative. However, the agreement between the general processes occurring in the simulation and the experimental observations is good.

The simulation modeled the resin particle as a perfect sphere since experimental observations had not indicated any difference in behavior dependent on the shape of the particle, and modeling a spherically symmetric particle greatly simplified the interpretation of the results. All temperature gradients, concentration gradients, stresses, and strains were then a function only of the radial spatial coordinate, and of time. The mesh shown in Figure 5 was generated, composed of axi-symmetric solid elements for coupled temperature-displacement analysis. This mesh represents a disc just above the equator of the particle, formed by rotating a 10-degree sector around the polar axis of the particle. Coupled temperature-displacement elements were used to analyze the thermal expansion/thermal stresses induced by the very large temperature changes.

The boundary conditions, placed on the mesh by the spherical symmetry, are that the top and bottom surfaces of the mesh, and the center surface (actually a point) of the innermost element, are required to be surfaces of symmetry (no heat flux or displacement). The outer surface of the outermost element exchanged heat with the surroundings assumed constant at 850°C, both through a convective film coefficient and through radiation. The initial condition was that the particle temperature was uniform at 25°C.

The physical properties (density, thermal conductivity, heat capacity, elastic modulus, yield strength, etc.) of the loaded resin were not known with much accuracy. As a reasonable

approximation, the physical properties of polystyrene were used as the properties of the resin, on the basis of the similarity of chemical structure of the resin.

When the resin particle is dropped into the calciner environment, its initial behavior is merely a transient heating from the exterior. Heat is transferred to the particle mainly by conduction through the gas film surrounding the particle, and by radiation from the hot calciner tube wall. The particle of resin is small enough that the heat transfer coefficient from the gas to the particle is relatively insensitive to the gas velocity past the particle. The convective motion of the gas past the particle will only reduce the external convective heat transfer resistance by 7 to 25 percent below that of a completely stagnant gas film, depending on the particle size (smaller decrease for the smaller particles). Consequently the gas around the particle can be regarded as mainly stagnant, and heat transfer from the gas to the resin particle is limited by the thermal conduction through this stagnant gas film.

The resin particle itself has a low thermal conductivity, and this limits the heat transfer into the interior of the particle. Consequently, the outer shell of the particle heats up before the interior. Even with the limitations caused by the low thermal conductivity and low heat transfer coefficient, the heat-up of the particle is very rapid because of the particle's small size. Figure 6 is a plot of the simulated temperature in the particle if there were no heat generated internally from the oxidation reaction. As can be seen, the particle would come to thermal equilibrium within about 1 second. As Figure 6 shows, the heating rate for the particles exceeds 40,000°C per minute, much more rapid than any rate ever performed in the batch calcination experiments. This calculated heating rate neglects any contribution from internal heat generation by the oxidation reaction, which will only intensify the heating rate.

When the particle enters the calciner, the rate of the oxidation reaction is negligible. However, the rate of reaction increases with increasing temperature. There is very little energy

released or absorbed by the resin until the resin reaches approximately 300°C. As the resin is heated, the outer surface of the resin particle reaches a temperature where the rate of oxidation becomes appreciable. Then this oxidation reaction releases heat faster than the low thermal conductivity of the resin can transfer the heat into the cooler interior of the particle, and faster than the stagnant gas film can transfer it to the bulk gas. The released heat then raises the temperature of resin particle in the immediate region of reaction. This rise in temperature increases the local rate of reaction even more, releasing even more heat.

The internal heat generation from the oxidation reaction was modeled as a temperature dependent rate of reaction in an Arrhenius type equation:

$$r=17,700*e^{(-10800/T)} \quad (1)$$

where r = rate of reaction (fraction converted per second)

T = Temperature (kelvin).

This reaction rate expression was estimated from some experiments with small quantities of resin in a large excess of air, and represents the maximum rate of reaction if the supply of oxygen is not limited by the rate of diffusion to the reaction site. As a first approximation to the reaction kinetics, the effects of limitation of the oxygen were neglected, and the above rate was used in the model as the local rate of reaction in an element until all of the resin in the element was consumed. The heat released by the complete reaction was 2000 cal/gm. The total extent of consumption of the resin was tracked by the use of solution-dependent state variables that integrated the instantaneous rate of reaction. If the total extent of reaction was less than 100 percent, then further rate of reaction was calculated from equation (1); if the total extent was equal to 100 percent, the rate of reaction was zero.

The simulated reaction, not limited by the supply of oxygen, occurs very rapidly. The ABAQUS temperature simulation in Figure 7 shows the entire particle converted within about 2 milliseconds. A problem with automatic control of the time increment occurred during modeling of the reaction process. The time increment increased during the initial transient heat-up of the particle before "ignition", but when the reaction started, this time step was too long, so that the entire reaction occurred during the next time step. However, if the time increment was kept fixed at a value small enough to accurately simulate the reaction, the number of increments required during the heat-up was excessive. The only solution found was to run the problem with automatic control of the time increment, note the time at which reaction started, and then use the ABAQUS restart feature to begin a second "step" at that point, with a much smaller time increment.

The extreme speed of the events occurring during the "ignition" of the oxidation reaction, and the need to include temperature, displacement, reaction rate, and total extent of reaction variables for each of the nine nodes of each of the 50 elements of the mesh created a very computationally intensive modeling problem. The oxidation reaction phase of the problem took place in about 2 milliseconds of "real" time, and accurate modeling required that this be divided up into about 20 incremental time steps of the model. Each time step required several iterations of the convergence routines for solving the temperature and displacement equations. While longer increments could be used during the transient heat-up prior to "ignition", and during cool-down after completion of the oxidation reaction, several hundred total increments were required to model the entire process. About 25-30 minutes of CPU time on an IBM 3090, Model 180, were required for one run of the model. A total of about 3.5 megabytes of memory were required to hold the values of all the variables during a modeling run. The necessity for restarting a modeling run at the point of "ignition", with a smaller time increment, (described in the previous paragraph) required the ability to quickly store the entire 3.5 megabytes of memory on external storage media and then restore it for the restarted run.

The temperatures simulated by the ABAQUS code shown in Figure 7 indicate a heating rate of over 90 million°C per minute during the reaction phase. In reality, the reaction rate will be limited by the rate at which oxygen can diffuse into the particle from the surrounding gas, and this will limit the consequent temperature rise. To model this oxygen-limited reaction would require the simultaneous modeling of the temperature, the oxygen diffusion, and the diffusion of the gaseous combustion products. Simultaneous modeling would be required, since the temperature depends on the rate of reaction, which depends on both temperature and oxygen concentration. Similarly the oxygen concentration would depend on the rate of consumption by reaction, and on the diffusion of the various gases. In addition, the very large temperature changes cause very large thermal expansions, so simultaneous displacement analysis is also required. No ABAQUS element currently exists for simultaneous analysis of temperature and concentration (even of one species, let alone two or more). Consequently, the ABAQUS code that is currently available cannot adequately model this diffusion-limited phenomenon. Even so, the simulation available currently does model the qualitative behavior of transient heat-up, "ignition" of the reaction, and propagation of the reaction by heat conduction.

The ABAQUS simulation also gives some insight into how the porosity is created in the particles during calcination. After the reaction has "ignited" and propagated into the interior of the particle, the interior temperatures are much higher than the surface temperatures. Simple thermal expansion of the interior, relative to the surface, can generate stresses exceeding the tensile strength of the particle manyfold. If the particle were heated uniformly to high temperature, thermal expansion would be uniform throughout the particle and no stresses would be created. However, because the interior is heated to higher temperatures than the exterior, the interior attempts to expand more than the exterior. This excess expansion of the interior puts the interior into a state of compression, and the exterior into a state of tension; much as the skin of a balloon is in a state of tension when the gas in the interior expands. The exact stresses generated will depend on the thermal expansion coefficient of the resin (which is unknown) and on the temperatures (which will

depend on the unknown thermal conductivity and heat capacity of the resin). However, the ABAQUS simulation, using values of the resin properties appropriate for polystyrene (which should be similar), predicted stresses that exceeded the tensile strength by a factor of about 10.

Figure 8 shows the maximum principal stress as a function of time. The maximum principal stress is always tensile, in the tangential direction, and occurs at the outer surface of the particle. Also shown in the figure is the literature value for the tensile strength of polystyrene. While the exact calculated values of the stresses are probably not correct, nor is the tensile strength, the stresses clearly are sufficient to crack and break the particle. Note that the stresses during the transient heat-up phase are not excessive, but that they become very large as soon as the reaction begins.

There is an additional process contributing to the cracking of the particle; the volume shrinkage that occurs during calcination. The conversion occurs progressively in thin shells, first near the surface and then propagating into the interior. As the outside is converted, this shell attempts to shrink, but the interior of the particle will not have converted appreciably and will still be near its original volume. If the particle shrank uniformly in size, no stresses would be induced. But this differential shrinkage will cause tensile stresses in the outer shell, and compression in the interior of the particle; the same type of stresses created by the differential thermal expansion. The volume shrinkage was also modeled in ABAQUS. The relative volume was assumed to vary linearly with the total extent of reaction, from 100 percent at no conversion, to 7 percent at complete conversion. Including the effect of volume shrinkage from conversion did not change the qualitative behavior of the results, only increasing the magnitude of the induced stresses. Stresses remained lower than the presumed tensile strength of the resin until reaction occurred, and then greatly exceeded any conceivable tensile strength.

The ABAQUS simulation of a particle in the calciner suggests that the temperatures at the particle interior, and therefore the stresses (and perhaps the degree of created intra-particle porosity), can be controlled by controlling either the amount or the rate of heat released during the runaway oxidation reaction.

The amount of heat released after "ignition" could be reduced by releasing some of the heat of reaction at lower temperatures before the "ignition" temperature of the runaway reaction is reached. This could be done by holding the particle for a prolonged period of time at some temperature below the "ignition" point, but yet still sufficient that the reaction would occur at a slow but controlled rate. Or, the rate of heat-up of the particle could be slowed, so that the "slow" reaction that occurred before "ignition" would already have released much of the stored chemical energy.

An ABAQUS simulation of a particle placed in surroundings that increase in temperature at 300°C per minute (as opposed to being plunged immediately into 850°C surroundings) only reaches a peak temperature of about 3800°C as shown in Figure 9 (instead of approximately 11,000°C, shown in Figure 7). If the surroundings are heated at 100°C per minute, the peak temperature never exceeds the temperature of the surroundings by more than 5°C, and the reaction is complete before the temperature reaches 570°C, as shown in Figure 10.

The rate of heat release after the runaway reaction has started could also be controlled by limiting the supply of oxygen to the reaction. The oxygen must diffuse in from the exterior surroundings of the particle. This rate of diffusion will be proportional to the concentration of oxygen in the surrounding gas. Consequently lowering the oxygen partial pressure in the gas will lower the rate of heat release during the reaction. As described above, this diffusion limited reaction has not yet been modeled by ABAQUS, but simple calculations support the feasibility of this proposed control method, and experiments have verified the predicted behavior.

CONCLUSIONS

Despite the major simplifications made in this model (spherical geometry, constant physical properties, linear elastic behavior, chemical reaction not limited by oxygen diffusion, etc.), the results have been very useful in understanding the phenomena that are occurring during this calcination process. In addition, the modeling has suggested several methods of controlling the phenomena to obtain the desired properties in the uranium oxide product. The modeling has indicated the approximate range of values that the control parameters should have, and this has proven to be a valuable guide to experimental studies.

The type of modeling done in this study (heat transfer, mass transfer, and stress/displacement analyses, preferably simultaneous) has potential applications to other areas of chemical engineering. Two brief examples are:

- Combustion of Pulverized Coal. This is very similar to the calcination process. The composition of the ash and the conditions of combustion, can lead to either very light, fluffy ash that is difficult to handle; to a dense, compact ash; or to ash that fuses together into large "clinkers". Modeling of the heat transfer, mass transfer, and stress during the combustion process can lead to better control of the process.
- Heterogeneous Catalyst Performance for Very Exothermic Reactions (i.e., flue gas oxidation). Very large temperature gradients can cause stresses that will fracture the catalyst particles, or inactivate the catalyst sites. Transient conditions during startup or process disturbances may be especially severe, and could be analyzed easily with this model.

SUMMARY

ABAQUS can effectively simulate the heat transfer and thermal expansion stresses that occur within a small particle during combustion. The simulation gives good insight into the processes that occur and explains differences in results observed under different conditions. The simulation also suggests methods to control the processes to achieve the desired characteristics of the ash product. The simulation has been very useful as a guide to additional experimentation and development.

ACKNOWLEDGMENT

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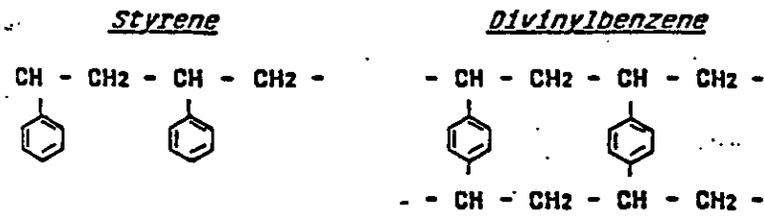
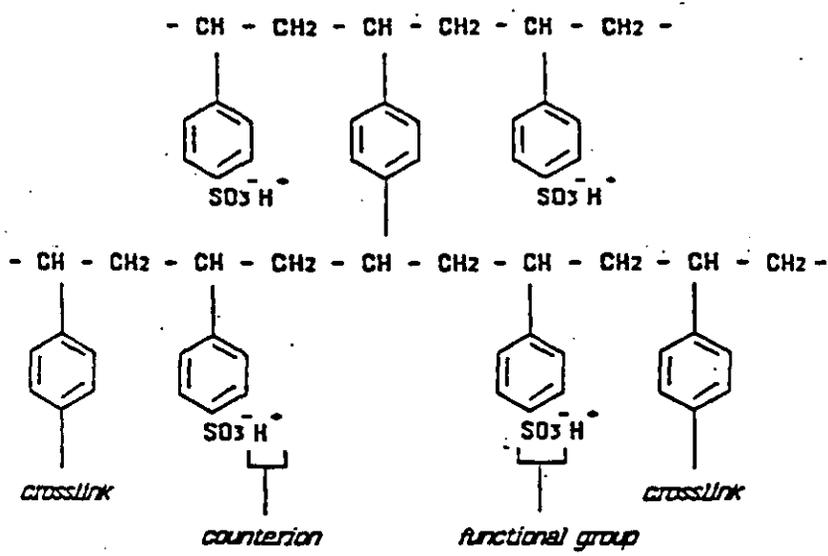


FIGURE 1. Structure of Strong-Acid Ion Exchange Resin

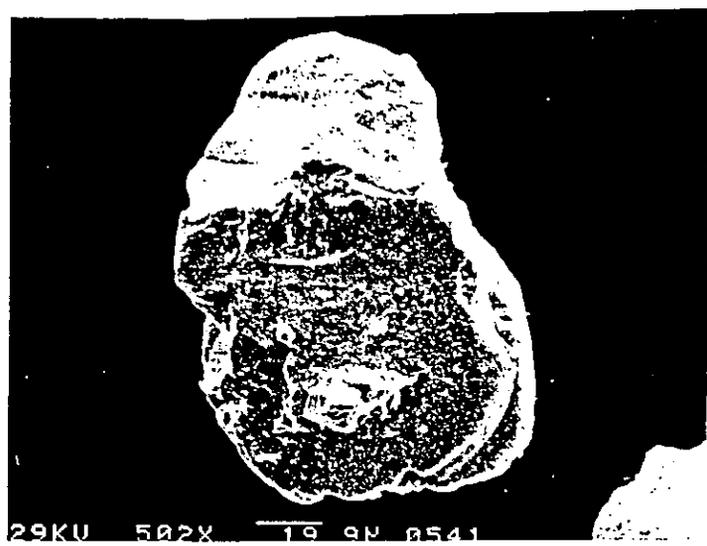


FIGURE 2. Scanning Electron Micrograph (SEM) of High Density Uranium Oxide Particle



FIGURE 3. SEM of Low Density Uranium Oxide Particle

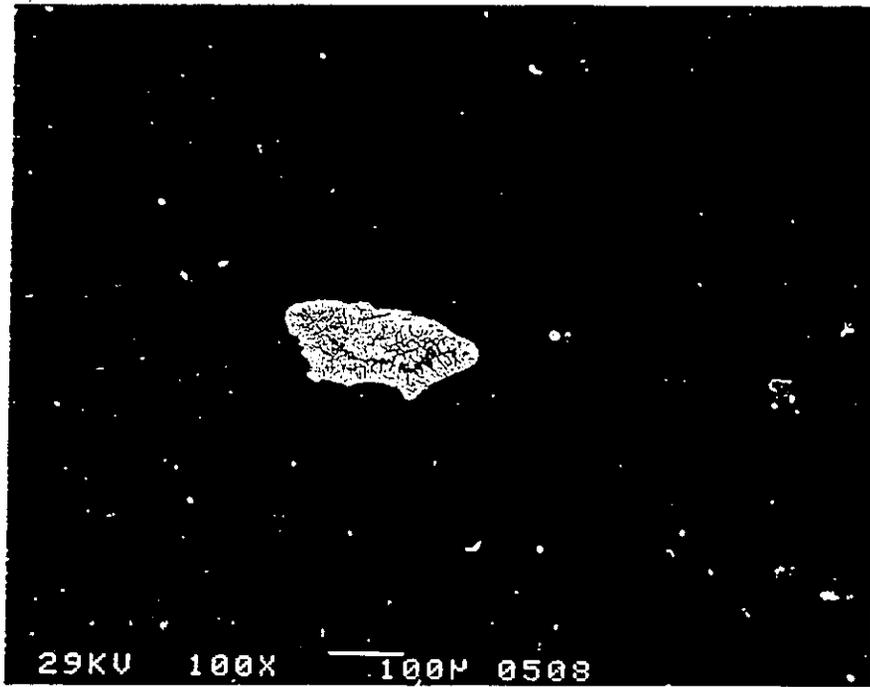


FIGURE 4. SEM of a Cross-Section through a Low Density Uranium Oxide Particle

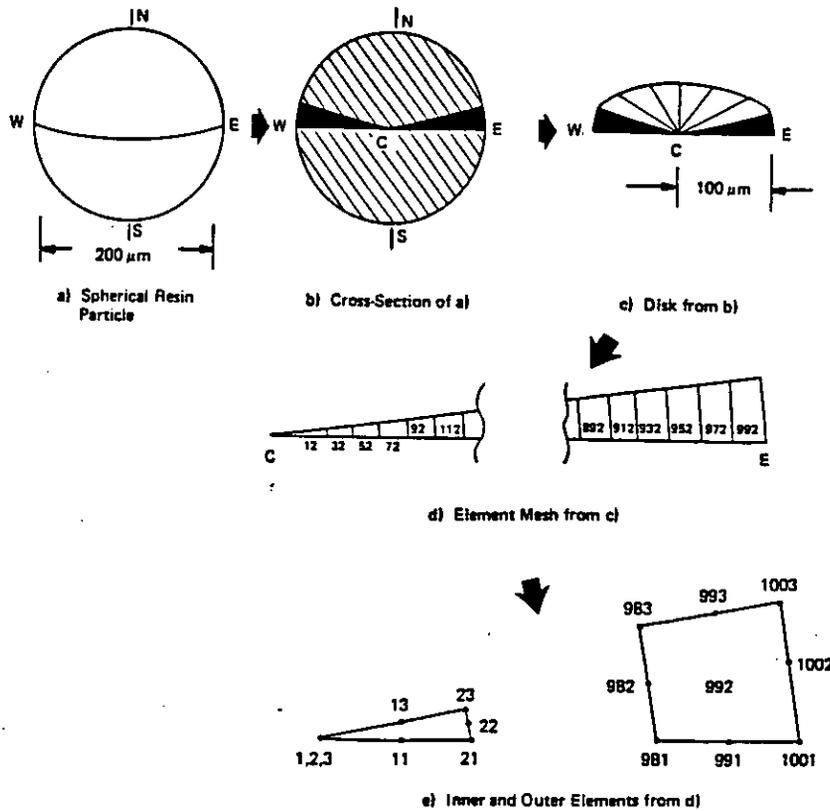


FIGURE 5. Finite Elements for Combustion Modeling

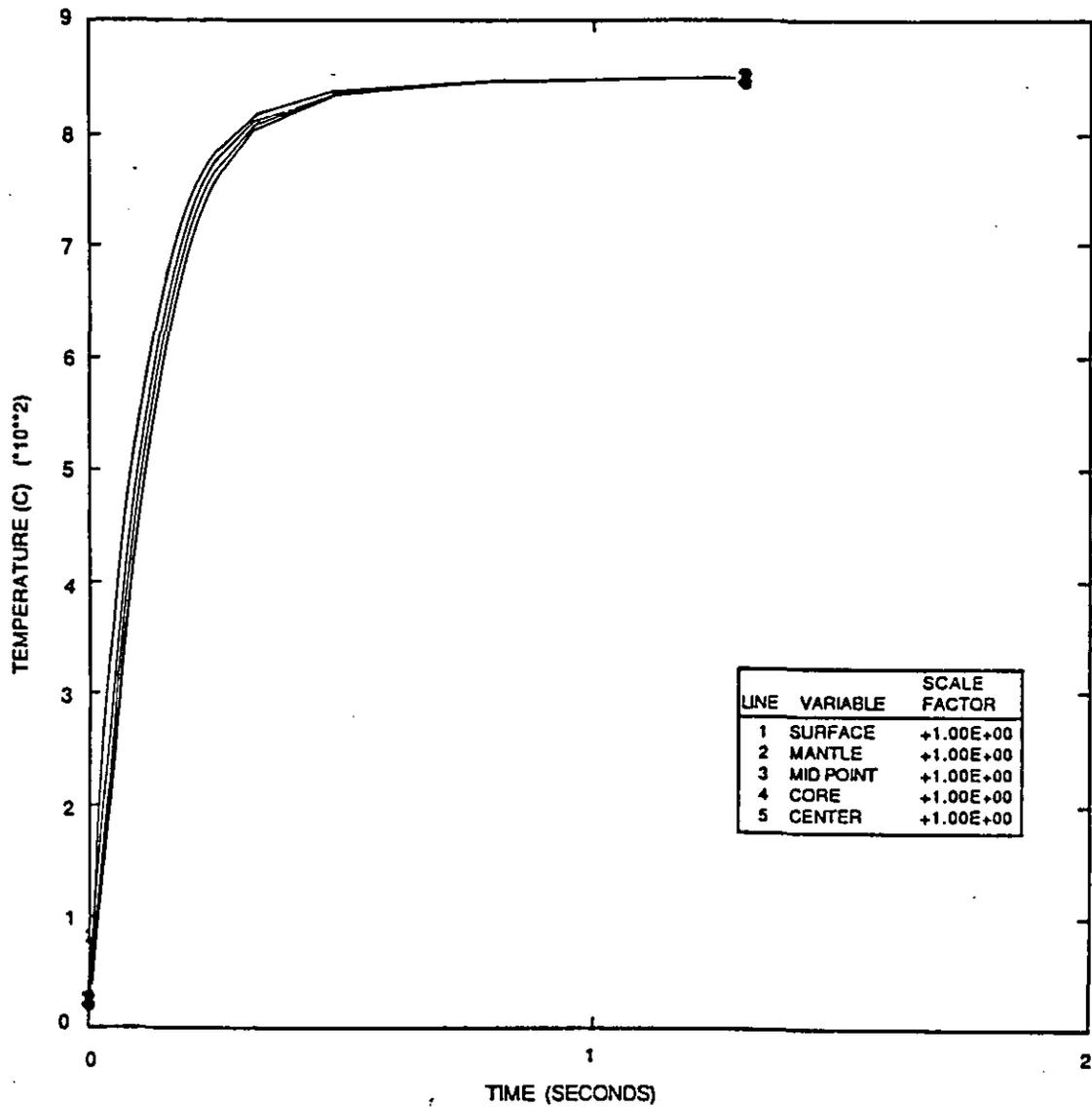


FIGURE 6. Temperature in a Resin Particle During Heating Without Combustion

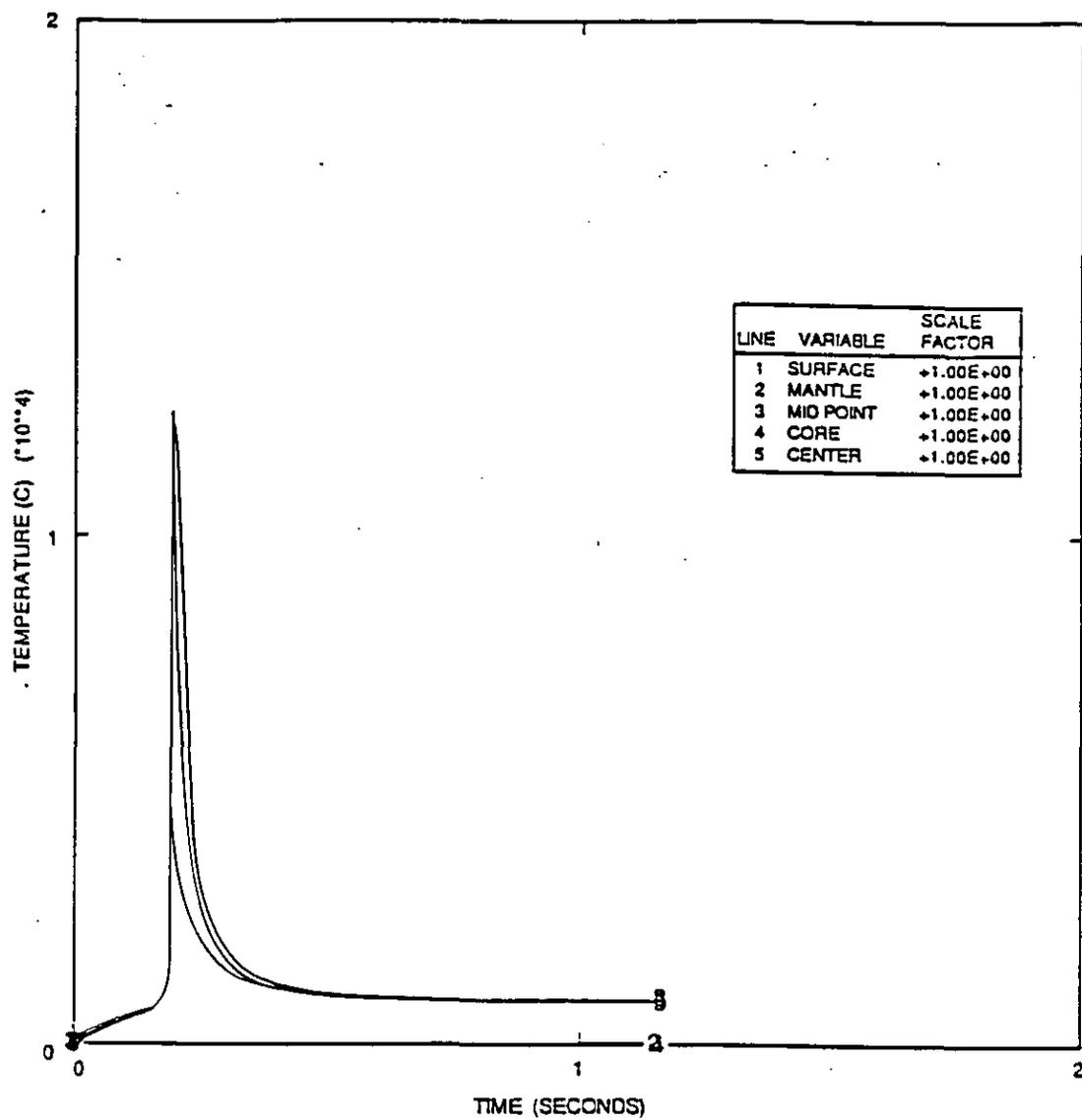


FIGURE 7. Temperature in a Resin Particle During Combustion

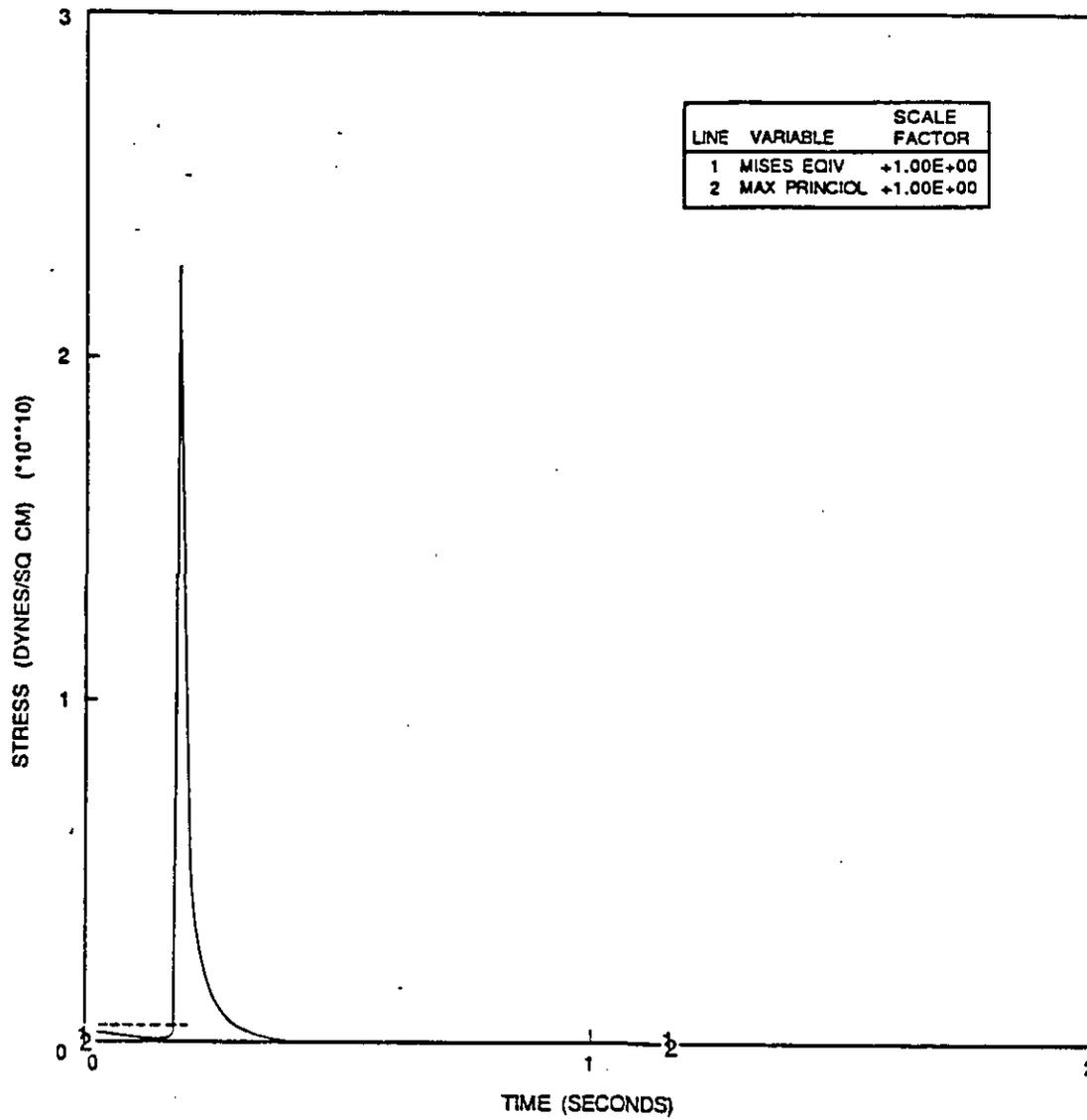


FIGURE 8. Thermal Expansion Stresses During Combustion

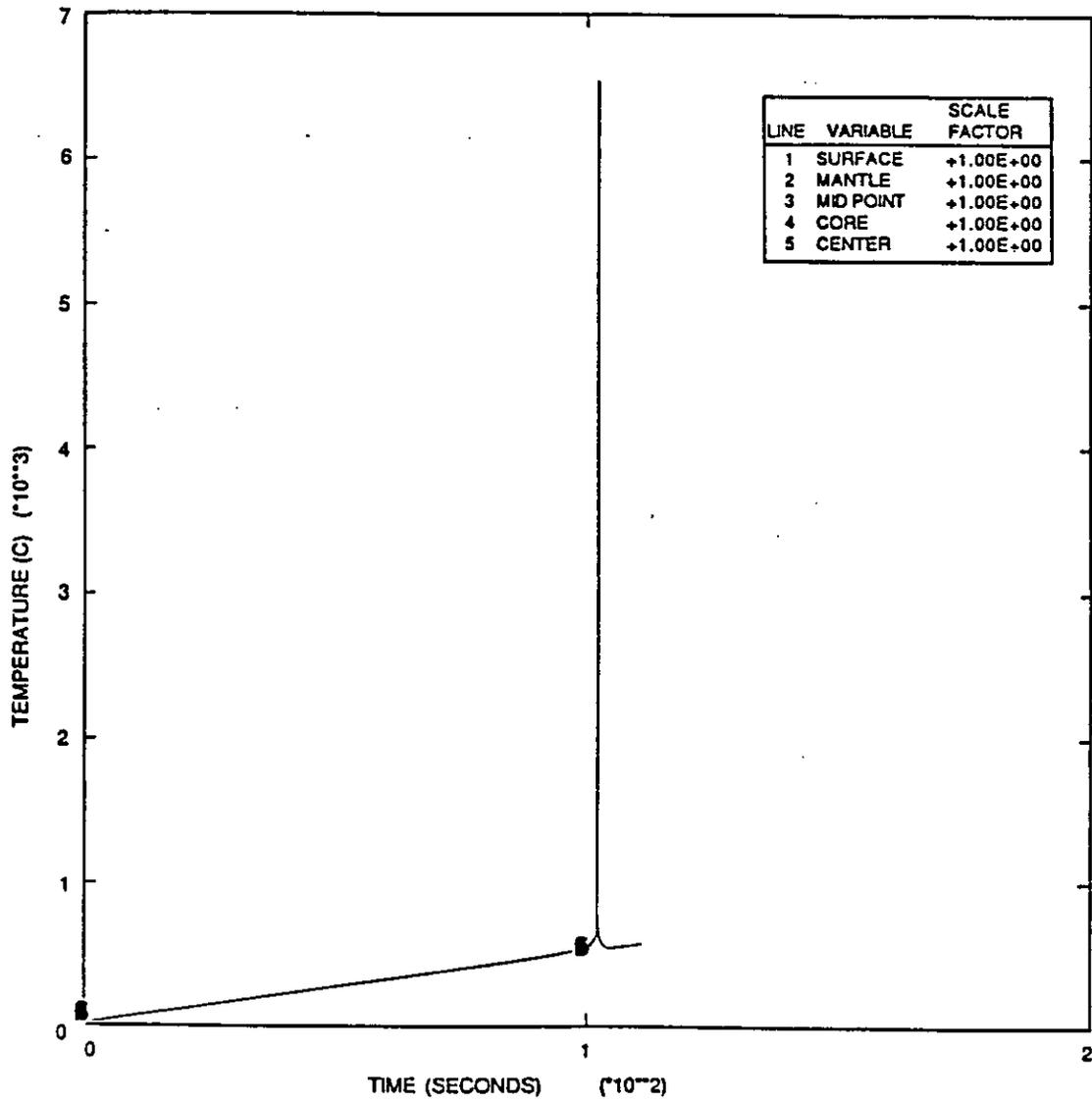


FIGURE 9. Temperature in a Resin Particle Heated at 300 Degrees/Minute

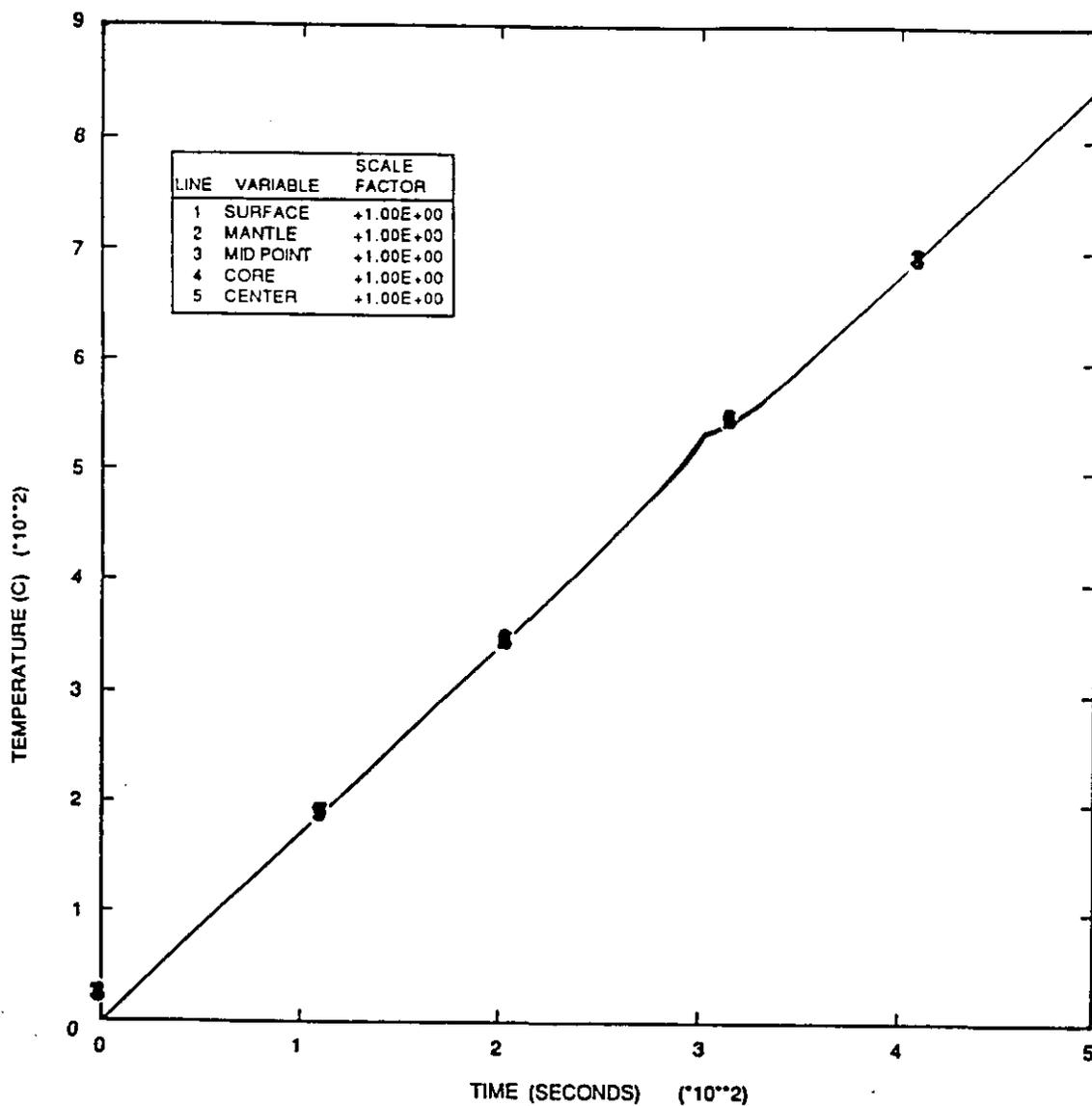


FIGURE 10. Temperature Change in a Resin Particle Heated at 100 Degrees/Minute

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Figure Captions:

- FIGURE 1. Structure of Strong-Acid Ion Exchange Resin
- FIGURE 2. Scanning Electron Micrograph (SEM) of High Density Uranium Oxide Particle
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Index Terms:

ABAQUS

Combustion

Diffusion

Finite-element modeling

Fracturing

Heat transfer

Stress/Strain

Uranium oxide

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Dave received his B.S. in Chemical Engineering in 1965 from Case Institute of Technology (now Case Western Reserve University). He received his M.S. in 1966 and his Ph.D. in 1970 (both in Chemical Engineering) from the University of Wisconsin, under the mentoring of Prof. E. N. Lightfoot. He joined the Du Pont Company in 1970 at the Savannah River Plant where he has had a variety of assignments in the nuclear field: gas centrifuge separation of isotopes, cryogenic distillation of hydrogen isotopes, laser isotope separation, and production of uranium oxide for nuclear reactor fuel. He became a Westinghouse employee in April 1989, when Westinghouse Savannah River Company took over as the operating contractor of the SRS. He is currently a Research Associate in the Nuclear Materials Planning Division.