SANDIA REPORT
SAND2001-1821
Unlimited Release
Printed July 2001

Filling Source Feedthrus With Alumina/Molybdenum CND50 Cermet: Experimental, Theoretical, and Computational Approaches

J. N. Stuecker, J. Cesarano III, E. L. Corral, K. A. Shollenberger, R. A. Roach, J. R. Torczynski, E. V. Thomas, and D. J. Van Ornum

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.doe.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/ordering.htm

SAND2001-1821
Unlimited Release
Printed July 2001

Filling Source Feedthrus With Alumina/Molybdenum CND50 Cermet: Experimental, Theoretical, and Computational Approaches

J. N. Stuecker, J. Cesarano III, and E. L. Corral
Ceramic Materials Center

K. A. Shollenberger, R. A. Roach, and J. R. Torczynski
Engineering Sciences Center

E. V. Thomas
Statistics and Human Factors Department

D. J. Van Ornum
Manufacturing Processes Department

Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-01349

ABSTRACT

This report is a summary of the work completed in FY00 for science-based characterization of the processes used to fabricate cermet vias in source feedthrus. In particular, studies were completed to characterize the CND50 cermet slurry, characterize solvent imbibition, and identify critical via filling variables. These three areas of interest are important to several processes pertaining to the production of neutron generator tubes. Rheological characterization of CND50 slurry prepared with 94ND2 and Sandi94 primary powders were also compared. The 94ND2 powder was formerly produced at the GE Pinellas Plant and the Sandi94 is the new replacement powder produced at CeramTec. Processing variables that may effect the via-filling process were also studied and include: the effect of solids loading in the CND50 slurry; the effect of milling time; and the effect of Nuosperse (a slurry "conditioner"). Imbibition characterization included a combination of experimental, theoretical, and computational strategies to determine solvent migration though complex shapes, specifically vias in the source feedthru component. Critical factors were determined using a controlled set of experiments designed to identify those variables that influence the occurrence of defects within the cermet filled via. These efforts were pursued to increase part production reliability, understand selected fundamental issues that impact the production of slurry-filled parts, and validate the ability of the computational fluid dynamics code, GOMA, to simulate these processes. Suggestions are made for improving the slurry filling of source feedthru vias.

Executive Summary

A scientific approach has been used to characterize and study the processes and methods used in the production of neutron tube source feedthrus. Particular attention was given to the preparation of CND50 cermet slurry and the subsequent use of the slurry for filling vias. Several interesting observations were made with regard to slurry characterization, solvent imbibition characterization and modeling, and identification of critical processing variables.

Slurry characterization:

- The rheological profiles of operator-preferred cermet slurries are similar and independent of the initial powder (Sandi94 or 94ND2). This occurs because the operators use an audible clicking sound created by the steel mixing balls as a guide. Even though different amounts of solvent are needed to reach this clicking sound, depending on the starting powder, the resulting rheologies are similar.
- As the slurry is mixed, the mixing balls change the powder morphology by breaking down the large, spray-dried alumina granules, effectively changing the solids loading by exposing the granule interior to solvent. As a result the slurry rheology increases with time and the clicking sound disappears.
- Significant slurry settling occurs within 10 to 15 seconds of not being milled, dramatically affecting the viscosity.
- Nuosperse had little to no effect as a dispersing agent, as verified by rheological studies and settling compaction behavior.

Solvent imbibition characterization:

- Microfocus x-ray experiments for planar imbibition can be modeled theoretically and simulated computationally with GOMA.
- Capillary imbibition experiments can also be modeled theoretically and simulated computationally with GOMA.
- Combining the results of previous studies, porous models can be created, allowing GOMA simulations of more complex geometries such as a cermet via.

Design of experiments on filling vias with CND50 slurry:

- Of the four factors thought to be critical in influencing production defects during slurry fill (applied vacuum level, solvent amount, slurry injection rate, time over vacuum after fill), only the time over vacuum was determined to be statistically important, with slight importance given to solvent amount. Longer vacuum times (20 s) are five times more likely to produce defect-free vias than short vacuum times (1 s).
- Each source feedthru has two vias that need to be filled with cermet slurry. Less defects were seen in the vias filled second when a high-solvent slurry was injected into the first via, suggesting that pre-wetting was occurring and helping to produce better fills. This effect was not as strong as the time-over-vacuum variable.
- In hopes of giving the operator a simple way to check via fill integrity, weighing of the dried filled parts was attempted. It was determined that there is too much variability in even the most careful weighing procedures to determine if defects are

present in the vias, necessitating 100% inspection with x-ray radiography unless a more reliable process is found.

Pragmatic implications:

- In an effort to make the slurry-filling process more reproducible (with the objective of improving supplier yields of source feedthrus) it is our opinion and recommendation that the work instruction (WI-704191-050) for filling source feedthrus be modified. We suggest including language that instructs the technician to apply a vacuum of at least 23 inches of mercury for a period of 20 seconds +/- 5 seconds. Furthermore, we suggest that a new (i.e., dry) piece of filter paper be used for each via. This will ensure that the slurry-filling kinetics are repeatable from via to via.

Table of Contents

List of Figures

List of Tables

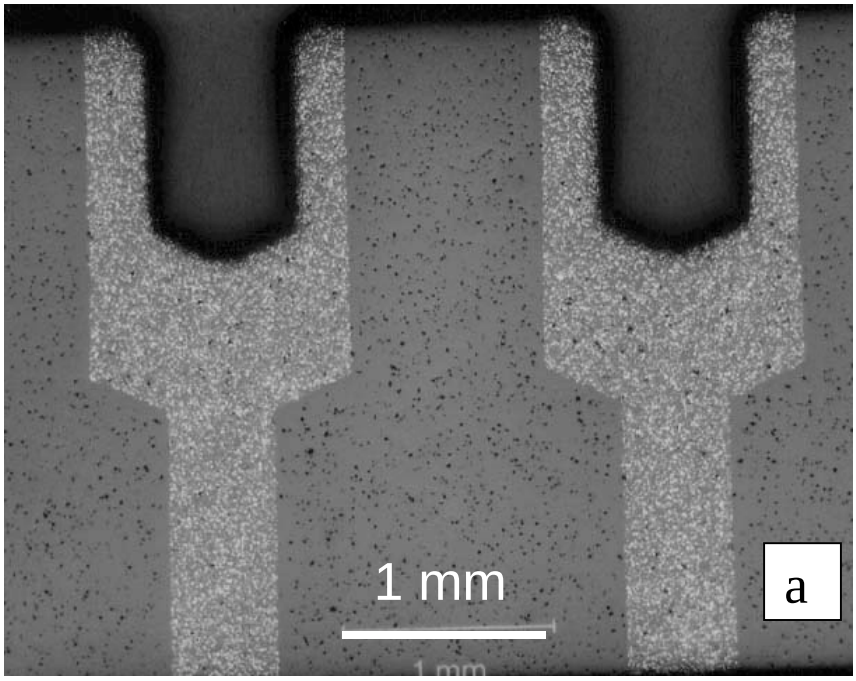
Filling Source Feedthrus With Alumina/Molybdenum CND50 Cermet: Experimental, Theoretical, and Computational Approaches

Background

Alumina/molybdenum CND50 cermet is used extensively in the production of neutron generator components. In this report, the source feedthru of the MC4277 neutron generator tube was investigated. The source feedthru has a dense ceramic body with hermetic pathways that are electrically conductive. A schematic is shown in Fig. 1. The ceramic part of the source feedthru is an electrically non-conductive 94% alumina body. The alumina powders used to manufacture the source feedthru body are either 94ND2 (formerly produced at the GE Pinellas Plant) or Sandi94 (produced at CeramTec). The electrically conductive pathways, termed 'vias' are made from an alumina / molybdenum cermet material. The current method of producing vias requires green machining holes into the 94% alumina body and filling the holes with a low-solids slurry (~25 vol%) of 50/50 wt% alumina/molybdenum cermet powder. Diethylene glycol monobutyl ether acetate (DGBEA) is the liquid used to make the slurry and Nuosperse is used as a dispersing aid. The starting cermet powder used to make the slurry is a 4-hour-dry-ball-milled blend of spray-dried alumina of 50-100 μm (Sandi94 or 94ND2) and molybdenum powder with an average size of 4-8 μm. The slurry is batched in a rotating mixing cup approximately 10 ml at a time and is injected into the hollow vias using vacuum assistance to pull the slurry into the via. Relevant work instructions are found in Appendix A: WI-704191-030 (dry blending), WI-704191-040 (slurry preparation), and WI-704191-050 (slurry fill). The vias are drilled into pressed 94% alumina pellets which are 50% porous (Figure 1). Once the vias are filled with slurry, the cermet particles consolidate as solvent imbibes (wicks) into the porous alumina. Excess slurry is placed over the vias to act as a material reservoir during consolidation. Subsequent drying, isostatic pressing, sintering, and grinding steps change the source feedthru dimensions to those required by neutron tube specifications.

The cermet slurry preparation and filling procedures have been determined to be the critical steps in creating defect-free source feedthru parts.[1] Inadequate via filling or

particle consolidation may result in cracking and warping within the via, compromising functionality (Figure 2). However, the work instructions fail to pinpoint the optimal slurry conditions for via filling, creating a situation based on operator discretion. For example, an operator may create slurries ranging from 20 to 35 vol% solids, resulting in a 250% change in viscosity, all within the specifications of the work instruction. For many variables, there are no boundaries provided to the operator. For example, during via filling, the amount of time the filled part is left over vacuum is defined as ‘let dry to a dull sheen’.



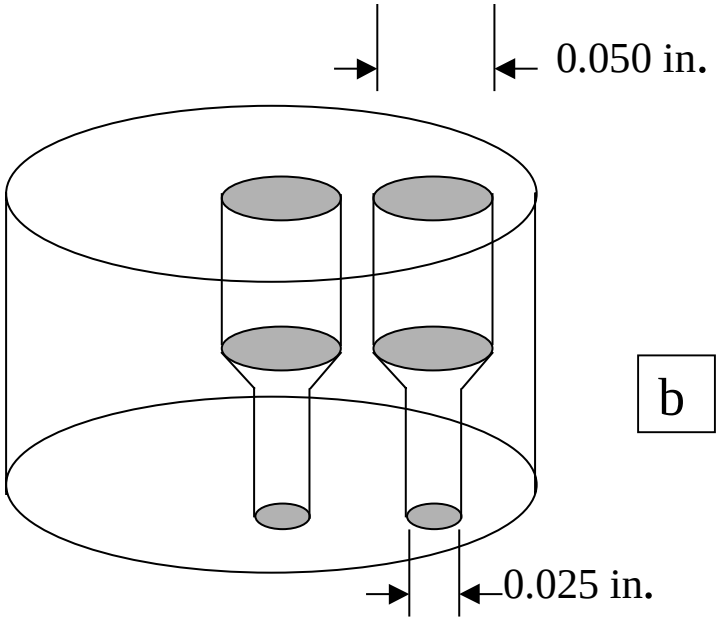


Figure 1: (a) SEM cross section of a sintered and machined source feedthru part. (b) Corresponding schematic diagram.

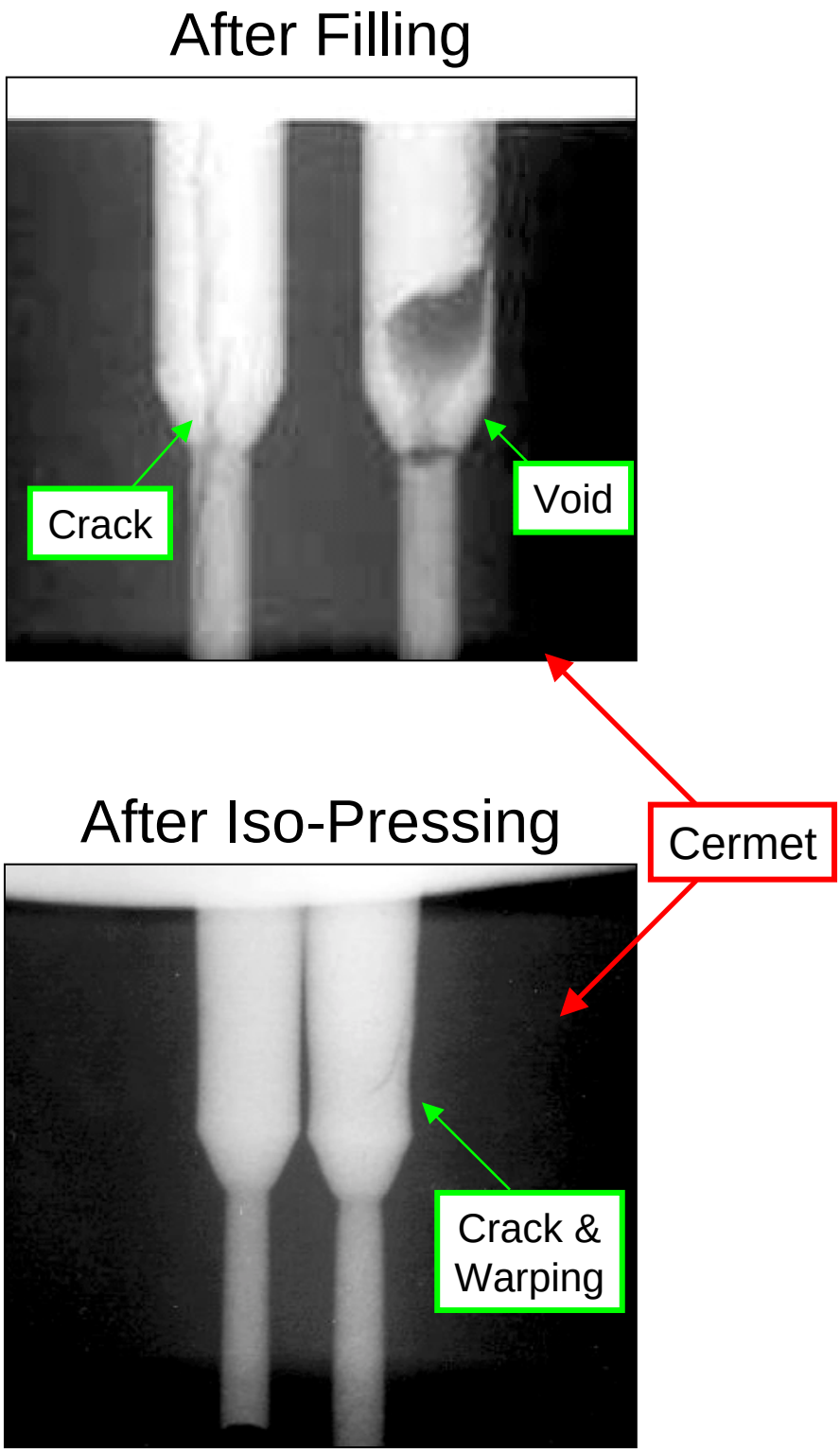


Figure 2: X-ray micrograph of a pair of vias poorly filled with cermet: top, after filling; bottom, after isopressing.

In order to obtain a defect-free cermet via, slurry must completely fill the via under vacuum assist and then uniformly consolidate during solvent imbibition into the surrounding porous alumina body. The time-scales when critical fundamental mechanisms influence via production are distinct but sometimes concurrent. For example, previous modeling work has been completed to suggest that vacuum-driven filling of the vias with the slurry takes 0.01-1 s. Appreciable consolidation due to vacuum-driven removal of liquid occurs from 5-50 s. Consolidation due to imbibition-driven removal of liquid occurs from (3-20 s) and gravitational settling (60-800 s). Through the years, experienced Sandia operators have migrated to a certain set of slurry-preparation and filling conditions that qualitatively manage the above critical stages and have improved yields up to 80%. The expense of a neutron generator suggests that 100% of cermet parts be tested for flaws. Although this level of inspection may not change, a favorable understanding of the slurry preparation and filling procedures could reduce training time for new operators and increase yields, thereby reducing waste and improving efficiency.

Work Objective

Three separate tasks were performed to characterize the cermet via production process. Although these tasks are separate, findings in one task commonly give insight into solving questions arising from other tasks. Tasks are as follows:

1. Characterizing the slurry, which included the effects on rheology of additive, solids loading, binder, and powder type (Sandi94 vs. 94ND2).
2. Modeling of slurry consolidation within the via through experimental, analytical and computational means.
3. Resolution of the critical variables in the manual slurry filling procedure.

As indicated in Task 1, slurry characterization is important for all subsequent experiments. Rheology change, which is determined by many factors including solids loading, could possibly affect via filling both during vacuum driven filling and subsequent consolidation. Because the powder morphology is a combination of spray-dried granules and micron-sized powder, processes such as mixing during the slurry

preparation procedure may alter the morphology and thus the rheology. Also, the new Sandi94 powder behaves differently than the 94ND2. Operators have noticed that a change in solids loading is required to closely match the rheology of Sandi94 to that of 94ND2. Several series of experiments are used to characterize the cermet slurry.

As indicated in Task 2, creating defect free cermet source feedthru parts requires that the critical variables/stages and the influence of these critical variables/stages on producing a defect-free cermet via be determined. One important processing stage is the consolidation of particles during solvent imbibition. Imbibition-driven packing competes with vacuum-driven filling and packing during consolidation. In order to characterize imbibition-driven packing, the imbibition of solvent through a porous medium was determined using experimental, theoretical, and computational techniques. The ability to model particle consolidation, which relies on imbibition-driven packing, affords the opportunity to explain or predict common processing flaws.

As indicated in Task 3, determining the critical factors during the manual filling procedure is critical to creating defect-free parts. There are several steps the operator must proceed through to fill a via. Operator experience and an examination of the history of low-yield part batches were used to select a set of critical variables. All remaining factors were then held as constants while a statistical design of experiments was conducted with the critical factors. Using statistical software packages, the influence of each factor, as well as combinations of factors, on defect creation was determined.

General Materials and Material Preparation

All materials were prepared within specification of the relevant work instructions. Spray-dried alumina containing 93.4% alumina, 4.4% silica, and 3 wt% binder (equal weights of methylcellulose and hydroxypropyl methylcellulose) (SS305195-200) is used to create both the cermet slurry and porous green compact. Slurry preparation has been briefly outlined above, with more detail available in the work instruction. Alumina compact fabrication (SS305195) yields a cylindrical compact of 0.875 in. diameter and 0.8 in. height. For the source feedthru, vias are drilled in this compact to specification (SS393650). Important via dimensions are found in Table 1.

Table 1: Cermet Source Feedthru Via Dimensions.

Via 1 Position	Center
Via 2 Position	Offset 0.086 in.
Large Diameter	0.0625 in.
Small Diameter	0.032 in.
Via Transition Depth	Undefined

It is important to note here that parts of the experimental design matrix are only applicable to this component with these dimensions. For example, lower-solids slurries still within range of the slurry preparation work instruction are also used to fill smaller diameter vias (0.010"). However, a large share of the analysis is applicable to any slurry-filling procedure.

Diethylene glycol monobutyl ether acetate (DGBEA) is used as the solvent, 99% pure (SS305003-200). Nuosperse 657 is used as an optional particle surfactant, the effectiveness of which will be determined later in the slurry characterization. Nuosperse is commonly used in screen printing inks to break up particle agglomerates by migrating to the solid-liquid interface. In all experiments, the solvent has Nuosperse added.

Slurry Characterization

The slurry work instruction does not specify the exact slurry solids loading, only a range of 7 - 12 ml solvent, 23.5 - 35 vol% respectively for a 20-g batch size of cermet powder. Operators have determined that as the stainless steel balls mix the slurry in the rotating mixing cup, the correct viscosity occurs when those milling balls make an audible clicking sound. So, through trial and error, this clicking sound is adopted as the viscosity indicator for the correct solids loading, corresponding to approximately 11.5 ml of solvent for Sandi94 powder, and 9.0 ml for 94ND2 (Figure 3). Further, there is a factor of ten difference in viscosities when comparing at the lowest solids loading to the highest solids loading for the 94ND2 case. At the lowest solids loading (7 ml solvent), Sandi94 was unable to be mixed in the normal mixing cup, so a solids loading of 29.5 vol% (~9ml of solvent) was used. Important to note in Figure 3, is the fact that the

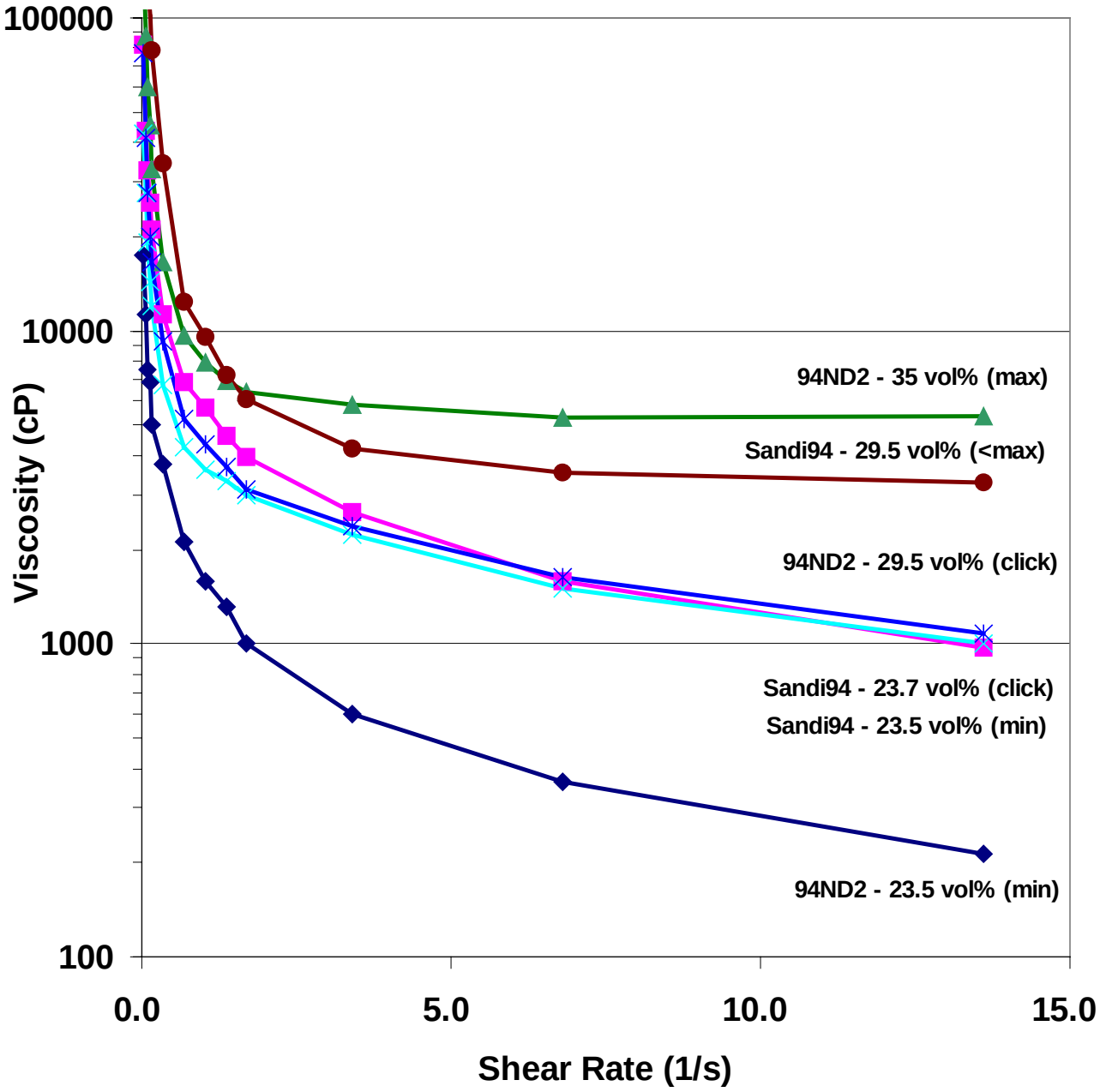


Figure 3: Rheology profiles covering the range of allowable cermet slurries for both 94ND2 and Sandi94.

commonly used ‘clicking’ slurries both have the same rheological profile even though the solids loadings are different for 94ND2 and Sandi94. Similar rheological profiles in these two systems with different solids loading indicate a difference in powder morphology. The spray-dried alumina granules change with milling time.[2] If the granules are of a uniform spherical shape, trapped air within the granule will change the effective density of the solid particles, decreasing the solids loading and decreasing the viscosity. However, if the granules are not well formed due to excess milling either wet or dry, the solids loading will be higher, increasing the viscosity. Presumably, this is the only difference between spray-dried Sandi94 and 94ND2, and dry-ball-milled mixtures with molybdenum. This logical supposition of changing powder morphology is supported by past work[2] and by Figure 4 in which rheology as a function of milling time is plotted.

Stability of the slurry has always been less than ideal with the solid particles visually observed to settle in minutes. For this reason, the mixing cup is always rotating throughout the via-filling process (1-3 hours). The actual viscosity change with time is shown in Figure 5 and suggests that if the slurry were not mixed for ~ 20 seconds prior to injection, a 10% change in viscosity would result, corresponding to a lower solids-loading injected slurry and possibly contributing defects to the final via. Also, it is therefore important to note that the viscosity change with time seen in Figure 4 may need to be taken into consideration. This change in viscosity has also been visually observed by operators, who have adjusted the viscosity to yield a ‘clicking’ slurry by adding a few more drops of solvent. Although it was originally thought that solvent evaporation (not likely due to the low vapor pressure) is the cause of the gradually increasing viscosity, it is more likely due to the powder morphology change.

The additive Nuosperse is optional in the slurry-preparation work instruction. Nuosperse was used initially in screen printing to break up particles by migrating to the solid/liquid interface. It is not used as a dispersant, only a surfactant. The additive was incorporated into the cermet slurry process because the process is patterned after a screen printing process used by Kodak in Schenectady, NY. Because the cermet process uses spray-dried alumina particles held together with binder, the usefulness of the surfactant is

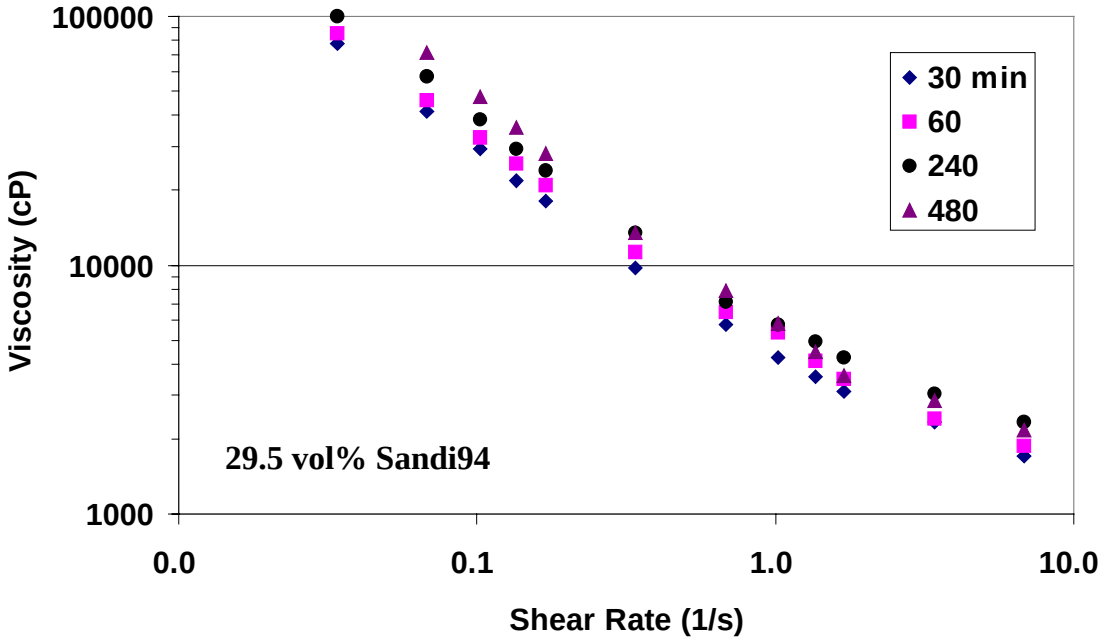


Figure 4: Rheology profile for a 29.5 vol% 'clicking' Sandi94 cermet slurry over a 480-minute test period while milling with the requisite 9 steel milling balls. Clicking stops after 240 minutes.

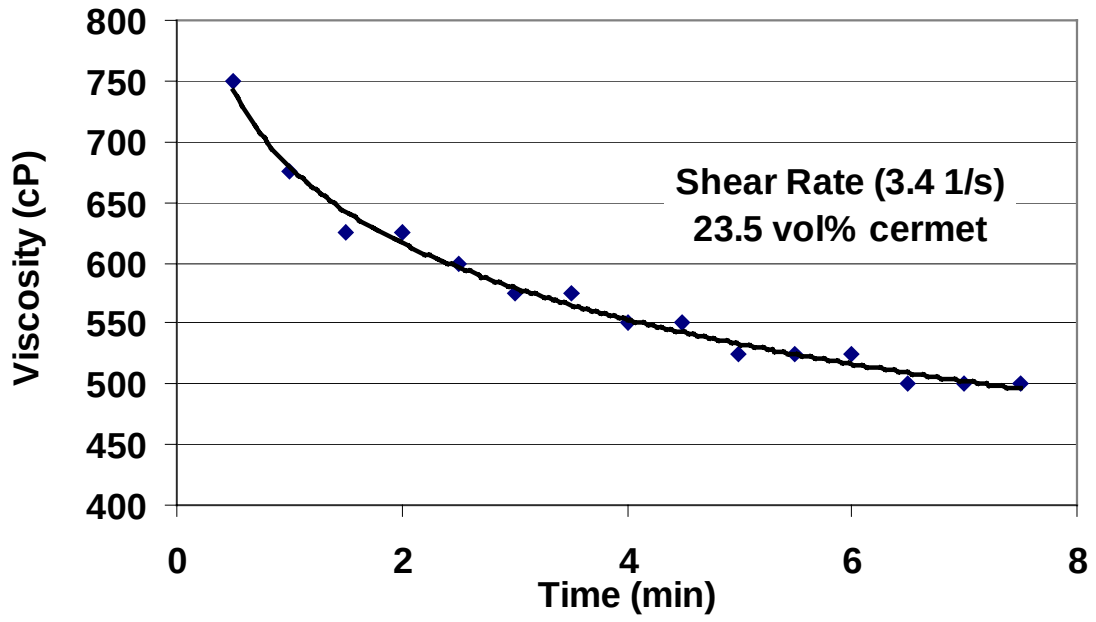


Figure 5: Viscosity versus time for a slurry that was mixed for 30 minutes, then left to settle.

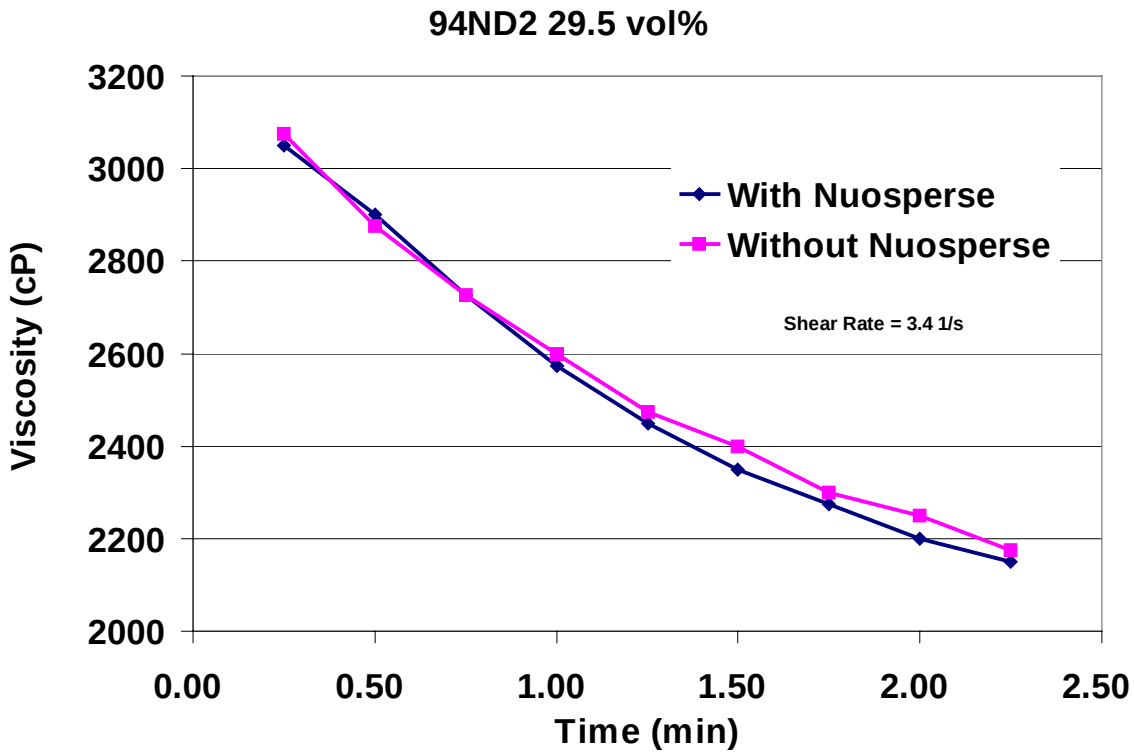


Figure 6: Rheology profile of two equal-solids-loading cermet slurries, one with Nuosperse and the other with an equal amount of added solvent.

questionable. The plot in Figure 6 shows the effect of Nuosperse on 29.5 vol% cermet slurries. One slurry with 83 μl (about 3 drops) of Nuosperse and another identical slurry with 83 μl of DGBEA solvent. The solids loadings of the slurries are equal, and both slurries were exposed to the same milling time. It can be observed that the effect of Nuosperse on viscosity is negligible, where in other circumstances, similar amounts of dispersant or surfactant have been seen to have a dramatic effect on viscosity (50-90% reduction).[3] Figure 7 shows that solids packing is increased by 1.5% with 0.08 g of Nuosperse (about 3 drops) based on examining sedimentation heights.

Several other questions were qualitatively addressed during this research as well. The solubility of the binder (methylcellulose and hydroxypropyl methylcellulose) was determined to be below 0.02 wt% using infrared light reflection techniques. This information is important for imbibition characterization, for which solvent properties are generally used in the models. Samples of Nuosperse have been observed to darken and thicken unexplainably. Contamination and aging were examined as possible causes. The aging of Nuosperse when exposed to sunlight and fluorescent lighting was determined to be negligible over a 6-month test period. Samples of Nuosperse were placed in glass vials and exposed to direct sun and fluorescent lighting and compared with bulk samples from a dark storage cabinet. There were no noticeable changes in color or viscosity, suggesting that contamination may change some physical properties of the liquid Nuosperse.

Solvent Imbibition Characterization

Introduction

Fluid imbibition was modeled using a combination of experiments, theoretical models, and computational models (GOMA). A list of parameters and materials properties used in imbibition characterization is provided in Table 2.[4] Experiments and theoretical models were used to validate the ability of GOMA to accurately simulate simple geometric imbibition cases, GOMA was ultimately applied to simulate the more complex via geometry. Two experimental geometries were investigated: planar imbibition and capillary imbibition. The results were then validated by comparison to theoretical models, and these situations were subsequently simulated using GOMA.

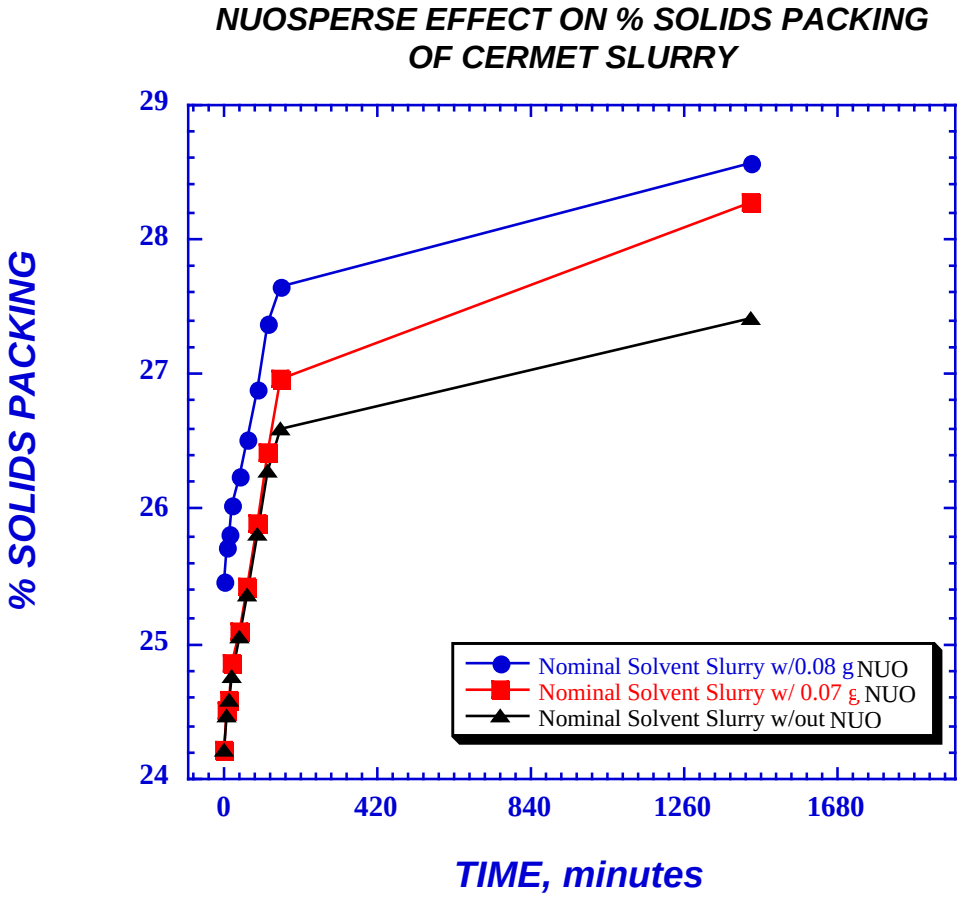


Figure 7: The effect of Nuosperse additions on solids packing of 19.5 vol% cermet slurries.

A detailed description of the experimental and theoretical procedures used to track the fluid saturation front in a porous medium has been compiled very completely in a previous report[4] but will be outlined in this report accordingly.

Table 2: Materials Parameters and Other Relevant Properties[4]

Parameter	Symbol	Value
Liquid Density (DGBEA)	ρ	0.978 g/cm^3
Liquid Viscosity (DGBEA)	μ	0.0515 g/(cm s) at 293
Liquid Surface Tension (DGBEA)	σ	22 dyne/cm at 293 K
Saturated Vapor Pressure (DGBEA)	p_{svp}	13 dyne/cm^2 at 293 K
Molybdenum Density	ρ_M	10.2 g/cm^3
Alumina Density (94% pure)	ρ_A	3.82 g/cm^3
Alumina Density (4 wt% binder)	ρ_B	3.56 g/cm^3
Alumina Density (4 wt% binder, 47% dense)	ρ_P	1.67 g/cm^3
Alumina Density (4 wt% binder 47% dense, sat.)	ρ_S	2.19 g/cm^3
Green Alumina Permeability	K	(1.25±0.25) 10^{-11} cm^2
Green Alumina porosity	ε	0.45
Green Alumina Pore Radius	R_p	0.432 10^{-4} cm
Green Alumina Contact Angle	θ_p	probably 0-30°
Glass Contact Angle	θ	probably 0-30°
Gravitational Acceleration	g	981 cm/s^2

Planar Imbibition

In brief, the saturation front was tracked for the planar-imbibition situation by immersing the planar face of a porous cylindrical alumina pellet into a dish of solvent. A wire screen allows the solvent access to all portions of the submerged planar face. The saturation front is then tracked using a microfocus x-ray system.[4] The saturated material's higher density decreases the transmitted intensity of x-rays, allowing the saturation front to be distinguishable (Figure 8). Image analysis at selected times throughout the experiment allows the saturation front to be plotted as a function of time (Figure 9), in which one-dimensional flow is observed (flat saturation front). Experimental results agree to within 5% of the theoretical model.

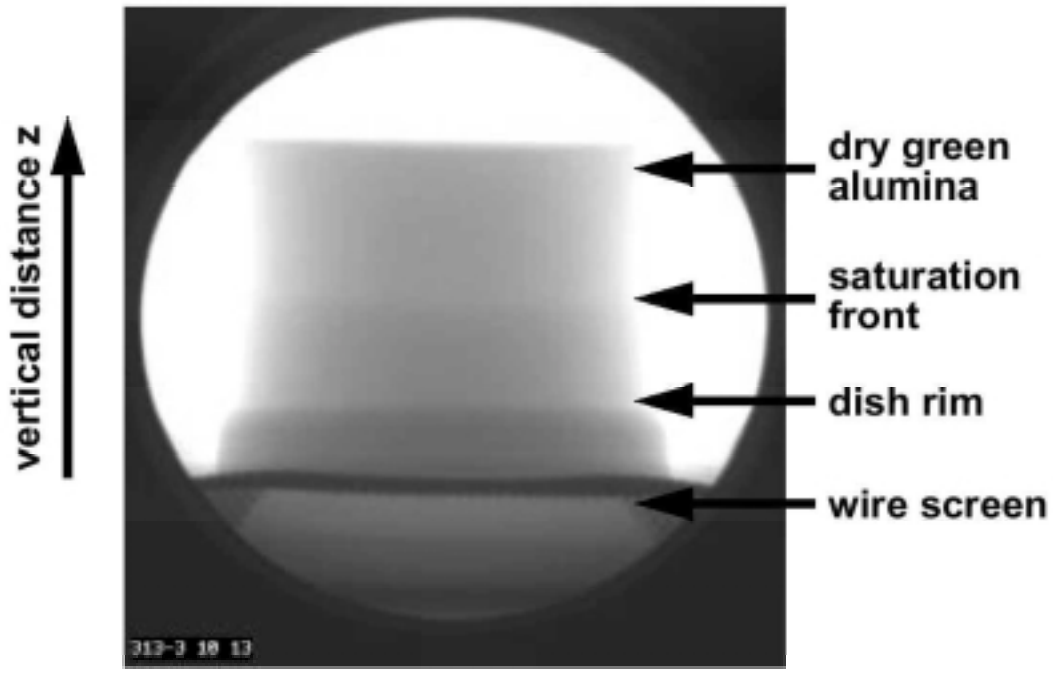


Figure 8: X-ray image of the solvent saturation front traveling up through a pressed alumina blank.[4]

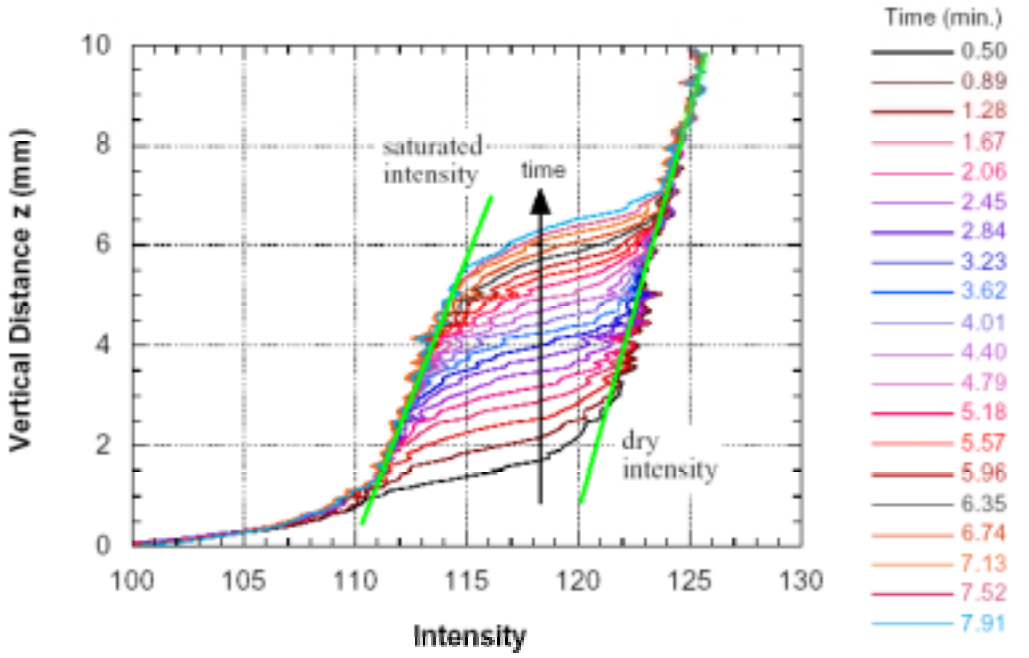


Figure 9: Transmitted X-ray intensity is reduced as the saturation front continues to propagate through the porous alumina blank with time.[4]

A theoretical model was created based on Darcy's Law, and knowledge of materials properties.[4] Capillary pressure is the driving force for imbibition with gravity, liquid evaporation, and air motion being negligible. The resulting equation derived for this planar system is:

$$h = \left(\frac{2\kappa p_c t}{\varepsilon \mu} \right)^{1/2} \text{ (front height),}$$

where p_c is the capillary pressure[4], t is time, with all other units being defined in Table 2. Inserting values, the equation solves to:

$$h = \left(0.106 \frac{mm^2}{s} \cdot t \right)^{1/2} \text{ (front height).}$$

The total uncertainty of the parameters in Table 2 used in the theoretical derivation total to 30%, driving the uncertainty of the theoretical model to 30%

GOMA uses a single-phase Darcy formulation to calculate the liquid-phase pressure in the porous substrate. A Van Genuchten model is used to relate the saturation level to liquid-phase pressure and for the relative liquid permeability model.[4] Vapor-pressure models tested included both Flat and Kelvin models. A set of mesh equations with quadratic elements is used to create a fine mesh to accurately determine saturation front motion. Using the same set of materials parameters and sample size as in the experimental and theoretical procedures, the saturation front was determined as a function of time (Figure 10). Resulting computations showed insensitivity to the type of vapor pressure model used.

A comparison summary of experimental, theoretical, and computational results for planar imbibition is provided (Figure 10). In summary:

- All methods illustrate that the saturation front height progresses as the square root of time.
- The best fit of the theoretical curve fits the experiments almost exactly, with nominal parameter values yielding an 8% deviation from experimental.
- GOMA computations using nominal parameter values also deviate 8% from experimental.

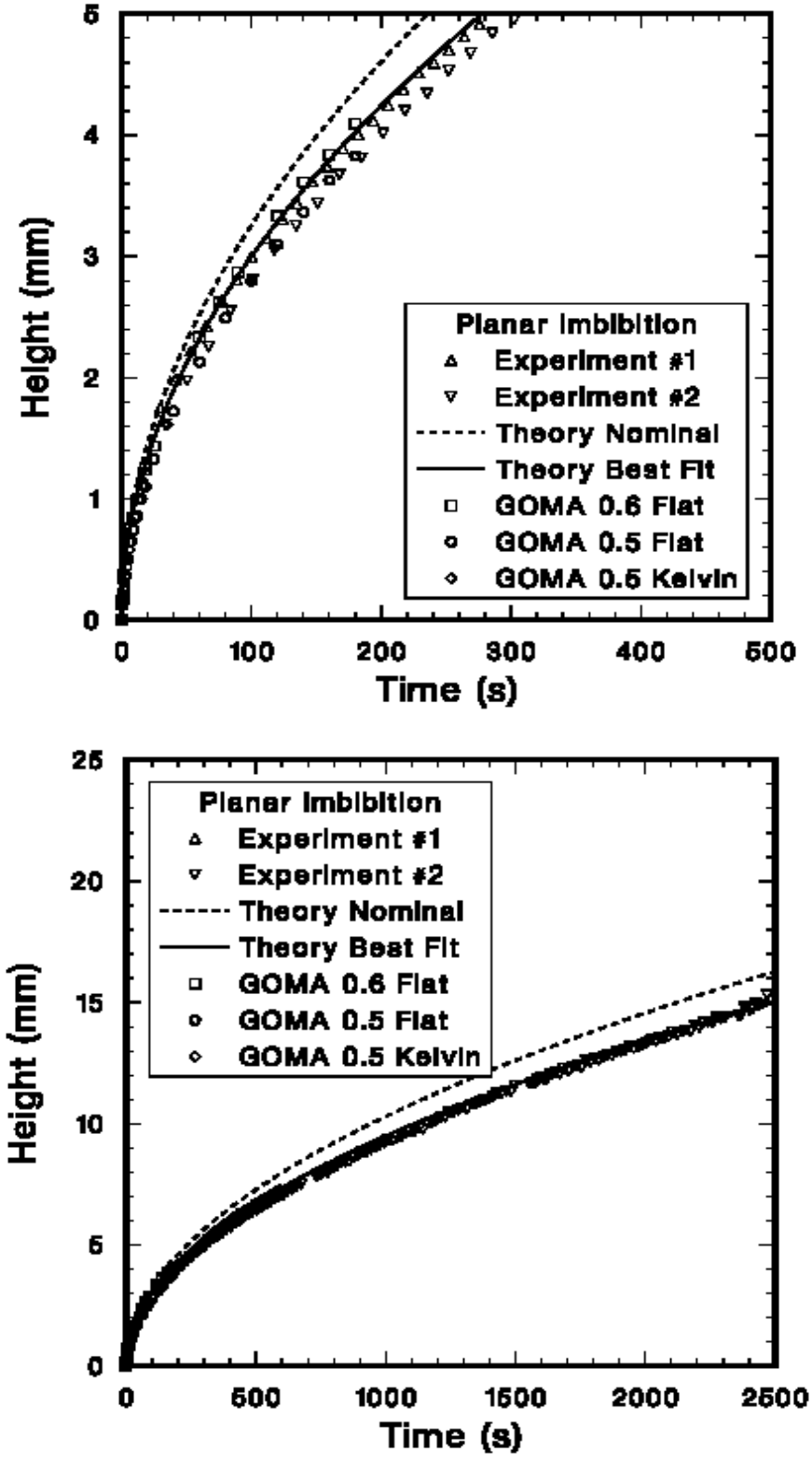


Figure 10: Comparison of experimental, theoretical, and computational results for (a) short and (b) long planar imbibition times.[4]

Capillary Imbibition

A slightly more complex geometry is investigated using a glass capillary tube (Wilmad Glass, Buena, NJ). The capillary tube (0.8 mm ID, 1.0 mm OD) is filled with solvent and brought into contact with the top planar surface of a porous cylindrical alumina pellet (Figure 11). A multi-axis positioning system is used to position capillary tubes repeatably on the porous substrate. The decreasing solvent height in the capillary tube is tracked as a function of time using digitally captured images. Saturation-front propagation is not observed but is presumed to be near hemispherical. This saturation-front shape depends on the type of depression the capillary tube creates in the porous substrate and the nature of the seal created between tube and porous substrate. Repeatability of experiments was increased to yield less than 10% variability once the importance of capillary contact was determined and controlled. An increase in capillary depression depth into the substrate corresponded to a decrease in volumetric flow rate. If the capillary tube was brought down just enough to introduce the pendant drop to the surface without the tube itself touching the surface, faster volumetric flow rates resulted. This phenomenon suggests that more advanced theoretical models be employed to describe these conditions accurately.

Theoretical models are employed in a similar manner to the planar imbibition case to describe the capillary experimental conditions.[4] Important modeling issues include whether the surface of the porous substrate is permeable and the type of depression created by the capillary tube. An impermeable surface situation dictates that imbibition can occur only through the contact area defined by the inner radius of the capillary tube (Figure 12), nearly the situation where the capillary tube is driven deep into the substrate. A permeable surface allows an external meniscus to be created outside of the capillary tube, allowing imbibition to occur over a much larger effective area (Figure 13). This is similar to the situation in which the capillary does not actually contact the substrate but imbibition is occurring. Extensive derivations were required to model these situations, with more effort required for the permeable-surface condition.[4] The difference between permeable and nonpermeable surface conditions can change the volumetric flow rate by a factor of three.

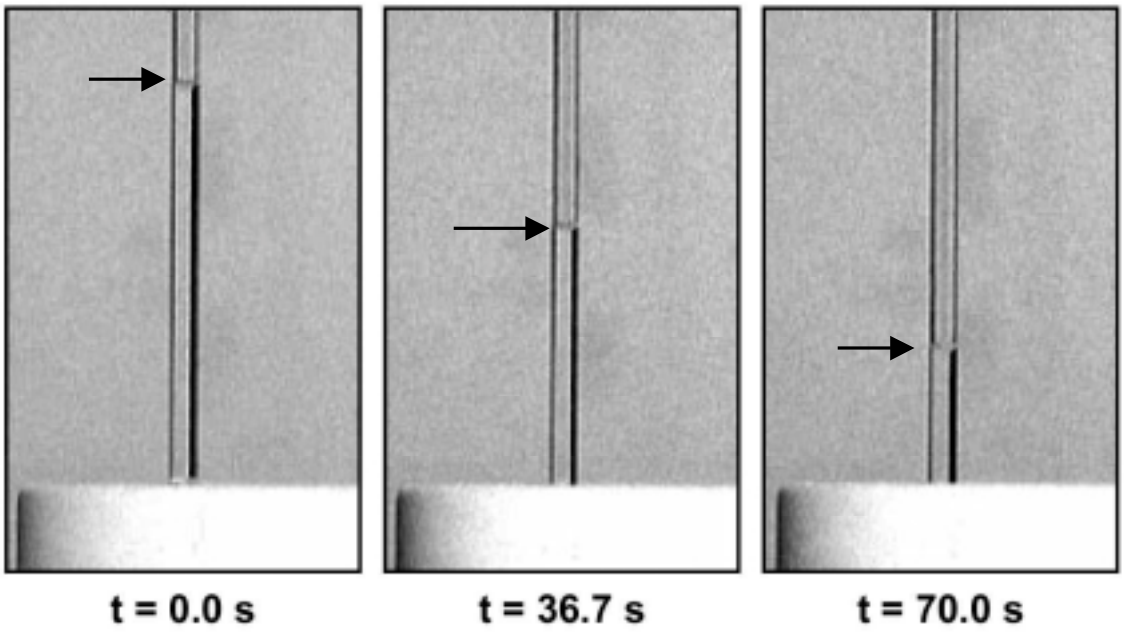


Figure 11: Sampling of experimental capillary imbibition test pictures used to determine imbibition rates.

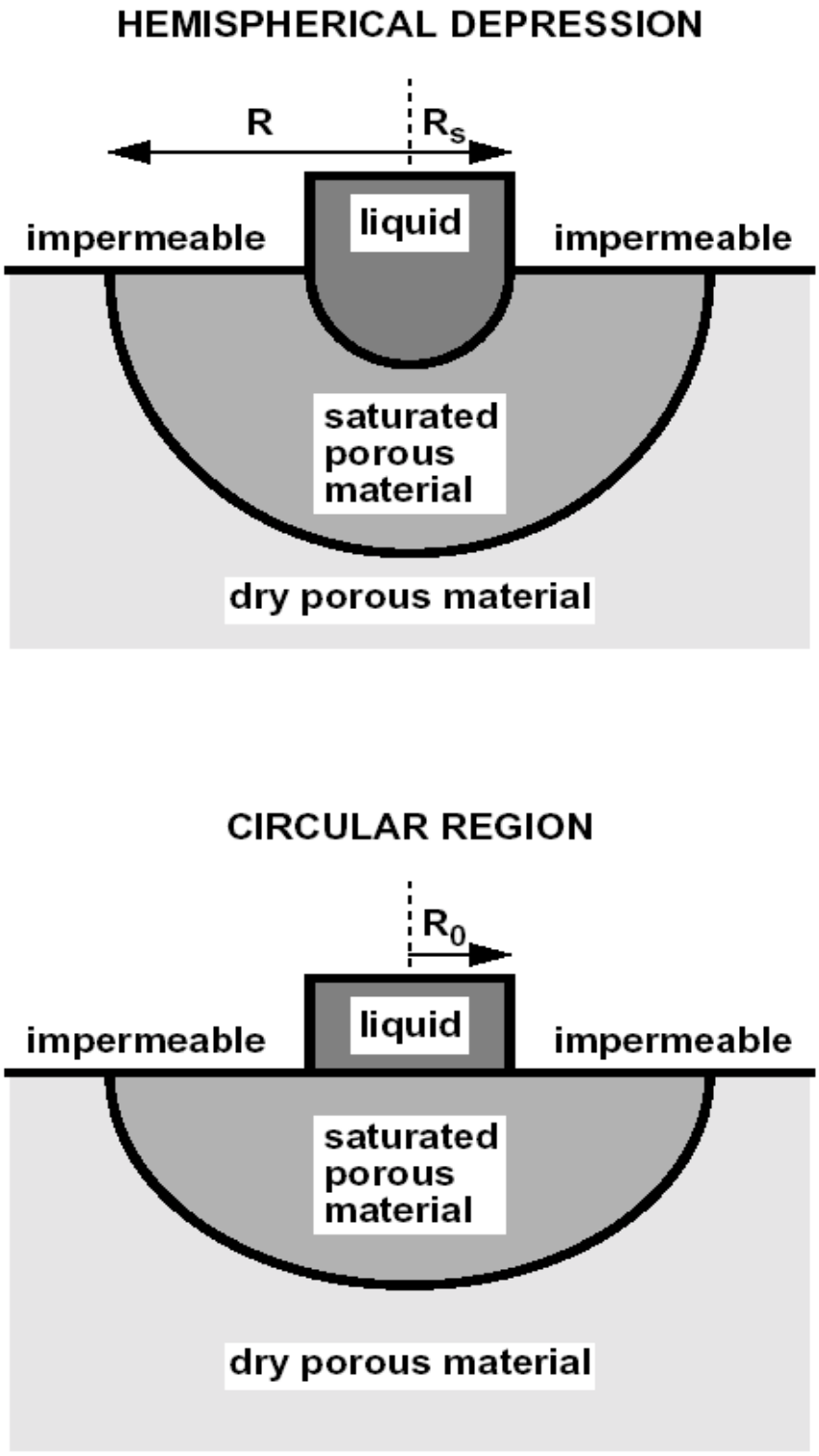


Figure 12: Limiting cases for the impermeable surface situation: (a) hemispherical depression; (b) circular region.[4]

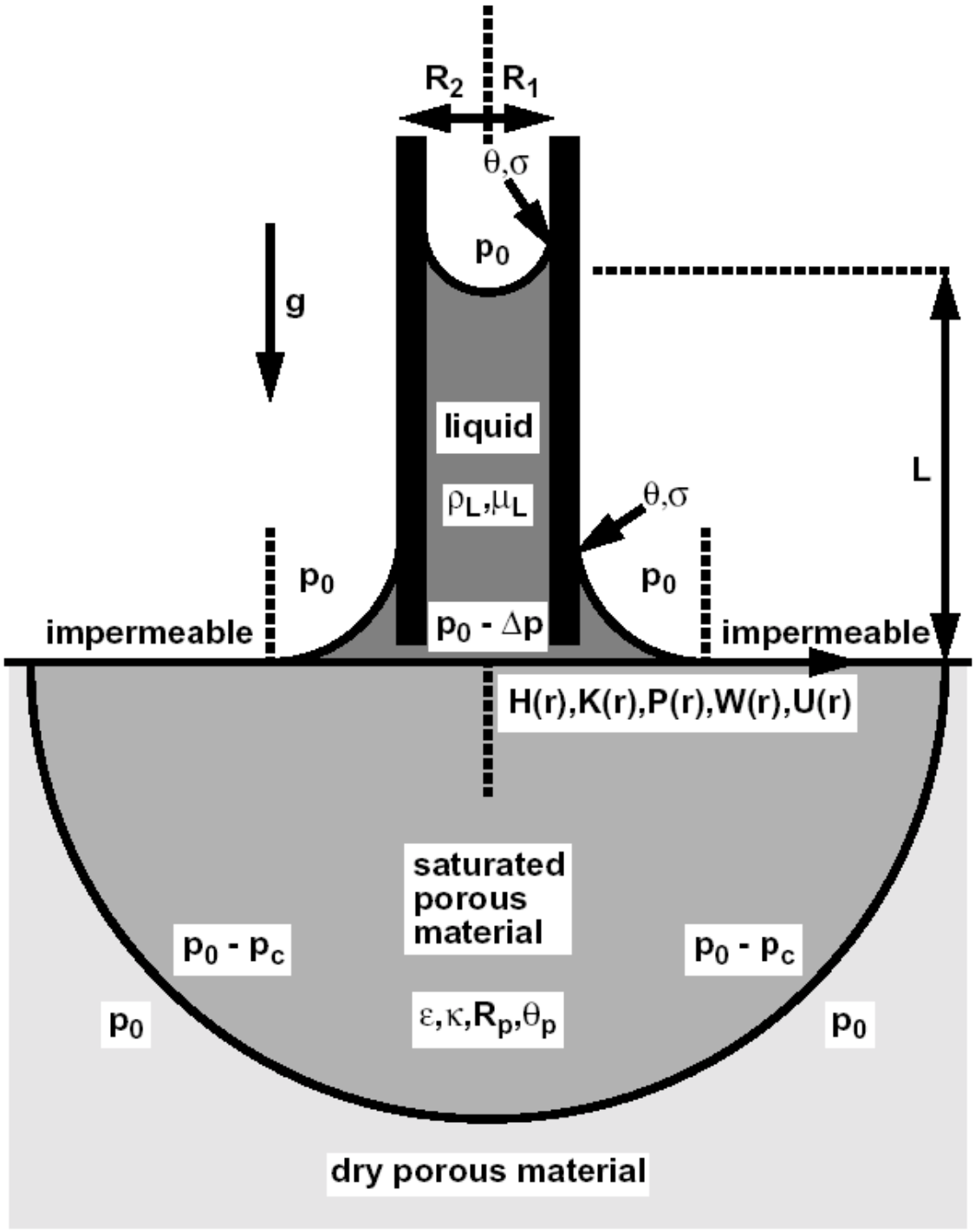


Figure 13: Permeable-surface situation for capillary imbibition where a meniscus outside the capillary tube can be formed (exaggerated separation distance).[4]

GOMA computations of the capillary-imbibition situation are similar to those for the planar-imbibition situation with addition of a two-dimensional mesh and a solvent-filled capillary tube (Figure 14). A Darcy-Continuous boundary condition is applied to the capillary tube-porous substrate interface. Kinematic and capillary boundary conditions are applied to the liquid surface in the capillary tube. An impermeable surface was set for the surface boundary condition, and the saturation front was tracked as a function of time (Figure 15). GOMA results suggest capillary imbibition rates 1.85 times faster than in planar imbibition after 4.5 s due to the larger volume available for saturation. Since and impermeable surface situation was examined using GOMA, the computational imbibition rate should be slower than the experimental rate. As with planar imbibition, the capillary-imbibition computations are insensitive to the vapor pressure model employed.

A comparison summary of experimental, theoretical, and computational results for planar imbibition is provided (Figure 16). In summary:

- All methods illustrate that the volumetric flow rate decreases with time.
- The impermeable-surface theory (Theory A) agrees well with GOMA computations (impermeable surface), as well as with the experiment in which the capillary was driven deep into the substrate (EXPT #4).
- The permeable-surface theory (Theory B) slightly underpredicts the experiment in which the capillary was not touching (EXPT #1) or was slightly pressed (EXPT #3) because the theory uses limiting values for the volumetric flow rate.

GOMA Via Simulations

Imbibition-driven packing of a cermet slurry filled via was simulated using the porous medium models derived through the planar and capillary imbibition models. The change in particle concentration during consolidation was determined using the Phillips model in conjunction with a Krieger model.[4] Instability of particle concentration predictions resulted when applying vacuum to the via, so for all simulations, the vacuum is removed. Initial particle concentration in the slurry is 25 vol%, with experimental data showing maximum particle consolidation to 45 vol%.

The mesh structure used for simulations is shown in Figure 17. Simulated consolidation of cermet slurry in a via for times of 0, 0.1, and 0.5 s are shown in Figure 18. GOMA simulations can be thus be used to describe cermet consolidation based solely on imbibition.

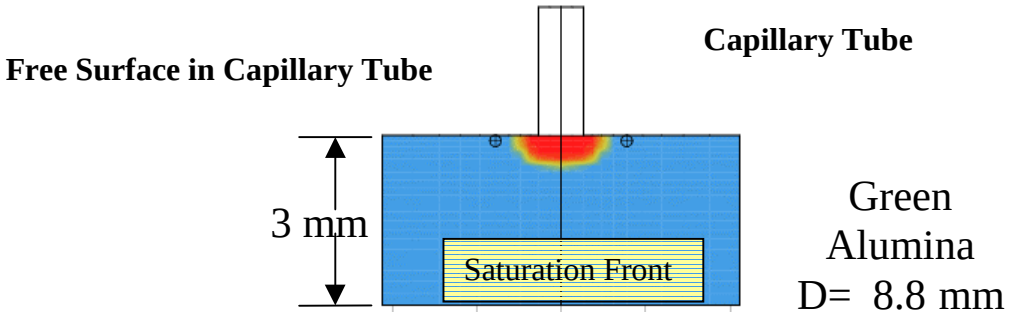


Figure 14: GOMA setup for capillary-imbibition simulations.[4]

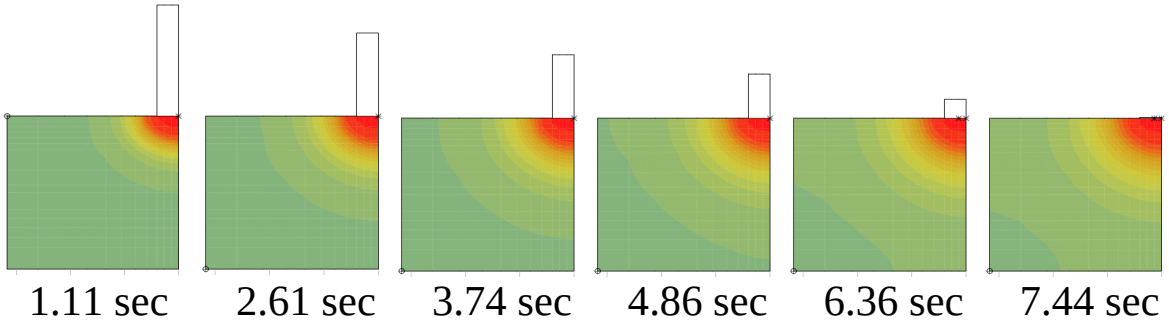


Figure 15: GOMA simulation for the imbibition of DGBEA into a porous alumina blank.[4]

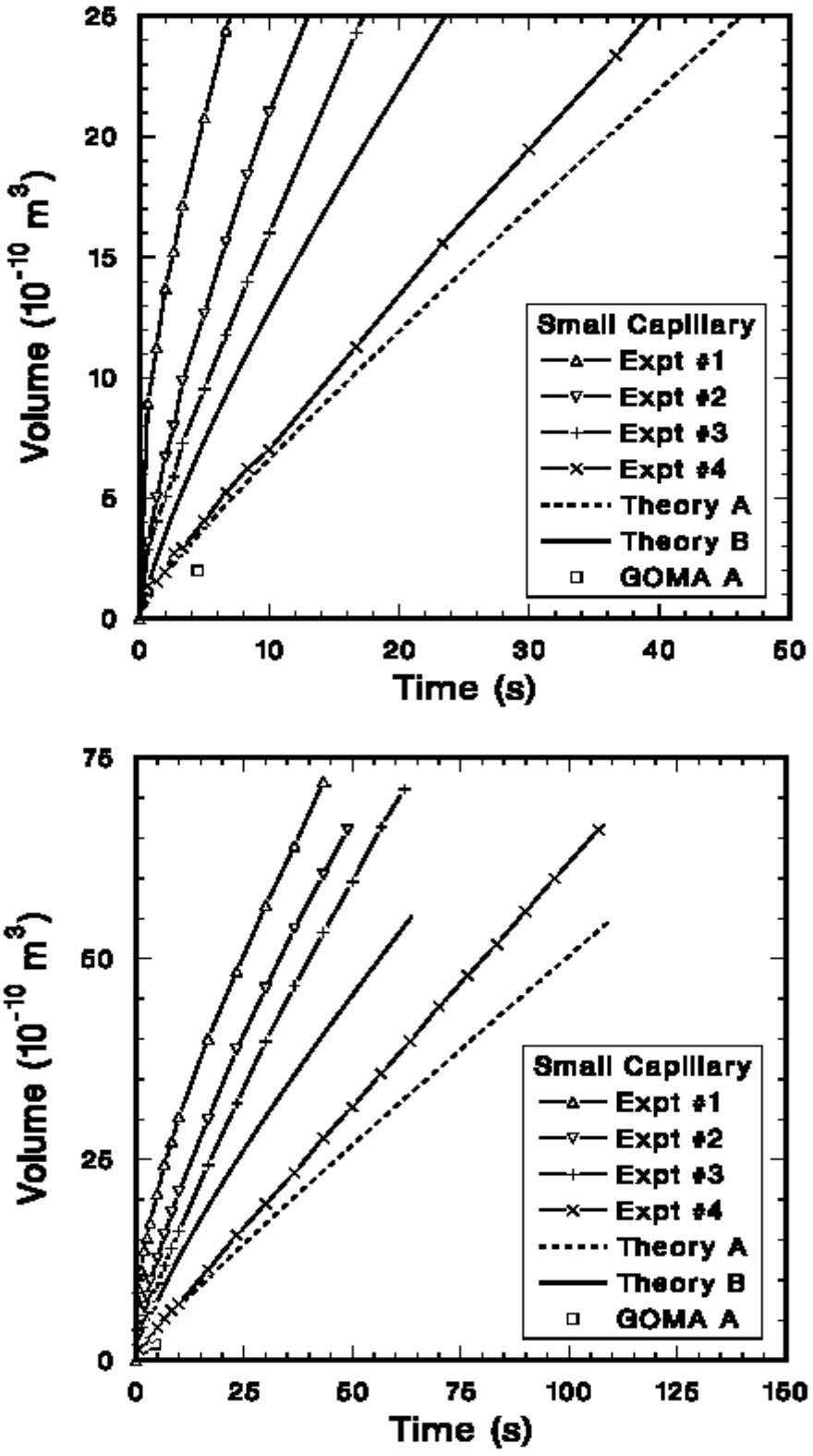


Figure 16: Comparison of experimental, theoretical, and computational results for (a) short and (b) long capillary-imbibition times.[4]

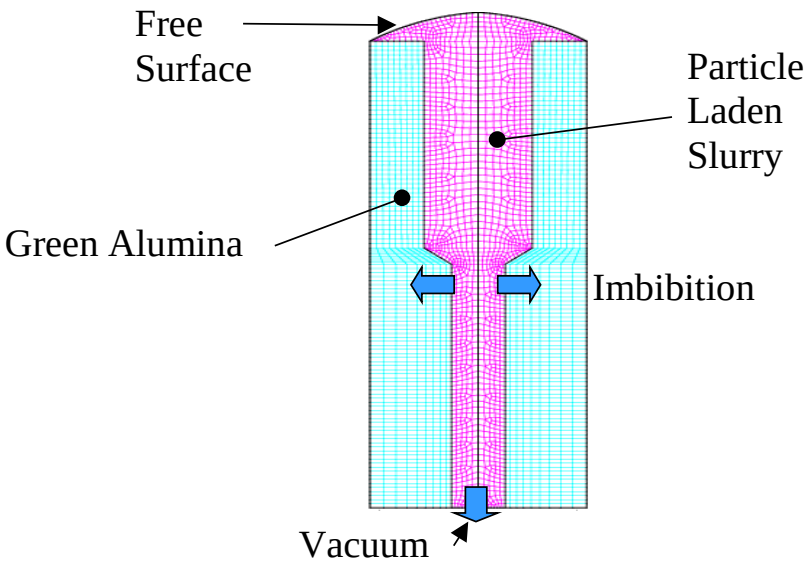


Figure 17: Computation mesh for GOMA simulations of imbibition within a via.[4]

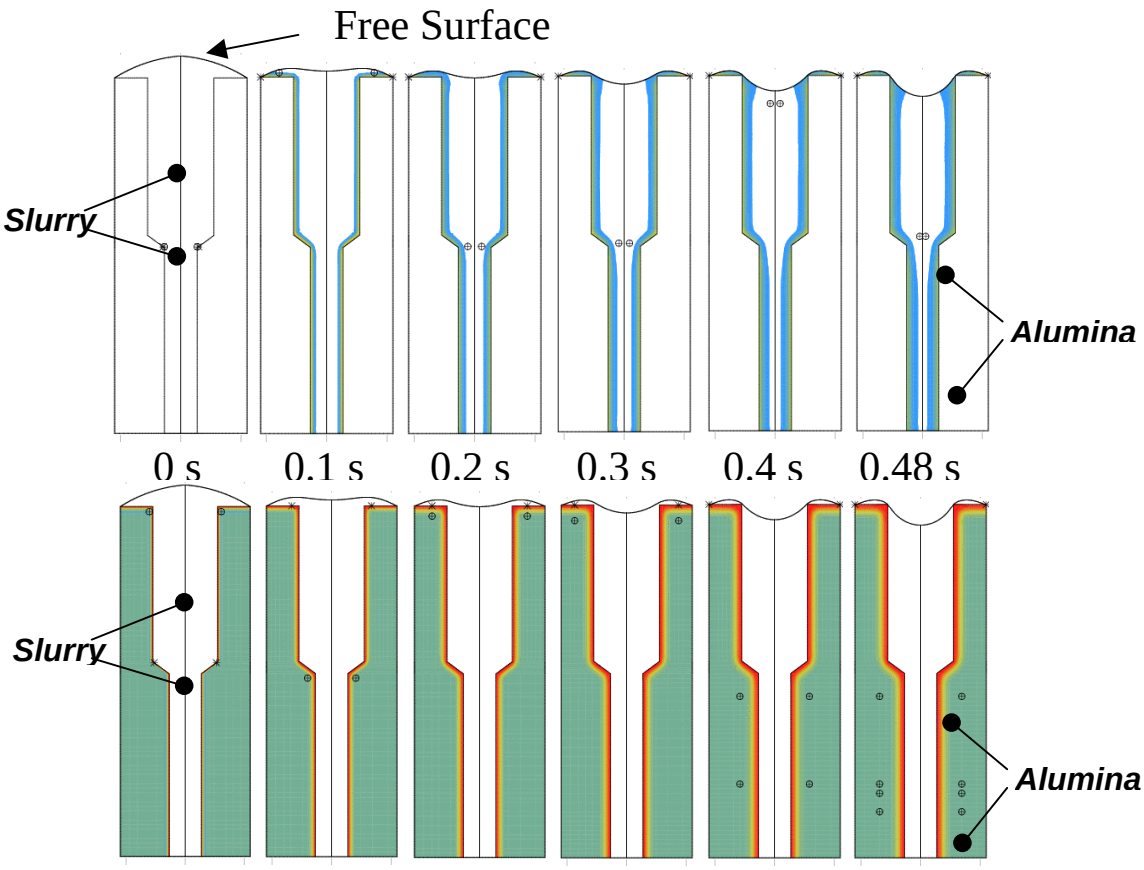


Figure 18: GOMA simulation results for the migration of solid (top) particles and solvent (bottom).[4]

Design of Experiments

Factor Selection

During the manual operation of filling a via with cermet slurry, the operator has several methods available towards achieving the goal of via filling. These methods are different for different operators, each having his/her own system. Although some operators have consistently achieved over 80% total process yields in production, this variability makes it difficult to determine causes for the occasional 100% loss of parts due to slurry-filling defects. Operator-controlled factors are shown in Table 3. The influence of each of these factors on the quality of the final product is not known in detail at present. Therefore, these operator-dependant factors must be controlled and characterized using statistics and experiments.

Experienced operators and process administration were brought together to determine which factors were to be characterized, and which were to be set constant.[5] Table 4 shows the results of these discussions, with four factors being selected. The mixture's volume fraction of solids was chosen due to the large range of viscosities allowed which can change how the material flows into the via under vacuum assist. Three ranges of viscosity (effectively solids) were selected; typical 'clicking' slurry viscosity, a higher viscosity (higher solids), and lower viscosity (lower solids). If it is possible to fill the via with a higher-solids-loading cermet mixture, it is believed that better fills may be produced. However, the higher viscosities associated with higher solids loadings may produce problems getting the mixture into the via initially, so the lower-viscosity mixture was chosen as well. The amount of actual pressure drop across the via produced by the vacuum is controlled by the type of filter paper. The most commonly used paper (Whatman 541) allows only a small pressure drop across the via (< 2 in. Hg). A higher flow filter was chosen which effectively brought the pressure drop to 6 in. Hg, in anticipation of better fills. The amount of time the part exposed to the filling vacuum is not controlled. Longer vacuum times may play a part in particle consolidation after the via is filled with cermet. A suggested long vacuum time exposure of 20 seconds was implemented, with a shorter time of 1 second as a complement. An operator fills the via, usually using a 10-ml syringe, by dropping the cermet mixture on top of the via and allowing the vacuum to pull the mixture into the via. The rate at which

cermet is deposited may have a critical effect because as a single drop of cermet mixture is brought into contact with the filter paper at the bottom of the via, the vacuum is thought to be cut off immediately, and any subsequent cermet will not experience the via filling vacuum. Therefore, operators have determined that a thin steady stream of cermet should be 'poured' quickly into the vacuum-exposed via. An automated pipette (Rainin EDP Plus, Woburn, MA) with a controlled rate of injection and a controlled volume was implemented to quantify these factors. Slow and fast injection rates were chosen which best mimicked the operators experiences.[5]

Table 3: Selected Operator Controlled Factors

Factor	Description	Allowable Range
slurry concentration	solids loading, affects viscosity	20-35 vol%
filter paper	low or high permeability	NS
vacuum time	how long the via is subject to vacuum after fill	NS
injection rate	time to deposit slurry over vacuum	NS
tip position	angle and height of syringe tip over alumina	NS
injection volume	amount of slurry dispensed into via	NS
Nuosperse volume	additive	0-3 drops

NS – Not Specified

Factors selected to remain constant were the placement and orientation of the tip with respect to the via, the amount of volume injected into/onto the via, and the amount of Nuosperse in the cermet mixture. Tip position and orientation were controlled using a three-axis positioning system shown in Figure 19. The programmable pipette is removable for filling with cermet, with a foot-controlled solenoid valve used to turn off vacuum to the cermet part. All cermet mixtures were created using 20.0 g of Sandi94 cermet powder and were mixed for 30 minutes using standard mixing procedures outlined in the work instruction.

Table 4: Controlled Factors for the Design of Experiments

Factor	Control Method	Selected Values
slurry concentration	weighed amounts of each component	10.85 – 24.4 vol% 11.52 – 23.3 vol% 13.00 – 21.2 vol%
filter paper	selected grades	Whatman 541 – 2.0 in. Hg Bunn coffee filter – 5.8 in. Hg
vacuum time	foot-operated solenoid	1, 20 s
injection rate	auto pipette	227, 765 μl/s
tip position	fill station positioning system	45° angle, xyz position set by eye using system
injection volume	auto pipette	100 μl
Nuosperse volume	weighed amounts	0.07 g

Experimental Design Matrix

A statistical design of experiments was created using solids loading (high, medium, low), vacuum drop (high, low), vacuum time (high, low), and injection rate (high, low) to create a $3^1 \times 2^3$ full factorial (24 experiments) set of experiments, using 5 repetitions per experiment and two vias per repetition.[6] Those 24 experiments were repeated randomly in order to observe repeatability, yielding 480 total vias for analysis (see Appendix B for experimental design outline). Each specific experiment yielded 10 parts with two vias each. Four of those parts were selected for subsequent fill mass determination, in which the mass was measured to within ±0.00005 g. The critical response for each experiment was the presence of defects within the small or large via diameters. The defect-presence analysis was conducted using maximum-likelihood estimation to estimate values of model parameters and their significance of producing a defect. Modules in Statistical Analysis Software, Proc Catmod and Proc Logistic, were used for analysis on defect formation, while Proc GLM was used on fill mass analysis.[7]

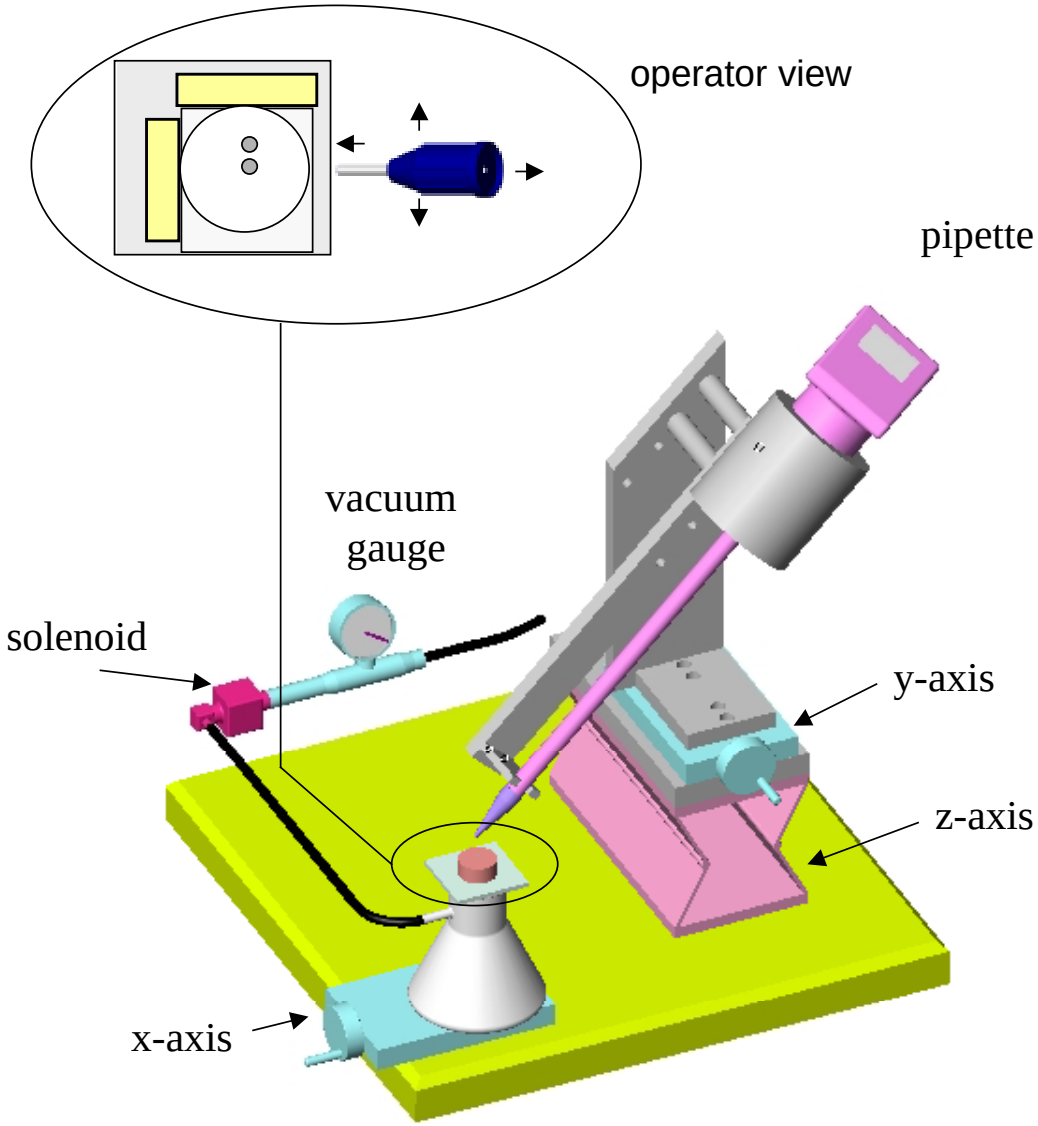


Figure 19: Controlled cermet-via-filling apparatus for use in a design of experiments.

Experimental Procedure

Mixing of 20.0 g cermet powder, the prescribed amount of DGBEA, and 0.07 g Nuosperse was accomplished according to the work instruction. A standard alumina blank with two drilled vias was placed on the filling station, and the center via was covered with parafilm to block the vacuum. After 30 minutes of equilibration by mixing, 100 μl of cermet mixture was drawn into the pipette. The pipette was then inserted into the fill station holder and the mixture dispensed over the off-center via, which is exposed to vacuum. The timer was manually started simultaneously with dispensing and the solenoid was engaged to disrupt vacuum pressure at the prescribed time period. The part was rotated on the stage in order to remove the off-center via's exposure to vacuum and the center via was filled in a similar manner. After the filling step was completed, the part was placed off to the side and subsequently dried at 120°C for 12 hours. A new pipette tip was used for each via fill, as was new filter paper. The appropriate samples used for fill mass determination were weighed prior to filling and after drying (with excess slurry being gently removed from the top of each via). Specific rheologies for all three cermet mixtures are found in appendix A.

Qualitative Results

Even though operator discretion was significantly reduced, fatigue was noticed. The tedious manual steps which occur even when variability is reduced still serves to wear on the operator. In this particular set of experiments, two operators were employed, one to create cermet mixtures and the other to fill parts, with filling parts being the more stressful of the two tasks. Such repetitive procedures are commonly performed by machines to reduce operator fatigue and produce parts more reliably.

Statistical Results

Defect Presence Analysis

With the response variable set as the presence or absence of defects, both large-diameter and small-diameter vias were examined. Maximum likelihood estimation was used to estimate the values and significance of model parameters. The first result discovered was that the first repetition of experiments (Rep1) produced different results

from the second experimental repetition (Rep2). Higher variability in Rep1 was the cause for this discrepancy, and as a result, less information was able to be gained from Rep1. During Rep1, the separation height between the tip and alumina blank was increased to compensate for high-solvent slurry that was being prematurely drawn into the via by the vacuum, further invalidating results obtained from Rep1. It was also found that in no instance was there a defect in the large diameter portion of the via (LDV) and not in the small diameter portion of the via (SDV). The influence of each factor (vacuum time, solvent amount, pressure drop, injection rate) on the response variable (defect presence or absence) is reported as a probability value (p-value). Smaller p-values imply more significance. A factor with a p-value < 0.001 is deemed highly significant. A factor with a p-value < 0.05 is deemed significant. A factor with a p-value > 0.05 is deemed not significant. Table 5 shows the results for the defect results on the off-center via, filled first in this study, distinguishing between defects found in the LDV and SDV only for Rep2. Table 6 shows similar results for the center via.

Table 5: Factor Influence (p-value) on the Off-Center Via

Off-Center Via	Large Diameter	Small Diameter
Vacuum Time	**<0.0001**	all fills bad – no p obtainable
Solvent	NE	0.01
Filter Paper	NE	NE
Injection Rate	NE	NE

NE – No Effect

Table 6: Factor Influence (p-value) on the Center Via

Center Via	Large Diameter	Small Diameter
Vacuum Time	**<0.0001**	**0.004**
Solvent	0.01	0.01
Filter Paper	NE	NE
Injection Rate	0.0362	NE

NE – No Effect

One noticeable phenomenon was the change in influence of solvent amount. In the center via (filled last), increased solvent amount did not reduce the probability of defects. However, increasing solvent in the off-center via weakly reduced defect formation. Although this effect is slight, it may be interpreted to indicate that some prewetting of the center via by imbibed solvent from the off-center via may be reducing the tendency for the cermet to clog the via. This prewetting is an optional procedural step in the work instruction and is not generally used by operators for this particular via. However, prewetting has been shown to increase the probability of achieving good part fills for smaller diameter vias in other cermet-related parts.[5] Another contributor to better fills is the injection rate. It is believed that the higher injection rates avoid the issue of vacuum-shut off by initially deposited material in the via which occurs when filling the via slowly. The amount of vacuum experienced by the via did not have any significant effects on defect presence. The most influential factor was the amount of vacuum time the via experienced after filling. Longer vacuum times are believed to aid in consolidation, pulling wet cermet from the reservoir on top of the part into existing voids. It may be interesting here to observe the filling of vias drilled into a clear material to confirm this suspicion. Table 7 illustrates the influence of vacuum time on defect presence for data from the more reliable Rep2.

Table 7: Vacuum Time Influence on the Fabrication of Defect-Free Vias

	Number of Vias with Defects	Number of Vias without Defects
Low Vacuum Time (1 s)	**94**	26
High Vacuum Time (20 s)	19	**101**

The statistical software package allows combinatorial effects of factors to be examined as well as singular effects mentioned previously. Longer vacuum times combined with higher injection rates ($p = 0.058$) were seen to produce better fills for the small-diameter center via. These results only support the previous discussion of these variables.

Fill Mass Analysis

Table 8 compares the p-value of influence for each of the four factors considered on fill mass changes. Lower fill mass would indicate defect presence. Average fill mass values for Rep1 and Rep2 were 0.0278 and 0.0198 g respectively. Table 8 correlates well with results found in the defect presence analysis, with vacuum time having the most significant influence on fill mass. Rep2 shows better correlation with vacuum time, most likely due to the variability exhibited by the operator in Rep1. There was no good correlation of fill mass with via integrity based on examining the vias with a microfocus x-ray (see Appendix C). There was simply too much variability in the procedure to achieve a good measurement of the fill density.

Table 8: Factor Influence on Fill Mass

	Rep 1 (1-24)	**Rep 2 (25-48)**
Vacuum Time	**0.0093**	**<0.0001**
Solvent	NE	NE
Filter Paper	NE	NE
Injection Rate	NE	0.0229

Overall Results for the Design of Experiments

It was originally believed that an operator might be able to determine the quality of fill by carefully using the via fill mass technique. However, it was determined that the technique simply wasn't sensitive enough to detect flaws, even larger flaws. However, eliminating many of the factors led toward an understanding of the truly important factor, namely, the beneficial consolidation effect of the vacuum.

Moreover, statistical results suggested several new factors that might influence via filling. The slightly better fills achieved in the via filled second suggested that prewetting the hole may be an important factor. Changing the tip height above the part while filling had an influence on via filling, which suggests that the angle at which the tip is held may be important. Eliminating the angle by holding the pipette vertically may change filling dynamics. Lastly, holding the part over vacuum for even longer periods of time may further remove existing defects within the via. These factors are proposed for a second design of experiments.

Recommendations

Insight into the cermet-via-filling process has been obtained through the use of experimental, theoretical, and computational approaches. There are now only a few recommendations to address to fully optimize the filling process using a science-based method.

1. Filling and consolidation models were developed by GOMA to simulate those separate processes. The next step is to combine the models to simulate the simultaneous occurrence of these processes. The simulations should again be validated experimentally.
2. An additional design of experiments should be performed varying the parameters of injection angle, prewetting, and longer vacuum times. With this information, recommendation 3 can be performed.
3. Processing 'maps' should be created so that operators have a guideline to more accurately fill vias. Processing maps will be referenced by the operator after performing simple tests to determine if conditions are optimal for the slurry filling process.
4. The effect of slurry mixing time on via filling and electrical performance should be investigated.
5. An electrical characterization test should be developed in order to quantify the results of all above experiments. A reduction in performance is not predicted, but there should be some comparison value (electrical properties) to insure the product at least meets prior performance.
6. User friendly fixtures and procedures will be created to reduce operator fatigue, a factor influencing variability and low yields.
7. The supplier benefiting from these changes (CeramTec) should implement these improvements and quantify the new yields.
8. A more reliable fill method using high solids slurries should be investigated.

References

1. K. G. Ewsuk, Sandia National Laboratories, 1999, private communications.
2. E. L. Corral, K. G. Ewsuk, *Cermet Slurry Preparation Study*, Summer Research Final Report, Org. 01843, Sandia National Laboratories, 1999.
3. J. Cesarano III, I. A. Aksay, *Processing of Highly Concentrated Aqueous α-Alumina Suspensions Stabilized with Polyelectrolytes*, J. Am. Ceram. Soc., **71** [12]1062-1067, 1988.
4. J. R. Torczynski, K. A. Shollenberger, R. A. Roach, J. Cesarano III, J. N. Stuecker, *Liquid Imbibition into Green Alumina Substrates Used to Fabricate Cermet Vias*, Sandia internal memorandum to Distribution, June 26, 2000.
5. D. J. Van Ornum, T.V. Montoya, Sandia National Laboratories, 2000, private communication.
6. E. V. Thomas, Sandia National Laboratories, 2000, private communications.
7. E. L. Corral, *A Critical Analysis of the Processing of Alumina/Molybdenum Cermets*, Summer Research Final Report, Org. 01843, Sandia National Laboratories, 2000.

Appendix A

Statistical design of experiments used to analyze critical processing regime.

Experiment #	**Design Parameters** **L**ow, **N**ominal, **H**igh	**Solvent** g	**Pressure Drop** mm Hg	**Vacuum Time** seconds	**Injection Rate** micro L / s
1	**N H H L**	11.52	5.8	20	227
2	**H L H H**	13.00	2	20	765
3	**L L H L**	10.85	2	20	227
4	**N L H L**	11.52	2	20	227
5	**N H H H**	11.52	5.8	20	765
6	**H H H H**	13.00	5.8	20	765
7	**H H L L**	13.00	5.8	1	227
8	**L L L L**	10.85	2	1	227
9	**L H H H**	10.85	5.8	20	765
10	**L H H L**	10.85	5.8	20	227
11	**L H L H**	10.85	5.8	1	765
12	**N L H H**	11.52	2	20	765
13	**H L H L**	13.00	2	20	227
14	**N H L H**	11.52	5.8	1	765
15	**N H L L**	11.52	5.8	1	227
16	**L L H H**	10.85	2	20	765
17	**L H L L**	10.85	5.8	1	227
18	**N L L L**	11.52	2	1	227
19	**H L L H**	13.00	2	1	765
20	**H H H L**	13.00	5.8	20	227
21	**H L L L**	13.00	2	1	227
22	**L L L H**	10.85	2	1	765
23	**H H L H**	13.00	5.8	1	765
24	**N L L H**	11.52	2	1	765
25	**N L H L**	11.52	2	20	227
26	**H L H H**	13.00	2	20	765
27	**H L H L**	13.00	2	20	227
28	**L L L L**	10.85	2	1	227
29	**H H H H**	13.00	5.8	20	765
30	**H H H L**	13.00	5.8	20	227
31	**L L H H**	10.85	2	20	765
32	**L H L H**	10.85	5.8	1	765
33	**N H L H**	11.52	5.8	1	765
34	**L H L L**	10.85	5.8	1	227
35	**N L L L**	11.52	2	1	227
36	**L H H L**	10.85	5.8	20	227
37	**H H L L**	13.00	5.8	1	227
38	**H L L L**	13.00	2	1	227
39	**L L L H**	10.85	2	1	765
40	**N L H H**	11.52	2	20	765
41	**N L L H**	11.52	2	1	765
42	**N H L L**	11.52	5.8	1	227
43	**H H L H**	13.00	5.8	1	765
44	**L L H L**	10.85	2	20	227
45	**L H H H**	10.85	5.8	20	765
46	**N H H L**	11.52	5.8	20	227
47	**H L L H**	13.00	2	1	765
48	**N H H H**	11.52	5.8	20	765

Appendix B

Viscosity and Dispersant Affect on Cermet Slurry Results

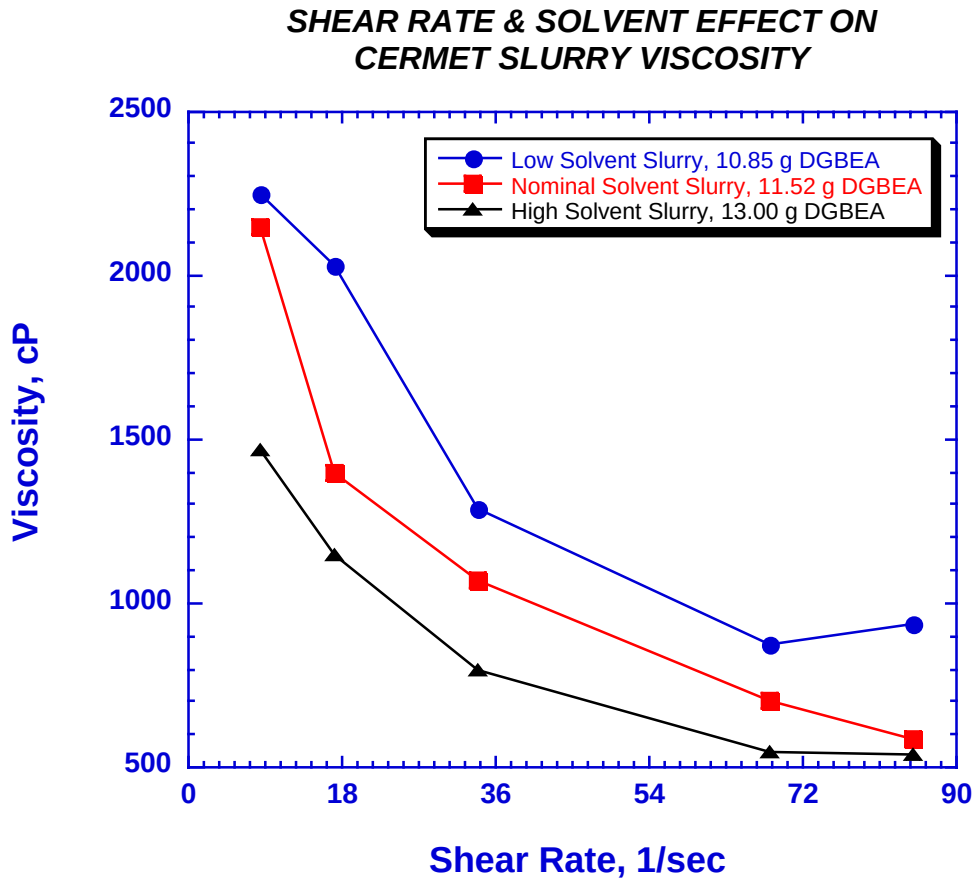


Figure 20: Rheology profiles for cermet slurries with low, nominal and high amounts of solvent a few seconds after mixing has stopped.

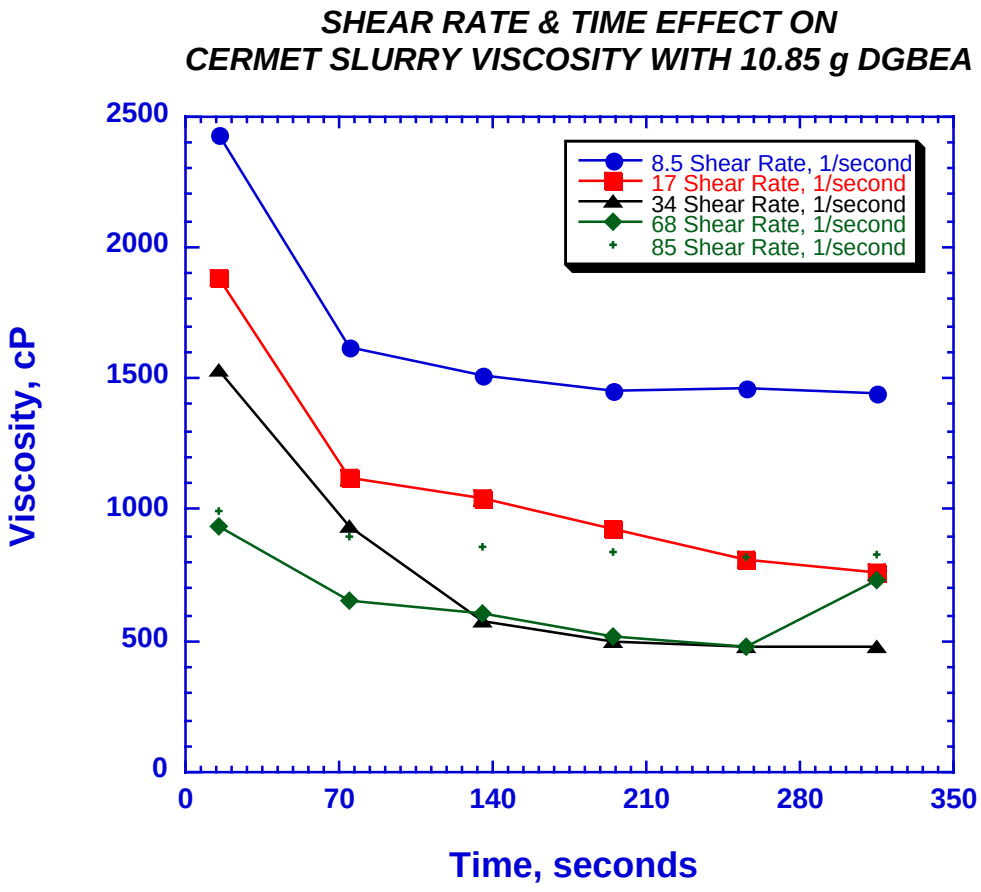


Figure 21: Viscosity of the cermet slurry with low solvent decreases rapidly until 75 seconds and levels off soon after.

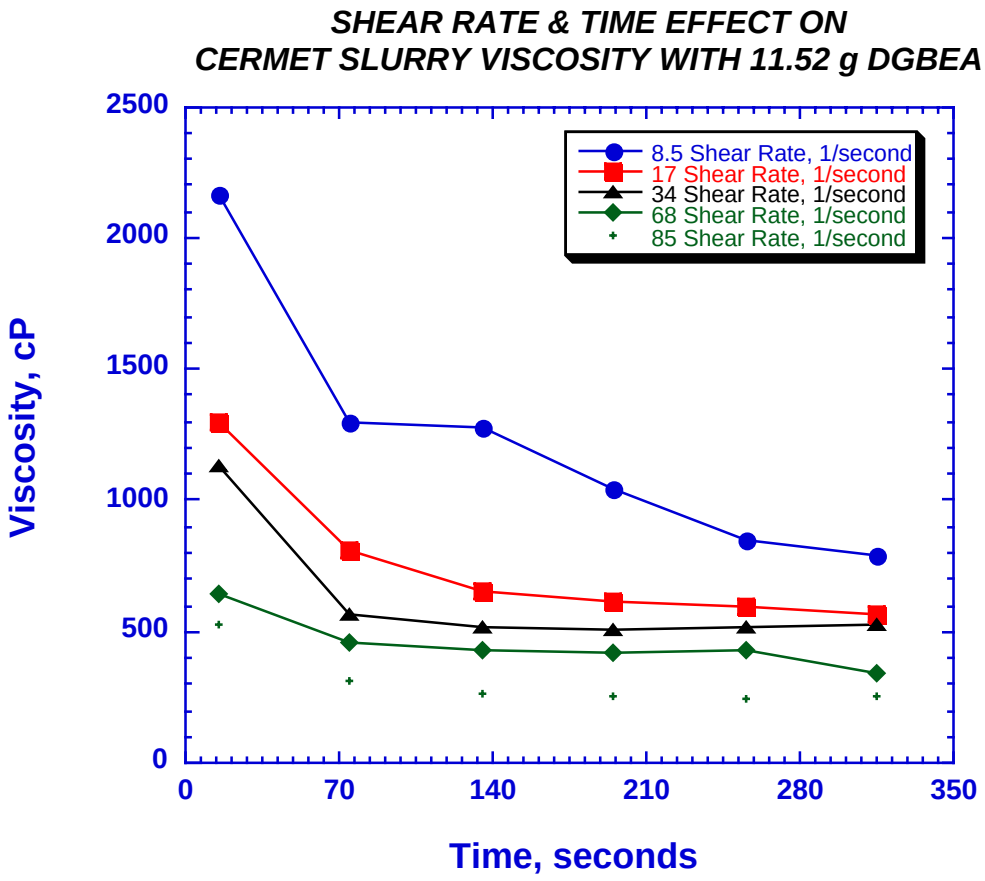


Figure 22: Viscosity of the cermet slurry with low solvent decreases rapidly until 75 seconds and levels off soon after.

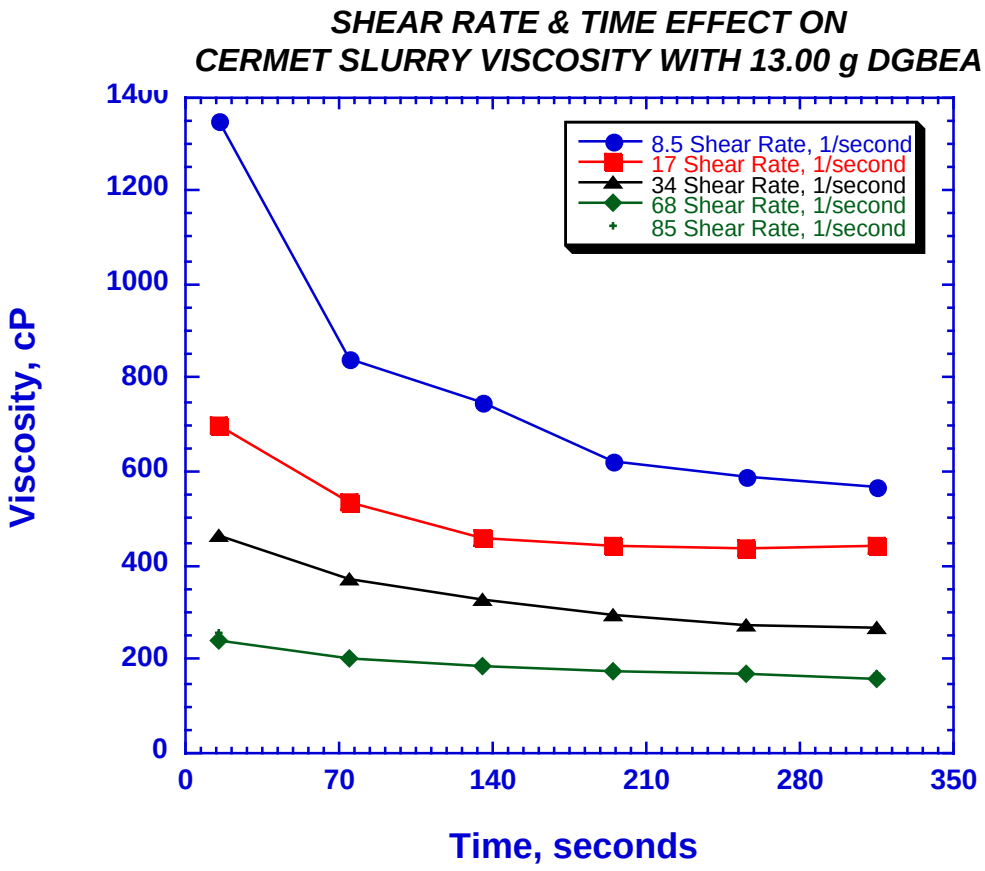


Figure 23: Graph shows the greatest decrease in cermet slurry viscosity as a function of time for the 8.5 shear rate.

Appendix C

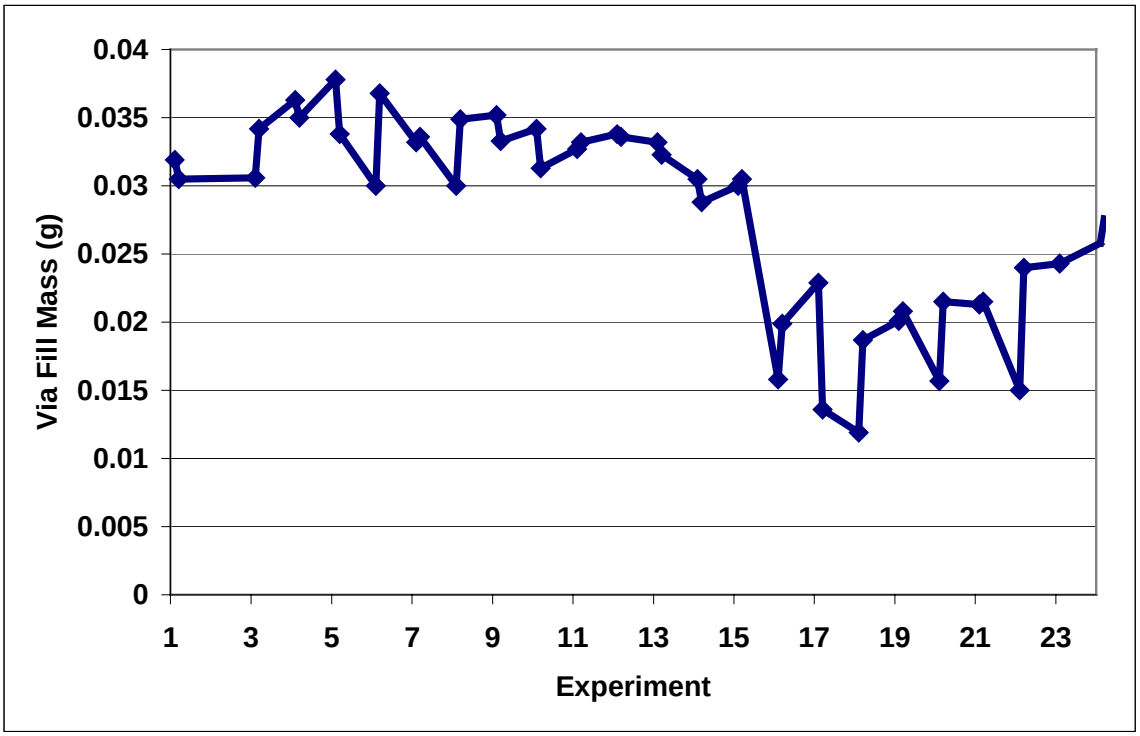


Figure 24: Fill density plot for the first 24 sets of experiments (2 data points per experiment). No correlation is observed with good or bad fills.

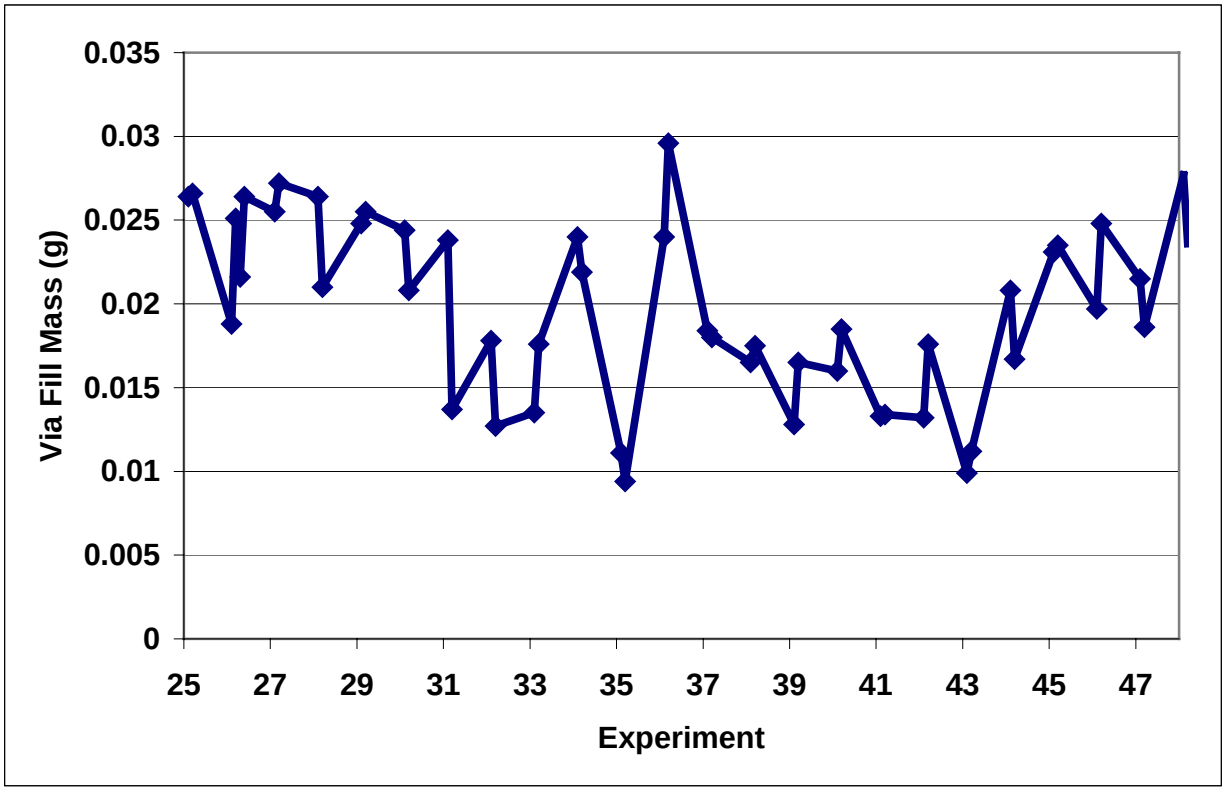


Figure 25: Fill density plot for the last 24 sets of experiments (2 data points per experiment). No correlation is observed with good or bad fills.

Distribution:

1	MS 1349	01843	J. N. Stuecker
1	MS 1349	01843	J. Cesarano III
1	MS 1411	01843	D. B. Dimos
1	MS 0841	09100	T. C. Bickel
1	MS 0824	09110	A. C. Ratzel
1	MS 0834	09112	K. A. Shollenberger
1	MS 0826	09113	W. L. Hermina
1	MS 0834	09114	P. R. Schunk
1	MS 0834	09114	R. A. Roach
1	MS 0834	09114	J. E. Johannes
1	MS 0836	09117	J. R. Torczynski
1	MS 0836	09117	M.R. Prairie
1	MS 0836	09117	R. O. Griffith
1	MS 0847	09126	S. N. Burchett
1	MS 0612	09612	Review and Approval Desk, For DOE/OSTI
2	MS 0899	09616	Technical Library
1	MS 0829	12323	E. V. Thomas
1	MS 0961	14100	F. P. Gerstle
1	MS 0868	14400	K. G. McCaughey
1	MS 0871	14405	N. A. Lapetina
1	MS 0856	14409	G. L. Theroux
1	MS 9018	89451	Central Technical Files
1	MS 0561	141812	D. J. Van Ornum