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Synthesis and densification of gel-derived powders in the Alb₂sOb₃s Bb₂sOb₃s SiOb₂s system

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Synthesis and densification of gel-derived powders in the $Al_2O_3 \cdot B_2O_3 \cdot SiO_2$ system

Bull, Jeffrey D., M.S.

San Jose State University, 1989

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SYNTHESIS AND DENSIFICATION OF GEL-DERIVED POWDERS
IN THE $Al_2O_3 \cdot B_2O_3 \cdot SiO_2$ SYSTEM

A Thesis

Presented to

The Faculty of the Department of Materials Engineering
San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Jeffrey D. Bull

May, 1989

APPROVED FOR THE DEPARTMENT OF
MATERIALS ENGINEERING

Dr. Patrick Pizzo

Dr. Guna Selvaduray

Dr. Daniel Leiser

APPROVED FOR THE UNIVERSITY

ABSTRACT
SYNTHESIS AND DENSIFICATION OF GEL-DERIVED POWDERS
IN THE $Al_2O_3 \cdot B_2O_3 \cdot SiO_2$ SYSTEM

by Jeffrey D. Bull

The sol-gel synthesis of inorganic materials proceeds by low temperature chemical reactions to produce an amorphous polymeric network of the desired composition. In this thesis an aluminoborosilicate (ABS) powder, high in alumina content, was synthesized by the sol-gel process utilizing four different methods. The effect that these methods had on the characteristics and densification behavior of the powders was studied.

Particle size, morphology, and thermochemical behavior was influenced by the method of synthesis. All powders, regardless of the method of synthesis, densified by similar mechanisms. Five regions of shrinkage in the temperature range 25 – 1184 °C were identified. Of these the greatest shrinkage occurred between T_g ($\approx 835^\circ\text{C}$) and T_i ($\approx 900^\circ\text{C}$). The primary mechanism of densification in this region was viscous flow. A multiphasic structure crystallized from the amorphous networks at T_i . Activation energies, relative contribution of shrinkage mechanisms and the amount of shrinkage varied according to the method of synthesis.

Polymeric modifications established during synthesis were retained at temperatures near 85% of the fusion point. The study shows the potential of sol-gel processing for producing inorganic materials of a single composition with varied high temperature behavior.

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LIST OF ACRONYMS AND ABBREVIATIONS

ABS	AluminoBoroSilicate
AIP	Aluminum Isopropoxide
ARL	Applied Research Laboratory
ASB	Aluminum SecButoxide
CHR	Constant Heating Rate
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
<i>EtOH</i>	Ethanol
ESCA	Electron Spectroscopy for Chemical Analysis
I.ABS.1	Synthesis Method I, aluminum isopropoxide based
I.ABS.2	Synthesis Method I, aluminum secbutoxide based
II.ABS.1	Synthesis Method II, aluminum isopropoxide based
II.ABS.2	Synthesis Method II, aluminum secbutoxide based
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
I/O	Input/Output
IR	Infrared Spectroscopy
LCTE	Linear Coefficient of Thermal Expansion
LVDT	Linear Variable Differential Transformer
M	Mean

$MeOH$	Methanol
$M(OR)_n$	Metal alkoxide with valence n
$M(OH)_n$	Metal hydroxide with valence n
MS	Mackenzie Shuttleworth model
n	Shrinkage coefficient
$\underline{n}$	Degrees of freedom
p	Level of probability
PC	Powder Compact
<u>RE</u>	Relative Error
RT	Room Temperature
R	An alkyl group
$R(OH)$	An alcohol
SEM	Scanning Electron Microscopy
TDA	Thermal Dilatometric Analysis
TEOS	TetraEthylOrthoSilicate
TGA	ThermalGravimetric Analysis
TMB	TriMethyl Borate
T_g	Glass transition temperature
T_t	Transformation temperature
XRD	X-Ray Diffraction

1 Introduction

Materials science and engineering is a discipline concerned with the interrelationship of structure and processing of materials to their properties and performance. If materials science is emphasized then the focus of this interrelationship is on understanding the nature of materials and how structure relates to composition, properties, and processing. This study is primarily concerned with exploring these latter interrelationships for a single composition within the $Al_2O_3 \cdot B_2O_3 \cdot SiO_2$ system synthesized by the sol-gel process.

The sol-gel process refers to wet chemical techniques which utilize solutions, sols and mixtures of solutions and sols as precursors for producing ceramic materials. The precursors can be polymerizable materials such as alkoxides, metal halides, and acetates, or, they can consist of colloidal suspensions. Gelling occurs either by electrolytic interaction of the colloid particles or by a chemical polymerization reaction with the metallic species. The process can be used to produce single component or multicomponent gels. Products obtained from the process include but are not limited to bulk glasses, fibers, thin films, and powders.

Yoldas¹ showed that in polymer systems derived from metal-organic gels, gelling occurs as an extended polymer network forms, as well as by the electrolytic effect. In these systems the network structures are formed by the kinetics of the reactions involved in the polymerization reactions. Molecular-structural variations which can result from the controlling kinetics may modify the properties of the resultant gel. Such variations can be introduced into metal-organic derived gels during synthesis. The effect of these variations extends to glass and ceramic materials ultimately

obtained from the gel and can even modify their high temperature behavior, e.g., sintering, crystallization, and viscosity.^{2,3}

Silica based systems derived from the sol-gel process have been shown to densify via several different mechanisms. Fitzner and Gadow⁴ summarized these mechanisms as follows: (1) physical desorption of water from micropore walls, (2) pyrolysis of residual organic groups, (3) condensation polymerization, (4) formation and collapse of micropores and (5) viscous sintering. Brinker and Mukherjee⁵ showed that there were at least three possible densification mechanisms operative during the gel to glass conversion of monolithic multicomponent gels: volume relaxation, condensation reactions, and conventional sintering. Similar results have been reported for different types of silica gel structures (xerogels and aerogels*).

The polymerized network that constitutes the gel microstructure can be approximated as a low density glass; a dried amorphous gel differs from a glass in its texture. Two models for the densification of low-density glass have been proposed. Both of these are derived from Frenkel's theory of viscous sintering,⁸ i.e., that the energy dissipated in viscous flow is equal to the energy gained by the decrease in surface area during sintering. Mackenzie and Shuttleworth⁹ calculated the rate of densification of a low-density glass containing closed spherical particles from which the *closed pore* model was developed. A densification model for low-density glass containing open nonspherical pores was proposed by Scherer¹⁰ and is known as the *open pore* model. These models were applied to the special case of the gel to glass transformation by Zarzycki.¹¹ Generally, densification in gel-derived materials

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*A xerogel is a gel structure from which all unbound water has been extracted. A gel dried at 60 or 100 °C is a dried gel and in most cases, not rigorously a xerogel. An aerogel is a gel structure which has been hypercritically dried, usually resulting in a crack-free gel monolith.^{6,7}

is due to chemical processes at low and intermediate temperatures, while physical processes—structural relaxation and viscous sintering—dominate at higher temperatures.

Ceramics in the $Al_2O_3 \cdot B_2O_3 \cdot SiO_2$ (ABS) system with high alumina content have the capability to resist high temperatures, in excess of $1400^\circ C$, with considerable retention of room temperature properties.¹² The ABS phase diagram is shown in Figure 1 with the studied composition indicated by N . The addition of B_2O_3 (boria) to the $Al_2O_3 \cdot SiO_2$ binary decreases the *apparent* viscosity of the system and yet retards devitrification because it occupies available nucleation sites.¹⁴ Thus, the addition of boria should assist in the retention of an amorphous phase. It would be advantageous, however, not to have the boria present at extremely high temperatures because of the reduced viscosity. A unique aspect of the ABS system is the vaporization of boria at elevated temperatures. This phenomenon has been reported by several authors.^{12,15,16} Reference to the phase diagram for this system indicates that, as boria volatilizes, the refractory compounds $3Al_2O_3 \cdot 2SiO_2$ (mullite) and $9Al_2O_3 \cdot 2B_2O_3$ (aluminum borate) are formed as a solid solution under conditions of equilibrium. Therefore, the ABS system has the potential to produce a high temperature glass or ceramic with low processing temperatures.

Unfortunately, glass formation in the ABS system is rather sporadic with respect to composition and conventional quenching from the melt usually results in devitrification.¹⁵ Sol-gel processing of materials in the ABS system can be used to circumvent this problem and thereby provide another means of obtaining the glass. Not only does the sol-gel process provide a secondary method of producing glass in this composition, but it also offers several distinct advantages relative to traditional

Figure 1. $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ Phase Diagram Indicating The Studied Composition, N (after ref. [13]).

processing as well as a few new and exciting prospects related to a "bottom-up" approach in the development of inorganic materials. Product purity, enhanced sinterability, compositional control, homogeneity, and reductions in cost due to energy requirements and equipment are some of the advantages in processing glass and ceramics via the sol-gel route. A few disadvantages are the cost of the precursors, their shelf life and toxicity. For bulk applications the disadvantages often outweigh the advantages and the sol-gel processing of sheet glass for example is not economically wise. On the other hand for specialized applications, such as the manufacture of $Pb_{1-1.5x}La_xZr_{1-y}Ti_yO_3$ (PLZT) transparent ceramics, the sol-gel process may be the most efficient and cost effective route. Additionally, the sol-gel process has the potential for structural control on a nanometer scale. This implies a capability to engineer materials from constituent molecular units where the unit is determined by the functionality of the precursor. This type of engineering may result in materials with novel properties relative to those of conventional processing.

Although structural control at the molecular level was alluded to by Yoldas,¹ no concerted effort has been made to investigate the extent of this control in multi-component systems, particularly in non-silica based systems. Many researchers^{1,17,18} have elaborated on the various parameters one must consider in synthesizing a multicomponent gel to attain a true homogeneous product. Indeed, in many cases homogeneity is the sole reason for using the process. In multicomponent systems however, the deliberate introduction of micro-inhomogeneities into the gel's microstructure via the sol-gel process and their influence on the gel's texture and subsequent properties warrant investigation. Specifically, the effects of such control on the properties of ABS powders, their mechanisms of densification, and agreement with current models merits study.

In this study, it is proposed that alterations in the method and material used in the sol-gel synthesis of an aluminoborosilicate gel will affect its structure and thereby determine the densification behavior of the resultant powder. Both variables, method and material, were chosen so as to alter the developing microstructure of the gel in the early stages of polymerization. The method is little more than the reversal of order in the addition of reactants. The material is the substitution of reactants in the synthesis, allowing their different chemical reactivity to influence the polymerization reaction. By altering the method of synthesis, the introduction of structural modifications at the molecular level should be induced. This is accomplished by utilizing the different chemical reactivities of the precursors, as well as those of polymeric species present in the sol, to determine the type and extent of bonding that will occur in the polymerization reactions.

It is expected that these variations in the early stages of the gel synthesis will determine the gel's microstructure, and hence, influence the densification behavior of the resultant amorphous powders as well as their physical properties. To best characterize the structural evolution of these powders a variety of analytical tools were employed. Spectroscopy techniques were used to qualitatively ascertain the type of intermolecular bonding in the polymer network. Thermochemical and compositional analysis were used to characterize the chemical makeup of the powders. Particle size analysis, x-ray diffraction (XRD), and scanning electron microscopy (SEM) were used for structural characterization. Physical properties were determined by bulk and apparent densities and microhardness measurements. Although density measurements alone could suffice to determine the mechanisms of densification, the more accurate technique of thermal dilatometry was employed for this task. The results of isothermal shrinkage experiments were used to determine the

mechanisms of densification and both isothermal and constant heating rate (CHR) shrinkage experiments were conducted to calculate the governing activation energies. The values were compared with those of other gel-derived materials in various systems. Correlations between shrinkage data, structural changes and physical properties were made in support of the observed densification behavior.

2 Sol-Gel Processing with Metal Alkoxides

The sol-gel process is the chemical synthesis of an inorganic glass network by a polymerization reaction in solution at or near room temperature. A sol formed from metal alkoxide(s) can be defined as a liquid mixture or solution of single or mixed alkoxide compounds. Metal alkoxide-derived sols differ from colloidal sols in that the former is composed of polymeric species rather than dense glass-like aggregates typical of the latter. Gelation of the alkoxide sol occurs when the liquid phase is occluded by the coalescence of polymerized species. Coalescence can occur by hydrogen bonding or electrostatic forces between the polymerized particles. The transition from the liquid sol into a gelatinous mass is what characterizes the process and gives it the expression "sol-gel process."

Metal alkoxides are often used in the sol-gel process because their chemistry provides a means of controlling the gel structure. Such control is not possible with other sol precursors like the colloids. Alkoxides are members of a class of compounds termed "metal-organics*" which includes all compounds having organic groups bound directly to the metal.²⁰ The chemistry of metal alkoxides is discussed in detail by Bradley *et al.*²¹ Metal alkoxides of groups III and IV metals, which constitute a large portion of glass and ceramic compositions, are easily hydrolyzed to precipitate the hydroxide. However, the hydrolysis reaction of alkoxides, particularly those in which the metal is a network former such as *Si, B, Ti, Zr*, or the intermediate *Al*, can be controlled so as to promote polymerization and the formation of a gel. The difference between the sol, gel, and precipitate is illustrated in Figure 2. The gels so formed consist of small particles which configure the network

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*The classical definition of the term "organometallic" would exclude all compounds except those in which at least one carbon of the organic constituent is bound directly to the metal atom.¹⁹

of the corresponding oxide glasses and/or ceramics.

The reactions leading to an inorganic oxide polymer and gel formation from metal alkoxides $M(OR)_n$ occur according to the following reactions. First hydrolysis forms a alcogel

followed by condensation via dehydration

or dealcoholation

R is an alkyl C_xH_{2x+1} group in the above reactions and M the metallic element. As reactions (2) and (3) proceed they promote extensive crosslinking of the gel by polycondensation. The resulting polymeric oxide is produced in the form of extremely small particles ranging from 2 - 10 nm.^{19,22} Metal alkoxides are dissolved in a mutual solvent, usually a low molecular weight alcohol, and the water necessary for hydrolysis is added in diluted form, either adsorbed from the atmosphere or from a wet alcoholic solution. For reagents exhibiting slow reactivity towards hydrolysis, e.g., $Si(OC_2H_5)_4$, a controlled amount of acid such as HCl or HNO_3 , or a base such as $NH_4(OH)$, can be added. The gelling time depends on the solution pH, temperature, and amount of water present.

Reactions (1)-(3) occur simultaneously and generally are incomplete. The extent of localized polymerization produced from them determines the skeletal structure of the polymer and ultimately the particle size of the gel. As these reactions proceed, partially hydrolyzed species, e.g., $M(OR)_{n-1}(OH)$, $M(OR)_{n-2}(OH)_2$, etc.,

Figure 2. Difference Between Sol, Gel, and Precipitate in the Sol-Gel Process (after ref. [11]).

created by reaction (1) are incorporated into the polymer network. These species have their own unique chemical reactivities and hence influence to some extent the developing polymer. In a multicomponent gel, the different metals M and M' are usually introduced so as to promote $M - O - M'$ linkages and to minimize self-condensation, $M - O - M$ and $M' - O - M'$, within the polymeric network.²³ The products of reactions (2) and (3) generally remain soluble in a controlled hydrolysis due to the absence of sufficient hydroxyls to cause formation of insoluble polymers. Molecular-structural variations such as these in the resultant network structure of the gel are affected by parameters that affect the kinetics and interaction of the reactions as well as by environmental conditions present after gelation. Yoldas and Schmidt have classified these parameters into several categories.^{24,25} Of these parameters, those which have the greatest influence on the resulting material's properties are:

- Sol composition;
- Reaction conditions;
- Post-gelation processing.

These parameters alter the network structure of the gel and hence its properties by changing the governing kinetics. Under any given set of reaction conditions the hydrolysis product will contain mixtures of various types of polymeric species whose distribution will be determined by statistical interactions. Nevertheless, as a major reaction product, a particular type of polymer may be obtained by the manipulation of the above parameters. If the control permitted by the synthesis parameters is sufficiently large, then a particular gel structure dominates and this structure will have unique properties at elevated temperatures as long as that structure is retained. Each of these parameters will be briefly discussed in the following sections.

2.1 Sol Composition

The starting compounds define the sol composition, but several different complications disrupt this simple assertion. Alkoxides and the chosen solvent can have a significant influence on the hydrolysis product as alluded to earlier. The condensation reactions represented by Eqs. (2) and (3) require diffusion of the partially hydrolyzed species, which is in turn affected by the size of the alkyl groups attached to these species. For a given metal alkoxide, steric effects due to the alkyl groups influence the coordination of the alkoxides in solution. Steric effects either increase or decrease the rate of hydrolysis according to the bulk of the alkyl substituents and the coordination they impose. For example, aluminum *tert*-butoxide is a cyclic dimer in solution as shown in Figure 3(a). The corresponding isopropoxide, on the other hand, is tetrameric at room temperature (RT), Figure 3(b), but reported to be trimeric at elevated temperatures.^{18,19} Yoldas¹ has shown that gels formed from aluminum secbutoxide and isopropoxide have different constitutions which are attributable to their different rates of hydrolysis. Alkoxides with lower molecular weight alkyls generally produce larger polymeric units; consequently, the oxide components of their gel are higher.

If alkoxides with high vapor pressure are used then steps must be taken to prevent the evaporation of the volatile component. This is the case with most boron alkoxides during the synthesis of borosilicate glasses according to the following reaction.

The indicated equilibrium is established by thermodynamic conditions. It follows

Figure 3. (a) *Tert*-butoxide Cyclic Dimer. (b) Tetrameric *Iso*-propoxide (after ref. [19]).

that a loss of boron, as the methoxide or ethoxide, especially in open systems, can be expected. Slow hydrolyzing alkoxides which result in unreacted or partially reacted monomers may remain and evaporate during drying or heating, resulting in a decreased yield of the corresponding oxide. Reesterification can also lead to the formation of volatiles with the same results as those indicated in Eq. (4).

The host medium affects the diffusion rates of the reacting species, i.e., H_2O and the partially hydrolyzed alkoxides. For this reason, hydrolysis products produced in lower alcohols have a higher equivalent oxide content, indicating a greater extent of polymerization. For example, when $Ti(OC_2H_5)_4$ is hydrolyzed in ethanol and dried at $100^\circ C$ the oxide content of the gel by weight is approximately 84%. This figure drops to about 73% when the hydrolysis is performed in *sec*-butanol.¹ The host medium may also take an active part in affecting the hydrolysis rates by the mechanism with which it interacts with the alkoxide. In addition to the sought-after solvation, coordination, coordination polymerization, ligand-exchange, and polycondensation may also occur. These interactions are illustrated in Figure 4. The polymer structure also depends on the functionality of the metal-organics. For example, from monofunctional and difunctional siloxane precursors, e.g., R_3SiOR and $R_2Si(OR)_2$, only linear polymers can be formed, whereas the use of compounds with higher functionality, e.g., $RSi(OR)_3$, leads to a highly branched polymeric network.

The effect of the reactant ratio $H_2O/M(OR)_n$ on the gel structure and on the ceramics and glasses obtained from them is dramatic, especially at elevated temperatures. As the reactant ratio increases, so too does the oxide content of the gel.

Figure 4. Different Structure-Forming Reactions in Solution: (a) Solvation; (b) Coordination; (c) Coordination Polymerization; (d) Ligand Exchange; (e) Condensation (after ref. [18]).

Hence the reactant ratio determines the extent of polymerization and the dimensionality of the oxide network. Structural studies for various gel systems show significant differences in the microstructure of the polymerized oxides according to the quantity of water used in hydrolysis.² The same studies indicate that these microstructural differences strongly influence any subsequent structural transformations.

The reactant ratio may be kept constant and the reactants diluted with a neutral host medium, e.g., alcohol. This has the effect of separating the reactants and favors those reactions which depend less on the diffusion of larger species, particularly bulky oligomers or other polymeric species. This means that as dilution increases, hydrolysis reactions are favored more than polymerization. Consequently, the polymeric network can be expected to decrease in size as the alkoxide concentration decreases. Highly diluted systems will also be accompanied by a decrease in the oxide content.

Summarizing, the sol composition is a dynamic solution which must be controlled if the microstructure of the gel is to be developed in a controlled fashion. The choice of alkoxides and host medium are instrumental in determining the reactivity of the sol. The reactant ratio and concentration will influence the gelling time, oxide content and the developing polymer network.

2.2 Reaction Conditions

Conditions such as sol temperature, pH, and the rate and order of reactant addition influence the controlling kinetics in gel formation. Assuming the sol composition to be fixed, these reaction conditions are dominant during the sol to gel transition. It has been shown that the properties of gels, especially their ability to

be dried and densified, is strongly dependent on reaction conditions.¹⁸ It is assumed that these differences in gel properties are in turn due to the different polymeric structures[†] formed in the initial polycondensation reactions. This assumption leads to the following question: At which stage of the reaction are stable structures formed and what reaction parameters are most influential in their formation? This is the subject of a great deal of current research in sol-gel technology.

Most metal alkoxides hydrolyze quite vigorously. But for those slow to hydrolyze, such as the alkoxysilanes, the use of catalysts can greatly accelerate the rates of hydrolysis as well as polycondensation. The hydrolysis reaction of Eq. (1) can be catalyzed by the addition of an acid or base. Depending on the sol pH and water content, the hydrolysis of tetraethylorthosilicate (TEOS) can result in the formation of polymeric species ranging from polysiloxane chains to colloidal particles of essentially pure SiO_2 .²⁶ Differences in structure can occur at a given concentration of water because the reaction mechanisms responsible for hydrolysis and condensation are different. At low pH values (< 2.5) hydrolysis occurs by a mechanism involving electrophilic attack on an alkoxide oxygen, as illustrated for TEOS in Figure 5. At intermediate to high pH values (> 2.5) hydrolysis occurs by a mechanism involving nucleophilic attack on silicon as illustrated in Figure 6. Polymer growth does not result in the formation of a colloidal silica in either case. Small and intermediate angle x-ray scattering has shown that hydrolysis of 1 mole of TEOS with 4 moles of water results in primarily linear, or randomly branched, polymers at pH 1, Figure 7(a), and in discreet, more highly branched polymeric clusters at pH 7, Figure 7(b). Colloid formation can be expected, however, for hydrolysis carried out in a large excess of water and at high pH values, Figure 7(c).

[†]These structures may contain reactive intermediates which are not easy to isolate or identify. Consequently, their role in sol-gel chemistry will not be pursued here.

Figure 5. Acid-Catalyzed Hydrolysis of Silicon Alkoxide by Electrophilic Reaction Mechanism (after ref. [27]).

Figure 6. Base-Catalyzed Hydrolysis of Silicon Alkoxide by Nucleophilic Reaction Mechanism (after ref. [28]).

Figure 7. Schematic Representation of Gelation in Acid and Base Catalyzed Gels and a Colloidal Gel; (a) Acid-Catalyzed-Entangled Primary Linear Molecules Crosslinked at Junctions; (b) Base- Catalyzed-Agglomerated Branched Clusters; (c) Aqueous Silica Linked Colloidal Particles (after ref. [27]).

Generally, higher reaction temperatures during the hydrolysis reactions facilitate diffusion, thus leading to the formation of larger polymers with higher oxide contents.

The hydrolysis reaction can be considered as a source for reactive monomers or oligomers. In multicomponent systems the rate of hydrolysis, and therefore the initial rate of polycondensation, varies significantly for different compounds. Hence, the sequence of reactant addition in these systems is an important parameter. Structural effects based on non-random-like distributions of the different elements in multicomponent gels can lead to local inhomogeneities in the network structure. As a general rule, the sequence of reactant addition in multicomponent systems should proceed from the least reactive to the most reactive reactant in order to obtain a homogeneous polymer.

Polycondensation reactions develop the polymeric structure of the gel. A reaction mechanism for the condensation of TEOS is illustrated in Figure 8. As with hydrolysis, the nucleophilicity of the metal alkoxide changes with increasing substitution of ligands. Indications are that other alkoxides behave in a similar fashion. Polycondensation of multicomponent systems leading to a random distribution of elements, and hence a homogeneous structure, is difficult to achieve due to the differences in chemical reactivity of the alkoxides; at the low temperatures and atmospheric pressures under which these reactions are conducted the enthalpy of the reaction is the driving force and this as a rule does not result in a randomly distributed amorphous network.²⁵

Since the driving force tends to establish thermodynamically metastable or

kinetically stabilized intermediates, the final polymeric structure will reflect a configuration of inordinately high free energy. Therefore structural variations in a given bulk structure can sometimes be eliminated by high temperature treatment which equilibrates the high energy configurations. To what extent these structural variations are retained at elevated temperatures has been an issue in sol-gel science. In some cases, e.g., phase separation in sols, these differences are not eliminated and result in glass-ceramics with a variety of tailorable properties. With respect to multicomponent systems the different reaction rates and nano-inhomogeneities of the gel can lead to measurable differences in the driving force for densification.

2.3 Post-Gelation Processing

Gelation occurs when the growing polymers aggregate or entangle and occlude the host medium. Because of the sharp increase in viscosity accompanying gelation, it may be considered a rapid solidification process, that is, a structure at a given state in the polymerization is essentially frozen-in. Thus, the final structure of the dry gel will depend heavily on the structure of the wet gel originally formed in solution; it will be a contracted or distorted version of the latter.

Some structural changes can also occur during dessication of the gel. A gel dessicated under ambient conditions forms a porous xerogel. Removal of solvent by evaporation results in increased surface tension forces which, in effect, exert a positive pressure on the gel structure. More weakly cross-linked gels exhibit greater shrinkage in response to these forces than do more highly cross-linked gels. Acid-catalyzed gels prepared with a low water content dry to a relatively dense xerogel exhibiting extremely fine continuous porosity. If the water content or the sol pH is

increased, xerogel density decreases. This is due to a large quantity of macropores formed during removal of the hydrolysis reaction by-products. Irrespective of the gel's initial state, the skeletal features of the structure, i.e, the polymer backbone, will become more glass-like, i.e, more highly polymerized and densified.²⁸

The dried amorphous gel differs from a glass primarily due to its texture. Zarzycki²² proposed different structural models of dried gels. These models are shown in Figure 9(a) through 9(c) and are described as: (a) aggregates of dense particles of approximately the same size; (b) aggregates of particles formed by primary particles, with ultrapores; (c) aggregates of a more complex nature in which three levels of particles can be distinguished as well as micro and macropores. As shown in Figure 9, the gel is essentially an agglomerate of elementary particles the size of which may be on the order of 10 nm, arranged more or less compactly. The porosity may vary considerably according to the reaction conditions and sol composition established. The residual space represents pores which may be closed for a dense arrangement of particles as in Figure 10(a) or open when the texture consists of more or less regular "lattices" of particles, leaving large interstices as in Figure 10(b). The constituent particles may be coated with residual OH^- or OR^- groups which have to be eliminated during the transition from a particulate texture towards a continuous solid, dense glass and/or ceramic. This can be achieved during a calcination step which will drive polymerization to completion, to the extent permissible by initial gel structure and packing geometry, and eliminate physically adsorbed water and residual solvent. The remaining chemically bound OH^- and OR^- should be considered constituents of the gel's chemical composition unless additional steps are taken to completely remove them, e.g., calcination in a chlorine atmosphere.

Figure 8. Nucleophilic Condensation Reaction Mechanism (after ref. [27]).

Figure 9. Different Structural Models of Dried Gels: (a) Dense Aggregates of Equal Size; (b) Aggregates with Macropores; (c) Secondary Aggregates of Primary Particles (after ref. [22]).

In summary, sol-gel processing with metal alkoxides begins with a wet-chemical synthesis in which several physico-chemical conditions are active at each stage of the process. These conditions include: determination of the sol composition which places an emphasis on the choice of alkoxides, host medium and reactant ratios; the size of the primary particles at the moment of gelation as well as their concentration and structure; the sol pH and temperature and other treatment in the gel's wet state; the aging and drying environment during the wet to dry gel transition. Other contributing factors in the processing of sol-gel materials not discussed here are external parameters such as mechanical forces, temperature and the time and atmosphere present during drying, pre-calcination and calcination.

Figure 10. Schematic of Texture in Gels: (a) Dense Agglomerate of Particles with Closed Pores; (b) Lattice of Particles with Open Pores (after ref. [22]).

3   **Densification of Polymeric Gels**

Densification of the dry gel is the final step in the processing of gel- derived materials. Gel densification is essentially a process by which the dessicated or dry gel is transformed into a dense solid glass. All gel systems and compositions, except for those intentionally made multiphasic, encounter a glass phase before the onset of transformations which would produce a ceramic or glass-ceramic. Figure 11 represents the basic stages of sol-gel processing.

As is the case with most glass and ceramic materials, powders are compacted into a useful form or shape and these green bodies are then fired at a temperature sufficient to develop useful properties. If the dessicated gel is a xerogel, this procedure can be used to indirectly determine the properties of the powder. If the dessicated gel is a monolith or aerogel the properties are determined directly from firing of the monolithic gel. This discussion, as in the previous section, is directed towards xerogel powders derived from alkoxides although the principles are applicable to gel-derived materials in general.

Many of the phenomena associated with the firing of conventional ceramics are applicable to gel-derived materials as well. However, the densification achieved on firing of gels, is the result of a competition between processes leading to crystallization and those promoting viscous flow.¹¹ During the firing process structural changes may initially occur because of decomposition or devitrification. On further heating of the fine-grained porous compact two major changes commonly occur. There is an increase in grain size and there is a change in pore shape, size and quantity, usually leading to decreased porosity.²⁹ If the gel devitrifies during the densification process,

a microcrystalline phase dispersed in a glassy matrix, a glass-ceramic, would result.

Densification of conventional ceramics usually occurs by solid-state sintering mechanisms for which there is a common driving force: the decrease in surface area and lowering of the surface free energy by the elimination of solid-vapor interfaces. This normally takes place with the coincidental formation of new but lower energy solid-solid interfaces.²⁹ This driving force certainly exists in gel-derived materials as well, but its magnitude and dependence on the gel structure are what differentiate a gel densification from that of conventional glasses and ceramics.

Solid-state sintering is not the dominant process by which gels densify. Gels may densify by several other mechanisms at considerably lower temperatures than those required for their conventional counterparts. Several researchers have identified and classified these mechanisms for various types of gels: colloid and polymer based xerogels and aerogels.⁴⁻⁷ Brinker, Scherer, and coworkers³⁰⁻³² showed in constant heating rate experiments of silica based gels that at least four mechanisms are operative during the gel to glass conversion in alkoxide-derived gels. These are: (I) capillary contraction; (II) condensation; (III) structural relaxation; (IV) viscous sintering. These mechanisms do not necessarily act independently of one another as any one of them may predominate in a given temperature range. Hence, gel shrinkage is a complex process involving several mechanisms or competing mechanisms. Chemical processes dominate at low and intermediate temperatures while physical processes, e.g., structural relaxation and viscous flow, control high temperature processes. The temperature ranges where these mechanisms are predominant, as well as their contribution to the total shrinkage, is dependent on the gel's structure and chemical composition and the heating rate. In order to optimize the processing

of gel-derived materials, specifically the thermal treatment or firing conditions, it is necessary to know how a particular gel will respond to these mechanisms.

3.1 Driving Force

Densification, being a spontaneous process, is accompanied by a decrease in free energy. As suggested by Roy³³ and Brinker, et al.,³¹ gels contain a large amount of free energy due to their large surface area, large amount of chemically bound water present and the large quantity of porosity characteristic of a low density crosslinked structure. Other factors, like concentration gradients and non-equilibrium structures can also increase the gel's free energy. The contribution made to the total free energy depends on the gel structure and consequently on the preparation conditions discussed in Chapter 2.

Densification is an irreversible process in which the decrease in free energy is accompanied by a decrease in surface area, a reduction in pore size and volume and elimination of excess free volume and other non-equilibrium structures.^{5,34} A lowering of surface free energy is obtained by the elimination of solid-vapor interfaces, i.e., particle consolidation. As the reactions represented by Eqs. (2) and (3) proceed, higher crosslinked chains and clusters are formed, excess free volume and hydroxyls are gradually reduced, and the skeletal density of the gel increases. The geometrical changes which actually evolve during skeletal densification depend on the shape, size, size distribution and modes of packing of particles and clusters. The extremely small size of the fundamental gel particle, 2-10 nm, provides a large driving force for densification by viscous flow as will be shown in Section 3.4. A low crosslink density results in an initial large shrinkage because of its relaxation to a more stable

structure but can prevent densification at higher temperatures. Agglomeration can have a negative influence on the uniform sintering of a body. Therefore, highly densified gels occur when there is a uniform microstructure with a controlled particle geometry, narrow size and size distribution, free from agglomeration.³⁴ The temperature range where the different densification mechanisms occur and the increase in density for each region is composition-dependent.

A schematic representation of free energy versus temperature for gels, glasses, and crystals is shown in Figure 12. From this figure, the available paths for structural evolution of the gel are apparent. The conversion of a gel to a glass is encountered as a step during the transformation of a xerogel to a stable crystalline material. The higher free energy of dessicated gels relative to glass of similiar composition permits the transformation of the gel to a glass at a temperature well below the melting point of a particular composition. It is also apparent from this figure that the various structural configurations instilled into the gel during the sol-gel process can lead to higher free energies and thus a higher densification rate. The enhanced sintering of compositionally diphasic xerogels in the $Al_2O_3 \cdot SiO_2$ system was explained by Hoffman and coworkers³⁵ under the hypothesis that diphasic and multiphasic xerogels must store more available metastable energy than the single phase gels since the heats of reaction of the different nanophases must also be added into the total free energy of the system.

Figure 11. The Gel to Glass Process (after ref. [11]).

Figure 12. Schematic Representation of Free Energy - Temperature Relationships for Gels, Glass, and Crystalline Structures (after ref. [33]).

3.2 Capillary Contraction

Capillary contraction corresponds to a temperature interval where considerable weight loss occurs with negligible shrinkage. Such a weight loss is due to desorption of physically adsorbed water and alcohol. For a borosilicate alkoxide gel fired under CHR conditions a measured value of 3% shrinkage was observed for capillary contraction in the temperature range of 25 – 150 °C.³¹

3.3 Condensation and Structural Relaxation

Shrinkage from condensation reactions results in skeletal densification which occurs concurrently with weight loss from the by-products of these reactions, e.g., water and alcohol. For the previously cited borosilicate gel this mechanism is active in the temperature range 150 – 525 °C and accounts for 33% of the total shrinkage. However, depending on the heating rate, a decrease in the rate of weight loss and a densification process with a different activation energy from that of condensation alone appears in the temperature interval 400 – 525 °C. This additional shrinkage is attributed to structural relaxation, i.e., the approach of the structure toward a configuration characteristic of the metastable liquid³¹ (see Figure 12). Structural relaxation occurs by the diffusive motion of atoms, without expulsion of water or other species. Both mechanisms, condensation and structural relaxation, result in skeletal densification.

3.4 Viscous Sintering

Viscous sintering, often referred to as viscous flow, results in rapid shrinkage without weight loss and is usually the predominant mechanism of densification in

gels. Rapid shrinkage results from the collapse of the micropores as viscous flow proceeds. For the borosilicate gel discussed in Sections 3.2 and 3.3, viscous flow occurs in the temperature range 525 – 700°C and accounts for 63% of the total shrinkage. In monolithic gels this sintering often results in complete densification if fired in air.

The boundary between condensation/structural relaxation and viscous flow is near the glass transition temperature T_g of the liquid glass where the viscosity is $\approx 10^{12}$ Pa·s.^{31,32} The condensation of hydroxyls and structural relaxation may continue to occur during viscous sintering. The effects that this has on viscous sintering will not be addressed here. The interested reader is referred to ref. [32] for an explanation of these effects.

Viscous flow is the primary mechanism of sintering for amorphous materials. Theoretical models of viscous sintering have been developed using a variety of assumptions for various initial geometries but all are based on the principles originally established by Frenkel.⁸ He showed that the deformation of a compact of spherical particles of radius r takes place through flow driven by surface tension, resulting in neck growth and the approach of particle centers, i.e., shrinkage. Frenkel equated the rate of energy gained from the reduction in surface area to the energy dissipated (heat) in viscous flow. Using this energy balance, an expression for the rate of viscous deformation, i.e., neck growth rate, of spherical particles of equal size during the *initial* stages of sintering can be obtained. The model leads to the following equation for the neck radius x as a function of sintering time t ,

$$\frac{x}{r} = \sqrt{\frac{3\gamma t}{2\eta r}} \quad (5)$$

where γ and η are the surface tension and viscosity respectively, at the sintering

temperature (see ref. [30] p. 492). The shrinkage which takes place is determined by the approach of particle centers. The rate of this approach is given by $d(x^2/2r)/dt$. Eq. (5) has been generalized to give the linear shrinkage of an array of spherical particles according to the expression³⁴

$$\frac{\Delta L}{L_o} = \frac{3\gamma t}{8\eta r} \quad (6)$$

where ΔL is the change in length and L_o is the initial length of a given dimension. The initial rate of shrinkage is directly proportional to the surface tension, inversely proportional to the viscosity, and inversely proportional to the particle size. Since γ, η and r are generally assumed to be constant, Eq. (6) establishes a linear relationship between the fractional linear shrinkage $\Delta L/L_o$ and time t . Frenkel's model provides a satisfactory description of the early stage of viscous sintering, $\Delta L/L_o \leq 10\%$.³⁴

Isothermal shrinkage data can usually be described by a simple generalization of Frenkel's model. The form of this equation describes the linear shrinkage in the form of a parabolic rate law expressed as

$$\frac{\Delta L}{L_o} = Kt^n \quad (7)$$

where K is characteristic of the material and dependent on temperature, and n is the coefficient of shrinkage which is related to the sintering mechanism. For viscous flow, $n = 1$, whereas for diffusional processes n is between 0.3 and 0.5.^{7,36}

Experimental studies^{37,38} have verified Frenkel's prediction of the time dependence of sintering. Other work has shown that compacts of non-spherical particles depart markedly from the behavior predicted for spheres.³⁹ Of course the sintering rate depends on the microstructure of the body, and as it evolves during the

course of sintering, deviations from Frenkel's model occur. Several other viscous sintering models have been proposed which encompass a broader range of sintering than does the Frenkel model. In the final stages of sintering the body will contain isolated spherical pores, Figure 10(a), whose rate of collapse will depend on both the pore radius and the permeability of the pores to gaseous products. Mackenzie and Shuttleworth⁹ developed a model, the MS or *closed pore* model, for the case of sintering in a body which contains isolated spherical pores and which is applicable for any initial value of porosity. A model that describes the early and intermediate stages of sintering in a body with open pores, Figure 10(b), was proposed by Scherer.¹⁰

3.4.1 Closed Pore Model

In the final stages of sintering the relative density, $\rho/\rho_s \geq 90\%$, in which densification results from the shrinkage of uniform spherical pores in a viscous matrix, the rate of pore closure is

$$\frac{dR}{dt} = -\frac{\gamma}{2\eta\rho} \quad (8)$$

where R is the mean pore radius. The kinetic equation of sintering

$$K(t - t_o) = \frac{2}{3} \left(\frac{3}{4\pi} \right)^{1/3} \int_0^D \frac{dD}{(1 - D)^{2/3}} \cdot D^{1/3} \quad (9)$$

where $t - t_o$ is the time necessary to reach the relative density $D = \rho/\rho_s$, ρ being the bulk density and ρ_s the density of the solid phase, i.e., the skeletal density.* For the reduced time, $K(t - t_o)$, t_o is a fictitious time when $\rho = 0$ and K is given by

$$K = \frac{\gamma n^{1/3}}{\eta} \quad (10)$$

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*There is disagreement among authors as to the correct definition of ρ_s . Some authors define it as the apparent density¹¹ while others define it as the true density.³⁴ Of course with gels, the difference is minimal and its assignment as the accepted value for theoretical density, i.e., 2.2 g/cm³ for vitreous silica, would not be incorrect.

where n , the number of pores per unit volume of solid phase, not to be confused with the shrinkage coefficient, can be expressed by

$$n = \frac{P}{4\pi R^3/3} \quad (11)$$

where P is the number of pores per particle. As shown in Figure 13, this model predicts a sigmoidal variation of density with time. The dimensionless time variable is $\gamma n^{1/3} t / \eta$. For a given pore volume, the pore radius decreases as n increases. The rate of sintering increases as the pore size and viscosity decrease and as the surface tension increases.

3.4.2 Open Pore Model

Scherer developed a model which consists of a regular cubic lattice of intersecting cylinders of radius a and edge l as shown in Figure 14(a). The parameters a and l are related respectively to the radius of elementary particles and to the spacing of the pseudo-lattice. As in the MS model, Scherer obtained an analytical relationship between the relative density and the reduced time (see Figure 13)

$$K(t - t_o) = 2 \int_0^x \frac{dx}{x^{2/3}} (3\pi - 8\sqrt{2}x)^{1/3} \quad (12)$$

where $x = a/l$, t is the sintering time, and t_o is the fictitious time at which $x = 0$. $K = \gamma / \eta l_o (\rho_s / \rho_o)^{1/3}$ and $\rho / \rho_s = 3\pi x^2 - 8\sqrt{2}x^3$ where l_o is the initial length of the cubic unit cell, ρ_s is the theoretical density of the solid, and ρ_o the initial compact density prior to sintering. Since the pore is trapped within the unit cell in the final stages of sintering, then

$$n^{1/3} = \frac{1}{L_o} (\rho_s / \rho_o)^{1/3} \quad (13)$$

Evaluation of $n^{1/3}$ can be accomplished by measuring the bulk density and the pore

Figure 13. Relative Density vs. Reduced Time, for Closed Pore Model, ref. [9] (—), and Open Pore Model, ref. [10] (- - -); t_f is the Time at Which $\rho/\rho_s = 1$; Upper Abscissa Applies to Open Pore Model Where t_0 is the Time When $\rho/\rho_s = 0$.

size or surface area from the expressions:

$$D = \rho/\rho_s = 3\pi x^2(1 - cx) \quad (14)$$

where $c = 8\sqrt{2}/3\pi$

$$S = \frac{1}{l\rho_s} \left[\frac{(2 - 3cx)}{x(1 - cx)} \right] \quad (15)$$

and the mean pore diameter may be approximated by

$$d = \frac{2l(1 - 2x)}{\sqrt{\pi}}. \quad (16)$$

Knowledge of D , S , or d is sufficient to determine the parameters x and l . Scherer's model also predicts a sigmoidal relationship between relative density and reduced time $K(t - t_o)$ as shown in Figure 13. At relative densities greater than 94% both curves coincide and the MS model can be applied. Figure 14(c) shows the condition for $x/l = 0.50$ ($D \approx 0.942$). To reduce their surface area, the cylinders tend to become shorter and thicker; when neighboring parallel cylinders touch, the pores are isolated and thereafter the MS model applies. Figure 13 also shows that the densification kinetics predicted for Scherer's model are very close to those predicted by the MS model when the relative density is ≥ 0.2 . The close agreement suggests that the shape of the unit cell does not have a strong effect on the predicted sintering kinetics. The virtue of the cylindrical array model is that the structure retains its form during densification. Frenkel's spheres lose their sphericity almost immediately, so the sintering kinetics must deviate from his prediction at an early stage. The cylindrical array changes only in scale, so it applies to both the initial and intermediate stages of sintering. The cylindrical model predicts densification kinetics identical to Frenkel's model over the range of shrinkage to which Frenkel's model applies.³³

Figure 14. Microstructural Model Consisting of Cylinders in Cubic Array (after ref. [31]). (a) Unit Cell Showing Edge Length, l , and Cylinder Radius, a ; (b) Model of Low Density Microstructure, $\rho/\rho_s = 0.05$; (c) Model of Microstructure with $\rho/\rho_s = 0.50$.

4 Experimental Methods and Techniques

4.1 Synthesis Methods

The methods of synthesis of ABS powders were adapted from those employed by Brinker and Mukherjee⁵ as well as those of Yoldas^{40,41} and Fleming⁴² all of which pertain to the chemical synthesis of multicomponent oxides. Synthesis parameters that were to remain constant for all methods, e.g., concentration and reactant ratios, were formulated on these authors' results with silica based gels. The main objective in the syntheses was to efficiently produce gels with maximum oxide content and with monolithic characteristics. Therefore, an acidic catalyst was used and a high concentration of oxide precursors (alkoxides) was maintained during all syntheses. The sought after advantage in using these conditions is that they produce microstructures comprised of very fine fundamental particles, 5-10 nm, with narrow size distribution.⁴² These gels will usually dry and fire without comminuting to very fine particles and in most cases retain the bulk shape of the gel, i.e., a gel monolith.

A nominal molar ratio of 3:1:2, $Al_2O_3 \cdot B_2O_3 \cdot SiO_2$, was sought in the gel syntheses. This ratio corresponds to 62% Al_2O_3 · 14% B_2O_3 · 24% SiO_2 by weight or a molar ratio of 50.3% Al_2O_3 · 16.6% B_2O_3 · 33.1% SiO_2 . This composition, *N*, is shown in Figure 1.

Two different methods of synthesis were developed to study their effect on the densification behavior and properties of the resulting powders. Their development was based on the hypothesis that different polymeric structures, i.e., the type and extent of $M - O - M'$ linkages, could be obtained by simply altering the sequence of reactant addition. Additionally, the hydrolysis reactivity of two aluminum alkoxides

and their effect on the densification behavior was investigated by their incorporation into each of the previously mentioned methods. The same hypothesis is applicable to the alkoxide substitution, except that in this case their reactivity towards hydrolysis is the basis. Alumina is the major component in the studied composition and it was anticipated that any effect(s) that this substitution has on the subsequent densification behavior would be much greater in magnitude than a similar substitution among the other components, and therefore, more likely to be measurable.

The two methods were designated as Method I and II with the alumina precursors extending each designation by an arabic numeral, i.e., the isopropoxide alumina precursor of Method I is designated I.ABS.1 and the secbutoxide precursor of Method II is II.ABS.2, for a total of four methods. Table 1 identifies the grade and source of the reagents used in the synthesis of ABS powders.

The proposed reaction steps and mechanisms for Methods I and II are described in Tables 2 and 3 respectively. These mechanisms are ideal in that they describe only well established paths to stable monomeric species. The actual mechanisms are undoubtedly more complex, with not only the formation of the shown monomers, but the formation of many dimeric, trimeric, and other intermediates as well. Nevertheless, the proposed mechanisms provide a necessary guide to the method of synthesis and the required stoichiometry. Flow diagrams detailing Methods I and II are shown in Figures 15 and 16 respectively. Each of these figures represent the respective sol-gel process as it was executed, in its entirety, from sol to powder. Major products corresponding to the numbered steps of Tables 2 and 3 are indicated at the appropriate points in each diagram. Ethanol serves as the host medium*

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*A host medium or mutual solvent, mother liquor, common solvent, etc., is an inert liquid which takes no active role in the reactions but serves as a vehicle for mass transport of the reactants.

Table 1. Grade and Supplier of Reagents Used in The Synthesis of ABS Powders

Reagent	Designated Grade	Supplier
Aluminum <i>iso</i> -propoxide $Al(OC_3H_7)_3$	98 + %	Alfa Products
Aluminum tri-(<i>sec</i> -butoxide) $Al(OC_4H_9)_3$	Double Distilled	Chattem Chemicals
Tetraethylorthosilicate $Si(OC_2H_5)_4$	Reagent	Fisher Scientific Co.
Trimethyl Borate $B(OC_2H_5)_3$	Practical	Eastman Kodak Co.
Ethyl Alcohol C_2H_5OH	U.S.P.	U.S. Industrial Chemicals Co.
Water H_2O	Distilled & Deionized > 18 Megaohm	Barnstead Co.
Nitric Acid HNO_3	78% Baker Instra-Analyzed	J.T. Baker Chemical Co.

Table 2. Proposed Reaction Steps and Mechanisms in the Synthesis of ABS Powders, Method I

Step	Reaction Mechanism
1.	$Si(OEt)_4 + H_2O \longrightarrow Si(OH)(OEt)_3 + EtOH.$
2.	$Si(OH)(OEt)_3 + B(OMe)_3 \longrightarrow (EtO)_3SiOB(OMe)_2 + MeOH.$
3.	$3Al(OR)_3 + (EtO)_3SiOB(OMe)_2 + 14H_2O \longrightarrow 3Al(OH)_3 + (HO)_3SiOB(OH)_2 + 9ROH + 3EtOH + 2MeOH.$
4.	$6Al(OH)_3 + 2(HO)_3SiOB(OH)_2 \longrightarrow 3Al_2O_3 \cdot B_2O_3 \cdot 2SiO_2 + 14H_2O.$
$R = (C_3H_7)^{iso}$ for I.ABS.1 and $(C_4H_9)^{sec}$ for I.ABS.2. $EtOH = C_2H_5OH$ (ethanol). $MeOH = CH_3OH$ (methanol).	

Table 3. Proposed Reaction Steps and Mechanisms in the Synthesis of ABS Powders, Method II

Step	Reaction Mechanism
1.	$Si(OEt)_4 + H_2O \longrightarrow Si(OH)(OEt)_3 + EtOH.$
2.	$Si(OH)(OEt)_3 + 3Al(OR)_3 \longrightarrow (EtO)_3SiOAl(OR)_2 + 2Al(OR)_3 + ROH.$
3.	$(EtO)_3SiOAl(OR)_2 + 2Al(OR)_3 + B(OMe)_3 + 14H_2O \longrightarrow$ $(HO)_3SiOAl(OH)_2 + 2Al(OH)_3 + B(OH)_3 + 3EtOH +$ $8ROH + 3MeOH.$
4.	$2(HO)_3SiOAl(OH)_2 + 4Al(OH)_3 + 2B(OH)_3 \longrightarrow$ $3Al_2O_3 \cdot B_2O_3 \cdot 2SiO_2 + 14H_2O.$
$R = (C_3H_7)^{iso}$ for II.ABS.1 and $(C_4H_9)^{sec}$ for II.ABS.2. $EtOH = C_2H_5OH$ (ethanol). $MeOH = CH_3OH$ (methanol).	

Figure 15. Flow Diagram for Synthesis of ABS powders, Method I. Circled Numbers Correspond to Reaction Steps of Table 2.

Figure 16. Flow Diagram for Synthesis of ABS powders, Method II. Circled Numbers Correspond to Reaction Steps of Table 3.

for all oxide precursors, their hydrolysis products, and water. In Method I, an ethanolic solution of TEOS was partially hydrolyzed and then an ethanolic solution of trimethyl borate (TMB) was added while stirring. This borosiloxane sol was then added to a slurry of aluminum isopropoxide (AIP) or aluminum secbutoxide (ASB), depending on the method, and vigorously stirred. Final hydrolysis of this mixture was performed by adding, dropwise, an aqueous ethanolic solution with continued stirring. Method II is similar to Method I except that the alumina precursor is added where the boria precursor was in the former. An ethanolic solution of TMB was then added to the corresponding aluminosiloxane sol. This mixture was then hydrolyzed as in Method I. The mixing was accomplished so that the concentration of the resultant sols totaled 5 wt.% equivalent oxide. This concentration and the use of an acidic catalyst, HNO_3 , were to encourage extensive polymerization and the formation of a network structure of the constituent oxides. All steps of the syntheses were performed in air at atmospheric pressure with no precautions taken to prevent premature hydrolysis from atmospheric moisture. Each process was evaluated by observing gel formation, powder characteristics and subsequent densification behavior.

4.2 Powder Characterization

Chemical and structural characterization of the ABS powders was based on techniques which would provide information pertinent to their subsequent high temperature behavior. The analytical techniques chosen were also those which were readily available and could be operated at little or no cost. With this premise, the following categories of characterization were established: thermochemical, including thermogravimetric and differential thermal analysis; compositional; structural,

including micro- and macrostructural characterization; and physical properties, including bulk density, apparent density, and microhardness measurements. Powder compact (PC) composition, physical properties, and microstructure were monitored as a function of temperature to provide additional characterization of the densification process.

4.2.1 Thermochemical Analysis

Thermal analysis identifies the physico-chemical behavior of a material as a function of temperature. Two techniques of thermal analysis were employed in this study, thermal gravimetric analysis (TGA) and differential thermal analysis (DTA). TGA was used to measure the weight change of the materials continuously, both as a function of increasing temperature and at a preselected temperature over a period of time. DuPont's 951 Thermogravimetric Analyzer was used in conjunction with the same manufacturer's 990 Thermal Analyzer for TGA. To complement TGA, DTA was used to measure the temperature at which heat-related transitions occur. This type of characterization provided qualitative data about any physical or chemical changes in the powders involving an endothermic or exothermic process. Hence, first order transitions such as decompositions or phase transformations and the temperature at which they occurred were indentified with DTA. DuPont's 910 Differential Scanning Calorimeter (DSC), equipped with a 1600 °C high temperature cell, was used in conjunction with DuPont's 1090 Thermal Analyzer. ABS powders were thermally analyzed after drying. A constant rate of heating, 5 °C/min, was used in all thermal analysis. Equal weights of powder were used in DTA.

4.2.2 Compositional Analysis

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and electron spectroscopy for chemical analysis (ESCA) provided quantitative and semi-quantitative elemental composition respectively. Together, these techniques yielded enough information to reconstruct the total chemical composition of the ABS powders.

Sample dissolution is required for elemental analysis with Applied Research Laboratories (ARL) Model 3510 Inductively Coupled Spectrometer. About 100 mg of the powder, PCs were first broken and then ground with a porcelain mortar and pestle, was dissolved in a $1M\ HF/0.8M\ HNO_3$ solution for analysis. The powder was analyzed for both major and trace elements after pre-calcination. For compositional analysis as a function of temperature only the major elements were analyzed. ARL's Model 3510 reports the results in parts per million (ppm) so it was necessary to convert them to their equivalent concentration as percent oxide by weight, with the assumption that all metals were present as oxides, a gross but useful assumption.

Additional chemical information and a hint of the structural organization was provided by ESCA. This technique determines the elemental and chemical composition of a material surface and is capable of detecting all elements with the exception of hydrogen. Thus, the halogens and elements of the second period, not readily detectable by ICP-AES, are revealed by ESCA. ESCA is also able to analyze electrical insulators such as the ABS powders. Several ABS powder compacts (PCs) representative of each process were supplied to Surface Science Laboratories of Mountain

View, California, for analysis. One PC of each process was lightly etched in P-etch[†] in order to remove surface contamination. Due to degassing difficulties—a 10^{-8} Torr vacuum is typically required—it was necessary to section the PCs and as a result of the additional time required only a few were analyzed. Several regions of $600\text{ }\mu\text{m}^2$ of the samples were analyzed from 0 - 1100 eV. High resolution investigations were conducted around major peak locations in an effort to elucidate localized bonding.

4.2.3 Structural Analysis

Structural analysis embodied both micro- and macrostructural characterization of the powders and PCs. Because structure was considered fundamental to this study, in view of its interrelationship with processing and properties, several analytical techniques were employed for its characterization. These provided information concerning: particle size, shape and distribution, intermolecular bonding, crystallinity, and microstructure. Analytical techniques included: particle size analysis, infrared spectroscopy (IR), powder x-ray diffraction (XRD), and scanning electron microscopy (SEM).

Several different techniques were employed to characterize the macrostructure of the ABS powders. For particle size analysis, Shimadzu's SALD-1000 Laser Diffraction Particle Size Analyzer was used. This technique is based on the optical diffraction of a laser beam off suspended particles in an aqueous liquid. The diameter and intensity of distribution in the resulting ring-like diffraction patterns are correlated with the particle size and distribution. The ABS powders were analyzed after pre-calcination with no dispersing agents.

[†]P-etch is a 5 % *HF* and 3.3 % *HNO*₃ by volume aqueous solution.

The bulk powders were also analyzed with SEM imaging techniques in conjunction with Quantel's "Crystal" particle size analysis package. This two-dimensional technique provided semi-quantitative results on the mean diameter and distribution of agglomerates in the powders. A description of the scanning electron microscope used in this analysis and required sample preparation will be discussed in the appropriate section.

The infrared spectrum of a material is an objective reflection of its structure. Absorptions within the frequency range $4000\text{--}500\text{ cm}^{-1}$ ($2.5\text{--}25\text{ }\mu\text{m}$) due to intermolecular bonding were examined. Samples, in powder form, were prepared using the potassium bromide (*KBr*) disc method and analyzed with the Nicolet MX-1 FT-IR Spectrometer. A disc, pressed from dehydrated *KBr*, was first scanned in the frequency range to determine absorptions due to the *KBr* disc. This scan was then automatically subtracted from the sample's IR spectrum for each subsequent run. Plots of percent transmission vs. wavenumber (cm^{-1}) were obtained for each run after an automatic expansion sequence was performed. Powders were characterized by IR after pre-calcination and as a function of temperature. PCs were broken up and reduced to a fine powder for analysis.

SEM provided microstructural information about the powders and PCs. Agglomerate and PC morphology were characterized with this technique. Micrographs were taken with Hitachi's Model S-415A Scanning Electron Microscope. Powders and PC segments were sputtered with *Au* or *Au/Pd* to reduce charging effects.

Additional structural characterization was done with powder XRD. Identification of crystalline phases in the powders was made possible by this technique. XRD

was also conducted as a function of temperature and like the IR samples, PCs were first ground to a fine powder. The powder was then packed uniformly into a sample holder using a standard procedure. Scintag's Pad V Automatic Diffraction System was utilized for this characterization. Diffraction conditions were maintained at 40 kV and 40 mA, with a step size of $0.1^\circ 2\theta$ and a θ slew speed of $10^\circ 2\theta/\text{min}$. $\text{Cu } K_\alpha$ radiation was used with a curved graphite monochromator at the detector.

As will be later shown, the ABS powders crystallize at high temperature. This permitted additional characterization of particle size. A dimension of the crystallites, diffraction domains, giving rise to a characteristic reflection can be measured by XRD according to the Scherrer equation

$$B = \frac{K\lambda}{t \cos \theta} \quad (17)$$

where B is the broadening of a diffraction line at full width half maximum, in radians, λ the wavelength of the incident radiation, K is a constant (usually 0.94), θ is the position of the peak being used for the size determination and t is the diameter of the crystallite in angstroms.⁴³ The broadening of the diffraction line is that leftover after subtracting the breadth due to instrumental effects. These effects were determined using an annealed α -alumina powder, finely ground and considered to be strain free. The Scherrer formula is applicable only to particle sizes in the range 5 - 100 nm. Scintag's software package, CSIZE, automatically makes the necessary corrections and computes the particle size based on the Scherrer formula. It was used for the crystallite size determinations in this experiment.

4.2.4 Physical Properties

Physical properties of the powders and PCs were determined as a function of temperature in order to relate them with the structural and chemical observations made during the densification process. Properties determined were bulk and apparent density and microhardness. Bulk density was determined by dimensional and mass measurements. Apparent density measurements were made with Beckman's Model 930 Air Comparison Pycnometer using helium as the working gas. Vickers microhardness testing was done using a diamond indenter and an applied load of 1 kg.

4.3 Powder Compaction

Pre-calcined powders were sieved through a 80 mesh, 180 μm , sieve. Agglomerates not able to pass through the sieve were ground with a porcelain mortar and pestle until they passed freely through the sieve, two passes were all that was necessary.

The powder was pressed in a single action carbon steel die using a Carver Laboratory Press Model B. The applied pressure was based on an optimum green density of 45%, relative to glass. The pressure necessary to achieve this density varied with the method of synthesis. Hence, a compaction study of the powders was conducted. The variation in relative bulk density ρ/ρ_u , where ρ_u is the density of fused silica, 2.2 g/cm³, with compaction pressure for ABS powders is shown in Figure 17. The required pressure could be obtained by interpolation from this plot and ranged from 100 - 160 MPa, 14.5 - 23.2 ksi. The pressure was applied to the

sample for a total of five minutes in one minute stages.

Zinc stearate was used as a lubricant and sprayed on the die components prior to each compaction. This lubricant greatly facilitated sample removal and reduced sample contamination from the die walls. The ABS green compacts were very tenacious and excess zinc stearate was easily removed by tapping the compacts lightly against a firm surface followed by blowing or brushing residual material away. The average dimensions of a green compact were 0.515 inches in diameter and 0.240 inches in thickness. These dimensions gave a thickness to diameter ratio of 0.47, a value reflective of minimal bulk density gradients.⁴⁴

4.4 Thermal Dilatometric Analysis

Thermal treatment, firing at intermediate and high temperatures, to effect additional densification of the PCs was accomplished in air with a tube furnace. The tube furnace is a component of Harrop's TD-726 dilatometer with which the dimensional densification behavior of the PCs was analyzed. Dilatometry or thermal dilatometric analysis (TDA) is a means of measuring expansion or contraction of a sample as a function of temperature. From the data of TDA, the mechanisms of densification were identified. As suggested by Bannister and Woolrey,⁴⁵ absolute values of shrinkage were obtained by monitoring a sample dimension continuously during the heating and isothermal periods. In this way, both shrinkage rate and absolute shrinkage data were compiled directly from the TDA data. The initial length L_0 and initial time t_0 of the PCs at an initial temperature T_0 were determined directly from these data.

Conversion, scaling, and recording of the dilatometric data from a sample were

made with an IBM personal computer-based data acquisition system interfaced with the dilatometer. The dilatometer and data acquisition system comprise the TDA system. Description, principles, calibration, and operation of the TDA system are detailed in Appendix A.

Generally, dilatometry consisted of firing the sample in air from room temperature to the designated hold temperature at a CHR of 5 °C/min—the ramp stage. The sample was held at this temperature for one hour—the dwell stage—and then furnace cooled to room temperature. Data were acquired throughout the ramp-dwell cycle in increments of 30 seconds in order to reliably establish initial time and sample lengths. This method of data collection provided enough information to fully characterize the isothermal and CHR densification of the PCs. Samples representative of each method of synthesis were fired at designated temperatures. These temperatures were established from the DTA results and an initial CHR dilatometric run, 5 °C/min from RT to 1184 °C. Each sample's weight and dimensions were recorded before and immediately after each run.

As discussed in Appendix A, a correction factor for system expansion was applied to the collected data. A second correction factor, that due to the thermal expansion of the sample, was also applied. No data, i.e., coefficient of thermal expansion, could be found for this composition in the literature. Nor for that matter would such a coefficient be applicable for these synthesized powders as their composition was less than 100% oxide. The alternative was to measure the linear coefficient of thermal expansion (LCTE) of an ABS PC. A representative PC was fired at 5 °C/min to 700 °C and held there for several hours. After a second firing to 700 °C an expansion curve was obtained from which a LCTE of approximately

$3.8 \times 10^{-6}/^{\circ}\text{C}$ was calculated. This value was used in all subsequent processing of raw thermal dilatometric data.

The complete post-synthesis processing of the ABS powders is depicted in Figure 18.

Figure 17. Variation in Relative Bulk Density with Compaction Pressure for Synthesized ABS Powders.

Figure 18. Flow Diagram of Post-Synthesis Processing of ABS Powders.

5 Gel Synthesis and Powder Characteristics

The synthesis of ABS powders proceeded according to the flow diagrams of Figures 15 and 16. Several batches of each method of synthesis were prepared over the course of this study. This procedure permitted checks on compositional accuracy and reproducibility of the method as well as provided sufficient material to conduct the densification phase of the study. Each synthesis was based on a 10.0 gram equivalent total oxide content. The corresponding quantity of reagents used for both methods were: TEOS (8.89 ml), TMB (4.57 ml), 20.15 ml of water and 0.25 ml of a 1.56 *M* HNO_3 solution. For the methods based on AIP as an alumina precursor, 24.84 g of AIP was used, while ASB based powders used 29.96 g of ASB.

5.1 Composition

Chemical analysis of the ABS powders revealed slight deviations from the 3:1:2 ratio of $Al_2O_3 \cdot B_2O_3 \cdot SiO_2$ as shown in Table 4. The largest deviations occurred in the Al_2O_3/SiO_2 ratio and are positive. The SiO_2/B_2O_3 ratio is nearest in agreement with the calculated ratio. Hence, the deviations are most likely due to depletions in the boria and silica content of the powder. The presence of *Al*, *Si*, and *B* as non-oxides, e.g., hydroxides, would also contribute to the relative errors. Preliminary results from ESCA indicated that the majority of the metals were present as oxides and so this contribution was negligible. Depletions in the silica content could be due to the vaporization of unreacted silanol species during drying and pre-calcination. Xiaoming and Yuguang⁴⁶ observed significant boria deviations in an ABS system with Al_2O_3 as the minor constituent and attributed the loss to hydrolysis of the TMB with atmospheric moisture. They showed that the compositional deviation

increased with decreasing SiO_2/B_2O_3 molar ratio, the greatest deviation (88.9 %) occurring at a ratio of 2.08. A minute adjustment in the quantity of TMB and TEOS was made to reduce the deviations. The values shown in Table 4 and subsequent tables reflect this adjustment.

Table 5 lists the major oxide constituents and their abundance in the pre-calcined powders. The results are the mean values from three batches. The values in Table 5 show that all synthesized ABS powders are of equal composition. The powders contained approximately 14% by weight non-oxide material at this stage of processing. The mass difference was due to residual organics and physically and chemically bound water. Table 6 lists the quantities of minor oxide constituents, impurities, detected in the initial batch of powders. It is obvious from this table that ABS powders based on the ASB precursor contain lower levels of impurities than those based on AIP. The difference was attributed to the initial purity of the alumina precursors.

The chemical composition of an ABS PC as determined by ICP-AES and ESCA are compared in Table 7. The agreement is relatively good. ESCA shows that the mass difference previously observed is due primarily to residual organics. High resolution techniques with ESCA in the vicinity of the peaks due to *Al* and *Si* show that these metals are present as oxides. The same technique shows *B* present as a mixture of oxide and hydroxide. The close agreement between the analyzed values and the calculated value implies that at this level of analysis the PCs are chemically homogeneous and consist primarily of oxides.

Table 4. Comparison of Calculated and Analyzed Molar Oxide Ratios in Synthesized ABS Powders

Method	Oxide Molar Ratio ^a		
	Al_2O_3/SiO_2	Al_2O_3/B_2O_3	SiO_2/B_2O_3
I.ABS.1	1.69	3.18	1.88
<u>RE</u>	12.7	6.0	-6.0
I.ABS.2	1.64	3.18	1.94
<u>RE</u>	9.3	6.0	-3.0
II.ABS.1	1.69	3.18	1.88
<u>RE</u>	12.7	6.0	-6.0
II.ABS.2	1.64	3.37	2.06
<u>RE</u>	9.3	12.3	3.0
Calculated	1.50	3.00	2.00

^aResults based on ICP-AES analysis performed after pre-calcination of powders. Average of 3 batches.

Table 5. Major Oxide Concentrations in Synthesized ABS Powders

Method	<u>n</u>	Oxide, wt. %		
		<i>Al₂O₃</i>	<i>B₂O₃</i>	<i>SiO₂</i>
I.ABS.1	3			
<u>M</u>		55.4	12.0	19.7
<u>SD</u>		4.5	1.6	1.6
I.ABS.2	3			
<u>M</u>		55.4	12.4	20.1
<u>SD</u>		4.1	2.3	1.3
II.ABS.1	2			
<u>M</u>		55.4	11.7	19.3
<u>SD</u>		3.9	2.0	1.3
II.ABS.2	2			
<u>M</u>		54.6	11.0	20.0
<u>SD</u>		2.6	0.7	0.3

Note. Results based on elemental analysis by ICP-AES after pre-calcination of the powders.

Table 6. Impurity Levels in Synthesized ABS Powders

Method	Impurity Concentration, wt. %					
	<i>Na₂O</i>	<i>K₂O</i>	<i>Li₂O</i>	<i>MgO</i>	<i>CaO</i>	<i>Fe₂O₃</i>
I.ABS.1	≤LQD	0.26 ^a	≤LQD	0.015	0.007 ^a	0.004 ^a
I.ABS.2	≤LQD	0.18 ^a	≤LQD	≤LQD	0.007 ^a	≤ LQD
II.ABS.1	≤LQD	0.26 ^a	≤LQD	0.015	0.007 ^a	0.003 ^a
II.ABS.2	≤LQD	0.24 ^a	≤LQD	≤LQD	0.005 ^a	≤LQD

Note. Results based on elemental analysis by ICP-AES after pre-calcination of powders.

All results have an accuracy of ±1% except where indicated.

LQD = Lowest quantity determinable.

^aValues are ±10% of that reported.

5.2 Synthesis and its Evaluation

Observations of the sol-gel synthesis methods revealed only minor visual fluctuations among them. In the methods where AIP was used, it was necessary to vigorously stir and slowly bring the ethanolic slurry of AIP to a temperature of $70 \pm 5^\circ\text{C}$ for approximately five minutes in order to achieve a uniform slurry of the alkoxide. After the temperature was reduced to ambient the slurry appeared to remain homogeneous, even after standing for 30 minutes. A slight difference in opacity accompanied this thermal cycling of ethanolic AIP. With its introduction to ethanol at room temperature, the AIP formed an opaque white slurry. On mild heating this slurry gave way to a somewhat translucent one with the exception of settled clumps that did not immediately enter the slurry. As the temperature approached 65°C , the translucency of the slurry gradually changed to an opaque white resembling the original slurry except that at this point it was quite uniform, i.e., no clumps. When cooled to room temperature, the appearance of the slurry remained unchanged.

The thermal cycling required for AIP was not necessary for the liquid ASB. Upon introduction to ethanol at room temperature, with stirring, it rapidly formed a homogeneous white slurry. In contrast, the silanol solution of both methods was completely clear as was the borosiloxane solution formed in the initial steps of Methods I.ABS.1 and I.ABS.2.

Once all the oxide precursors were introduced into the sol and given a designated time to react, according to the governing method, the resulting (metal-alo)metalosiloxane sol was hydrolized with excess water to produce a gel. Ethanolic

Table 7. Calculated and Analyzed Chemical Composition of an ABS Powder Compact as Determined by ESCA and ICP-AES

Element	Atom Percent			Analytical Agreement, atom %
	Calculated	ESCA ^a	ICP-AES ^b	
<i>Al</i>	23.1	24.2	23.2	1.0
<i>B</i>	7.7	6.0	6.6	0.6
<i>Si</i>	7.7	9.6	7.0	2.4
<i>C</i>		3.7	4.4 ^d	0.7
<i>O</i>	61.5	56.5	58.8 ^c	2.3

^a I.ABS.1 after 100 Å ion milling, probe area = 600 μm².

Accuracy is reported to be 10% of the relative abundance.

^b I.ABS.1, accuracy of ±1% of reported value.

^c Calculated from stoichiometric oxide content of listed metals.

^d Difference from mass balance.

water was added dropwise via an addition funnel at a rate of ≈ 4 ml/min. The sol to gel transition, which occurred at different times during this hydrolysis, varied with the method of synthesis. The transition was accompanied by changes in gel appearance and viscosity. Viscosity of the gels was not determined. However, the appearance and quantity of water added up to the gelling point in the final hydrolysis step for each method are given in Table 8.

All sols gelled before the complete addition of excess stoichiometric water. Hence, in order to complete this addition, the gels were mechanically broken up so that the remaining water of hydrolysis would be equally dispersed within the gel. With the excess water added and additional vigorous stirring, the gel formed a new slurry of particulates. After stirring for one hour, the slurries were oven dried at 70 °C in a Blue M Single Wall Transite Oven to volatilize the large mass of alcohol and reaction by-products. Drying was continued to the point where the gel could be removed for comminution. The time required for drying was again dependent on the method of synthesis. Generally, those methods with AIP as an alumina precursor were dried for 24 hours while those using ASB were dried for 48 hours. The dried gels consisted of large white friable chunks and powder. The chunks were ground to a fine powder with a porcelain mortar and pestle, transferred to a drying dish, and dried for an additional 4 hours at 70 °C. Powder fines were transferred to a dessicator and stored under vacuum.

5.3 Powder Characteristics

ABS powders resulting from the previously described syntheses appeared as “bleach” white particulates after drying. After pre-calcination, the powders took

Table 8. Gel Formation and Appearance for Various Methods of Synthesizing ABS Powders

Method	Water Required ^a for Gelation, mol	Gel Appearance ^b
I.ABS.1	0.49	Homogeneous, blue-gray
I.ABS.2	0.38	Precipitate, white
II.ABS.1	0.36	Homogeneous, blue-grey
II.ABS.2	0.32	Precipitate, white

^a Total amount of water added up to gelation.

^b Gel appearance recorded 30 minutes after gelation.

on different hues of whiteness corresponding to the extent of oxidation of the organic constituents. Oxidation of organics and other weight loss phenomena were revealed in the thermal analysis of the prepared powders and are presented in the following section. Physical properties of the powders and particle morphology are presented in Section 5.3.2 and 5.3.3 respectively.

5.3.1 Thermochemical Analysis

Results of TGA of the different powders are shown in Figure 19. The curves of weight loss vs. temperature are all characterized by a rapid weight loss between 25 and 300 °C followed by a gradual transition to a slower but more constant weight loss in the temperature range 300 – 1000 °C. Finally, an increase in weight loss between 1000 and 1200 °C. Between 40 and 53% of the initial powder weight was lost in the entire temperature range of 25 – 1200 °C, the total loss being dependent on the method of synthesis. Almost 90% of this weight loss occurred in the temperature range 25 – 600 °C for all powders.

The initial rapid weight loss, between 30 and 35% of the total, was due to the elimination of solvent and reaction by-products (H_2O & ROH) and the desorption of excess water.^{5,35,47,48} Figure 20 shows DTA thermograms for the different powders. In the temperature range 25 – 100 °C of this figure a somewhat compressed, but nonetheless distinct, endotherm was observed in all cases. These endotherms correspond to the range of high weight loss observed in Figure 19 for the same temperature range. Endotherms in this temperature range are due to the elimination of water, solvent, and organics. Reaction by-product removal is particularly evident in the 100 – 200 °C range by an inflection of those curves belonging to ASB

Figure 19. Percent Weight Loss with Temperature, from TGA of Synthesized ABS Powders. Heating Rate = 5 °C/min.

based methods, i.e., I & II.ABS.2. This inflection, not present in the AIP based methods, is due to the lower vapor pressure of secbutanol relative to isopropanol resulting in a depressed rate of vaporization in the later. The exotherms around 300°C in Figure 20 are due to combustion of organics.^{47,48} These exotherms occur in the transition region between high and low weight loss of Figure 19.

The region of weight loss in the temperature range 300 – 1000°C is characterized by a slow but constant increase in weight loss due to condensation reactions similar to that shown in Figure 8.⁵ There is no significant change in weight loss around 900°C and so the exotherm in Figure 20 near this temperature were attributed to a structural transformation. The change of slopes in the DTA at $\approx 835^\circ\text{C}$ is common to all powders and indicative of a change in their specific heat capacity. Such a change occurs at the onset of the gel to glass transition, and hence, 835°C corresponds to the glass transition temperature (T_g) of the ABS powders. Xiaoming and Yuguang⁴⁶ reported a T_g of approximately 930°C for high silica bearing gels in the ABS system and a $\text{SiO}_2/\text{B}_2\text{O}_3 = 3.93$. Sowman⁴⁹ reported an exotherm in the DTA of aluminum borosilicate gels, similar in composition to those studied here, in the temperature range 850 – 870°C. His subsequent XRD analysis revealed the coincident formation of a novel crystalline species (“reverse mullite”) in this temperature range.

The increase in slope of the TGA curves in the temperature range 1000 – 1200°C accounted for an additional 1 – 5% weight loss. No thermal event was revealed in the corresponding temperature range of the DTA thermograms. The slopes are all similar with the exception of I.ABS.2 which is considerably greater.

Figure 20. Temperature Difference vs. Temperature, from DTA of Synthesized ABS Powders. Heating Rate = 5 °C/min.

Collaboration with other experimental results is necessary before suggesting a plausible origin for this anomaly.

5.3.2 Apparent Density

Physical property characterization of the powders and PCs began with their apparent density ρ_a , i.e., density due to the solid phase and the isolated pores within the solid phase. It was assumed that the relative amounts of isolated pores were small compared to the continuous pores.⁵⁰ After drying, the powders exhibited a mean value of apparent density approximately equal to 1.72 g/cm³. This characterization was continued at several stages of processing as indicated in Figure 18 and the results are given in Table 9. The values of apparent density increased by $\approx 28\%$ during pre-calcination. This increase indicated a considerable consolidation of the gel particulate during this stage of processing. The increase occurred with a decrease in volume large enough to offset the corresponding decrease in weight as indicated by the TGA results of Figure 19. The needed volume contraction could have occurred as a result of the polycondensation reactions within individual particles and agglomerates. The result of these reactions occurring simultaneously with the expulsion of combustion and condensation reaction by-products is the collapse of macropores in the gel resulting in a decreased porosity and a strengthening of the gel skeletal structure. The apparent density of the ABS powders after pre-calcination is approximately that of silica glass (2.20 g/cm³).⁵⁰ This value is retained as the initial apparent density of the PCs. As indicated in Table 9, the measurements of apparent density are accompanied by relatively large determinate errors. These errors were due to calibration difficulties with the pycnometer. Because of these errors, no definitive statement can be made regarding differences in apparent density

Table 9. Apparent Density of Synthesized ABS Powders after Several Stages of Processing

Method	Apparent density, g/cm ³		
	Powder after ^a 70 °C, 24-48 h	Powder after ^a 600 °C, 2 h	Powder compact as pressed
I.ABS.1	1.68	2.15	2.24 ^b
I.ABS.2	1.67	2.28	2.09 ^c
II.ABS.1	1.87	2.18	2.16 ^d
II.ABS.2	1.67	2.22	2.15 ^c

Note. Apparent density determined with an air comparison pycnometer using helium as the working gas.

^aAccuracy of these values is assumed to be no greater than that determined from the powder compacts, $\approx 6\%$.

^b $\underline{SD} = 0.14$, $\underline{n} = 13$.

^c $\underline{SD} = 0.12$, $\underline{n} = 13$.

^d $\underline{SD} = 0.20$, $\underline{n} = 12$.

with respect to the method of synthesis.

5.3.3 Particle Size and Morphology

The influence of the methods of synthesis was most significant in the particle size, distribution, and morphology. Table 10 lists the mean particle size and distribution for each method as analyzed by laser diffraction and the mean diameter of agglomerates as analyzed by SEM imaging. From a statistical analysis of the data, the T-test at a 95% confidence interval, it was confirmed that the mean particle size was significantly different not only between methods based on the two different alumina precursors but also between Methods I and II for ASB based powders. Particle size analysis, determined after the powders were pre-calcined, showed that AIP based powders consisted of larger agglomerates but had a smaller mean particle size and distribution than those powders based on ASB. The particle distribution differed significantly between I.ABS.1 and I.ABS.2.

Particle morphology was revealed by SEM. Figures 21(a) and (b) show an agglomerate from AIP and ASB based powders respectively, both having been exposed to 600°C for 2 hours. The agglomerates from methods based on AIP were found to be more regularly shaped than those based on ASB. The latter's agglomerates were more shard-like in shape. Figures 21(c) and (d) are a higher magnification of the enclosed region in the micrographs of Figures 21(a) and (b) respectively. Figure 21(c) shows that the AIP based agglomerate is composed of submicron particulates as well as what appears to be well ordered rod-like structures. The ASB agglomerate shown in Figure 21 (d) revealed a featureless morphology common in many glasses.^{47,48}

Table 10. Particle Size and Distribution of Synthesized ABS Powders

Method	Particle Size, μm	Particle ^a		Agglomerate Diameter, μm
		Distribution, μm		
		95%	5%	
I.ABS.1 ^b				
<u>M</u>	9.5 _†	34.6 _†	2.2	53
<u>SD</u>	0.6	2.1		
I.ABS.2 ^c				
<u>M</u>	15.31 _{†,†}	43.5 _†	2.5	46
<u>SD</u>	0.05	0.1		
II.ABS.1 ^c				
<u>M</u>	8.9 _†	39.5		53
<u>SD</u>	1.6	7.3		
II.ABS.2 ^b				
<u>M</u>	12.7 _{†,†}	41.9	2.9	40
<u>SD</u>	0.4	1.3		

Note. Determination of particle size and distribution based on laser diffraction using Rosin-Rammler distribution function and a measuring range of 1.86-135 μm . Agglomerate mean diameters from SEM imaging. Means having the same subscript are significantly different at $p < 0.05$, two-tailed.

^aCumulative percentage less than by volume.

^bn = 5 for particle size and distribution statistics.

^cn = 3 for particle size and distribution statistics.

A

80 μm

B

C

15 μm

D

Figure 21. SEM Micrographs of ABS Agglomerates Prepared from Different Methods. (a) AIP Based Agglomerate. (b) ASB Based Agglomerate. (c) 5X Magnification of Boxed Region in (a). (d) 5X Magnification of Boxed Region in (b).

6 Densification of ABS Powder Compacts

6.1 Thermal Dilatometry

TDA of all samples began by firing the ABS PCs in a tube furnace at a controlled heating rate of 5°C/min from room temperature to 1184°C. The results of these initial runs are shown in Figure 22. All PCs exhibited similar densification behavior. Between 18 and 23% shrinkage was observed for the ABS PCs with I.ABS.1 shrinking the most and I.ABS.2 the least. Method II AIP and ASB based PCs differed by only 0.6% in total shrinkage. Similar comparisons for AIP based methods gives 2% and with ASB a difference of 3.4%. Linear shrinkage, $\Delta L/L_o$, in the ABS PCs was characterized by five major regions of shrinkage. These regions were designated Regions A – E from low to high temperature and are indicated as such in Figure 22. Region A covers room temperature to 100°C, Region B from 100 – 400°C, Region C from 400 – 800°C, Region D from 800 to about 890°C, and finally Region E from about 890 – 1184°C. Less than 0.1% of the total shrinkage was recorded in Region A, about 2% in Region B, another 3% in Region C, 13% in Region D, and 3% in Region E. I.ABS.1 exhibited more CHR shrinkage than any of the other methods in all regions. II.ABS.1 did not undergo any measurable shrinkage in Region E under CHR conditions.

Several temperatures in Regions C – E were selected for isothermal TDA as well as two from Region B. ABS PCs were heated at 5°C/min from room temperature to the selected temperature and held at that temperature for one hour. Appendix B contains the tabulated results of isothermal TDA. Sample temperature, apparent shrinkage, and time were recorded automatically every 30 seconds during the ramp

Figure 22. Linear Shrinkage vs. Temperature, for Synthesized ABS Powders Showing Five Major Regions of Shrinkage. Heating Rate = 5°C/min.

and dwell cycle. Analysis of these data showed when the selected temperature was stabilized, within $\pm 2^\circ\text{C}$. From this initial temperature, the initial time and length L_o were determined. From these initial data, subsequent data were collected at 3 minute intervals for further processing and tabulation. This procedure resulted in eighteen degrees of freedom (n) for most regression analyses.

Tables 17-68 in Appendix B identify the isothermal shrinkage and L_o for each sample. Raw data consisted of the recorded temperature, apparent shrinkage and time. The magnitude of the correction factor and the LCTE that were applied to the raw data are given in Appendix A and Section 4.4 respectively. Eq.(7) describes isothermal shrinkage due to viscous flow and solid state diffusional processes. The coefficient of shrinkage n can be found from a log-log plot of the isothermal shrinkage data. At the bottom of each table for Regions B, C, and E, the results of linear regression of $\log(\Delta L/L_o)$ vs. $\log t$ are given.

Most samples taken above 845°C were distorted from their original cylindrical shape. This was a result of density gradients in the PCs. Some of the samples that were taken above 845°C fractured in the radial direction. Data from samples that fractured severely were usually quite scattered and resulted in a poor linear fit. Linear regression results that gave a value of $R^2 < 0.75$ were rejected. Cases for which this occurred are indicated in the tabulated data of Appendix B by the omission of linear regression results.

Linear shrinkage and log-log plots for all significant runs in all regions investigated are given in Appendix C. The slopes of the log-log plots and their applicable

regions are listed in Table 11. The values listed in this table indicate similar coefficients of shrinkage for all methods in both Regions C and E. Therefore, it would appear as though similar densification mechanisms were at work in these regions. Method II.ABS.1 gave rather anomalous data for all regions except Region D. It was determined that all ABS PCs densified by viscous flow in Region D. Linear shrinkage plots of this region are characterized by an initial high rate of shrinkage, gradually tapering off, according to the sintering temperature and method of synthesis. The log-log plots show this same trend. The initial values, for $t < 10$ min, of the slope in these plots were always very nearly one. Then as the curves in these figures suggest, the value gradually decreased, in some cases to almost zero. With most PCs 10% shrinkage was observed in this region at 845°C and 8% at 864°C. According to Orgaz-Orgaz³³ then, the Frenkel model is applicable for this region (also see Section 3.4). Figure 23 shows the variation in shrinkage of the ABS PCs for temperatures within Regions C – E. The PCs in this figure show, visually, the densification behavior presented thus far.

6.2 Compositional Evolution

Weight loss occurred during the densification of ABS PCs. There was no significant difference in the weight loss between powders prepared by different methods. Figure 24 shows the mean recorded weight loss of the PCs in the temperature interval studied along with the mean fractional shrinkage in percent. Figure 24 shows that more than 50% of the total weight loss occurred at the relatively low temperature of 522°C. Before the compacts enter Region D, up to 78% of the total weight was eliminated. Only about 1% weight loss occurred in Region D so that the remaining 20% of the total was given up in Region E. Most of this was lost

Table 11. Mean Coefficients of Shrinkage for Regions B, C, and E from Isothermal Densification of ABS Powder Compacts

Method	Shrinkage Coefficient, n		
	<u>Region B</u>	<u>Region C</u>	<u>Region E</u>
I.ABS.1			
<u>M</u>		0.65 ^c	0.81 ^b
<u>SD</u>		0.16	0.18
I.ABS.2			
<u>M</u>		0.77 ^c	0.67 ^c
<u>SD</u>		0.07	0.10
II.ABS.1			
<u>M</u>		0.87 ^c	
<u>SD</u>		0.22	
II.ABS.2			
<u>M</u>	0.70 ^a	0.68 ^c	0.72 ^c
<u>SD</u>	0.04	0.08	0.20

^a $\bar{n} = 1$.

^b $\bar{n} = 2$.

^c $\bar{n} = 3$.

between 1146 and 1184 °C. The characteristics of PC weight loss closely parallels the results of TGA shown in Figure 19.

Along with the weight loss there was an increase in the oxide content of the PCs. This is reflected in Figure 25 which shows the concentration of the major oxides and their total with increasing temperature. An increase of 14% in the total oxide content occurred between 600 and 1049 °C. At 1049 °C the total oxides present accounted for 96% of the weight. The majority of the increase in the oxide content occurred between 700 and 800 °C with the major oxide, Al_2O_3 , showing the greatest increase. Only a slight decrease ($\approx 1\%$) was observed in the temperature range 1049 – 1184 °C. Table 12 summarizes the chemical composition of the synthesized powders and its variation during different stages of processing.

6.3 Structural Evolution

Structural evolution with temperature was characterized with XRD, SEM, and IR. The results from XRD are presented in Figures 26(a) and (b) for Methods I.ABS.1 and I.ABS.2 respectively and Figures 27(a) and (b) for Methods II.ABS.1 and II.ABS.2 respectively. The powders were amorphous up to a temperature of 845 °C except for II.ABS.2 which retained its amorphous structure up to 864 °C. The diffraction lines at 2θ values of approximately 38 and 45° in the low temperature patterns were attributed to the decomposition products of zinc stearate, the die lubricant. These peaks were not present in XRD patterns of the same powders run before compaction.

Both AIP based powders exhibit some ordering at 845 °C whereas the ASB powders do not. A weakly crystallized species is present at 864 °C except for II.ABS.2

Figure 23. Variation in Shrinkage of ABS Powder Compacts with Temperature after Exposure to the Indicated Temperature for 1 h.

Table 12. Summary of Chemical Composition in Synthesized ABS Powders

Oxide	Weight, %			Percent Change in Thermal Treatment (C - B)/B X 100%	Deviation from Nominal Composition (C - A)/A X 100%
	Nominal A	After Pre-Calcination B	Final 1049°C C		
Al_2O_3	62.0	54.5	62.4	14.5	0.7
SiO_2	24.0	19.3	21.9	13.5	-8.7
B_2O_3	14.0	10.6	12.1	14.2	-13.6
Total	100	84.4	96.4	14.2	-3.6

Note. Results based on elemental analysis by ICP-AES.

Figure 24. Mean Recorded Weight Loss and Fractional Shrinkage of ABS Powder Compacts as a Function of Temperature. Recorded Weight Loss was the Mean after 1 h at Each Temperature.

Figure 25. Mean Oxide Levels in ABS Powder Compacts and Their Change with Temperature. Levels Determined from ICP-AES after 1 h at Each Temperature.

Figure 26. X-Ray Diffraction Patterns of Method I ABS Powders after 1 h at Several Different Temperatures; (a) I.ABS.1, (b) I.ABS.2. Numbers in Pattern Indicate Temperature in °C.

Figure 27. X-Ray Diffraction Patterns of Method II ABS Powders after 1 h at Several Different Temperatures; (a) II.ABS.1, (b) II.ABS.2. Numbers in Pattern Indicate Temperature in °C.

which displays only a slight ordering at this temperature. Ultimately, all the powders crystallize to the same structure. Intensities of the diffraction lines increased with increasing temperature corresponding to crystallite growth. Apparent shifts in the intensities of the major diffraction lines, i.e., $2\theta = 16.5, 26.4$, and 41.4° , with temperature were examined as a possible indication of structural reordering. But most of these changes were $< 10\%$ and hence attributed to preferred orientation.

The XRD pattern of well crystallized ABS powders is quite complex. Figure 28(a) shows the XRD pattern and d -spacings of II.ABS.2 after 1 h at 1400°C . This pattern is representative of all ABS powders with the exception of minor fluctuations in line intensities. This indicates that no significant structural change occurred in II.ABS.2 from 1184 to 1400°C except for additional grain growth. There was approximately a 45% increase in line intensity, $d_{h,k,l} = 3.37$, for this temperature interval.

Identification of the crystalline structure(s) present in the ABS powders was attempted with this sample because of its sharper diffraction pattern. Figure 28(b) shows the same pattern as in 28(a) along with stick patterns of three candidate compounds that may be present. A listing of diffraction lines for the three structures and those of II.ABS.2 are given in Table 13. Agreement of diffraction lines in the ABS powder with the suspected compounds is indicated in this table. Mullite and aluminum borate are equilibrium compounds as indicated in the phase diagram of Figure 1. Many of the diffraction lines of the candidates have the same or nearly the same d -spacing. Line superposition and the fact that agreement is obtained for some d values but not for all the corresponding intensities, as in the three major lines previously discussed, means that, at best, only tentative identification is possible.

Figure 28. (a) XRD Pattern of ILABS.2 after 1 h at 1400°C Showing Intensity and d-Spacing of Diffraction Lines. (b) Same as (a) But Showing Stick-Pattern of Three Compounds Identified in the ABS Powders.

Clearly, the ABS powders are multiphasic above 1000 °C with differing amounts of each candidate present in a glass matrix.

Phase separation in aluminosilicate systems have been reported.^{51,52} The absence of some lines, e.g., $d_{h,k,l} = 2.21$ of mullite, and the lack of agreement in intensities also suggests that these phases are metastable. The amount of each phase present was not determined and considered beyond the scope of this study. No free alumina was detected in any of the powders.

As a part of structural characterization with XRD, crystallite size analysis was performed as discussed in Section 4.2. The results are shown in Table 14. The crystallites are quite small and their size is close to that reported as the ultimate particle size in alkoxide gels (see Section 2.1). Crystallite growth occurs with an increase in temperature. An average of 52% growth was observed for Method I powders and 32% for Method II powders. The statistical significance of the recorded values is not known.

The IR spectra of I.ABS.1 and II.ABS.2 for various temperatures are shown in Figures 29(a) and (b) respectively. There were only slight differences in the spectra of the different methods and these two examples best illustrate those differences. Table 15 lists the absorption bands, designated by the bold letters **a- h** in Figure 29, their frequencies and assignments.^{44,51,52,53}

There were several interesting features in the IR spectra of ABS powders. The intensity of the absorption band at **a** gradually diminished with increasing temperature and shifted to a lower frequency. The band at **b** decreased with increasing temperature. Neither of these bands appeared in the powders at 845 °C. The weak

Table 13. Major Diffraction Lines of Crystalline Phases of ABS Powder, Mullite, Aluminum Oxide Borate, and Aluminum Borate

<u>ABS Powder</u>		<u>$3Al_2O_3 \cdot 2SiO_2$</u>		<u>$5Al_2O_3 \cdot B_2O_3$</u>		<u>$9Al_2O_3 \cdot 2B_2O_3$</u>	
$d_{h,k,l}$	I_{rel}	$d_{h,k,l}$	I_{rel}	$d_{h,k,l}$	I_{rel}	$d_{h,k,l}$	I_{rel}
		5.39	50				
5.37	80			5.38	100	5.37	100
						5.30	18
				4.37	30	4.36	50
3.42	42	3.43	95			3.75	16
3.39	46	3.39	100				
3.37	100			3.38	70	3.37	40
2.84	19						
2.69	63	2.69	40	2.69	80	2.68	40
2.51	44			2.51	20	2.50	25
2.42	18						
		2.29	20				
2.27	27						
		2.21	60				
2.18	75			2.19	20	2.18	25
2.12	47	2.12	25	2.12	25	2.12	20
1.83	23			1.84	15		
1.69	24			1.69	20		
1.59	21	1.60	20				
1.52	62	1.52	35	1.51	30	1.51	19

Note. Diffraction lines were considered to be in agreement if the $d_{h,k,l}$ were within ± 0.01 of each other.

Table 14. Crystallite Size Variation with Temperature in Synthesized ABS Powders

Temperature, °C	Crystallite Size, Å			
	I.ABS.1	I.ABS.2	II.ABS.1	II.ABS.2
864	90	99	99	
1049	110	108	119	108
1184	137	150	129	145

Note. Values determined after 1 hour at the indicated temperature. Determinations based on the Scherrer technique with 0.94 as the calibration constant and using $26.402^\circ 2\theta$.

Figure 20. Infrared Spectra of Synthesized ABS Powders after Firing at 1 h at the Indicated Temperature; (a) AIP Based Powder, (b) ASB Based Powder.

Table 15. Infrared Absorption Bands Observed in ABS Powders and Their Assignments

IR Absorption ^a Frequency, cm ⁻¹	Letter Designation	Functional Group
3480	a	<i>H₂O, OH</i>
1650	b	<i>H₂O</i>
1415	c	<i>B – O – Si</i> Stretch
1290	d	<i>B – O – B</i> Stretch
880	e	<i>Al – O – B^b</i>
1050	f	<i>Al – O – Si</i> Stretch
1100	g	<i>Si – O – Si</i> Stretch
690	h	<i>B – O – Si</i> Bend

^aAbsorption band frequency after 1 hour at 522°C.

^bNot confirmed.

absorption band at **a** is still present in the IR spectra at temperatures greater than 690°C, but it was also present in the IR spectrum of the blank *KBr* disc and therefore not related to the structure of the ABS powder. At 864°C these bands reappear in ASB based material and once again are absent at higher temperatures. No absorption bands attributable to organic groups were observed in the spectra.

The strongest absorption band in the IR spectra was observed around 1100 cm^{-1} . This broad band encompassed two absorptions **g** and **f**. The absorption band **g** at 1100 cm^{-1} was assigned to the stretching vibrations of *Si - O - Si* in amorphous *SiO₂*.^{46,53} The absorption band labeled **f** at 1050 cm^{-1} , slightly less than that of **g**, was assigned to the stretching vibrations of *Al - O - Si*.^{46,53} As the temperature increased, the former shifted to higher wavenumbers and the intensity of the bands strengthened and separated. Between 1049 and 1184°C a shoulder was evident from the gradual resolving of the absorption due to *Al - O - Si*. The absorption band at **d** in the IR spectra was assigned to *B - O - B* and it also strengthened and shifted to higher wavenumbers with increasing temperature. In contrast, the absorption band at 1415 cm^{-1} , labeled **b**, decreased in intensity and shifted to lower wavenumbers with increasing temperature. This band remained only as a shoulder at 864°C and did not appear above that temperature in ASB based powders. The band was not present at all above 845°C in AIP based powders.

The IR absorption band labeled **e** around 880 cm^{-1} was temporarily assigned to *Al - O - B*. As temperature increased, this band sharpened and shifted to higher wavenumbers. At still higher temperatures, it was observed that the absorption band actually consisted of several absorptions. These absorptions are indicated by the shoulders in the broader main band of 880 cm^{-1} . The absorption band around

690 cm^{-1} , designated **h**, decreased in intensity and shifted to lower frequencies with increasing temperature, from 522 to 845 °C. Xiaoming and Yuguang⁴⁶ assigned this absorption band to $\text{Si} - \text{O} - \text{B}$. In this temperature range **h** also became more distinct because of the shift of the adjacent absorption **e** to higher wavenumbers. Between 845 and 864 °C this band seemed to blend into a lower frequency shoulder. At temperatures greater than 864 °C, the higher frequency region of the band at **h** evolved into a sharp absorption at 740 cm^{-1} . This IR absorption is characteristic of $\text{B} - \text{O} - \text{B}$.⁴⁶ Absorptions in the IR spectra due to metal hydroxyls could not be located as they would be buried in the large band at **a**.

Microstructural changes in the ABS PCs that occurred with increasing temperature were additionally characterized with SEM. The fractured surfaces of a green PC pressed from powder based on AIP are shown in Figures 30(a) and (c). Another PC from the same powder is shown in Figures 30(b) and (d) after exposure to 1184 °C for 1 hour. Likewise, green PCs prepared from ASB based powder are shown in Figures 31(a) and (c) while Figures 31(b) and (d) show an ASB based PC after 1 hour at 1184 °C. In Figures 30 and 31 (b), secondary cracks are evident from cleavage of the PC. None appear in the corresponding green PCs. The cracks are reflective of the increased brittleness which occurs on firing of the PCs. The particulate nature of both AIP and ASB based PCs is clearly apparent from these micrographs. Particle growth and coalescence is also evident by comparison of the higher magnification micrographs before and after firing. Particle growth appears from the micrographs to be of similar magnitude in both AIP and ASB powders. The particulates are submicron before and after firing. Regions in Figures 30(a) and 31(a) that appear smooth and featureless, are shown in Figures 30(c) and 31(c) to consist of a dense fine particulate. There are more of these regions in AIP based

PCs than in the ASB based PCs.

Several of the PCs fired at 1184°C for 1 hour were etched in P-etch for 30 seconds in an effort to reveal their bulk microstructure. The results are shown in Figures 32 and 33. A inhomogeneous PC morphology was observed for both AIP and ASB based methods. An AIP based PC is shown in Figures 32(a)-(d) and an ASB based PC in Figures 33(a)-(d). The features in the AIP based PC are much smaller and obviously different from those in the ASB based PC. Figure 32(a) and (b) show overlapping fields of view at the same magnification in the AIP based PC. Two distinct structures were observed in this PC. Highly porous regions, one of which is enclosed within the highlighted box of Figure 32(a), and more dense regions, one indicated within a similar box in Figure 32(b) are evident. Figures 32(c) and (d) are higher magnifications of the boxed areas in Figures 32(a) and (b) respectively. The porous region of Figure 32(a) and (c) consists of rod-like structures extending three dimensionally throughout the region. The rods have sintered together to form larger rods and locally sintered plates. Microporosity existed throughout this region. The densified regions of Figure 32(b) are all highly irregular in shape with well defined boundaries. From Figure 32(d) the apparently featureless surface of one such region is seen to consist of extremely small particles. Larger particulate debris can be seen on its surface. The main body of this region contains little microporosity. Effects of sintering can be observed in certain areas of this region.

The ASB based PC of Figures 33(a)-(d) show two different microstructures as well. A large highly dense region and a less dense region with regularly shaped formations are present in the overlapping fields of view in Figures 33(a) and (b). The dense region of Figure 33(a), a portion of which is highlighted by a box, is

Figure 30. SEM Micrographs of Fractured Surface of AIP Based Powder Compacts; (a) As Pressed; (b) After 1 h at 1184 °C; (c) 10X Magnification of Boxed Area in (a); (d) 10X Magnification of Boxed Area in (b).

Figure 31. SEM Micrographs of Fractured Surface of ASB Based Powder Compacts; (a) As Pressed; (b) After 1 h at 1184 °C; (c) 10X Magnification of Boxed Area in (a); (d) 10X Magnification of Boxed Area in (b).

seen to consist of sintered material with microporosity as shown in Figure 33(c). Hexagonal and layered structures are evident in Figure 33(d) with no indication of sintering. This region is very porous.

6.4 Powder Compact Properties

Apparent density, bulk density, and microhardness measurements were taken as a function of temperature to gauge physical properties of the ABS PCs. Bulk density, ρ_b —a measure of the relative amounts of solid phase, isolated pores and continuous pores (i.e., open pores)—of the PCs initially decreased slightly with increasing temperature as shown in Figure 34*. Brinker *et al.*,⁵⁶ have reported similar behavior but also observed a decrease in apparent density accompanying the decrease in bulk density. They attributed this to desorption of physically adsorbed water and solvents from the gel and pyrolysis of unhydrolyzed alkoxy groups. This would result in an apparent increase in surface area. No such decrease was observed in the apparent density of ABS PCs.

Above 690°C a sharp inflection occurred in the bulk density. This was accompanied by a slight increase in the slope of the curve for apparent density. This is indicative of rapid bulk and skeletal densification, assuming apparent density is reflective of the skeletal structure. The maximum bulk density was achieved at 864°C. Above this temperature the bulk density remained approximately constant. The apparent density continued to increase with increasing temperature from 690 - 1184°C. Only a slight decrease in the slope of apparent density occurred at 864°C corresponding to the rapid change in bulk density observed at this temperature.

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*Similar behavior in the bulk density of all PCs was observed and so only the mean bulk density is presented. The same applied to apparent density.

Figure 32. SEM Micrographs of an Etched AIP Based Powder Compact Showing Varied Microstructure; (a) and (b) Overlapped Fields of View of Equal Magnification; (c) and (d) 5X Magnification of Boxed Areas in (a) and (b) Respectively.

Figure 33. SEM Micrographs of an Etched ASB Based Powder Compact Showing Varied Microstructure; (a) and (b) Overlapped Fields of View of Equal Magnification; (c) 10X Magnification of Boxed Area in (a); (d) 5X Magnification of Boxed Area in (b).

Figure 34. Variation in Mean Apparent Density, ρ_a , and Mean Bulk Density, ρ_b , of ABS Powder Compacts with Temperature. Densities Measured after 1 h at the Indicated Temperature.

The results for apparent density are difficult to interpret because of the large determinate error in the apparent volume readings. A maximum mean bulk density of 1.8 g/cm^3 and a mean apparent density of approximately 2.9 g/cm^3 were measured. The PCs increased in bulk density by 80% and in apparent density by approximately 32%. Thus, PC densification was characterized by a large decrease in volume with a gradual elimination of porosity.

Vickers microhardness testing was conducted on II.ABS.1 PCs fired at different temperatures. As shown in Figure 35 the hardness increased with increasing temperature up to 864°C . Above this temperature the hardness value drops to that measured at 845°C . There was only a slight additional increase in hardness at higher temperatures. These results parallel the behavior in bulk density as a function of temperature.

Figure 35. Vickers Microhardness as a Function of Temperature for II.ABS.1 Powder Compacts.

7 Synthesis and Densification; Interrelationships

7.1 Activation Energies

The ordinate intercept of the log-log plots in Figures 45-49(b) and 54-57(b) of Appendix C is the logarithm of the material constant K . It follows from Eq. (7) that K is dependent on the temperature and nature of the material. Apparent activation energies of the different regions of densification were calculated by making the assumption that K obeyed an Arrhenius relationship; that is

$$K = K_o \exp(-Q/RT) \quad (18)$$

where K_o is a constant, Q the activation energy, and T the absolute temperature. A $\log K$ vs. $1/T$ plot is a straight line with $-0.43Q/R$ slope. However, to apply Eq. (18) the shrinkage coefficient n in Eq. (7) must be constant. Within experimental error, this is the case for Regions C and E. Arrhenius plots for each method of synthesis in Regions C and E are shown in Figures 36 and 37 respectively. Insufficient data was collected for II.ABS.1 in Region E and hence is not included in Figure 37.

To be discussed in greater detail in Section 7.2.2 is the behavior of the curves in Region D for all methods of synthesis. This region of densification was attributed to viscous sintering for which n in Eq. (7) equals one. The decreasing shrinkage rate that is observed in Figures 50-53 of Appendix C prevented the application of Eq. (17). However, since sintering occurred by viscous flow, CHR experiments were applied using Frenkel's model (see Section 3.4). Assuming that $\eta = A \exp(Q/RT)$

Figure 36. Activation Energy Plot for Region C.

Figure 37. Activation Energy Plot for Region E.

and expressing the heating rate by $\nu = dT/dt$, Eq. (6) becomes

$$\frac{d}{dt} \left(\frac{\Delta L}{L_o} \right) = \left(\frac{\gamma}{2rA\nu} \right) \exp(-Q/RT) \quad (19)$$

Assuming γ and the frequency factor A are independent of temperature, this equation can be integrated and becomes^{7,57}

$$\frac{\Delta L}{L_o} = \left(\frac{\gamma RT^2}{2rA\nu Q} \right) \exp(-Q/RT) \quad (20)$$

Thus a plot of $\log(\Delta L/L_o \cdot 1/T^2)$ vs. $1/T$ will be linear and have a slope of $-0.43Q/R$. Such a plot was constructed for the different powders in Region D. The results are combined in the plot of Figure 38. The absolute shrinkage data for this plot were collected directly from the ramp portion of TDA runs in Region E, from 800°C to the observed transformation temperature T_t . Tables 69-76 in Appendix D contain the CHR shrinkage data for these experiments. These tables are set up in a manner similar to those of Appendix B. The caption of these tables includes the crystalline transformation temperature which demarcates Regions D and E.

Apparent activation energies calculated from the slopes of the plots in Figures 36-38 are given in Table 16. Values ranging from 29 – 91 kJ/mol were calculated for Region C. These values are in close agreement with those previously reported in other gel systems. Prassas⁷ calculated activation energies from 21 to 42 kJ/mol for a silica aerogel in the temperature range 500 – 850°C. These values are of the same order of magnitude as those for the reaction

Brinker *et al.*,⁵⁶ found that the heat of formation in $M - O - M$ bonds resulting from dehydration is very sensitive to the $M - O - M$ bond angle ϕ . As the bond

Figure 38. Activation Energy Plot for Region D.

Table 16. Apparent Activation Energies for Major Regions of Shrinkage in Synthesized ABS Powders

Method	Activation Energy, kJ/mol		
	Region C ^a	Region D ^b	Region E ^a
I.ABS.1			
<u>M</u>	29.2	489	232
<u>SD</u>	0.5	25	182
I.ABS.2			
<u>M</u>	55	414	254
<u>SD</u>	9	17	11
II.ABS.1			
<u>M</u>	91	410	
<u>SD</u>	15	13	
II.ABS.2			
<u>M</u>	54	448	298
<u>SD</u>	18	8	82

^an = 2. Values calculated from $\log K$ vs. $1/T$, °K⁻¹.

^bn = 18. Values calculated from $\log(\Delta L/L_o \cdot 1/T^2)$ vs. $1/T$, °K⁻¹.

angle decreases and the structure becomes more strained the heat of formation increases. For example, $\phi = 150^\circ$ in vitreous silica and the reaction of Eq. (21) has a heat of formation of -17 kJ/mol. However, if ϕ is reduced to 87° , which is known for edge-sharing tetrahedra in the SiO_2 structural form of silica (2-fold rings) the energy increases to +209 kJ/mol. Brinker obtained a value of +184.3 kJ/mol for dehydration above $525^\circ C$ in an acid-catalyzed borosilicate monolithic gel.

The apparent activation energies of Region C agreed closely for ASB based gels and differed by a factor of three for AIP based gels. In spite of the low sampling number for this region, the difference in these values for AIP based methods and the agreement with ASB based methods suggest that different polymeric structures were present in the former and also between AIP and ASB based methods. There is about 29 kJ/mol difference between AIP and ASB based methods.

The different activation energies calculated in Region C for AIP based powders extended to Region D. A difference of 79 kJ/mol was calculated for I.ABS.1 and II.ABS.1 in Region D. Significant differences existed among the other methods as well except between I.ABS.2 and II.ABS.1 which had the same value within experimental error. Though some of the mentioned differences were slight, they were considered significant in view of the large number of observations made. The activation energies listed in Table 16 for viscous flow are low, but not unusually so, for gel-derived materials. For SiO_2 aerogels Prassas' calculated a value of 368 kJ/mol from CHR dilatometry. Scherer³¹ reported activation energies ranging from 125 to 510 kJ/mol for viscous flow of an acid-catalyzed borosilicate gel. This wide range was found to be linearly related to the OH^- content of the gel. Differing values of activation energies are reported for the viscous flow of fused silica. These

differences are also due to residual hydroxyl content. Prassas gave values of 502 – 711 kJ/mol corresponding to hydroxyl concentrations of 1300 – 3 ppm respectively. Orgaz-Orgaz³³ reported 710 kJ/mol, comparable to the value accepted for pure fused silica, for base-catalyzed silica gels. Activation energies for viscous flow are also dependent on composition. Orgaz-Orgaz reported activation energies of viscous flow for sintered colloidal gel-derived glasses of 598 kJ/mol for pure SiO_2 and 460 kJ/mol for silica with three percent by weight B_2O_3 added.

Apparent activation energies for Region E are midway between those of Regions C and D. There was considerable error in this region due to erratic shrinkage and scatter of data. No differences could be assigned to the activation energies of this region except for II.ABS.1 which consistently exhibited virtually no shrinkage whatsoever except at 1184°C. The activation energies calculated in this range are considerably less than the 593 – 627 kJ/mol reported for solid state diffusion sintering.⁵⁷ Therefore the mechanism(s) of densification in Region E were due to several competing mechanisms.

7.2 Densification Mechanisms and Processes

The mean coefficients of shrinkage for Regions C and E for different methods of synthesis are listed in Table 11. As explained in Section 6.1, all methods of synthesis have been assigned a value of one as the shrinkage coefficient for Region D. Region B had a coefficient approximately equal to the mean of Region C for II.ABS.2 and similar values are expected for the other methods in this region. The processes responsible for the reported values of n and their correlation with the method of synthesis will be discussed in the following sections.

7.2.1 Evaluation of Regions B and C

The mean shrinkage values reported for Region C in Table 11 show that a common mechanism exists for all methods with an overall mean value of $n = 0.74$. The mechanism(s) operative in Region B were still operative in Region C as the difference in the means of the two regions is insignificant*. Figures 46-49 in Appendix C show the expected trend of increasing shrinkage with increasing temperature. Only about 0.1% shrinkage was observed for most PCs in the temperature range 522 – 567°C. The shrinkage more than tripled over the temperature range 567 – 690°C with between 0.3 and 0.4% recorded after 1 hour at 690°C. Observed shrinkage in Region B (see Figure 45) shows that more shrinkage occurred at 240°C than at 287°C, about 0.25% after 1 hour at the former.

Observed weight loss data in Region B for the ABS powders and PCs (see Figures 19 and 24) showed a rapid decrease between 25 and 300°C. This weight loss is concurrent with little change in apparent density and only a slight decrease in bulk density. IR spectra show a decreasing absorption due to water and hydroxyls and their removal in this temperature range. An explanation to account for this behavior is proposed as follows. A great deal of atmospheric moisture was physically adsorbed onto the highly reactive surface of the powders after pre-calcination. The vaporization of this water accounts for the initial high weight loss observed in Figure 24. The diffusion of water from the PC was responsible for the higher densification at the lower temperature of Region B. As this water is gradually depleted the dominant densification mechanism changes to the condensation reactions

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*No data was obtained from Region A. This region was particularly unresponsive to both shrinkage and weight loss. From observations made in Regions B and C it was gathered that capillary contraction occurred in this region. However, this would have occurred during the pre-calcination stage of processing.

already in progress. The transition from Region B to Region C is subtle and the processes described here from the isothermal shrinkage data and characterization are not readily apparent from the CHR curves of Figure 22. This scenario also explains why no initial decrease in apparent density was observed in the temperature range corresponding to the decrease in bulk density (see the results presented in Section 6.4). The skeletal structure had already been largely developed during the pre-calcination stage of processing as evidenced by the 28% increase in apparent density. Therefore, additional firing of the PCs at the temperatures of Region B had little effect on the apparent density. The changes in apparent density do not come about until sufficient energy is available to drive additional condensation reactions. The required energies are listed in Table 16. This scenario also explains why the greatest compositional deviation occurred at 522°C with the PCs (see Figure 25) after the powders have been pre-calcined.

The densification of the PCs after the vaporization of water was nearly constant up to 624°C. The value of 0.74 for the shrinkage coefficient in Region C is too large for the densification mechanism to be due to condensation reactions alone. It is well established that condensation reactions are diffusion-controlled and hence $n = 0.5$.³³ Therefore, densification in this region is due to at least one other mechanism acting in concert with condensation. The continued weight loss throughout this region (see Figures 19 and 24) is due to the elimination of condensation reaction by-products. Another contributing mechanism could be structural relaxation. Structural relaxation is achieved by the diffusive motions of atoms, without the expulsion of water or other species. It occurs as the gel structure seeks a configuration more characteristic of corresponding metastable liquid. Scherer³¹ reported structural relaxation in a borosilicate gel in the temperature interval 400 - 525°C.

If the gels have different structures at the onset then the contribution of structural relaxation will differ, the shrinkage coefficients will differ, and the activation energies will differ. A mechanism which assists the structure in seeking a more stable state will increase the amount of densification and therefore increase the shrinkage coefficient and decrease the activation energy. This is what is observed in Region C and in the values of n for Region B. Structural relaxation results in an increase in the angle ϕ which reduces the strain in the local polymeric network. Hence, the observed variations in activation energies for Region C were most likely due to different magnitudes of structural relaxation which in turn was dependent on the initial gel structure. Structural relaxation would further densify the skeletal structure resulting in an increase in apparent density. This was observed (see Figure 34). The slight decrease in bulk density in these regions shows that the weight loss was slightly greater than the volume contraction.

7.2.2 Evaluation of Region D

Viscous flow in synthesized ABS powders occurred in the narrow temperature range of $800 - T_i$. Region D was the region where the most shrinkage and greatest densification occurred. Figures 50-53 in Appendix C show that densification in this region was very sensitive to temperature. Generally, greater shrinkage occurred at 845°C than at higher temperatures in this region. This was more closely obeyed by Method II powders than by Method I. The slopes of the log-log plots in this region were equal to unity for short periods of time and then decreased as time increased. The rate of change in the slope was greater at higher temperatures than at lower temperatures. This is particularly evident in Figure 50(a) which includes a separate run at 875°C . Only 2% shrinkage was observed at this temperature and all of this

shrinkage occurred within the first five minutes of the run.

Figure 34 shows that a rapid increase in bulk density occurred from 690 to 845 °C while the apparent density increased more gradually. Both Figures 19 and 24 show that little weight loss occurred in Region D. The inflection of the lower curve in Figure 34 was due to a sharp decrease in the bulk volume with little loss in weight. Compared to Region C, the weight loss in Region D was very little, so condensation reactions apparently did not contribute substantially to this shrinkage. A rapid reduction in the bulk volume due to the collapse of open pores could account for these changes in properties. These observations are characteristic of viscous flow. The effects of viscous flow are apparent in the microstructure of the PCs after etching (Figures 32 & 33).

The deviation of Region D shrinkage data from ideal viscous sintering, as modeled by Frenkel, appeared to be due to a rising viscosity. Similar behavior in the viscous sintering of alkoxide-derived gels has been reported.^{31,33} The viscosity of glass is dependent on the hydroxyl content and temperature. The viscosity decreases with increasing $[OH^-]$. Brinker *et al.*,⁵⁶ reported that the densification of gels under standard laboratory conditions, $\approx 50\%$ RH, is known to result in glasses with high hydroxyl contents, e.g., > 20 times that of glass. Retained water and hydroxyls in the ABS gels up to 690 °C was evident from the IR spectra of Figures 29(a) and (b). It has been shown that increasing water content depresses T_g .⁵⁹ Figure 20 shows a change in slope of the DTA thermogram for all methods at about 835 °C which was indirectly attributed to T_g . Because similar behavior was observed in the DTA, it was assumed that the $[OH^-]$ was approximately the same for all powders. The relatively high water and hydroxyl content that was retained upon

entry into Region D reduced the viscosity at the lower temperature, permitting a higher rate of initial shrinkage. As sintering proceeded, the $[OH^-]$ decreased and dampened the shrinkage rate.

Scherer³¹ pointed out that structural relaxation as well as the condensation of hydroxyls can occur during viscous sintering and have an important influence on the rate of shrinkage. His estimates on a borosilicate alkoxide gel at 525°C suggest that structural relaxation may cause a significant fraction of the viscosity increase, but that changing hydroxyl content is probably the dominant factor. Relaxation will cause smaller changes in shrinkage during isothermal holds at higher temperatures as relaxation will occur during heating to the hold temperature. However, hydroxyl loss will also be less at higher temperatures as it is loss during the ramp as well. Hence, both mechanisms may be active and distinguishing between them is difficult.

Because structural relaxation and condensation mechanisms were active in Region C prior to the onset of viscous flow, it was concluded that both mechanisms were active in Region D. The more salient features of data accumulated from this region suggest that residual $[OH^-]$ was more influential than structural relaxation. It was assumed that the $[OH^-]$ was about the same for all powders as mentioned previously. It was also noted that the smaller particle size of AIP based powders did not significantly increase the amount of shrinkage in Region D between methods as predicted by Eq. (6). The previous observation of large water/hydroxyl content from the IR spectra at 690°C and its virtual elimination at 845°C along with the consistently higher rates of initial shrinkage at the higher temperatures of Region D support this reasoning. The curves at 845°C follow Frenkel's model for a longer period of time than do those at higher temperatures. The viscosity increased slowly

with the gradual elimination of hydroxyls and greater shrinkage occurred. At higher temperatures the hydroxyl content was less than that at lower temperatures and actually was a glass of a small but significantly different composition. This composition initially sintered at a higher rate because there was an initial shrinkage component leftover from the ramp, through the majority of Region D up to the hold temperature. Now, there were less hydroxyls in this high temperature composition and so the viscosity increased more rapidly. This resulted in less shrinkage than that at the lower temperature. The IR spectrum for ASB based powders, shows that this process resulted in the trapping of some water and hydroxyl within their structure. This suggests that the ASB structure is initially more dense than the AIP, also apparent from the agglomerate morphology of Figure 21, but unfortunately not detected by density measurements. At 845 °C the ASB structure sintered at a low enough rate to allow water vapor to escape, whereas at 864 °C, the higher rate of sintering sealed in the vapor.

There is one other pertinent feature in Region D from the IR spectra. This is the gradual elimination of the absorption band at 1415 cm^{-1} assigned to $Si-O-B$. This adsorption rapidly decreases in the short temperature interval of 845-864 °C. It is proposed that what is being observed here is bond cleavage in the $Si-O-B$ network during viscous sintering and the dissolution of Si^{+4} and B^{+3} into the glass structure. The result is the formation of a borosilicate phase-separated glass. Therefore, viscous flow involved the breakage of $Si-O-B$ bonds.

7.2.3 Evaluation of Region E

The overall mean value of n for Region E is 0.73 and nearly equal to that of Region C. The apparent activation energy, however, is considerably higher. These data alone indicate that different mechanism(s) are responsible for high temperature shrinkage than those of the lower region. The transition from Region D to Region E was marked by an abrupt change in shrinkage for CHR TDA (see Figure 22). XRD showed that an ordered structure was forming at the temperatures corresponding to this transition. Analysis of CHR data revealed within $\pm 2^\circ\text{C}$ the temperature of this transformation. It was found that Method I powders had a average $T_t = 888^\circ\text{C}$ while Method II powders had an average $T_t = 895^\circ\text{C}$.

An examination of Figures 54-57 in Appendix C show irregular behavior for the ABS PCs in Region E. For ASB based powders and I.ABS.1 similar values of shrinkage occurred at 950, 1049, and 1184°C. These values were about equal to those of Region C. Oddly enough, the greatest shrinkage for all powders occurred at 1146°C rather than at 1184°C. Shrinkage at this temperature was only slightly greater for I.ABS.1, nonexistent for II.ABS.1 and dramatic for ASB based powders. Observed changes in structure and properties provided little support for these shrinkage phenomena. Apparent density continued to increase showing additional skeletal densification but at a slower rate than that observed for Region D. Bulk density changed little and IR spectroscopy indicated only a continued strengthening of bonds within the now crystallized structure. The single observation which may have had some correlation with the observed densification behavior was the increase in weight loss at the higher temperatures of this region. This increase is not large relative to the total observed. Those mechanisms discussed previously

cannot account for the observations made in Region E and so it was believed that this behavior was related to the increased rate of weight loss.

The differences among the methods in this region were due to the remnants of structural differences leftover from the earlier densification. The majority of change in the way the powders densified in Region E was due to the different alumina precursors and to a lesser extent on Methods I and II. It is proposed that the various structures bond boron in the polymer differently. Eventually, the type and extent of oxygen-boron-oxygen-metal linkages will determine the amount of boria that enters into the phase-separated glass. Hence, the chemical potential of boria is not the same for all powders. The result is a variable vapor pressure of boria in the different powders which causes one to release the boria more readily than another. The vaporization was greater with ASB based powders than AIP based and subsequently greater shrinkage was observed in the temperature range where vaporization occurred. It is thought that the boria vapor acted as an internal flux enhancing the rate of densification. Speculation as to the narrow temperature range was made on the basis that most of the boria was tied up in the crystalline borate compounds, so that only free boria was released from the amorphous phase.

From Tables 52-67 of Appendix B, it can be seen that the shrinkage coefficients are lowest at 1146 °C. Zheng¹⁴ showed that the vaporization of boria is diffusion-controlled and hence if the shrinkage mechanism was due solely to the vaporization of boria n would equal 0.5. The micrographs of Figures 30(a) -(d) as well as the results of crystallite size determination showed that grain growth occurred in this region. The activation energies are too small to be due to grain growth alone. The shrinkage coefficients are too large to be due to solid state diffusion ($0.3 < n < 0.5$).

Therefore, densification in Region E is due to several concurrent processes, the most striking of which is a boria fluxed densification. Powder compacts from II.ABS.1 powders were static in Region E except for minimal shrinkage at 1184°C.

7.3 Synthesis

The effects that the different methods of synthesis had on the densification behavior have been discussed. All powders, regardless of the method of synthesis, densify by similar mechanisms. The driving force and amount of densification differs based on the method of synthesis. This section will address how these differences could have come about from the different methods of synthesis.

To what extent the reactions in Tables 2 and 3 were followed is not known. However, the extent to which they were followed was manifested in the structure and properties of the corresponding gels and powders. These were measurable and a qualitative extrapolation can be made as to the origin of the observed behavior.

The opacity that changed with thermal cycling of the AIP sol was probably due to a change in particle size of the aluminum alkoxide. Aluminum isopropoxide was reported to be tetrameric in solution at room temperature and trimeric at higher temperatures (see Section 2.1 and Figure 3). The observed optical properties of the AIP sol are probably due to this transformation. If the trimeric species is retained after cooling to room temperature then the alumina sol would have been more reactive, due to the change in coordination, than had it reverted. Based on the results of Yoldas[†] and the well known tendency of Al^{+3} to seek a higher

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[†]Yoldas[†] showed that both aluminum isopropoxide and secbutoxide when hydrolyzed in excess hot water form the monohydroxide, $AlO(OH)$, which showed no significant conversion to the trihydroxide, $Al(OH)_3$, when the temperature was reduced to room temperature.⁶⁰

coordination number,^{16,19} it is believed that this sol was primarily composed of trimeric AIP prior to the addition of the other alkoxides. Hence, structure-forming reactions, i.e, coordination (see Figure 4) occurred in the early stages of synthesis of AIP based gels.

According to the proposed reaction mechanisms, 0.56 moles of water were required to fully hydrolyze the alkoxides. The values given in Table 8 show that gelation occurred before this amount of water was added. Therefore, extensive crosslinking of the polymer chains must have occurred to result in this premature gelling. This would have given the gel a low oxide content. The wet gel, however, was not given the opportunity to retain this structure as excess water was added. The effect of the excess water on the methods of synthesis was apparent soon after completion of the syntheses.

ASB based gels tended to form a precipitate on standing while the AIP based gel remained homogeneous. This indicated that the ASB based gels had a larger hydroxide content or were less polymerized than the corresponding AIP gels. Chemical developments such as these are a reflection of the different reactivity towards hydrolysis of AIP and ASB. As the gels dried and concentrated, the particulate slurry may have separated, though this was not observed, forming laminar structures in the agglomerates. Such features are visible in the ASB agglomerate of Figure 21(b). It is believed that similar fragments remained intact throughout processing and are responsible for the dense irregular regions seen in the micrograph of Figure 32(a) and (b).

Structural developments which occurred during gelation became quite evident

in the resultant agglomerate size and morphology. The particulate nature of the AIP agglomerate is apparent in Figure 21(b). Also apparent in this figure are rod-like formations. The AIP powders are amorphous after exposure to the conditions of pre-calcination. Hence, these formations could be a reflection of directional polymer growth. The rods indicate that linear polymeric chains were formed during synthesis. Similar texture did not exist in the ABS based powder but rather a featureless agglomerate was observed (see Figure 21(d)). Hence, polycondensation reactions in ASB gels were not as directional as those of its counterpart nor as extensive, i.e., a lower molecular weight polymer was formed. The smaller mean particle size of AIP based powders could be a measure of its particulate morphology and/or the friable nature of the agglomerates. The particle characteristics became influential in powder compaction (see Figure 17). The smaller diameter AIP based powders showed a higher tap density than those of ASB and then converged with increased pressure. However, as discussed in the previous section, the particle size effects were not evident in subsequent densification behavior. The latter behavior was a function of the ultimate particle size of the gel.

None of the methods showed any significant compositional variations in the analyses performed. ASB based powders were purer than AIP powders due to the initial purity of the alumina precursor. No correlation in the densification behavior with impurity levels was observed. The final composition exhibited a 2% by weight deviation in silica and boria. These deviations were due to the volatilization of unpolymerized precursors during synthesis and drying. The large depletion of boria reported by Xiaoming and Yuguang⁴⁶ for a $SiO_2/B_2O_3 = 2.04$ in an ABS system of high silica content was not observed in this system. The increase in oxide content of the powders was proportional to the abundance of the individual oxide. Accordingly,

as no large concentration of hydroxyls were detected in IR or ESCA, this increase was primarily due to the loss of absorbed water.

Compositionally, the powders evolved in a similar fashion with temperature. The same did not quite apply to the structure. XRD and IR characterization showed subtle changes between methods. Although the IR spectra appeared similar at temperatures below T_g , the bonding was not very well developed at this point and the absorption bands are diffuse. There may be obscured absorptions in these bands which could be revealed by high resolution or other IR techniques. The gradual formation of an ordered structure occurred more quickly for Method I powders than those of Method II based on XRD and the recorded T_i . The crystalline phase(s) that formed were identical for all methods. Several compounds crystallized from the glassy ABS powders as shown in Figure 27(b). The diffraction lines at $d_{h,k,l} = 1.83$ and 1.69 are unique to $5Al_2O_3 - B_2O_3$. This compound is a metastable structure which contains the boroxyl, BO_3 , species in the unit cell $[Al_5(BO_3)O_8]$. The presence of this compound is undoubtedly reflective of the starting gel configuration. It is indicative of micro-inhomogenities in bridging networks that contain boron. Mullite forms from a solid state reaction in most aluminosilicates.^{51,53} A similar reaction was assumed to have occurred for aluminum borate. It and mullite have the same structure, orthorhombic, so both probably reacted to form a solid solution. Such a solid solution is also indicated on the phase diagram (see Figure 1). No free alumina was detected although the hexagonal structure in Figure 33(d) suggests its presence. Therefore, the presence of boria in the powders served to tie up the alumina in the observed phases and prevented its nucleation. The presence of boria did not prevent the crystallization of a pseudo-mullite structure. An additional reaction step beyond those given in Tables 2 and 3 to account for these observations

is given as follows.

The aluminum oxide borate structure is not given as a product in this reaction because it is a non-equilibrium compound.

Method I powders showed 20% more grain growth in the temperature range 864 – 1184°C than did Method II powders (see Table 14). Measurements of properties were insensitive to changes among the methods. Most fell within the error level of the measurement and could not be reported as significant.

Based on the single observation of the PC, II.ABS.2, taken to 1400°C for 1 hour, it appears that structural differences in these powders are retained at considerable temperatures. This sample showed the same structure as that observed at 1184°C for the same period of time. Only a small increase in intensity of the major diffraction lines were observed. Thus, the structure of the powder at 1184°C remained unaltered at the higher temperature. It has been shown that structural variations generated in the synthesis were retained beyond T_g and were influential at temperatures as high as 1184°C. Assuming that the lone observation is indicative of the other powders as well, then it appears that these same variations may exist at temperatures approaching 85% of the fusion temperature.

8 Summary and Conclusion

Aluminoborosilicate powders with the molar ratio 3:1:2 ($Al_2O_3 \cdot B_2O_3 \cdot SiO_2$) were prepared by the sol-gel route. A method of synthesis was developed to produce a gel with maximum oxide content and a three dimensional polymeric network. Four modifications of this method were developed to show the potential for structural control as revealed by differences in the densification behavior. Structural irregularities incorporated into the gels by these methods resulted in diverse densification behavior at low, intermediate and high temperatures.

Differences observed in the syntheses were attributed to the different hydrolysis reactivity of the alumina precursors. These differences extended to the powder particle size, morphology, compaction conditions, and thermochemical behavior. AIP based methods produced powders with mean particle diameters $5\mu m$ less than those of ASB based powders. AIP based methods resulted in regularly shaped particulate agglomerates while those based on ASB produced featureless, irregular shard-like agglomerates. Powder compaction behavior was reflective of these particle characteristics. Greater compact densities at lower compaction pressures were achieved with AIP based powders. Thermochemical analysis showed similar behavior among the different powders. A glass transition temperature of $\approx 835^\circ C$ was common to all powders. Crystallization occurred at $888 \pm 2^\circ C$ for Method I powders and at $895 \pm 2^\circ C$ for Method II powders. All powders crystallized in multiphasic structures consisting of phase separated glass and non-equilibrium forms of mullite, aluminum oxide borate and aluminum borate. An increase in weight loss was observed above $1100^\circ C$ and is believed to be due to the vaporization of boria. The exact temperature and magnitude of the increase again varied according to the method of

synthesis.

A 28% increase in the apparent density of all powders occurred during pre-calcination indicating extensive skeletal densification during this stage of processing. Hence the structure of the powders was well established before compaction. Subsequent densification resulted in a gradual increase in apparent density while the bulk density increased by almost 50% in a 100°C temperature range (800 – 900°C) corresponding to an abrupt increase in oxide content.

ASB based powders contained less trace impurities than AIP based powders and was attributed to the chemical purity of the alumina precursor. No correlation between these contaminants and the densification behavior was evident.

Five regions of densification were observed in the temperature range 25 – 1184°C for all powders. The regions were labeled A - E from low to high temperature. Region A (25 – 100°C) was probably due to capillary contraction. This was not observed directly because it occurred during the pre-calcination stage of processing. Hence, the observed Region A was inert with no shrinkage and no measurable weight loss. Region B (100 – 400°C) was due to the elimination of adsorbed water and condensation reactions. Region C (400 – 800°C) was due to condensation reactions and structural relaxation. ASB based methods had the same activation energy in this region while I.ABS.1 had the least. I.ABS.1 densified considerably more in this region than all other powders. II.ABS.1 had an activation energy roughly three times that of I.ABS.1. Region D (800 – T_f) was due to viscous sintering. Shrinkage due to viscous sintering decreased with increasing viscosity. The increase in viscosity was attributed primarily to a decrease in the $[OH^-]$ during sintering.

This too was dependent on the method of synthesis. Generally, greater shrinkage was observed at temperatures nearer to T_g than those near T_i . $Si - O - B$ bond disruption occurred in this region and indicated the formation of a phase-separated glass. Region E ($T_i - -1184^\circ\text{C}$) was due to several competing mechanisms. It is believed that grain growth and structural relaxation occurred and were assisted by boron fluxed densification. ASB based powders densified considerably more in this region than AIP based powders. II.ABS.1 exhibited no measurable shrinkage in this region except at 1184°C . Unlike densification in monolithic gels, these PCs exhibited a component of shrinkage due to structural relaxation over a much broader temperature range.

Physical property measurements were relatively insensitive to these changes among the different methods. Hardness measurements paralleled bulk density measurements with the greatest hardness appearing in Region D.

Because the greatest shrinkage due to viscous flow occurred near T_g , this temperature would prove optimal for processing glass from the synthesized powders. This is some 400°C less than that required for processing of a conventionally prepared powder of the same composition. Although some difficulty in obtaining the right composition was encountered due to the volatility of some precursors, this can easily be compensated for. The payoff in decreased impurity levels, reproducible compositions, and increased homogeneity are worth the investment for specialty applications.

No continuous correlation existed between the different methods and the densification behavior. Nonetheless, it is quite obvious that methods as simple as those

employed in this study can influence the polymeric structure of the gel. Apparent activation energies, the contribution of each shrinkage mechanism and the amount of shrinkage varied among the different methods. This behavior is reflective of the different polymeric networks established during synthesis and their domination of physical processes at elevated temperatures. Particularly striking in this respect is the contrast in shrinkage between the AIP based powders in Region E. Whatever structural configuration that existed in II.ABS.1 prevented its shrinkage in Region E. This information could be used in designing dimensionally stable ABS materials for high temperature applications. Likewise the enhanced densification of ASB based powders in Region E could be used to advantage as a sintering aide.

It appears that the ABS powders retain their structural variations at temperatures approaching the fusion point ($\approx 0.85 T_m$ for II.ABS.2). If this is indeed true, then a more carefully executed synthesis of any single composition could provide tailored materials with structures and properties otherwise unattainable in that composition and they may retain these properties at considerable temperatures. This shows the potential of sol-gel processing in relation to the "bottom-up" approach in engineering inorganic materials of the same composition but with varied high temperature behavior.

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APPENDIX A

TDA System; Principles, Calibration, and Operation

Dilatometry, or thermal dilatometric analysis (TDA), is an analytical technique which measures dimensional changes in a sample as a function of temperature. This appendix describes the principles, installation and operation of the Harrop Model TD-726 dilatometer with an IBM personal computer-based data acquisition system.

Figure 39 is a view of the dilatometer showing the location of major components.⁶¹ The sample is heated in a tube furnace mounted on a movable slide for easy positioning over the sample. The furnace incorporates a multi-shunt heating element which provides $\pm 1^\circ\text{C}/\text{in}$ temperature uniformity over a four inch hot zone thus minimizing sample temperature gradients. The sample is placed in a ceramic holder in contact with a freely suspended ceramic probe rod. A detailed illustration of the sample holder/probe rod assembly is shown in Figure 40. Holder, probe, and sample are inserted into the furnace whose temperature is precisely controlled by Harrop's microprocessor-based programmable controller. As the sample temperature changes and the sample expands or contracts, the change in length, ΔL , is transmitted by the probe rod to the core of a linear variable differential transducer (LVDT) located in the measurement head. Figure 41 is a photograph of the measurement head showing the location of the discussed components. The LVDT converts this displacement into a proportional voltage signal which is routed to the data acquisition system. Two type R thermocouples, *Pt - Pt/13%Rh*, are used to measure temperature T . One of the thermocouples rests on the alumina sleeve of the furnace with its output routed to the programmable controller. The second is placed within a few millimeters or in contact with the sample and its output is fed directly to the data acquisition system. The resultant continuous plot

of ΔL vs. T is the basic TDA curve.

Conversion, scaling and recording of the dilatometric data, i.e., ΔL and T , from the dilatometer was made with an IBM personal computer-based data acquisition system. The interface hardware and software were set up for thermal expansion measurements but were equally applicable for shrinkage measurements. The required interface hardware was purchased from MetraByte Corporation and consisted of two interconnected component boards. Metrabyte's EXP-16 expansion multiplexer/conditioner contains 16 fully differential inputs that can be multiplexed into a single input channel of an analog to digital (A/D) converter. The output of the LVDT and the sample thermocouple are connected to the EXP-16 via screw terminal connections and occupy only 2 of the 16 available channels. The EXP-16 has a dip-switch selectable gain for amplification of the input signals to a level sufficient for input into the A/D converter and also contains a temperature sensor to provide cold junction compensation for the sample thermocouple.

The A/D converter is contained within MetraByte's DAS-8 board. It is an 8 channel 12 bit high speed successive approximation A/D converter and timer/counter board with average conversion times of 25 microseconds. The DAS-8 plugs directly into one of the IBM PC's expansion slots with connection to the EXP-16 made via a standard 37 pin type "D" connector. IBM personal computer buss power (+5, +12, -12 VDC) is provided along with all other input/output (I/O) signals to the EXP-16 through the rear connector of the DAS-8. A diagram illustrating the data acquisition interface is shown in Figure 42.

Although Metrabyte provided utility software demonstrating the use of these

Figure 39. View of Thermal Dilatometer Showing Major Components.

Figure 40. Illustration of Sample Holder and Probe Rod Assembly.

Figure 41. Close-Up View of Measurement Head Showing Individual Components.

Figure 42. Illustration of Data Acquisition Hardware for TDA System.

interface boards, they were found to be inadequate for the specialized task of converting the outputs from the dilatometer to a systematic data display and logging format that was "user friendly." Therefore, programs were developed in IBM BASIC to accomplish this task. The programs require the presence of MetraByte's machine language I/O driver, DAS8.BIN, to run. The I/O driver controls the A/D converter, timer and I/O channel functions via BASIC CALL functions. It selects the multiplexer channels, sets scan limits and performs software commanded A/D conversions. Commands to DAS8.BIN are given from subroutines in the BASIC programs ZERO.BAS and THEXP.BAS, hereafter referred to by ZERO and THEXP respectively. Likewise, the output from DAS8.BIN is received from these two programs and converted, scaled, displayed and/or recorded according to user input. The program ZERO is a stand-alone program for nulling the output of the LVDT. TDA is run in conjunction with the program THEXP which records ΔL and T of the sample as well as elapsed time. The documented program code for these programs are listed in Appendix A.1 and A.2 for ZERO and THEXP respectively.

The procedure used for operating the TDA system consisted of the following:

- (1) Power was applied to all components of the system and allowed to stabilize for 30 minutes as suggested by the manufacturer.
- (2) The sample was placed in the sample holder with the leaf spring at a set distance from the spring block. This step was to ensure that a constant compressive load was maintained on all samples.
- (3) The BASIC program ZERO was loaded and run using a constant gain setting on both the EXP-16 and the dilatometer. The gain settings were set according to the magnitude of the expected change in sample dimensions over the temperature range considered. For this study, the dilatometer gain setting was 10, a coarse setting, corresponding to the maximum linear range of the LVDT, $\Delta L = \pm 0.100$ in.
- (4) The

program ZERO was run and LVDT core travel registered by the data acquisition system was checked against that of the micrometer. Zero was established by moving the micrometer until a null signal was displayed. (5) Run parameters for furnace control, eg., maximum temperature, heating rate, dwell time, etc., were entered in the programmable controller and verified. (6) The BASIC program THEXP was loaded and run to initiate data acquisition. This program provides the operator with a real time display of time, sample temperature, and ΔL . (7) Once the data acquisition parameters, e.g., gain settings, duration of run, sampling rate, etc., are entered, the program then waits for a keystroke to begin data acquisition. With the program controller set for the desired heating schedule, the run was initiated by simultaneously pressing a key on the PC keyboard and the program controller.

The collected data was saved as displayed and after a run was complete the operator had the option of saving the data to disk as a LOTUS 1-2-3 compatible import file, to a MetraByte compatible file for immediate graphical presentation, or to simply scroll through the collected data on the monitor. The raw data was processed in the spread-sheet environment of LOTUS 1-2-3.

Because the sample holder and probe rod assembly expand when heated, the measuring system needs to be calibrated, or rather, a base line established for a particular measuring system, alumina or fused silica. If the sample probe rod were butted up against the end of the sample holder and both were heated, the thermal expansion of the two would tend to cancel one another so that the LVDT would sense no movement. The sample, however, displaces a certain portion of the probe rod, so in essence, the sample holder is longer, by the length of the sample, than the probe rod. Therefore, the expansion of the sample holder over the length of

the sample causes an apparent expansion at the LVDT to be less than the expansion of the sample. If the sample is shrinking, the expansion of the sample holder over the length of the sample is in the same direction as the shrinkage. Hence, the recorded shrinkage is equivalent to the sum of sample shrinkage and system expansion, or, if you will, the apparent shrinkage of the measuring system.⁶² This effect was compensated for by calibrating the measuring system, alumina in this case, in the temperature range 25 – 1200°C with a 2 X 3/8 inch 998 alumina standard supplied by the manufacturer. A plot of percent expansion with temperature is shown in Figure 43 for 998 alumina. From this plot the LCTE of the alumina standard was calculated to be $\alpha_{Al} = 8.8 \times 10^{-6}/^{\circ}\text{C}$.

The measured percent expansion per unit sample length L_c with temperature is shown in Figure 44 along with the percent expansion of the 998 alumina standard obtained from the previously calculated expansion coefficient. Ideally, L_c should have been zero at all temperatures, but dissimilar temperature profiles on the push rod and sample holder caused the measured differential expansion. This base line and the known thermal expansion characteristics of the alumina standard were used to calculate the length $L(T)$ of a sample at any temperature T by the following relationship⁶¹

$$L(T) = L_o + \Delta L_a + L_o \left(\int_{T_o}^T \alpha_{Al} dt - L_c \right) \quad (23)$$

where T_o is the initial temperature, L_o the initial sample length and ΔL_a the apparent expansion of the system. This equation can be evaluated, assuming alpha is independent of temperature, to give a more convenient representation in the following form

$$\Delta L(T)/L_o = \Delta L_a/L_o + (\alpha_{Al}\Delta T - L_c) \quad (24)$$

or simply

$$\Delta L(T)/L_o = \Delta L_a/L_o + c \quad (25)$$

where c , the calibration constant, equals $\alpha_{Al}\Delta T - L_c$. The calibration constant is the difference between the curves shown in Figure 44. A value of $c = 6.8 \times 10^{-6}/^{\circ}\text{C}$ was calculated from this figure. This value was used in the conversion of raw data to the processed data tabulated in Appendices B & D.

Figure 43. Expansion Characteristics of 998 Alumina.

Figure 44. System and 998 Alumina Expansion Curves from Room Temperature to 1200°C.

A.1 Listing of IBM BASIC Program ZERO

```

100 ' *****
110 ' *
120 ' *      NASA-Ames Research Center
130 ' *      Thermal Protection Branch (RTM)
140 ' *      Zero LVDT Program      Rev 1.01 JDB 10-31-1988
150 ' *
160 ' *****
170 '
180 ' ----- Initialize -----
190 '
200 SCREEN 0,0 : WIDTH 80 : KEY OFF : CLS
210 CLEAR, 49152!
220 DEF SEG = 0
230 LOCATE 12, 12 : PRINT "(< Wait - Loading DAS8.BIN driver & DAS8.ADR >)"
240 LOCATE 25,1 : PRINT " NASA-Ames Research Center";
250 SG = 256 * PEEK(&H511) + PEEK(&H510)
260 SG = SG + 49152!/16
270 DEF SEG = SG
280 BLOAD "DAS8.BIN", 0
290 OPEN "DAS8.ADR" FOR INPUT AS #1
300 INPUT #1, BASADRX
310 CLOSE #1
320 DAS8 = 0
330 FLAG% = 0
340 MDX = 0
350 CALL DAS8 (MDX, BASADRX, FLAG%)
360 IF FLAG% (<) 0 THEN PRINT "INITIALIZATION ERROR"
370 '
380 ' ----- Zero LVDT & Check -----
390 '
400 CHX = 0 'DAS-8 channel the EXP-16 is connected to as determined by J4 ju
410 mper position of EXP-16
420 CLS: PRINT
430 INPUT "Gain setting of Harrop dilatometer (10 or 100)X1 ";AT
440 IF AT = 10 THEN
450 COEF(1)=.000062 : COEF(2)=3.0008 : COEF(3)=.5303 : COEF(4)=-12.121 : COEF(5)
460 =-8.2731 : COEF(6)=-194.4105
470 IF AT = 100 THEN
480 COEF(1)=.00006 : COEF(2)=.44444 : COEF(3)=-13.835 : COEF(4)=746.78 : COEF(5)
490 =-18589 : COEF(6)=177197!
500 ELSE PRINT "Not a valid setting " : GOTO 420
510 PRINT : INPUT "EXP-16 gain setting (100, 200, 1000 etc.) ";AV
520 CLS : PRINT
530 LOCATE 12,22 : PRINT "LVDT travel =          inches"
540 LOCATE 24,1 : PRINT "Press any key to exit"
550 'Convert data to volts then scale to inches IAW dilatometer attenuation
560 CMD$ = " " : WHILE CMD$ = " " : COLOR 7,14
570 LTX(0) = CHX : LTX(1) = CHX : MDX = 1 'Lock DAS-8 to channel 0
580 CALL DAS8 (MDX, LTX(0), FLAG%)
590 IF FLAG% (<) 0 THEN PRINT "ERROR IN SETTING CHANNEL" : END
600 SUBX = 1
610 MDX = 14
620 CALL DAS8 (MDX, SUBX, FLAG%)
630 IF FLAG% (<) 0 THEN PRINT "ERROR IN EXP CHANNEL NUMBER" : END
640 MDX = 4 'Do one A/D conversion and write to DX for display
650 CALL DAS8 (MDX, DX, FLAG%)
660 IF FLAG% (<) 0 THEN PRINT "ERROR IN PERFORMING A/D CONVERSION"
670 V = (DX*8)/(AV*2048)
680 GOSUB 700
690 LOCATE 11,35 : PRINT USING "###.#####";1*AMP
700 CMD$ = INKEY$ : COLOR 7,0 : WEND : END
710 '-----SUBROUTINE FOR SCALING LVDT OUTPUT TO INCHES -----
720 '
730 AMP=COEF(1)
740 FOR CNTX = 5 TO 1 STEP -1
750 AMP = AMP + COEF(CNTX + 1) * V ^ CNTX
760 NEXT CNTX
770 RETURN

```

A.2 Listing of IBM BASIC Program THEXP

```

100 : *****
110 : *
120 : *          NASA-Ames Research Center
130 : *          Thermal Protection Branch (RTM)
140 : *          Thermal Expansion Program          Rev 1.01 JDB 10-31-1988
150 : *
160 : *****
170 :
180 : ----- Initialize -----
190 :
200 SCREEN 0,0 : WIDTH 80 : KEY OFF : CLS
210 CLEAR, 49152!
220 DEF SEG = 0
230 LOCATE 12, 12 : PRINT "(< Wait - Loading DASB.BIN driver & DASB.ADR >)"
240 LOCATE 25,1 : PRINT " NASA-Ames Research Center";
250 SG = 256 * PEEK(&H511) + PEEK(&H510)
260 SG = SG + 49152!/16
270 DEF SEG = SG
280 BLOAD "DASB.BIN", 0
290 OPEN "DASB.ADR" FOR INPUT AS #1
300 INPUT #1, BASADRX
310 CLOSE #1
320 DASB = 0
330 FLAGX = 0
340 MDX = 0
350 CALL DASB (MDX, BASADRX, FLAGX)
360 IF FLAGX (> 0) THEN PRINT "INITIALIZATION ERROR"
370 :
380 : ----- Load Thermocouple Data -----
390 :
400 GOSUB 1040
410 CLS
420 INPUT "EXP-16 gain setting (100, 200, 1000 etc.) ";AV
430 PRINT : INPUT "Duration of run (ramp + dwell) in minutes ";DR
440 PRINT : INPUT "Scan interval (seconds) ";SI
450 PRINT : INPUT "Maximum temperature of run (deg. C) ";MAXT
460 PRINT : INPUT "Gain setting of dilatometer (10 or 100)X1";AT
470 IF AT = 10 THEN
480 COEF(1)=.000062 : COEF(2)=3.0008 : COEF(3)=.5303 : COEF(4)=-12.121 : COEF(5)
=-8.2731 : COEF(6)=-194.4105
490 IF AT = 100 THEN
500 COEF(1)=.00006 : COEF(2)=.44444 : COEF(3)=-13.835 : COEF(4)=746.78 : COEF(5)
=-18589 : COEF(6)=177197!
510 ELSE PRINT "Not a valid setting " : GOTO 460
520 ND = (60*DR)/SI
530 PRINT : PRINT "Total number of data points = ";ND
540 PRINT : INPUT "Data acquisition parameters correct -(Y/N) ";A$
550 IF A$ = "Y" OR A$ = "y" THEN GOTO 570 ELSE IF A$ (<) "" THEN GOTO 410
560 :
570 'Dimension data array for A/D data and check for sufficient memory
580 :
590 IF (FRE(0) - 2000 - ND*3) (< 0) THEN PRINT "WARNING! There is insufficient mem
ory within BASICA to hold this data" : PRINT "Re-run program" : END
600 DIM TM(ND+1), T1(ND+1), DELTAL(ND+1), DX(2), ASD(2)
610 CLS : LOCATE 12,12 : COLOR 7,4 : PRINT "(< PRESS ANY KEY TO START DATA ACQU
ITION >);": COLOR 7,0
620 IF INKEY$ = "" GOTO 620
630 :
640 : ----- Begin Data Acquisition -----
650 :
660 NL = 0
670 CLS : LOCATE 24,1 : COLOR 0,7 : PRINT "-Press (Ctrl-Break) to terminate data
acquisition-";: COLOR 7,0
680 LOCATE 1,10 : PRINT "Delta L      =          inches"
690 LOCATE 2,10 : PRINT "Temperature =          degrees C"
700 LOCATE 3,10 : PRINT "Time into run ="
710 MDX = 1 : LTX(0) = 1 : LTX(1) = 1 'Get initial CJC & Temp.
720 CALL DASB (MDX, LTX(0), FLAGX)
730 IF FLAGX (> 0) THEN PRINT "ERROR IN SETTING CJC CHANNEL" : END
740 MDX = 4 : CJX = 0
750 CALL DASB (MDX, CJX, FLAGX)
760 IF FLAGX (> 0) THEN PRINT "ERROR IN CJC A/D CONVERSION" : END
770 CJX = CJX/10
780 CHX = 0
790 MDX = 1 : LTX(0) = CHX : LTX(1) = CHX 'Get initial temp.
800 CALL DASB (MDX, LTX(0), FLAGX)
810 IF FLAGX (> 0) THEN PRINT "ERROR IN SETTING CHANNEL 0" : END
820 MDX = 14 : SUBX = 0
830 CALL DASB (MDX, SUBX, FLAGX)
840 IF FLAGX (> 0) THEN PRINT "ERROR IN EXP-16 CHANNEL NUMBER" : END

```

```

850 MDX = 4 : DX(SUBX) = 0
860 CALL DASB (MDX, DX(SUBX), FLAGX)
870 IF FLAGX ( ) 0 THEN PRINT "ERROR IN PERFORMING A/D CONVERSION" : END
880 ASD(SUBX) = DX(SUBX)
890 TIMER ON
900 TIME$ = "0"
910 ON TIMER(SI) GOSUB 1560
920 TM(NL) = NL*SI
930 IF NL = ND + 1 THEN TIMER OFF : GOTO 1920
940 IF CINT(T1(NL)) > MAXT + 10 THEN BEEP
950 FOR I = 0 TO 1
960 IF I = 0 THEN V = ASD(I)*5/(AV*2048) : GOSUB 1360 : T1(NL) = TC
970 LOCATE 3,25 : COLOR 7,4 : PRINT USING "#####.##";T1(NL)
980 IF I = 1 THEN V1 = ASD(I)*8/(AV*2048) : GOSUB 3130 : DELTA(NL) = -1*AMP
990 LOCATE 1,25 : COLOR 0,2 : PRINT USING "###.#####";DELTA(NL)
1000 NEXT I
1010 LOCATE 5,25 : COLOR 7,1 : PRINT TIME$
1020 GOTO 1010
1030 '
1040 '----- Table lookup data for R type thermocouple -----
1050 '
1060 'Number of points, voltage step interval (mV), starting voltage (mV)
1070 DATA 212, .1, 0
1080 READ NR, SIR, SVR
1090 'Temperature at 0mV, 0.1mV, 0.2mV etc.
1100 DATA 0.0, 18.1, 34.8, 50.6, 65.4, 79.3, 93.6, 107.0, 120.0, 132.6
1110 DATA 145.0, 157.1, 169.0, 180.7, 192.3, 203.6, 214.8, 225.0, 236.7, 247.3
1120 DATA 258.2, 268.8, 279.3, 289.7, 300.0, 310.2, 320.4, 330.5, 340.5, 350.4
1130 DATA 360.3, 370.1, 379.3, 389.6, 399.3, 408.9, 418.5, 428.0, 437.5, 446.9
1140 DATA 456.3, 465.7, 475.0, 484.3, 493.5, 502.7, 511.0, 521.0, 530.1, 539.1
1150 DATA 548.1, 557.1, 566.1, 575.0, 583.9, 592.7, 601.5, 610.4, 619.1, 627.8
1160 DATA 636.5, 645.0, 653.6, 662.4, 671.0, 679.6, 688.1, 696.5, 705.0, 713.4
1170 DATA 721.8, 730.0, 738.5, 746.8, 755.0, 763.3, 771.5, 779.8, 787.3, 795.8
1180 DATA 804.1, 812.0, 820.3, 828.4, 836.4, 844.4, 852.4, 860.3, 868.3, 876.1
1190 DATA 884.0, 891.9, 899.8, 907.6, 915.3, 923.1, 930.9, 938.6, 946.3, 954.0
1200 DATA 961.7, 969.3, 976.3, 984.6, 992.2, 999.8, 1007.3, 1014.8, 1022.4, 1029.9
1210 DATA 1037.4, 1044.8, 1052.2, 1059.7, 1067.1, 1074.5, 1081.9, 1089.3, 1096.6, 1103.9
1220 DATA 1111.3, 1118.6, 1125.9, 1133.1, 1140.4, 1147.7, 1155.0, 1162.2, 1169.4, 1176.7
1230 DATA 1183.9, 1191.1, 1198.3, 1205.5, 1212.7, 1219.9, 1227.0, 1234.1, 1241.3, 1248.4
1240 DATA 1255.6, 1262.7, 1269.9, 1277.0, 1284.1, 1291.2, 1298.3, 1305.4, 1312.5, 1319.6
1250 DATA 1326.7, 1333.8, 1340.9, 1347.9, 1355.0, 1362.1, 1369.2, 1376.3, 1383.4, 1390.5
1260 DATA 1397.5, 1404.6, 1411.7, 1418.8, 1425.9, 1433.0, 1440.1, 1447.1, 1454.2, 1461.3
1270 DATA 1468.4, 1475.5, 1482.6, 1489.7, 1496.8, 1503.9, 1511.1, 1518.2, 1525.3, 1532.4
1280 DATA 1539.6, 1546.7, 1553.8, 1561.0, 1568.2, 1575.4, 1582.6, 1589.8, 1597.0, 1604.2
1290 DATA 1611.4, 1618.6, 1625.8, 1633.1, 1640.4, 1647.6, 1654.9, 1662.2, 1669.5, 1676.8
1300 DATA 1684.1, 1691.3, 1698.5, 1706.3, 1713.0, 1721.3, 1728.0, 1736.4, 1744.0, 1751.7
1310 DATA 1759.5, 1767.3
1320 DIM TR(NR-1)
1330 FOR I = 0 TO NR-1:READ TR(I):NEXT I
1340 RETURN
1350 '
1360 '----- Interpolation routine to find R thermocouple temperature -----
1370 '
1380 'Entry variables:-
1390 'CJC = cold junction compensator temperature in deg. C.
1400 'V = thermocouple voltage in volts
1410 'Exit variables:-
1420 'TC = temperature in degrees Centigrade
1430 'TF = temperature in degrees Fahrenheit
1440 'Execution time on std. IBM P.C. = 46 milliseconds
1450 'Perform CJC compensation for R type
1460 VR = 1000*V + .141 + (CJC-25)*.00595 'VR in mV
1470 'Find look up element
1480 ER = INT((VR-SVR)/SIR)
1490 IF ER(0) THEN TC=TR(0):GOTO 1530 'Out of bounds, round to lower limit
1500 IF ER(NR-2) THEN TC=TR(NR-1):GOTO 1530 'Out of bounds, round to upper limit
1510 'Do interpolation
1520 TC = TR(ER) + (TR(ER+1) - TR(ER))*(VR-ER*SIR-SVR)/SIR 'Centigrade
1530 TF = TC*9/5 + 32 'Fahrenheit
1540 RETURN
1550 '
1560 '----- Subroutine to convert EXP-16 channels to number of bits -----
1570 '
1580 NL = NL + 1
1590 MDX = 1 : LTX(0) = 1 : LTX(1) = 1 'Lock DAS-8 to channel 1 for CJC
1600 CRASE DX, ASD
1610 CALL DASB (MDX, LTX(0), FLAGX)
1620 IF FLAGX ( ) 0 THEN PRINT "ERROR IN SETTING CHANNEL 1" : END
1630 '
1640 '----- Get cold junction compensation temperature -----

```



```

1650 '
1660 MDX = 4 : CJX = 0
1670 CALL DASB (MDX, CJX, FLAGX)
1680 IF FLAGX ( ) 0 THEN PRINT "ERROR IN PERFORMING CJC A/D CONVERSION" : END
1690 CJC = CJX/10 'Change output in bits to temp., 0.1 deg.C./bit
1700 '
1710 '----- Get delta L and thermocouple data -----
1720 '
1730 MDX = 1 : LTX(0) = CHX : LTX(1) = CHX
1740 CALL DASB (MDX, LTX(0), FLAGX)
1750 IF FLAGX ( ) 0 THEN PRINT "ERROR IN SETTING CHANNEL 0" : END
1760 'Now set EXP-16 to mode 14 and collect temp. & delta L data, average 5 A/Ds

1770 FOR SUBX = 0 TO 1
1780 MDX = 14
1790 CALL DASB (MDX, SUBX, FLAGX)
1800 IF FLAGX ( ) 0 THEN PRINT "ERROR IN EXP-16 CHANNEL NUMBER" : END
1810 NC = 0 : SDX = 0
1820 MDX = 4
1830 CALL DASB (MDX, DX(SUBX), FLAGX)
1840 IF FLAGX ( ) 0 THEN PRINT "ERROR IN PERFORMING A/D CONVERSION" : END
1850 NC = NC + 1
1860 SDX = SDX + DX(SUBX)
1870 IF NC < 10 THEN GOTO 1830
1880 ASD(SUBX) = SDX/NC
1890 NEXT SUBX
1900 RETURN 920
1910 '
1920 '----- Terminate data acquisition, save data prompts -----
1930 '
1940 COLOR 7,0 : CLS : LOCATE 12,22 : COLOR 7,14 : PRINT "<< TERMINATED DATA COL
LECTION >>)" : COLOR 7,0
1950 LOCATE 25,1 : PRINT " - Press any key to continue -"
1960 IF INKEY$ = "" GOTO 1960
1970 '
1980 '----- Choose type of file required -----
1990 '
2000 CLS : PRINT "Choose from the following:"
2010 PRINT:PRINT" (1) - Generate a Lotus 1-2-3 compatible import file"
2020 PRINT:PRINT" (2) - Generate a data file & plot using the DAS-8 graphics pa
ckage"
2030 PRINT:PRINT" (3) - Display data on screen"
2040 PRINT:PRINT" (4) - Exit to BASIC"
2050 PRINT:PRINT"Enter selection number (1-3) : ";
2060 A$= INKEY$: IF A$= "" GOTO 2060
2070 PRINT A$
2080 IF VAL(A$)=1 THEN GOTO 2810
2090 IF VAL(A$)=2 THEN GOTO 2140
2100 IF VAL(A$)=3 THEN GOTO 2320
2110 IF VAL(A$)=4 THEN CLS:END
2120 PRINT[";A$;"] is not a valid entry. Please re-enter": GOTO 2050
2130 '
2140 '--- Generate DAS-8 graphics package data file & plot -----
2150 '
2160 CLS: DIM AR(ND+1) : LOCATE 1,1:INPUT"DATA FILE NAME [DRIVE]:NAME.EXT";FILX$
2170 OPEN FILX$ AS #1 LEN = 30
2180 FIELD #1, 15 AS X$, 15 AS Y$
2190 '
2200 'Get display mode, dot, line or no plot
2210 '
2220 LOCATE 3,1:COLOR 0,7:PRINT"L";:COLOR 7,0:PRINT"line, OR ";:COLOR 0,7:PRINT"D
";:COLOR 7,0:PRINT"ot plot mode?"
2230 LOCATE 3,29:INPUT"A$
2240 IF A$="L" OR A$="1" THEN M=1:GOTO 2280
2250 IF A$="D" OR A$="d" THEN M=0:GOTO 2280
2260 LOCATE 4,1:PRINT"RE-ENTER":LOCATE 3,1:PRINT SPC(79):GOTO 2220
2270 '
2280 ' Get time axis units
2290 '
2300 PRINT : INPUT "What is desired time axis units : (H) hours, (M) minutes or
(S) seconds ";A$
2310 '
2320 IF A$ = "H" OR A$ = "h" THEN TAX = 3600 : GOTO 2360
2330 IF A$ = "M" OR A$ = "m" THEN TAX = 60 : GOTO 2360
2340 TAX = 1 'seconds or default
2350 '
2360 ' Choose y-axis
2370 '
2380 LOCATE 10,1 : PRINT "Data for y-axis -" : COLOR 0,7 : PRINT "T";: COLOR 7,
0 : PRINT "emp.; or ";: COLOR 0,7 : PRINT "D";: COLOR 7,0 : PRINT "elta L ?"
2390 LOCATE 10,30 : INPUT "" ,A$

```

```

2400 IF A$ = "T" OR A$ = "t" THEN AR=T1 : GOTO 2440
2410 IF A$ = "d" OR A$ = "D" THEN AR=DELTA1 : GOTO 2440
2420 LOCATE 11,1 : PRINT "RE-ENTER" : LOCATE 10,1 : PRINT SPC(70) : GOTO 2300
2430 '
2440 'Enter number of data points and plot mode in record 1
2450 '
2460 LSET X$ = MKS$(ND) : LSET Y$ = MKS$(M)
2470 PUT #1,1
2480 'Enter data in remaining records
2490 FOR I=2 TO ND+1
2500 LSET X$=MKS$(TM(I-2)/TAX) : LSET Y$=MKS$(AR(I-2))
2510 PUT #1, I
2520 NEXT I
2530 'Write file
2540 CLOSE #1
2550 '
2560 'Generate LINPLT.LNK plotting file for LINPLT.BAS to use
2570 '
2580 OPEN "RLINPLT.LNK" AS #1 LEN = 30
2590 FIELD #1, 30 AS RLNK$
2600 LSET RLNK$ = MKI$(1) 'one data file
2610 PUT #1, 1
2620 CLS
2630 INPUT "Enter graph Y axis label : ",Y$
2640 IF LEN(Y$) > 30 THEN Y$ = LEFT$(Y$,30)
2650 LSET RLNK$ = Y$ 'Y axis label
2660 INPUT "Enter graph X axis label : ",X$
2670 IF LEN(X$) > 30 THEN X$ = LEFT$(X$, 30)
2680 PUT #1, 2
2690 LSET RLNK$ = X$ 'X axis label
2700 PUT #1, 3
2710 LSET RLNK$ = FILX$ 'data file name
2720 PUT #1, 4
2730 CLOSE #1
2740 RUN"LINPLT 'run plotting program
2800 '
2810 '----- Generate a Lotus 1-2-3 .PRN import file -----
2820 '
2830 CLS : INPUT "LOTUS 1-2-3 import file name e.g., A:\DATA (automatic .PRN fil
e extension) ";F$
2840 F$ = F$ + ".PRN"
2850 OPEN F$ FOR OUTPUT AS #1
2860 FOR I = 0 TO ND
2870 PRINT #1, T1(I), DELTA(I), TM(I)
2880 NEXT I
2890 CLOSE #1
2900 GOTO 1980
2910 '
2920 '----- Display data on screen and return to menu -----
2930 '
2940 CLS
2950 LOCATE 25,1 : PRINT "Press any key to STOP/START display, (ESC) key to retu
rn to data storage menu " : LOCATE 1,1
2960 PRINT "Time, sec. Temp., deg. C Delta L, inches"
2970 PRINT "-----"
2980 PRINT
2990 FOR I = 0 TO ND
3000 PRINT TM(I), T1(I), DELTA(I)
3010 A$ = INKEY$
3020 IF A$ = CHR$(27) THEN I = ND + 3
3030 IF A$ <> "" THEN GOTO 3090
3040 NEXT I
3050 IF I = ND + 3 GOTO 1980
3060 COLOR 0,7 : PRINT "Press any key to return to data storage menu " : COLOR 7
3070 IF INKEY$ = "" GOTO 3070
3080 GOTO 1980
3090 FOR K = 1 TO 50 : NEXT K 'delay
3100 IF INKEY$ = "" GOTO 3100
3110 GOTO 3040
3120 END
3130 '
3140 '----- Subroutine for scaling LVDT output to inches -----
3150 '
3160 AMP = COEF(1)
3170 FOR CNTX = 5 TO 1 STEP -1
3180 AMP = AMP + COEF(CNTX + 1) * V1 ^ CNTX
3190 NEXT CNTX
3200 RETURN

```

APPENDIX B

Table 17. Isothermal Shrinkage Data for Region B,

II. ABS. 2 Sample 3, Lo = 0.2370 inches, 240 deg. C.

Temperature, degrees C	Apparent Shrinkage inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage,	Log Linear Shrinkage	Log Time
238.1	-0.002160	6.0	0.000332	-0.001829	-0.000106	0.236887	0.000446	-3.3506	0.7782
239.3	-0.002243	9.0	0.000334	-0.001909	-0.000186	0.236808	0.000784	-3.1055	0.9542
239.3	-0.002295	10.0	0.000334	-0.001962	-0.000233	0.236755	0.001007	-2.9970	1.0000
239.5	-0.002289	12.0	0.000334	-0.001956	-0.000233	0.236761	0.000981	-3.0082	1.0792
238.8	-0.002330	15.0	0.000333	-0.001998	-0.000275	0.236719	0.001159	-2.9359	1.1761
240.4	-0.002360	18.0	0.000335	-0.002025	-0.000301	0.236693	0.001272	-2.8956	1.2553
240.1	-0.002424	21.0	0.000335	-0.002089	-0.000366	0.236628	0.001546	-2.8109	1.3222
240.3	-0.002471	24.0	0.000335	-0.002136	-0.000413	0.236582	0.001743	-2.7588	1.3802
240.4	-0.002500	27.0	0.000335	-0.002165	-0.000442	0.236553	0.001866	-2.7292	1.4314
239.9	-0.002495	30.0	0.000335	-0.002160	-0.000437	0.236557	0.001844	-2.7343	1.4771
240.3	-0.002524	33.0	0.000335	-0.002189	-0.000466	0.236529	0.001965	-2.7067	1.5185
240.8	-0.002547	36.0	0.000336	-0.002211	-0.000488	0.236507	0.002061	-2.6860	1.5563
240.1	-0.002559	39.0	0.000335	-0.002224	-0.000501	0.236493	0.002115	-2.6747	1.5911
241.0	-0.002583	42.0	0.000336	-0.002246	-0.000523	0.236472	0.002208	-2.6560	1.6232
240.5	-0.002594	45.0	0.000335	-0.002259	-0.000536	0.236459	0.002260	-2.6458	1.6532
239.9	-0.002618	48.0	0.000335	-0.002282	-0.000559	0.236436	0.002360	-2.6271	1.6812
240.4	-0.002659	51.0	0.000334	-0.002283	-0.000560	0.236434	0.002364	-2.6264	1.7076
241.2	-0.002676	54.0	0.000335	-0.002324	-0.000600	0.236394	0.002533	-2.5963	1.7324
241.2	-0.002676	57.0	0.000337	-0.002340	-0.000617	0.236379	0.002602	-2.5847	1.7559
240.7	-0.002700	60.0	0.000336	-0.002364	-0.000641	0.236354	0.002704	-2.5679	1.7782

n = 0.67 ± 0.03, Log(K) = -3.75 ± 0.04, R Squared = 0.958

Table 18. Isothermal Shrinkage Data for Region B,

11. ARS.2 Sample 14, $L_0 = 0.2287$ inches, 287 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, min.	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
285.7	-0.001568	6.0	0.000361	-0.001207	-0.000081	0.228642	0.000353	-3.4519	0.7782
285.1	-0.001598	9.0	0.000360	-0.001237	-0.000111	0.228611	0.000485	-3.3143	0.9542
285.8	-0.001574	10.0	0.000361	-0.001213	-0.000086	0.228637	0.000378	-3.4224	1.0000
285.9	-0.001598	12.0	0.000362	-0.001236	-0.000110	0.228613	0.000480	-3.3186	1.0792
285.5	-0.001645	15.0	0.000362	-0.001282	-0.000156	0.228568	0.000681	-3.1667	1.1761
287.0	-0.001656	18.0	0.000363	-0.001293	-0.000167	0.228557	0.000729	-3.1371	1.2553
287.4	-0.001674	21.0	0.000364	-0.001310	-0.000184	0.228541	0.000803	-3.0951	1.3222
286.0	-0.001703	24.0	0.000362	-0.001341	-0.000215	0.228508	0.000941	-3.0265	1.3802
285.7	-0.001703	27.0	0.000363	-0.001340	-0.000214	0.228510	0.000936	-3.0287	1.4314
287.7	-0.001750	30.0	0.000364	-0.001386	-0.000260	0.228455	0.001135	-2.9450	1.4771
287.9	-0.001744	33.0	0.000365	-0.001380	-0.000253	0.228472	0.001108	-2.9535	1.5185
287.4	-0.001762	36.0	0.000364	-0.001398	-0.000272	0.228453	0.001188	-2.9251	1.5563
287.0	-0.001774	39.0	0.000363	-0.001410	-0.000284	0.228440	0.001242	-2.9059	1.5911
287.2	-0.001809	42.0	0.000364	-0.001445	-0.000319	0.228405	0.001394	-2.8557	1.6232
287.3	-0.001832	45.0	0.000364	-0.001469	-0.000342	0.228382	0.001496	-2.8250	1.6532
287.0	-0.001832	48.0	0.000363	-0.001469	-0.000343	0.228381	0.001498	-2.8244	1.6812
287.6	-0.001861	51.0	0.000364	-0.001497	-0.000371	0.228353	0.001623	-2.7897	1.7076
287.8	-0.001861	54.0	0.000364	-0.001497	-0.000371	0.228354	0.001622	-2.7900	1.7324
288.3	-0.001879	57.0	0.000365	-0.001514	-0.000388	0.228338	0.001695	-2.7708	1.7559
287.9	-0.001856	60.0	0.000365	-0.001491	-0.000365	0.228360	0.001595	-2.7973	1.7782

$n = 0.73 \pm 0.03$, $\log(K) = -4.06 \pm 0.03$, $R \text{ Squared} = 0.977$

Table 10. Isothermal Shrinkage Data for Region C,

I.08S.1 Sample 4, $L_0 = 0.2308$ inches, 522 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
521.2	-0.007978	6.0	0.000707	-0.007271	-0.000073	0.230700	0.000326	-3.4866	0.7782
521.5	-0.008013	9.0	0.000708	-0.007305	-0.000110	0.230665	0.000477	-3.3219	0.9542
521.0	-0.008031	10.0	0.000707	-0.007324	-0.000128	0.230647	0.000556	-3.2550	1.0000
522.0	-0.008048	12.0	0.000708	-0.007340	-0.000145	0.230631	0.000626	-3.2032	1.0792
521.5	-0.008095	15.0	0.000707	-0.007388	-0.000192	0.230583	0.000833	-3.0795	1.1761
521.4	-0.008119	18.0	0.000707	-0.007411	-0.000216	0.230559	0.000935	-3.0291	1.2553
522.0	-0.008160	21.0	0.000708	-0.007451	-0.000256	0.230520	0.001109	-2.9551	1.3222
522.3	-0.008142	24.0	0.000709	-0.007433	-0.000238	0.230538	0.001031	-2.9867	1.3802
521.3	-0.008165	27.0	0.000707	-0.007458	-0.000263	0.230512	0.001139	-2.9434	1.4314
522.0	-0.008212	30.0	0.000708	-0.007504	-0.000309	0.230467	0.001338	-2.8736	1.4771
522.2	-0.008212	33.0	0.000708	-0.007504	-0.000309	0.230467	0.001337	-2.8739	1.5165
522.4	-0.008235	36.0	0.000709	-0.007527	-0.000332	0.230445	0.001437	-2.8426	1.5563
522.5	-0.008242	39.0	0.000709	-0.007533	-0.000337	0.230439	0.001461	-2.8352	1.5911
522.8	-0.008283	42.0	0.000709	-0.007573	-0.000378	0.230399	0.001538	-2.7858	1.6232
522.9	-0.008283	45.0	0.000710	-0.007573	-0.000378	0.230399	0.001537	-2.7859	1.6532
522.3	-0.008289	48.0	0.000709	-0.007580	-0.000385	0.230391	0.001666	-2.7783	1.6912
522.3	-0.008318	51.0	0.000709	-0.007609	-0.000414	0.230362	0.001793	-2.7463	1.7076
522.7	-0.008341	54.0	0.000709	-0.007632	-0.000437	0.230340	0.001892	-2.7324	1.7324
522.8	-0.008371	57.0	0.000709	-0.007661	-0.000466	0.230311	0.002019	-2.6949	1.7559
523.0	-0.008347	60.0	0.000710	-0.007638	-0.000442	0.230335	0.001916	-2.7176	1.7782

$n = 0.74 \pm 0.02$, $\log(K) = -4.00 \pm 0.03$, $R \text{ Squared} = 0.982$

Table 20. Isothermal Shrinkage Data for Region C,

1.888.1 Sample 5, $L_0 = 0.2307$ inches, 567 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
566.9	-0.009526	6.0	0.000773	-0.008753	-0.000135	0.230561	0.000584	-3.2337	0.7782
566.7	-0.009562	9.0	0.000773	-0.008789	-0.000170	0.230526	0.000737	-3.1323	0.9542
566.7	-0.009573	10.0	0.000773	-0.008800	-0.000182	0.230514	0.000788	-3.1033	1.0000
567.6	-0.009532	12.0	0.000774	-0.008858	-0.000239	0.230458	0.001036	-2.9847	1.0792
567.7	-0.009561	15.0	0.000774	-0.008887	-0.000268	0.230428	0.001163	-2.9343	1.1761
567.6	-0.009556	18.0	0.000775	-0.008881	-0.000262	0.230434	0.001137	-2.9442	1.2533
568.5	-0.009702	21.0	0.000776	-0.008927	-0.000308	0.230389	0.001337	-2.8740	1.3222
568.5	-0.009720	24.0	0.000776	-0.008945	-0.000326	0.230371	0.001413	-2.8499	1.3802
568.5	-0.009732	27.0	0.000776	-0.008956	-0.000338	0.230360	0.001464	-2.8346	1.4314
568.7	-0.009720	30.0	0.000776	-0.008944	-0.000326	0.230372	0.001411	-2.8503	1.4771
568.3	-0.009679	33.0	0.000775	-0.008904	-0.000285	0.230412	0.001236	-2.9079	1.5185
568.4	-0.009691	36.0	0.000775	-0.008915	-0.000287	0.230400	0.001286	-2.8906	1.5563
568.7	-0.009738	39.0	0.000776	-0.008962	-0.000343	0.230354	0.001488	-2.8274	1.5911
568.6	-0.009697	42.0	0.000776	-0.008921	-0.000302	0.230395	0.001311	-2.8825	1.6232
568.5	-0.009726	45.0	0.000776	-0.008950	-0.000332	0.230365	0.001438	-2.8422	1.6532
568.9	-0.009738	48.0	0.000776	-0.008962	-0.000343	0.230355	0.001487	-2.8278	1.6812
569.0	-0.009753	51.0	0.000776	-0.008979	-0.000360	0.230337	0.001562	-2.8063	1.7076
568.4	-0.009796	54.0	0.000775	-0.009021	-0.000402	0.230295	0.001744	-2.7584	1.7324
568.3	-0.009808	57.0	0.000775	-0.009033	-0.000414	0.230283	0.001796	-2.7458	1.7559
568.5	-0.009808	60.0	0.000776	-0.009033	-0.000414	0.230283	0.001794	-2.7461	1.7782

$n = 0.41 \pm 0.04$, $\log(K) = -3.48 \pm 0.05$, R Squared = 0.870

Table 21. Isothermal Shrinkage Data for Region C,

1. A88.1 Sample 1, $L_0 = 0.2282$ inches, 624 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
622.9	-0.010189	6.0	0.000490	-0.005699	-0.000105	0.228062	0.000461	-3.3363	0.7782
623.1	-0.010266	9.0	0.000490	-0.005776	-0.000181	0.227986	0.000794	-3.1001	0.9542
623.3	-0.010272	10.0	0.000490	-0.005781	-0.000187	0.227960	0.000880	-3.0862	1.0000
623.3	-0.010289	12.0	0.000490	-0.005799	-0.000204	0.227953	0.000895	-3.0480	1.0792
623.3	-0.010337	15.0	0.000490	-0.005847	-0.000252	0.227915	0.001106	-2.9562	1.1761
623.6	-0.010343	18.0	0.000491	-0.005852	-0.000258	0.227910	0.001130	-2.9468	1.2533
623.8	-0.010407	21.0	0.000491	-0.005917	-0.000322	0.227846	0.001412	-2.8500	1.3222
623.6	-0.010396	24.0	0.000491	-0.005905	-0.000311	0.227857	0.001362	-2.8659	1.3802
624.1	-0.010495	27.0	0.000491	-0.010004	-0.000410	0.227758	0.001797	-2.7454	1.4314
624.7	-0.010454	30.0	0.000492	-0.009963	-0.000368	0.227800	0.001615	-2.7919	1.4771
624.6	-0.010495	33.0	0.000491	-0.010004	-0.000410	0.227759	0.001795	-2.7459	1.5185
624.6	-0.010507	36.0	0.000491	-0.010016	-0.000421	0.227747	0.001847	-2.7336	1.5563
625.3	-0.010519	39.0	0.000492	-0.010027	-0.000433	0.227737	0.001896	-2.7223	1.5911
624.3	-0.010572	42.0	0.000491	-0.010081	-0.000466	0.227682	0.002131	-2.6715	1.6232
624.9	-0.010595	45.0	0.000492	-0.010103	-0.000509	0.227660	0.002331	-2.6515	1.6532
624.2	-0.010607	48.0	0.000491	-0.010116	-0.000521	0.227647	0.002388	-2.6411	1.6812
624.2	-0.010630	51.0	0.000491	-0.010139	-0.000545	0.227623	0.002533	-2.6220	1.7076
625.1	-0.010619	54.0	0.000492	-0.010127	-0.000532	0.227637	0.002333	-2.6380	1.7324
624.9	-0.010648	57.0	0.000492	-0.010156	-0.000562	0.227607	0.002463	-2.6086	1.7559
625.1	-0.010671	60.0	0.000492	-0.010180	-0.000585	0.227584	0.002565	-2.5909	1.7782

$n = 0.68 \pm 0.02$, $\text{Log}(K) = -3.78 \pm 0.03$, $R \text{ Squared} = 0.978$

Table 22. Isothermal Shrinkage Data for Region C,

1.ABS.1 Sample 6, Lo = 0.2299 inches, 690 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
688.6	-0.010882	6.0	0.000947	-0.009935	-0.000182	0.229690	0.000792	-3.1012	0.7782
688.3	-0.010929	9.0	0.000946	-0.009982	-0.000230	0.229643	0.000999	-3.0006	0.9542
689.2	-0.010958	10.0	0.000948	-0.010010	-0.000257	0.229616	0.001120	-2.9508	1.0000
689.5	-0.011005	12.0	0.000948	-0.010037	-0.000304	0.229569	0.001323	-2.8786	1.0792
688.8	-0.011075	15.0	0.000947	-0.010128	-0.000375	0.229497	0.001533	-2.7870	1.1761
689.7	-0.011163	18.0	0.000948	-0.010215	-0.000462	0.229411	0.002010	-2.6967	1.2553
689.5	-0.011210	21.0	0.000948	-0.010262	-0.000509	0.229364	0.002216	-2.6545	1.3222
690.6	-0.011269	24.0	0.000950	-0.010319	-0.000566	0.229308	0.002464	-2.6084	1.3802
690.2	-0.011304	27.0	0.000949	-0.010355	-0.000602	0.229272	0.002620	-2.5817	1.4314
689.9	-0.011339	30.0	0.000949	-0.010391	-0.000638	0.229236	0.002775	-2.5568	1.4771
690.8	-0.011422	33.0	0.000950	-0.010472	-0.000719	0.229156	0.003126	-2.5050	1.5185
690.1	-0.011439	36.0	0.000949	-0.010490	-0.000737	0.229137	0.003207	-2.4938	1.5563
690.4	-0.011480	39.0	0.000949	-0.010531	-0.000778	0.229096	0.003384	-2.4706	1.5911
691.2	-0.011504	42.0	0.000951	-0.010553	-0.000800	0.229075	0.003481	-2.4582	1.6232
691.3	-0.011551	45.0	0.000951	-0.010600	-0.000847	0.229028	0.003685	-2.4336	1.6532
691.3	-0.011545	48.0	0.000951	-0.010594	-0.000841	0.229034	0.003659	-2.4366	1.6812
691.1	-0.011586	51.0	0.000950	-0.010635	-0.000883	0.228992	0.003839	-2.4158	1.7076
691.6	-0.011627	54.0	0.000951	-0.010676	-0.000923	0.228952	0.004015	-2.3953	1.7324
691.1	-0.011656	57.0	0.000950	-0.010706	-0.000953	0.228922	0.004145	-2.3824	1.7559
691.5	-0.011668	60.0	0.000951	-0.010717	-0.000964	0.228911	0.004194	-2.3774	1.7782

n = 0.75 ± 0.02, Log(K) = -3.67 ± 0.02, R Squared = 0.988

Table 23. Isothermal Shrinkage Data for Region C,

I.ABS.2 Sample 6, $L_0 = 0.2323$ inches, 522 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
521.7	-0.005860	6.0	0.000712	-0.005148	-0.000052	0.232322	0.000226	-3.6462	0.7782
522.5	-0.005872	9.0	0.000714	-0.005158	-0.000063	0.232312	0.000271	-3.5664	0.9542
522.5	-0.005896	10.0	0.000714	-0.005182	-0.000087	0.232289	0.000372	-3.4290	1.0000
522.1	-0.005901	12.0	0.000713	-0.005188	-0.000093	0.232282	0.000400	-3.3975	1.0792
521.9	-0.005901	15.0	0.000713	-0.005189	-0.000093	0.232281	0.000402	-3.3959	1.1761
522.0	-0.005937	18.0	0.000713	-0.005224	-0.000128	0.232246	0.000553	-3.2576	1.2553
522.9	-0.005954	21.0	0.000714	-0.005240	-0.000145	0.232231	0.000623	-3.2057	1.3222
522.6	-0.005966	24.0	0.000714	-0.005252	-0.000157	0.232219	0.000675	-3.1709	1.3802
522.2	-0.005972	27.0	0.000713	-0.005259	-0.000163	0.232212	0.000703	-3.1532	1.4314
523.3	-0.005978	30.0	0.000715	-0.005263	-0.000167	0.232208	0.000721	-3.1421	1.4771
523.6	-0.006013	33.0	0.000715	-0.005298	-0.000202	0.232174	0.000870	-3.0603	1.5185
522.7	-0.006019	36.0	0.000714	-0.005305	-0.000209	0.232166	0.000901	-3.0452	1.5563
523.0	-0.006048	39.0	0.000714	-0.005334	-0.000238	0.232137	0.001026	-2.9889	1.5911
523.3	-0.006071	42.0	0.000715	-0.005357	-0.000261	0.232115	0.001125	-2.9489	1.6232
522.7	-0.006066	45.0	0.000714	-0.005352	-0.000256	0.232119	0.001103	-2.9574	1.6532
523.0	-0.006130	48.0	0.000714	-0.005416	-0.000320	0.232055	0.001379	-2.8603	1.6812
522.8	-0.006130	51.0	0.000714	-0.005416	-0.000321	0.232055	0.001381	-2.8600	1.7076
522.9	-0.006148	54.0	0.000714	-0.005434	-0.000338	0.232037	0.001456	-2.8370	1.7324
523.1	-0.006154	57.0	0.000714	-0.005439	-0.000344	0.232032	0.001479	-2.8299	1.7559
522.3	-0.006183	60.0	0.000713	-0.005470	-0.000374	0.232001	0.001611	-2.7929	1.7782

$n = 0.86 \pm 0.03$, $\log(K) = -4.34 \pm 0.03$, $R \text{ Squared} = 0.983$

Table 24. Isothermal Shrinkage Data for Region C,

I. ABS.2 Sample 14, Lo = 0.2523 inches, 567 deg. C.

Temperature, degrees C.	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
565.8	-0.001668	6.0	0.000844	-0.000824	-0.00028	0.252319	0.000111	-3.9548	0.7782
565.8	-0.001668	9.0	0.000844	-0.000824	-0.00028	0.252319	0.000111	-3.9548	0.9542
565.9	-0.001686	10.0	0.000844	-0.000842	-0.00045	0.252302	0.000180	-3.7439	1.0000
566.1	-0.001686	12.0	0.000844	-0.000841	-0.00045	0.252302	0.000179	-3.7464	1.0792
566.3	-0.001668	15.0	0.000845	-0.000823	-0.00027	0.252320	0.000108	-3.9657	1.1761
566.6	-0.001703	18.0	0.000845	-0.000858	-0.00062	0.252286	0.000246	-3.6098	1.2553
567.6	-0.001674	21.0	0.000847	-0.000827	-0.00031	0.252318	0.000123	-3.9093	1.3222
566.7	-0.001691	24.0	0.000845	-0.000846	-0.00050	0.252298	0.000198	-3.7024	1.3802
567.4	-0.001738	27.0	0.000846	-0.000892	-0.00096	0.252253	0.000380	-3.4200	1.4314
567.7	-0.001703	30.0	0.000847	-0.000856	-0.00060	0.252289	0.000238	-3.6227	1.4771
568.1	-0.001709	33.0	0.000847	-0.000862	-0.00065	0.252284	0.000260	-3.5858	1.5185
567.7	-0.001738	36.0	0.000847	-0.000886	-0.00095	0.252253	0.000378	-3.4224	1.5563
567.7	-0.001733	39.0	0.000847	-0.000886	-0.00090	0.252259	0.000355	-3.4499	1.5911
567.7	-0.001750	42.0	0.000847	-0.000903	-0.00107	0.252242	0.000425	-3.3720	1.6232
567.6	-0.001791	45.0	0.000847	-0.000944	-0.00148	0.252200	0.000588	-3.2309	1.6532
567.9	-0.001768	48.0	0.000847	-0.000921	-0.00124	0.252225	0.000493	-3.3072	1.6812
567.7	-0.001803	51.0	0.000847	-0.000956	-0.00160	0.252189	0.000633	-3.1984	1.7076
567.9	-0.001768	54.0	0.000847	-0.000921	-0.00124	0.252225	0.000493	-3.3072	1.7324
568.1	-0.001774	57.0	0.000847	-0.000926	-0.00130	0.252219	0.000515	-3.2881	1.7559
568.2	-0.001779	60.0	0.000848	-0.000932	-0.00136	0.252214	0.000538	-3.2695	1.7782

n = 0.79 ± 0.09, Log(K) = -4.68 ± 0.12, R Squared = 0.798

Table 25. Isothermal Shrinkage Data for Region C,

1. ABS.2 Sample 2, Lo = 0.2330 inches, 624 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
622.5	-0.007796	6.0	0.000853	-0.006933	-0.000093	0.232832	0.000400	-3.3978	0.7782
622.3	-0.007825	9.0	0.000862	-0.006963	-0.000123	0.232803	0.000527	-3.2782	0.9542
623.5	-0.007813	10.0	0.000864	-0.006949	-0.000109	0.232817	0.000469	-3.3285	1.0000
623.1	-0.007825	12.0	0.000863	-0.006962	-0.000122	0.232805	0.000522	-3.2821	1.0792
623.2	-0.007890	15.0	0.000864	-0.007026	-0.000186	0.232740	0.000799	-3.0977	1.1761
623.5	-0.007919	18.0	0.000864	-0.007055	-0.000215	0.232712	0.000923	-3.0349	1.2553
623.5	-0.007948	21.0	0.000864	-0.007084	-0.000244	0.232682	0.001049	-2.9794	1.3222
623.0	-0.007943	24.0	0.000863	-0.007079	-0.000239	0.232687	0.001027	-2.9886	1.3802
623.6	-0.007989	27.0	0.000864	-0.007125	-0.000285	0.232642	0.001223	-2.9126	1.4314
624.0	-0.008007	30.0	0.000865	-0.007142	-0.000302	0.232625	0.001297	-2.8870	1.4771
623.7	-0.008036	33.0	0.000864	-0.007172	-0.000332	0.232595	0.001425	-2.8462	1.5185
625.0	-0.008066	36.0	0.000866	-0.007200	-0.000359	0.232569	0.001542	-2.8118	1.5563
625.2	-0.008054	39.0	0.000866	-0.007187	-0.000347	0.232581	0.001491	-2.8266	1.5911
624.7	-0.008089	42.0	0.000866	-0.007223	-0.000383	0.232544	0.001645	-2.7838	1.6232
624.4	-0.008077	45.0	0.000865	-0.007212	-0.000372	0.232555	0.001597	-2.7968	1.6532
624.6	-0.008101	48.0	0.000866	-0.007235	-0.000395	0.232532	0.001696	-2.7706	1.6812
624.4	-0.008136	51.0	0.000865	-0.007271	-0.000431	0.232497	0.001848	-2.7332	1.7076
625.3	-0.008201	54.0	0.000867	-0.007334	-0.000494	0.232434	0.002120	-2.6737	1.7324
624.7	-0.008160	57.0	0.000866	-0.007294	-0.000454	0.232474	0.001947	-2.7106	1.7559
624.6	-0.008154	60.0	0.000866	-0.007288	-0.000448	0.232480	0.001923	-2.7161	1.7782

n = 0.75 ± 0.03, Log(K) = -4.01 ± 0.04, R Squared = 0.976

Table 26. Isothermal Shrinkage Data for Region C,

I. ABS-2 Sample 4, $L_0 = 0.2310$ inches, 690 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage, inches	Log Linear Shrinkage	Log Time
688.4	-0.007743	6.0	0.000951	-0.006792	-0.000158	0.230828	0.000683	-3.1656	0.7782
689.1	-0.007802	9.0	0.000952	-0.006850	-0.000215	0.230771	0.000932	-3.0304	0.9542
689.6	-0.007802	10.0	0.000953	-0.006849	-0.000215	0.230772	0.000930	-3.0317	1.0000
689.4	-0.007849	12.0	0.000952	-0.006896	-0.000262	0.230725	0.001134	-2.9454	1.0792
689.3	-0.007890	15.0	0.000952	-0.006937	-0.000303	0.230683	0.001312	-2.8820	1.1761
690.1	-0.007954	18.0	0.000954	-0.007001	-0.000366	0.230621	0.001587	-2.7996	1.2553
690.1	-0.007950	21.0	0.000954	-0.007007	-0.000372	0.230615	0.001612	-2.7927	1.3222
690.0	-0.007989	24.0	0.000953	-0.007036	-0.000402	0.230585	0.001740	-2.7596	1.3802
690.2	-0.008036	27.0	0.000954	-0.007083	-0.000448	0.230539	0.001941	-2.7119	1.4314
690.2	-0.008060	30.0	0.000954	-0.007106	-0.000472	0.230515	0.002043	-2.6897	1.4771
690.8	-0.008113	33.0	0.000955	-0.007158	-0.000524	0.230464	0.002268	-2.6444	1.5185
690.8	-0.008119	36.0	0.000955	-0.007164	-0.000530	0.230458	0.002293	-2.6396	1.5563
691.2	-0.008195	39.0	0.000955	-0.007240	-0.000605	0.230383	0.002621	-2.5816	1.5911
691.0	-0.008212	42.0	0.000955	-0.007258	-0.000623	0.230365	0.002698	-2.5690	1.6232
690.8	-0.008242	45.0	0.000955	-0.007287	-0.000653	0.230335	0.002826	-2.5488	1.6532
691.2	-0.008277	48.0	0.000955	-0.007322	-0.000687	0.230301	0.002976	-2.5264	1.6812
691.4	-0.008289	51.0	0.000955	-0.007333	-0.000699	0.230289	0.003026	-2.5191	1.7076
691.8	-0.008306	54.0	0.000956	-0.007350	-0.000716	0.230273	0.003099	-2.5087	1.7324
691.5	-0.008347	57.0	0.000955	-0.007392	-0.000758	0.230231	0.003279	-2.4842	1.7559
691.5	-0.008359	60.0	0.000956	-0.007403	-0.000769	0.230219	0.003330	-2.4776	1.7782

$n = 0.69 \pm 0.01$, $\text{Log}(K) = -3.70 \pm 0.01$, $R \text{ Squared} = 0.996$

Table 27. Isothermal Shrinkage Data for Region C,

11.ABS.1 Sample 5, $L_0 = 0.2316$ inches, 522 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
521.7	-0.005570	6.0	0.000710	-0.005860	0.000018	0.231610	-0.000078		0.7782
521.4	-0.005582	9.0	0.000710	-0.005872	0.000006	0.231598	-0.000026		0.9542
522.1	-0.005599	10.0	0.000711	-0.005888	-0.000011	0.231582	0.000046	-4.3396	1.0000
521.9	-0.005635	12.0	0.000710	-0.005924	-0.000046	0.231546	0.000199	-3.7002	1.0792
522.1	-0.005664	15.0	0.000711	-0.005953	-0.000075	0.231517	0.000324	-3.4890	1.1761
521.6	-0.005681	18.0	0.000710	-0.005971	-0.000093	0.231498	0.000403	-3.3942	1.2553
521.7	-0.005723	21.0	0.000710	-0.006012	-0.000134	0.231458	0.000580	-3.2366	1.3222
522.2	-0.005717	24.0	0.000711	-0.006006	-0.000128	0.231465	0.000552	-3.2584	1.3802
522.8	-0.005758	27.0	0.000712	-0.006046	-0.000168	0.231425	0.000725	-3.1395	1.4314
522.6	-0.005781	30.0	0.000712	-0.006070	-0.000192	0.231401	0.000828	-3.0822	1.4771
522.5	-0.005787	33.0	0.000711	-0.006076	-0.000198	0.231395	0.000854	-3.0685	1.5185
523.2	-0.005810	35.0	0.000713	-0.006098	-0.000220	0.231373	0.000950	-3.0221	1.5563
522.5	-0.005828	39.0	0.000711	-0.006117	-0.000239	0.231354	0.001031	-2.9866	1.5911
522.1	-0.005840	42.0	0.000711	-0.006129	-0.000251	0.231341	0.001084	-2.9648	1.6232
522.6	-0.005875	45.0	0.000712	-0.006163	-0.000286	0.231307	0.001233	-2.9091	1.6532
523.4	-0.005893	48.0	0.000713	-0.006180	-0.000302	0.231292	0.001304	-2.8847	1.6812
523.0	-0.005887	51.0	0.000712	-0.006175	-0.000297	0.231296	0.001281	-2.8923	1.7076
522.3	-0.005893	54.0	0.000711	-0.006181	-0.000304	0.231289	0.001311	-2.8824	1.7324
522.5	-0.005910	57.0	0.000711	-0.006199	-0.000321	0.231272	0.001386	-2.8584	1.7559
522.9	-0.005928	60.0	0.000712	-0.006216	-0.000338	0.231255	0.001459	-2.8359	1.7782

$n = 1.06 \pm 0.05$, $\text{Log}(K) = -4.59 \pm 0.03$, $R \text{ Squared} = 0.975$

Table 28. Isothermal Shrinkage Data for Region C,

II. ABS.1 Sample 2, $L_0 = 0.2320$ inches, 567 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
567.4	-0.007280	6.0	0.000778	-0.006501	0.000043	0.232012	-0.000185		0.7782
566.6	-0.007327	9.0	0.000777	-0.006550	-0.000005	0.231963	0.000022	-4.6535	0.9542
567.2	-0.007338	10.0	0.000778	-0.006560	-0.000016	0.231952	0.000059	-4.1591	1.0000
567.6	-0.007344	12.0	0.000779	-0.006566	-0.000021	0.231948	0.000092	-4.0384	1.0792
567.0	-0.007368	15.0	0.000778	-0.006590	-0.000046	0.231923	0.000197	-3.7060	1.1761
567.6	-0.007420	18.0	0.000779	-0.006642	-0.000097	0.231872	0.000420	-3.3765	1.2553
567.2	-0.007415	21.0	0.000778	-0.006637	-0.000092	0.231876	0.000398	-3.4005	1.3222
567.6	-0.007479	24.0	0.000779	-0.006701	-0.000156	0.231813	0.000673	-3.1720	1.3802
568.2	-0.007456	27.0	0.000779	-0.006676	-0.000132	0.231838	0.000568	-3.2453	1.4314
568.2	-0.007503	30.0	0.000779	-0.006723	-0.000179	0.231791	0.000771	-3.1131	1.4771
568.0	-0.007485	33.0	0.000779	-0.006706	-0.000162	0.231808	0.000696	-3.1572	1.5185
568.7	-0.007544	36.0	0.000780	-0.006764	-0.000219	0.231751	0.000945	-3.0247	1.5563
568.4	-0.007544	39.0	0.000780	-0.006764	-0.000220	0.231750	0.000946	-3.0239	1.5911
567.9	-0.007532	42.0	0.000779	-0.006753	-0.000209	0.231761	0.000899	-3.0461	1.6232
568.5	-0.007591	45.0	0.000780	-0.006811	-0.000266	0.231703	0.001148	-2.9399	1.6532
568.2	-0.007591	48.0	0.000779	-0.006811	-0.000267	0.231703	0.001150	-2.9394	1.6812
568.9	-0.007591	51.0	0.000780	-0.006810	-0.000266	0.231704	0.001146	-2.9410	1.7076
568.7	-0.007632	54.0	0.000780	-0.006852	-0.000307	0.231653	0.001324	-2.8781	1.7324
568.5	-0.007632	57.0	0.000780	-0.006852	-0.000307	0.231662	0.001325	-2.8777	1.7559
568.8	-0.007673	60.0	0.000780	-0.006892	-0.000348	0.231622	0.001500	-2.8239	1.7782

$n = 1.06 \pm 0.07$, $\log(K) = -4.72 \pm 0.05$, R Squared = 0.940

Table 20. Isothermal Shrinkage Data for Region C,

11.ABS.1 Sample 11, $L_0 = 0.2301$ inches, 624 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
624.0	-0.004781	6.0	0.000854	-0.003927	-0.000087	0.230026	0.000379	-3.4218	0.7782
623.9	-0.004822	9.0	0.000854	-0.003969	-0.000128	0.229985	0.000358	-3.4536	0.9542
624.2	-0.004817	10.0	0.000854	-0.003962	-0.000122	0.229991	0.000330	-3.4755	1.0000
624.3	-0.004852	12.0	0.000854	-0.003997	-0.000157	0.229956	0.000582	-3.1660	1.0792
624.2	-0.004853	15.0	0.000854	-0.004009	-0.000169	0.229944	0.000734	-3.1341	1.1761
624.5	-0.004910	18.0	0.000855	-0.004056	-0.000215	0.229898	0.000936	-3.0286	1.2553
625.1	-0.004934	21.0	0.000856	-0.004078	-0.000238	0.229876	0.001034	-2.9854	1.3222
625.1	-0.004969	24.0	0.000856	-0.004113	-0.000273	0.229841	0.001187	-2.9255	1.3802
625.0	-0.004934	27.0	0.000855	-0.004078	-0.000238	0.229876	0.001035	-2.9850	1.4314
625.4	-0.004957	30.0	0.000856	-0.004101	-0.000261	0.229853	0.001134	-2.9452	1.4771
625.5	-0.004959	33.0	0.000856	-0.004113	-0.000273	0.229842	0.001185	-2.9264	1.5185
625.0	-0.004975	36.0	0.000855	-0.004120	-0.000279	0.229835	0.001214	-2.9159	1.5563
625.0	-0.005016	39.0	0.000855	-0.004161	-0.000320	0.229794	0.001392	-2.8564	1.5911
625.3	-0.005033	42.0	0.000856	-0.004178	-0.000337	0.229777	0.001466	-2.8337	1.6232
625.6	-0.005057	45.0	0.000857	-0.004200	-0.000360	0.229755	0.001565	-2.8055	1.6532
625.5	-0.005080	48.0	0.000856	-0.004224	-0.000384	0.229731	0.001669	-2.7776	1.6812
626.3	-0.005075	51.0	0.000857	-0.004217	-0.000377	0.229738	0.001638	-2.7856	1.7076
625.3	-0.005110	54.0	0.000856	-0.004254	-0.000414	0.229701	0.001797	-2.7454	1.7324
625.9	-0.005104	57.0	0.000857	-0.004247	-0.000407	0.229708	0.001769	-2.7524	1.7559
625.4	-0.005098	60.0	0.000856	-0.004242	-0.000402	0.229713	0.001746	-2.7580	1.7782

 $n = 0.65 \pm 0.02$, $\text{Log}(K) = -3.89 \pm 0.03$, $R \text{ Squared} = 0.977$

Table 30. Isothermal Shrinkage Data for Region C,

II. ABS.1 Sample 8, $L_0 = 0.2301$ inches, 690°C .

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Time
690.5	-0.008605	6.0	0.000550	-0.007655	-0.000161	0.229967	0.000700	0.7782
690.0	-0.008570	9.0	0.000550	-0.007720	-0.000226	0.229901	0.000984	0.9542
690.6	-0.008699	10.0	0.000550	-0.007749	-0.000255	0.229873	0.001108	1.0000
689.9	-0.008740	12.0	0.000949	-0.007791	-0.000297	0.229830	0.001291	1.0792
690.2	-0.008793	15.0	0.000550	-0.007843	-0.000349	0.229778	0.001518	1.1761
690.9	-0.008840	18.0	0.000951	-0.007889	-0.000395	0.229733	0.001717	1.2353
690.8	-0.008864	21.0	0.000951	-0.007913	-0.000419	0.229709	0.001820	1.3222
691.3	-0.008952	24.0	0.000952	-0.008000	-0.000506	0.229623	0.002199	1.3802
691.2	-0.008998	27.0	0.000951	-0.008047	-0.000553	0.229575	0.002404	1.4314
691.5	-0.008993	30.0	0.000952	-0.008041	-0.000547	0.229582	0.002376	1.4771
691.0	-0.009051	33.0	0.000951	-0.008100	-0.000606	0.229522	0.002635	1.5185
692.2	-0.009092	36.0	0.000953	-0.008139	-0.000646	0.229484	0.002805	1.5563
691.8	-0.009128	39.0	0.000952	-0.008175	-0.000681	0.229448	0.002961	1.5911
691.8	-0.009157	42.0	0.000952	-0.008205	-0.000711	0.229418	0.003088	1.6232
691.5	-0.009180	45.0	0.000952	-0.008229	-0.000735	0.229394	0.003193	1.6532
692.2	-0.009221	48.0	0.000953	-0.008269	-0.000775	0.229355	0.003366	1.6812
692.2	-0.009257	51.0	0.000953	-0.008304	-0.000810	0.229320	0.003520	1.7076
691.5	-0.009274	54.0	0.000952	-0.008322	-0.000828	0.229300	0.003600	1.7324
691.9	-0.009309	57.0	0.000952	-0.008357	-0.000863	0.229266	0.003751	1.7559
692.1	-0.009350	60.0	0.000953	-0.008398	-0.000904	0.229225	0.003928	1.7782

$n = 0.72 \pm 0.01$, $\text{Log}(K) = -3.69 \pm 0.01$, $R \text{ Squared } 0.995$

Table 31. Isothermal Shrinkage Data for Region C,

II. ABS. 2 Sample 5, Lo = 0.2332 inches, 522 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
521.6	-0.006042	6.0	0.000715	-0.005327	-0.000047	0.233145	0.000202	-3.6941	0.7782
521.5	-0.006107	9.0	0.000715	-0.005392	-0.000112	0.233080	0.000480	-3.3191	0.9542
521.6	-0.006095	10.0	0.000715	-0.005380	-0.000100	0.233092	0.000429	-3.3680	1.0000
521.6	-0.006124	12.0	0.000715	-0.005409	-0.000129	0.233062	0.000554	-3.2562	1.0792
521.9	-0.006118	15.0	0.000715	-0.005403	-0.000123	0.233069	0.000527	-3.2781	1.1761
523.3	-0.006159	18.0	0.000717	-0.005442	-0.000162	0.233031	0.000595	-3.1582	1.2553
522.3	-0.006148	21.0	0.000716	-0.005432	-0.000152	0.233041	0.000551	-3.1866	1.3222
522.4	-0.006189	24.0	0.000716	-0.005473	-0.000193	0.233000	0.000826	-3.0832	1.3802
522.7	-0.006171	27.0	0.000717	-0.005455	-0.000175	0.233018	0.000748	-3.1258	1.4314
522.6	-0.006201	30.0	0.000717	-0.005484	-0.000204	0.232989	0.000875	-3.0582	1.4771
522.9	-0.006206	33.0	0.000717	-0.005489	-0.000209	0.232983	0.000898	-3.0467	1.5185
522.6	-0.006259	36.0	0.000716	-0.005543	-0.000263	0.232930	0.001126	-2.9483	1.5563
523.0	-0.006253	39.0	0.000717	-0.005536	-0.000256	0.232937	0.001099	-2.9591	1.5911
523.3	-0.006265	42.0	0.000718	-0.005548	-0.000267	0.232926	0.001147	-2.9404	1.6232
523.6	-0.006277	45.0	0.000718	-0.005559	-0.000279	0.232915	0.001196	-2.9224	1.6532
522.8	-0.006277	48.0	0.000717	-0.005550	-0.000280	0.232913	0.001201	-2.9205	1.6812
522.5	-0.006294	51.0	0.000716	-0.005578	-0.000298	0.232895	0.001278	-2.8936	1.7076
522.7	-0.006312	54.0	0.000717	-0.005595	-0.000315	0.232877	0.001352	-2.8690	1.7324
522.9	-0.006318	57.0	0.000717	-0.005601	-0.000321	0.232872	0.001376	-2.8614	1.7559
522.9	-0.006330	60.0	0.000717	-0.005613	-0.000333	0.232860	0.001426	-2.8458	1.7782

$n = 0.71 \pm 0.04$, $\log(K) = -4.10 \pm 0.05$, $R \text{ Squared} = 0.946$

Table 32. Isothermal Shrinkage Data for Region C,

11.ABS.2 Sample 15, Lo = 0.2266 inches, 567 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage, inches	Log Linear Shrinkage	Log Time
566.5	-0.004359	6.0	0.000759	-0.003600	-0.00063	0.226494	0.000278	-3.5553	0.7782
566.2	-0.004371	9.0	0.000758	-0.003612	-0.00063	0.226482	0.000332	-3.4785	0.9542
566.3	-0.004355	10.0	0.000759	-0.003606	-0.00069	0.226488	0.000306	-3.5147	1.0000
566.2	-0.004394	12.0	0.000758	-0.003636	-0.00099	0.226458	0.000436	-3.3607	1.0792
566.2	-0.004406	15.0	0.000758	-0.003648	-0.00110	0.226446	0.000487	-3.3123	1.1761
566.3	-0.004424	18.0	0.000759	-0.003663	-0.00128	0.226429	0.000564	-3.2486	1.2553
567.4	-0.004424	21.0	0.000760	-0.003663	-0.00126	0.226432	0.000557	-3.2539	1.3222
566.7	-0.004459	24.0	0.000759	-0.003700	-0.00163	0.226395	0.000717	-3.1443	1.3802
567.2	-0.004471	27.0	0.000760	-0.003711	-0.00174	0.226384	0.000766	-3.1160	1.4314
567.3	-0.004488	30.0	0.000760	-0.003728	-0.00191	0.226367	0.000843	-3.0742	1.4771
567.4	-0.004471	33.0	0.000760	-0.003710	-0.00173	0.226385	0.000765	-3.1165	1.5185
567.6	-0.004488	36.0	0.000760	-0.003728	-0.00191	0.226367	0.000841	-3.0752	1.5563
567.8	-0.004500	39.0	0.000761	-0.003739	-0.00202	0.226356	0.000891	-3.0500	1.5911
568.2	-0.004529	42.0	0.000761	-0.003768	-0.00231	0.226328	0.001018	-2.9983	1.6232
567.4	-0.004553	45.0	0.000760	-0.003793	-0.00255	0.226302	0.001127	-2.9481	1.6532
568.1	-0.004512	48.0	0.000761	-0.003750	-0.00213	0.226345	0.000941	-3.0264	1.6812
568.3	-0.004564	51.0	0.000761	-0.003803	-0.00266	0.226293	0.001173	-2.9309	1.7076
568.1	-0.004529	54.0	0.000761	-0.003768	-0.00231	0.226328	0.001019	-2.9920	1.7324
568.1	-0.004570	57.0	0.000761	-0.003809	-0.00272	0.226287	0.001200	-2.9209	1.7559
568.3	-0.004558	60.0	0.000761	-0.003797	-0.00260	0.226299	0.001147	-2.9406	1.7782

n = 0.67 ± 0.03, Log(K) = -4.11 ± 0.04, R Squared = 0.969

Table 33. Isothermal Shrinkage Data for Region C,

11.088.2 Sample 9, $L_0 = 0.2319$ inches, 624 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
622.1	-0.004846	6.0	0.000858	-0.003988	-0.000059	0.231858	0.000254	-3.5954	0.7782
622.4	-0.004869	9.0	0.000858	-0.004011	-0.000082	0.231846	0.000353	-3.4518	0.9542
622.4	-0.004887	10.0	0.000858	-0.004029	-0.000100	0.231828	0.000430	-3.3570	1.0000
622.9	-0.004881	12.0	0.000859	-0.004022	-0.000093	0.231835	0.000401	-3.3970	1.0792
623.0	-0.004916	15.0	0.000859	-0.004057	-0.000128	0.231800	0.000532	-3.2584	1.1761
622.5	-0.004987	18.0	0.000858	-0.004128	-0.000199	0.231729	0.000858	-3.0663	1.2533
623.5	-0.004957	21.0	0.000860	-0.004097	-0.000168	0.231760	0.000726	-3.1393	1.3222
622.9	-0.005004	24.0	0.000859	-0.004145	-0.000216	0.231712	0.000932	-3.0308	1.3802
623.9	-0.004998	27.0	0.000860	-0.004138	-0.000209	0.231720	0.000900	-3.0456	1.4314
623.4	-0.005033	30.0	0.000860	-0.004174	-0.000245	0.231684	0.001055	-2.9766	1.4771
624.1	-0.005016	33.0	0.000861	-0.004155	-0.000226	0.231703	0.000975	-3.0111	1.5185
624.1	-0.005051	36.0	0.000861	-0.004190	-0.000251	0.231658	0.001127	-2.9482	1.5563
623.8	-0.005045	39.0	0.000860	-0.004185	-0.000256	0.231673	0.001103	-2.9574	1.5911
624.3	-0.005086	42.0	0.000861	-0.004225	-0.000296	0.231633	0.001277	-2.8938	1.6232
625.0	-0.005080	45.0	0.000862	-0.004218	-0.000289	0.231640	0.001248	-2.9039	1.6532
624.3	-0.005098	48.0	0.000861	-0.004237	-0.000308	0.231621	0.001328	-2.8768	1.6812
624.6	-0.005110	51.0	0.000862	-0.004248	-0.000319	0.231610	0.001376	-2.8613	1.7076
624.9	-0.005139	54.0	0.000862	-0.004277	-0.000348	0.231582	0.001501	-2.8237	1.7324
624.4	-0.005121	57.0	0.000861	-0.004260	-0.000331	0.231598	0.001428	-2.8452	1.7559
624.4	-0.005157	60.0	0.000861	-0.004295	-0.000366	0.231563	0.001580	-2.8013	1.7782

$n = 0.77 \pm 0.03$, $\log(K) = -4.16 \pm 0.04$, $R \text{ Squared} = 0.957$

Table 34. Isothermal Shrinkage Data for Region C,

11.485.2 Sample 4, $L_0 = 0.2321$ inches, 690 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
689.1	-0.007679	6.0	0.000957	-0.006722	-0.000200	0.231901	0.000860	-3.0657	0.7782
689.7	-0.007702	9.0	0.000957	-0.006745	-0.000222	0.231879	0.000957	-3.0192	0.9542
689.7	-0.007720	10.0	0.000957	-0.006762	-0.000240	0.231862	0.001033	-2.9851	1.0000
689.9	-0.007761	12.0	0.000958	-0.006803	-0.000280	0.231821	0.001208	-2.9179	1.0792
690.7	-0.007837	15.0	0.000959	-0.006878	-0.000355	0.231747	0.001532	-2.8149	1.1761
690.6	-0.007866	18.0	0.000959	-0.006907	-0.000385	0.231717	0.001659	-2.7803	1.2553
690.7	-0.007890	21.0	0.000959	-0.006931	-0.000408	0.231694	0.001759	-2.7547	1.3222
691.6	-0.007925	24.0	0.000960	-0.006965	-0.000442	0.231661	0.001906	-2.7200	1.3802
691.4	-0.007954	27.0	0.000960	-0.006994	-0.000472	0.231631	0.002033	-2.6918	1.4314
691.3	-0.008025	30.0	0.000960	-0.007055	-0.000542	0.231560	0.002337	-2.6313	1.4771
691.9	-0.008019	33.0	0.000961	-0.007098	-0.000536	0.231568	0.002308	-2.6368	1.5185
691.1	-0.008048	35.0	0.000959	-0.007089	-0.000566	0.231536	0.002440	-2.6127	1.5563
692.0	-0.008054	39.0	0.000961	-0.007093	-0.000571	0.231533	0.002459	-2.6092	1.5911
691.4	-0.008066	42.0	0.000960	-0.007106	-0.000583	0.231519	0.002513	-2.5997	1.6232
691.4	-0.008083	45.0	0.000960	-0.007123	-0.000601	0.231502	0.002589	-2.5869	1.6532
691.2	-0.008107	48.0	0.000960	-0.007147	-0.000625	0.231478	0.002691	-2.5700	1.6812
691.7	-0.008101	51.0	0.000960	-0.007141	-0.000618	0.231485	0.002663	-2.5746	1.7076
692.4	-0.008160	54.0	0.000961	-0.007198	-0.000676	0.231428	0.002911	-2.5360	1.7324
691.0	-0.008183	57.0	0.000959	-0.007224	-0.000701	0.231401	0.003021	-2.5198	1.7559
691.4	-0.008201	60.0	0.000960	-0.007241	-0.000718	0.231385	0.003095	-2.5094	1.7782

$n = 0.58 \pm 0.01$, $\log(K) = -3.53 \pm 0.02$, $R \text{ Squared} = 0.983$

Table 35. Isothermal Shrinkage Data for Region D,

I. ABS. 1 Sample 14, Lo = 0.2277 inches, 845 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
842.1	-0.010832	3.0	0.001158	-0.009695	-0.002111	0.225556	0.009271	-2.0329	0.4771
842.5	-0.013546	6.0	0.001158	-0.012387	-0.004804	0.222853	0.021098	-1.6758	0.7782
843.1	-0.016486	9.0	0.001159	-0.015327	-0.007744	0.219524	0.034008	-1.4684	0.9542
843.9	-0.019234	12.0	0.001160	-0.018074	-0.010490	0.217178	0.046070	-1.3366	1.0792
843.4	-0.021524	15.0	0.001160	-0.020364	-0.012781	0.214887	0.056130	-1.2508	1.1761
843.7	-0.023603	18.0	0.001160	-0.022443	-0.014859	0.212809	0.065258	-1.1854	1.2553
843.9	-0.025535	21.0	0.001160	-0.024375	-0.016791	0.210877	0.073743	-1.1323	1.3222
844.1	-0.027344	24.0	0.001161	-0.026183	-0.018600	0.209069	0.081686	-1.0879	1.3802
844.5	-0.029024	27.0	0.001161	-0.027883	-0.020279	0.207390	0.089061	-1.0503	1.4314
844.9	-0.030581	30.0	0.001162	-0.029419	-0.021835	0.205834	0.095896	-1.0182	1.4771
844.5	-0.032044	33.0	0.001161	-0.030882	-0.023299	0.204370	0.102322	-0.9900	1.5185
845.7	-0.033365	36.0	0.001163	-0.032202	-0.024619	0.203051	0.108120	-0.9661	1.5563
844.7	-0.034570	39.0	0.001162	-0.033408	-0.025825	0.201844	0.113416	-0.9453	1.5911
845.5	-0.035657	42.0	0.001163	-0.034494	-0.026911	0.200759	0.118184	-0.9274	1.6232
845.1	-0.036603	45.0	0.001162	-0.035440	-0.027857	0.199813	0.122341	-0.9124	1.6532
845.7	-0.037466	48.0	0.001163	-0.036303	-0.028720	0.198950	0.126131	-0.8992	1.6812
844.9	-0.038248	51.0	0.001162	-0.037086	-0.029503	0.198157	0.129568	-0.8875	1.7076
846.0	-0.038947	54.0	0.001163	-0.037784	-0.030200	0.197470	0.132632	-0.8774	1.7324
845.9	-0.039576	57.0	0.001163	-0.038412	-0.030829	0.196841	0.135353	-0.8684	1.7559
845.4	-0.040187	60.0	0.001163	-0.039024	-0.031441	0.196229	0.138080	-0.8599	1.7782

Table 36. Isothermal Shrinkage Data for Region D,

I. 888.1 Sample 3, $L_0 = 0.2035$ inches, 845 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
842.2	-0.035528	3.0	0.001035	-0.034493	-0.001902	0.201460	0.009347	-2.0293	0.4771
841.6	-0.037202	6.0	0.001034	-0.036168	-0.003577	0.199784	0.017579	-1.7550	0.7782
842.6	-0.038571	9.0	0.001035	-0.037635	-0.005045	0.198318	0.024791	-1.6057	0.9542
843.2	-0.039899	12.0	0.001036	-0.038863	-0.006272	0.197091	0.030821	-1.5112	1.0792
843.2	-0.041086	15.0	0.001036	-0.040050	-0.007459	0.195504	0.036534	-1.4359	1.1761
843.7	-0.042138	18.0	0.001037	-0.041101	-0.008510	0.194853	0.041819	-1.3785	1.2533
843.8	-0.043131	21.0	0.001037	-0.042094	-0.009503	0.193861	0.046598	-1.3307	1.3222
843.7	-0.044041	24.0	0.001037	-0.043004	-0.010414	0.192950	0.051174	-1.2910	1.3802
843.7	-0.044923	27.0	0.001037	-0.043885	-0.011295	0.192068	0.055505	-1.2557	1.4314
844.1	-0.045722	30.0	0.001037	-0.044684	-0.012094	0.191270	0.059429	-1.2260	1.4771
843.9	-0.046468	33.0	0.001037	-0.045431	-0.012840	0.190523	0.063057	-1.2000	1.5185
844.5	-0.047144	36.0	0.001038	-0.046106	-0.013515	0.189849	0.066414	-1.1777	1.5563
844.7	-0.047790	39.0	0.001038	-0.046752	-0.014151	0.189203	0.069589	-1.1575	1.5911
844.4	-0.048395	42.0	0.001038	-0.047357	-0.014767	0.188597	0.072564	-1.1393	1.6232
844.5	-0.048983	45.0	0.001038	-0.047945	-0.015354	0.188010	0.075451	-1.1223	1.6532
844.8	-0.049523	48.0	0.001038	-0.048485	-0.015895	0.187470	0.078106	-1.1073	1.6812
845.8	-0.049529	51.0	0.001040	-0.048989	-0.016299	0.187057	0.080091	-1.0964	1.7076
845.6	-0.050358	54.0	0.001039	-0.049318	-0.016728	0.186638	0.082200	-1.0851	1.7324
845.4	-0.050722	57.0	0.001039	-0.049683	-0.017092	0.186273	0.083992	-1.0758	1.7559
843.8	-0.051058	60.0	0.001037	-0.050031	-0.017441	0.185923	0.085705	-1.0670	1.7782

Table 37. Isothermal Shrinkage Data for Region D,

I.088.1 Sample 10, $L_0 = 0.2047$ inches, 864 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
859.9	-0.041820	3.0	0.001064	-0.040756	-0.004653	0.199827	0.019403	-1.7121	0.4771
860.5	-0.045216	6.0	0.001065	-0.044152	-0.008048	0.196432	0.033562	-1.4741	0.7782
860.8	-0.047578	9.0	0.001065	-0.046613	-0.010510	0.193971	0.043827	-1.3583	0.9542
861.5	-0.049541	12.0	0.001066	-0.048475	-0.012371	0.192110	0.051590	-1.2874	1.0792
861.4	-0.050886	15.0	0.001066	-0.049821	-0.013717	0.190764	0.057202	-1.2426	1.1761
862.3	-0.051981	18.0	0.001067	-0.050894	-0.014791	0.189591	0.061680	-1.2099	1.2533
862.3	-0.052766	21.0	0.001067	-0.051699	-0.015596	0.188887	0.065036	-1.1868	1.3222
863.0	-0.053324	24.0	0.001068	-0.052257	-0.016153	0.188330	0.067360	-1.1716	1.3802
862.6	-0.053799	27.0	0.001067	-0.052692	-0.016588	0.187894	0.069175	-1.1601	1.4314
862.8	-0.054129	30.0	0.001068	-0.053062	-0.016958	0.187525	0.070718	-1.1505	1.4771
863.2	-0.054429	33.0	0.001068	-0.053361	-0.017257	0.187226	0.071965	-1.1429	1.5185
863.3	-0.054629	36.0	0.001068	-0.053560	-0.017457	0.187026	0.072797	-1.1379	1.5563
864.0	-0.054817	39.0	0.001069	-0.053747	-0.017644	0.186840	0.073577	-1.1333	1.5911
863.1	-0.054928	42.0	0.001069	-0.053860	-0.017757	0.186726	0.074047	-1.1305	1.6232
863.5	-0.055028	45.0	0.001069	-0.053960	-0.017856	0.186627	0.074462	-1.1281	1.6532
863.2	-0.055104	48.0	0.001068	-0.054036	-0.017933	0.186550	0.074782	-1.1262	1.6812
863.1	-0.055157	51.0	0.001068	-0.054089	-0.017986	0.186497	0.075003	-1.1249	1.7076
863.4	-0.055240	54.0	0.001068	-0.054171	-0.018068	0.186416	0.075344	-1.1230	1.7324
863.9	-0.055269	57.0	0.001069	-0.054200	-0.018096	0.186387	0.075464	-1.1223	1.7559
864.2	-0.055281	60.0	0.001069	-0.054211	-0.018108	0.186376	0.075512	-1.1220	1.7782

Table 38. Isothermal Shrinkage Data for Region D,

I. ABS.1 Sample 11, $L_0 = 0.2379$, 864 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
850.6	-0.036920	3.0	0.001238	-0.035682	-0.006516	0.231187	0.027388	-1.5624	0.4771
851.1	-0.041844	6.0	0.001238	-0.040606	-0.011439	0.226265	0.048082	-1.3180	0.7782
852.0	-0.045487	9.0	0.001240	-0.044247	-0.015080	0.222624	0.063390	-1.1980	0.9542
852.4	-0.048101	12.0	0.001240	-0.046851	-0.017694	0.220011	0.074377	-1.1286	1.0792
853.4	-0.050093	15.0	0.001242	-0.048852	-0.019685	0.218021	0.082744	-1.0823	1.1761
853.2	-0.051627	18.0	0.001241	-0.050385	-0.021218	0.216487	0.089190	-1.0497	1.2553
854.3	-0.052637	21.0	0.001243	-0.051394	-0.022227	0.215480	0.093431	-1.0295	1.3222
854.2	-0.053125	24.0	0.001243	-0.051882	-0.022715	0.214992	0.095482	-1.0201	1.3802
853.2	-0.053442	27.0	0.001241	-0.052201	-0.023034	0.214672	0.096822	-1.0140	1.4314
853.5	-0.053636	30.0	0.001242	-0.052394	-0.023227	0.214479	0.097634	-1.0104	1.4771
853.7	-0.053742	33.0	0.001242	-0.052499	-0.023333	0.214374	0.098078	-1.0084	1.5185
853.9	-0.053836	36.0	0.001242	-0.052593	-0.023426	0.214280	0.098471	-1.0057	1.5563
855.0	-0.053812	39.0	0.001244	-0.052568	-0.023401	0.214306	0.098366	-1.0072	1.5911
855.0	-0.053806	42.0	0.001244	-0.052562	-0.023395	0.214312	0.098341	-1.0073	1.6232
854.6	-0.053847	45.0	0.001243	-0.052604	-0.023437	0.214270	0.098517	-1.0065	1.6532
855.2	-0.053836	48.0	0.001244	-0.052591	-0.023424	0.214283	0.098463	-1.0067	1.6812
854.9	-0.053812	51.0	0.001244	-0.052568	-0.023401	0.214306	0.098366	-1.0072	1.7076
854.1	-0.053818	54.0	0.001243	-0.052575	-0.023408	0.214298	0.098396	-1.0070	1.7324
854.3	-0.053841	57.0	0.001243	-0.052598	-0.023432	0.214275	0.098433	-1.0066	1.7559
854.9	-0.053783	60.0	0.001244	-0.052539	-0.023372	0.214336	0.098243	-1.0077	1.7782

Table 39. Isothermal Shrinkage Data for Region D,

I.085.1 Sample 15, Lo = 0.1902 inches, 874 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	Sytem Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
872.9	-0.045509	3.0	0.001004	-0.045505	-0.003225	0.186795	0.016957	-1.7706	0.4771
872.8	-0.047261	6.0	0.001004	-0.046257	-0.003977	0.186043	0.020912	-1.6796	0.7782
872.9	-0.047537	9.0	0.001004	-0.046533	-0.004254	0.185767	0.022363	-1.6505	0.9542
873.3	-0.047602	12.0	0.001005	-0.046597	-0.004318	0.185703	0.022701	-1.6440	1.0792
873.0	-0.047602	15.0	0.001004	-0.046598	-0.004318	0.185702	0.022703	-1.6439	1.1761
873.3	-0.047531	18.0	0.001005	-0.046527	-0.004247	0.185773	0.022330	-1.6511	1.2553
873.4	-0.047479	21.0	0.001005	-0.046474	-0.004194	0.185826	0.022051	-1.6566	1.3222
874.1	-0.047437	24.0	0.001006	-0.046432	-0.004152	0.185868	0.021831	-1.6609	1.3802
873.9	-0.047390	27.0	0.001005	-0.046385	-0.004105	0.185915	0.021585	-1.6658	1.4314
873.9	-0.047396	30.0	0.001005	-0.046391	-0.004111	0.185909	0.021616	-1.6652	1.4771
874.2	-0.047414	33.0	0.001006	-0.046408	-0.004129	0.18592	0.021706	-1.6634	1.5185
874.0	-0.047437	36.0	0.001005	-0.046432	-0.004152	0.185868	0.021831	-1.6609	1.5563
873.9	-0.047426	39.0	0.001005	-0.046420	-0.004141	0.185880	0.021770	-1.6621	1.5911
874.2	-0.047414	42.0	0.001006	-0.046408	-0.004129	0.185892	0.021706	-1.6634	1.6232
874.5	-0.047426	45.0	0.001006	-0.046420	-0.004140	0.185880	0.021766	-1.6622	1.6532
874.4	-0.047426	48.0	0.001006	-0.046420	-0.004140	0.185880	0.021767	-1.6622	1.6812
874.0	-0.047443	51.0	0.001005	-0.046438	-0.004158	0.185852	0.021862	-1.6603	1.7076
874.1	-0.047455	54.0	0.001006	-0.046450	-0.004170	0.185850	0.021924	-1.6591	1.7324
874.1	-0.047484	57.0	0.001006	-0.046479	-0.004199	0.185821	0.022078	-1.6560	1.7559
874.4	-0.047473	60.0	0.001006	-0.046467	-0.004187	0.185833	0.022014	-1.6573	1.7782

Table 40. Isothermal Shrinkage Data for Region D,

I.ABS.2 Sample 11, Lo = 0.2259 inches, 845 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
841.5	-0.018982	3.0	0.001148	-0.017834	-0.001884	0.223937	0.008338	-2.0789	0.4771
841.5	-0.020614	6.0	0.001148	-0.019466	-0.003516	0.222305	0.015564	-1.8079	0.7782
841.9	-0.022047	9.0	0.001148	-0.020898	-0.004948	0.220873	0.021904	-1.6595	0.9542
842.2	-0.023421	12.0	0.001149	-0.022272	-0.006322	0.219500	0.027985	-1.5531	1.0792
842.5	-0.024695	15.0	0.001149	-0.023546	-0.007596	0.218226	0.033624	-1.4733	1.1761
843.5	-0.025876	18.0	0.001151	-0.024725	-0.008775	0.217048	0.038844	-1.4107	1.2533
843.4	-0.027009	21.0	0.001151	-0.025859	-0.009909	0.215914	0.043863	-1.3579	1.3222
843.6	-0.028043	24.0	0.001151	-0.026892	-0.010942	0.214880	0.048438	-1.3148	1.3802
843.7	-0.029024	27.0	0.001151	-0.027873	-0.011923	0.213900	0.052780	-1.2775	1.4314
844.4	-0.029958	30.0	0.001152	-0.028806	-0.012856	0.212967	0.056910	-1.2448	1.4771
844.2	-0.030845	33.0	0.001152	-0.029693	-0.013743	0.212090	0.060838	-1.2158	1.5185
844.5	-0.031679	36.0	0.001152	-0.030527	-0.014577	0.211246	0.064529	-1.1902	1.5563
844.7	-0.032455	39.0	0.001152	-0.031302	-0.015352	0.210471	0.067961	-1.1677	1.5911
844.5	-0.033189	42.0	0.001152	-0.032037	-0.016087	0.209735	0.071213	-1.1474	1.6232
844.4	-0.033912	45.0	0.001152	-0.032760	-0.016810	0.209013	0.074412	-1.1284	1.6532
843.9	-0.034587	48.0	0.001151	-0.033436	-0.017486	0.208337	0.077406	-1.1112	1.6812
844.8	-0.035234	51.0	0.001153	-0.034081	-0.018131	0.207693	0.080261	-1.0955	1.7076
844.7	-0.035827	54.0	0.001152	-0.034675	-0.018725	0.207099	0.082889	-1.0815	1.7324
845.2	-0.036362	57.0	0.001153	-0.035209	-0.019259	0.206565	0.085253	-1.0693	1.7559
844.7	-0.036926	60.0	0.001152	-0.035773	-0.019823	0.206000	0.087753	-1.0567	1.7782

Table 41. Isothermal Shrinkage Data for Region D,

I. ABS.2 Sample 10, Lo = 0.2321 inches, 845 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
841.9	-0.012877	3.0	0.001180	-0.011697	-0.001660	0.229603	0.007153	-2.1453	0.4771
842.3	-0.014567	6.0	0.001181	-0.013386	-0.003350	0.227914	0.014433	-1.8407	0.7782
841.7	-0.016234	9.0	0.001180	-0.015054	-0.005018	0.226246	0.021619	-1.6652	0.9542
843.1	-0.017978	12.0	0.001182	-0.016796	-0.006759	0.224504	0.029122	-1.5358	1.0792
843.3	-0.019663	15.0	0.001182	-0.018480	-0.008444	0.222820	0.036380	-1.4391	1.1761
843.0	-0.021154	18.0	0.001182	-0.019972	-0.009936	0.221328	0.042808	-1.3685	1.2553
843.5	-0.022575	21.0	0.001182	-0.021393	-0.011356	0.219907	0.048928	-1.3104	1.3222
843.8	-0.023891	24.0	0.001183	-0.022708	-0.012671	0.218592	0.054593	-1.2629	1.3802
843.9	-0.025048	27.0	0.001183	-0.023865	-0.013828	0.217435	0.059577	-1.2249	1.4314
844.6	-0.026122	30.0	0.001184	-0.024938	-0.014902	0.216362	0.064204	-1.1924	1.4771
844.9	-0.027092	33.0	0.001184	-0.025907	-0.015870	0.215393	0.068378	-1.1651	1.5185
844.9	-0.028037	36.0	0.001184	-0.026853	-0.016816	0.214447	0.072452	-1.1399	1.5563
844.6	-0.028871	39.0	0.001184	-0.027687	-0.017651	0.213613	0.076048	-1.1189	1.5911
845.2	-0.029647	42.0	0.001185	-0.028462	-0.018425	0.212838	0.079385	-1.1003	1.6232
845.5	-0.030381	45.0	0.001185	-0.029196	-0.019159	0.212104	0.082547	-1.0833	1.6532
844.9	-0.031051	48.0	0.001184	-0.029866	-0.019830	0.211434	0.085436	-1.0684	1.6812
845.2	-0.031656	51.0	0.001185	-0.030471	-0.020434	0.210829	0.088041	-1.0553	1.7076
844.7	-0.032226	54.0	0.001184	-0.031042	-0.021005	0.210258	0.090499	-1.0434	1.7324
845.9	-0.032766	57.0	0.001186	-0.031580	-0.021544	0.209720	0.092820	-1.0324	1.7599
845.9	-0.033248	60.0	0.001186	-0.032062	-0.022025	0.209238	0.094896	-1.0228	1.7782

Table 42. Isothermal Shrinkage Data for Region D,

1.0BS.2 Sample 3, Lo = 0.2107 inches, 864 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
860.8	-0.042373	3.0	0.001096	-0.041276	-0.003007	0.198505	0.014271	-1.8455	0.4771
860.5	-0.044576	6.0	0.001096	-0.043480	-0.005211	0.196301	0.024731	-1.6068	0.7782
861.0	-0.046168	9.0	0.001097	-0.045072	-0.006802	0.194710	0.032285	-1.4910	0.9542
861.4	-0.047208	12.0	0.001097	-0.046111	-0.007842	0.193671	0.037218	-1.4292	1.0792
861.8	-0.047960	15.0	0.001098	-0.046863	-0.008593	0.192920	0.040785	-1.3895	1.1761
861.7	-0.048331	18.0	0.001098	-0.047233	-0.008964	0.192550	0.042542	-1.3712	1.2553
863.0	-0.048571	21.0	0.001099	-0.047472	-0.009203	0.192311	0.043678	-1.3597	1.3222
862.3	-0.048754	24.0	0.001098	-0.047655	-0.009386	0.192128	0.044546	-1.3512	1.3802
861.9	-0.048871	27.0	0.001098	-0.047773	-0.009504	0.192009	0.045107	-1.3459	1.4314
862.5	-0.048942	30.0	0.001099	-0.047843	-0.009574	0.191940	0.045438	-1.3426	1.4771
863.1	-0.048965	33.0	0.001099	-0.047866	-0.009596	0.191918	0.045545	-1.3416	1.5185
863.6	-0.048989	36.0	0.001100	-0.047889	-0.009619	0.191896	0.045654	-1.3405	1.5563
862.3	-0.048994	39.0	0.001098	-0.047896	-0.009627	0.191887	0.045690	-1.3402	1.5911
863.2	-0.048977	42.0	0.001099	-0.047877	-0.009620	0.191895	0.045656	-1.3405	1.6232
863.4	-0.048977	45.0	0.001100	-0.047877	-0.009608	0.191907	0.045599	-1.3410	1.6532
863.7	-0.049018	48.0	0.001100	-0.047918	-0.009648	0.191867	0.045792	-1.3392	1.6812
863.3	-0.048994	51.0	0.001100	-0.047895	-0.009626	0.191889	0.045684	-1.3402	1.7076
862.9	-0.049006	54.0	0.001099	-0.047907	-0.009638	0.191876	0.045742	-1.3397	1.7324
863.7	-0.049041	57.0	0.001100	-0.047941	-0.009672	0.191843	0.045904	-1.3382	1.7559
863.9	-0.049030	60.0	0.001100	-0.047929	-0.009660	0.191855	0.045847	-1.3387	1.7782

Table 43. Isothermal Shrinkage Data for Region D,

I. ABS.2 Sample 9, Lo = 0.2223 inches, 864 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
861.6	-0.029670	3.0	0.001158	-0.028512	-0.003776	0.218393	0.016986	-1.7699	0.4771
861.2	-0.032525	6.0	0.001157	-0.031368	-0.006632	0.215537	0.029832	-1.5253	0.7782
862.3	-0.034758	9.0	0.001159	-0.033599	-0.008863	0.213307	0.039868	-1.3994	0.9542
862.0	-0.036650	12.0	0.001158	-0.035491	-0.010755	0.211415	0.048380	-1.3153	1.0792
862.3	-0.038336	15.0	0.001159	-0.037177	-0.012441	0.209729	0.055964	-1.2521	1.1761
863.1	-0.039911	18.0	0.001160	-0.038751	-0.014014	0.208156	0.063042	-1.2004	1.2553
863.0	-0.041515	21.0	0.001160	-0.040355	-0.015619	0.206532	0.070259	-1.1533	1.3222
863.1	-0.042978	24.0	0.001160	-0.041818	-0.017081	0.205089	0.076840	-1.1144	1.3802
863.3	-0.044159	27.0	0.001160	-0.042999	-0.018262	0.203909	0.082151	-1.0854	1.4314
863.5	-0.045064	30.0	0.001160	-0.043903	-0.019167	0.203004	0.086220	-1.0644	1.4771
863.4	-0.045728	33.0	0.001160	-0.044567	-0.019831	0.202340	0.089208	-1.0496	1.5185
863.8	-0.046262	36.0	0.001161	-0.045102	-0.020365	0.201806	0.091611	-1.0381	1.5563
863.8	-0.046662	39.0	0.001161	-0.045501	-0.020765	0.201407	0.093408	-1.0296	1.5911
864.0	-0.047050	42.0	0.001161	-0.045889	-0.021152	0.201019	0.095151	-1.0216	1.6232
864.4	-0.047385	45.0	0.001162	-0.046223	-0.021486	0.200685	0.096655	-1.0148	1.6532
864.7	-0.047608	48.0	0.001162	-0.046446	-0.021709	0.200463	0.097657	-1.0103	1.6812
863.6	-0.047843	51.0	0.001161	-0.046682	-0.021946	0.200225	0.098722	-1.0056	1.7076
864.3	-0.047994	54.0	0.001161	-0.046822	-0.022086	0.200086	0.099352	-1.0028	1.7324
864.4	-0.048154	57.0	0.001162	-0.046993	-0.022256	0.199916	0.100117	-0.9995	1.7559
864.1	-0.048242	60.0	0.001161	-0.047081	-0.022345	0.199827	0.100516	-0.9978	1.7782

Table 44. Isothermal Shrinkage Data for Region D,

11.ABS.1 Sample 13, Lo = 0.2205 inches, 845 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
842.3	-0.015682	3.0	0.001122	-0.014561	-0.003239	0.217179	0.014690	-1.8330	0.4771
843.0	-0.018788	6.0	0.001122	-0.017665	-0.006344	0.214075	0.028770	-1.5411	0.7782
842.2	-0.021330	9.0	0.001121	-0.020209	-0.008887	0.211531	0.040305	-1.3946	0.9542
843.5	-0.023485	12.0	0.001123	-0.022362	-0.011040	0.209378	0.050070	-1.3004	1.0792
843.9	-0.025470	15.0	0.001124	-0.024347	-0.013025	0.207394	0.059070	-1.2286	1.1761
844.0	-0.027338	18.0	0.001124	-0.026214	-0.014893	0.205327	0.067541	-1.1704	1.2553
844.5	-0.029018	21.0	0.001125	-0.027894	-0.016572	0.203848	0.075156	-1.1240	1.3222
844.0	-0.030581	24.0	0.001124	-0.029457	-0.018135	0.202284	0.082246	-1.0849	1.3802
844.3	-0.031973	27.0	0.001124	-0.030849	-0.019527	0.200892	0.088558	-1.0328	1.4314
844.5	-0.033254	30.0	0.001125	-0.032129	-0.020808	0.199612	0.094355	-1.0252	1.4771
844.9	-0.034376	33.0	0.001125	-0.033251	-0.021939	0.198491	0.099452	-1.0024	1.5185
844.4	-0.035398	36.0	0.001125	-0.034274	-0.022952	0.197468	0.104091	-0.9826	1.5563
845.0	-0.036327	39.0	0.001125	-0.035201	-0.023880	0.196540	0.108298	-0.9654	1.5911
845.0	-0.037120	42.0	0.001125	-0.035994	-0.024673	0.195747	0.111895	-0.9512	1.6232
845.2	-0.037854	45.0	0.001126	-0.036729	-0.025407	0.195013	0.115224	-0.9385	1.6532
845.0	-0.038512	48.0	0.001125	-0.037387	-0.026065	0.194355	0.118210	-0.9273	1.6812
845.5	-0.039082	51.0	0.001126	-0.037956	-0.026635	0.193786	0.120792	-0.9180	1.7076
845.5	-0.039558	54.0	0.001126	-0.038532	-0.027210	0.193210	0.123403	-0.9087	1.7324
846.0	-0.040187	57.0	0.001127	-0.039060	-0.027739	0.192682	0.125798	-0.9003	1.7559
846.1	-0.040675	60.0	0.001127	-0.039548	-0.028226	0.192195	0.128009	-0.8928	1.7782

Table 45. Isothermal Shrinkage Data for Region D,

II.ABS.1 Sample 4, $L_0 = 0.2124$ inches, 845 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
842.0	-0.029976	3.0	0.001080	-0.028896	-0.002431	0.209866	0.011447	-1.9413	0.4771
842.5	-0.031973	6.0	0.001081	-0.030892	-0.004428	0.207869	0.020848	-1.5809	0.7782
842.8	-0.033741	9.0	0.001081	-0.032660	-0.006196	0.206102	0.029171	-1.5350	0.9542
843.7	-0.035263	12.0	0.001082	-0.034181	-0.007717	0.204582	0.036330	-1.4397	1.0792
843.5	-0.036667	15.0	0.001082	-0.035585	-0.009121	0.203177	0.042943	-1.3571	1.1761
844.4	-0.037972	18.0	0.001083	-0.036889	-0.010424	0.201873	0.049078	-1.3091	1.2553
843.7	-0.039206	21.0	0.001082	-0.038123	-0.011659	0.200640	0.054891	-1.2605	1.3222
844.2	-0.040351	24.0	0.001083	-0.039268	-0.012804	0.199493	0.060282	-1.2198	1.3802
844.4	-0.041403	27.0	0.001083	-0.040320	-0.013856	0.198444	0.065233	-1.1855	1.4314
845.1	-0.042384	30.0	0.001084	-0.041300	-0.014835	0.197464	0.069848	-1.1558	1.4771
845.4	-0.043336	33.0	0.001085	-0.042252	-0.015787	0.196513	0.074328	-1.1288	1.5185
844.6	-0.044212	36.0	0.001083	-0.043128	-0.016664	0.195635	0.078455	-1.1054	1.5563
844.8	-0.045058	39.0	0.001084	-0.043974	-0.017510	0.194790	0.082437	-1.0839	1.5911
846.1	-0.045851	42.0	0.001085	-0.044766	-0.018301	0.194000	0.086164	-1.0647	1.6232
845.8	-0.046603	45.0	0.001085	-0.045518	-0.019054	0.193247	0.089707	-1.0472	1.6532
845.9	-0.047302	48.0	0.001085	-0.046217	-0.019753	0.192548	0.092998	-1.0315	1.6812
845.9	-0.047966	51.0	0.001085	-0.046881	-0.020417	0.191884	0.096124	-1.0172	1.7076
845.7	-0.048583	54.0	0.001085	-0.047498	-0.021034	0.191266	0.099030	-1.0042	1.7324
846.1	-0.049171	57.0	0.001085	-0.048085	-0.021621	0.190680	0.101793	-0.9923	1.7559
845.8	-0.049711	60.0	0.001085	-0.048626	-0.022162	0.190139	0.104340	-0.9815	1.7782

Table 46. Isothermal Shrinkage Data for Region D,

II.ABS.1 Sample 10, Lo = 0.1897 inches, 864 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
861.2	-0.046691	3.0	0.000988	-0.045704	-0.003954	0.183351	0.0208	-1.6811	0.4771
862.1	-0.049335	6.0	0.000989	-0.048347	-0.006597	0.182909	0.0348	-1.4987	0.7782
862.5	-0.051274	9.0	0.000989	-0.050285	-0.008535	0.180970	0.0450	-1.3469	0.9642
862.7	-0.052790	12.0	0.000989	-0.051801	-0.010651	0.179455	0.0530	-1.2759	1.0792
862.2	-0.054018	15.0	0.000989	-0.053029	-0.011279	0.178226	0.0595	-1.2258	1.1761
863.1	-0.054969	18.0	0.000990	-0.053980	-0.012230	0.177276	0.0645	-1.1907	1.2553
864.1	-0.055668	21.0	0.000991	-0.054677	-0.012927	0.176580	0.0681	-1.1666	1.3222
864.0	-0.056285	24.0	0.000991	-0.055294	-0.013544	0.175962	0.0714	-1.1463	1.3802
863.7	-0.056773	27.0	0.000990	-0.055782	-0.014032	0.175474	0.0740	-1.1309	1.4314
864.6	-0.057172	30.0	0.000992	-0.056181	-0.014431	0.175077	0.0761	-1.1188	1.4771
863.7	-0.057495	33.0	0.000990	-0.056505	-0.014755	0.174752	0.0778	-1.1091	1.5185
864.1	-0.057713	36.0	0.000991	-0.056722	-0.014972	0.174335	0.0789	-1.1028	1.5563
864.4	-0.057871	39.0	0.000991	-0.056880	-0.015130	0.174377	0.0798	-1.0982	1.5911
864.0	-0.057989	42.0	0.000991	-0.056998	-0.015248	0.174259	0.0804	-1.0949	1.6232
864.0	-0.058065	45.0	0.000991	-0.057074	-0.015324	0.174183	0.0808	-1.0927	1.6532
864.5	-0.058130	48.0	0.000991	-0.057138	-0.015388	0.174119	0.0811	-1.0909	1.6812
864.5	-0.058141	51.0	0.000991	-0.057150	-0.015400	0.174107	0.0812	-1.0905	1.7076
864.8	-0.058159	54.0	0.000992	-0.057167	-0.015417	0.174090	0.0813	-1.0901	1.7324
864.7	-0.058182	57.0	0.000992	-0.057191	-0.015441	0.174067	0.0814	-1.0894	1.7559
865.1	-0.058194	60.0	0.000992	-0.057202	-0.015452	0.174056	0.0815	-1.0891	1.7782

Table 47. Isothermal Shrinkage Data for Region D,

II. ABS.1 Sample 15, $L_0 = 0.1885$ inches, 864 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
861.9	-0.043830	3.0	0.000982	-0.042848	-0.004241	0.184093	0.022501	-1.6478	0.4771
862.3	-0.046821	6.0	0.000982	-0.045838	-0.007232	0.181103	0.038365	-1.4161	0.7782
862.4	-0.049094	9.0	0.000983	-0.048112	-0.009505	0.178830	0.050427	-1.2973	0.9542
862.8	-0.050980	12.0	0.000983	-0.049897	-0.011291	0.177044	0.059900	-1.2286	1.0792
863.4	-0.052337	15.0	0.000984	-0.051354	-0.012747	0.175388	0.067626	-1.1699	1.1761
863.3	-0.053507	18.0	0.000984	-0.052523	-0.013917	0.174419	0.073828	-1.1318	1.2553
864.0	-0.054452	21.0	0.000985	-0.053468	-0.014862	0.173475	0.078842	-1.1032	1.3222
863.3	-0.055228	24.0	0.000984	-0.054244	-0.015638	0.172698	0.082960	-1.0811	1.3802
863.9	-0.055815	27.0	0.000984	-0.054831	-0.016225	0.172112	0.085072	-1.0651	1.4314
863.5	-0.056326	30.0	0.000984	-0.055342	-0.016736	0.171600	0.088786	-1.0517	1.4771
864.3	-0.056720	33.0	0.000985	-0.055735	-0.017129	0.171208	0.090469	-1.0416	1.5185
864.8	-0.057025	36.0	0.000985	-0.056040	-0.017434	0.170904	0.092486	-1.0339	1.5563
864.6	-0.057272	39.0	0.000985	-0.056287	-0.017681	0.170656	0.093796	-1.0278	1.5911
865.2	-0.057454	42.0	0.000986	-0.056468	-0.017862	0.170476	0.094758	-1.0234	1.6232
864.8	-0.057613	45.0	0.000986	-0.056627	-0.018021	0.170316	0.095602	-1.0195	1.6532
864.6	-0.057655	48.0	0.000985	-0.056680	-0.018074	0.170263	0.095884	-1.0183	1.6812
864.7	-0.057730	51.0	0.000985	-0.056745	-0.018139	0.170198	0.096226	-1.0167	1.7076
864.4	-0.057777	54.0	0.000985	-0.056792	-0.018185	0.170151	0.096477	-1.0156	1.7324
864.7	-0.057771	57.0	0.000985	-0.056786	-0.018180	0.170157	0.096444	-1.0157	1.7559
864.6	-0.057830	60.0	0.000985	-0.056845	-0.018238	0.170098	0.096756	-1.0143	1.7782

Table 48. Isothermal Shrinkage Data for Region D,

11.A85.2 Sample 12, Lo = 0.2225 inches, 845 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
842.3	-0.015682	3.0	0.001132	-0.014551	-0.003239	0.219195	0.014558	-1.8369	0.4771
843.0	-0.018788	6.0	0.001133	-0.017655	-0.006344	0.216091	0.028511	-1.5450	0.7782
842.2	-0.021330	9.0	0.001132	-0.020199	-0.008887	0.213547	0.039942	-1.3986	0.9542
843.5	-0.023485	12.0	0.001133	-0.022352	-0.011040	0.211395	0.049620	-1.3043	1.0792
843.9	-0.025470	15.0	0.001134	-0.024336	-0.013025	0.209411	0.058539	-1.2326	1.1761
844.0	-0.027338	18.0	0.001134	-0.026204	-0.014893	0.207543	0.066933	-1.1744	1.2553
844.5	-0.029018	21.0	0.001135	-0.027883	-0.016572	0.205864	0.074481	-1.1288	1.3222
844.0	-0.030581	24.0	0.001134	-0.029447	-0.018135	0.204301	0.081506	-1.0988	1.3802
844.3	-0.031973	27.0	0.001135	-0.030838	-0.019527	0.202909	0.087762	-1.0657	1.4314
844.5	-0.033254	30.0	0.001135	-0.032119	-0.020808	0.201629	0.093517	-1.0291	1.4771
844.9	-0.034376	33.0	0.001135	-0.033241	-0.021929	0.200508	0.098558	-1.0063	1.5185
844.4	-0.035398	36.0	0.001135	-0.034264	-0.022952	0.199484	0.103155	-0.9865	1.5563
845.0	-0.036327	39.0	0.001135	-0.035191	-0.023880	0.198557	0.107324	-0.9693	1.5911
845.0	-0.037120	42.0	0.001135	-0.035984	-0.024673	0.197764	0.110889	-0.9551	1.6232
845.2	-0.037854	45.0	0.001136	-0.036718	-0.025407	0.197030	0.114189	-0.9424	1.6532
845.0	-0.038512	48.0	0.001136	-0.037377	-0.026065	0.196371	0.117147	-0.9313	1.6812
845.5	-0.039082	51.0	0.001136	-0.037946	-0.026635	0.195803	0.119706	-0.9219	1.7076
845.5	-0.039558	54.0	0.001136	-0.038522	-0.027210	0.195227	0.122294	-0.9126	1.7324
846.0	-0.040187	57.0	0.001137	-0.039050	-0.027738	0.194699	0.124667	-0.9042	1.7559
846.1	-0.040675	60.0	0.001137	-0.039537	-0.028226	0.194212	0.126859	-0.8967	1.7782

Table 40. Isothermal Shrinkage Data for Region D,

II. A88.2 Sample 7, $L_0 = 0.2136$, 845 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
841.1	-0.028337	3.0	0.001085	-0.027252	-0.002279	0.211208	0.010671	-1.9718	0.4771
842.1	-0.030181	6.0	0.001086	-0.029095	-0.004122	0.209366	0.019300	-1.7144	0.7782
842.2	-0.031850	9.0	0.001086	-0.030763	-0.005791	0.207697	0.027110	-1.5669	0.9542
843.0	-0.033336	12.0	0.001087	-0.032249	-0.007276	0.206213	0.034064	-1.4677	1.0792
843.1	-0.034693	15.0	0.001087	-0.033606	-0.008633	0.204856	0.040417	-1.3934	1.1761
843.5	-0.036009	18.0	0.001088	-0.034921	-0.009949	0.203541	0.046376	-1.3318	1.2533
844.0	-0.037196	21.0	0.001089	-0.036107	-0.011135	0.202355	0.052129	-1.2889	1.3222
843.7	-0.038324	24.0	0.001088	-0.037236	-0.012263	0.201226	0.057412	-1.2410	1.3802
844.3	-0.039411	27.0	0.001089	-0.038322	-0.013349	0.200141	0.062497	-1.2041	1.4314
844.4	-0.040387	30.0	0.001089	-0.039297	-0.014325	0.199165	0.067063	-1.1735	1.4771
844.3	-0.041286	33.0	0.001089	-0.040196	-0.015224	0.198266	0.071272	-1.1471	1.5185
844.3	-0.042202	36.0	0.001089	-0.041113	-0.016140	0.197350	0.075564	-1.1217	1.5563
844.8	-0.043031	39.0	0.001090	-0.041941	-0.016968	0.196522	0.079440	-1.1000	1.5911
844.5	-0.043812	42.0	0.001089	-0.042723	-0.017750	0.195740	0.083100	-1.0804	1.6232
844.6	-0.044582	45.0	0.001090	-0.043492	-0.018520	0.194971	0.086703	-1.0620	1.6532
845.1	-0.045299	48.0	0.001090	-0.044208	-0.019236	0.194235	0.090056	-1.0453	1.6812
844.8	-0.045980	51.0	0.001090	-0.044890	-0.019918	0.193573	0.093248	-1.0304	1.7076
845.3	-0.046521	54.0	0.001091	-0.045530	-0.020557	0.192934	0.096243	-1.0166	1.7324
845.6	-0.047173	57.0	0.001091	-0.046082	-0.021110	0.192382	0.098827	-1.0051	1.7559
845.8	-0.047761	60.0	0.001091	-0.046669	-0.021697	0.191795	0.101577	-0.9932	1.7782

Table 50. Isothermal Shrinkage Data for Region D,

11. ABS.2 Sample 6, $L_0 = 0.2003$, 864 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage, inches	Log Linear Shrinkage	Log Time
859.8	-0.044594	3.0	0.001240	-0.043353	-0.004213	0.195127	0.021032	-1.5771	0.4771
859.7	-0.047572	6.0	0.001240	-0.045732	-0.007591	0.192748	0.037900	-1.4214	0.7782
860.4	-0.050804	9.0	0.001241	-0.049563	-0.010422	0.189918	0.052033	-1.2837	0.9542
861.1	-0.053084	12.0	0.001242	-0.051841	-0.012701	0.187640	0.063409	-1.1979	1.0792
861.5	-0.054864	15.0	0.001243	-0.053621	-0.014480	0.185561	0.072292	-1.1409	1.1761
861.8	-0.056215	18.0	0.001243	-0.054971	-0.015831	0.184510	0.079035	-1.1022	1.2553
862.7	-0.057184	21.0	0.001245	-0.055939	-0.016799	0.183543	0.083858	-1.0764	1.3222
862.2	-0.057789	24.0	0.001244	-0.056545	-0.017404	0.182937	0.086892	-1.0510	1.3802
861.8	-0.058106	27.0	0.001243	-0.056863	-0.017722	0.182519	0.088478	-1.0532	1.4314
862.0	-0.058394	30.0	0.001244	-0.057150	-0.018010	0.182332	0.089914	-1.0462	1.4771
862.6	-0.058576	33.0	0.001245	-0.057331	-0.018191	0.182151	0.090818	-1.0418	1.5185
862.5	-0.058576	36.0	0.001245	-0.057431	-0.018291	0.182051	0.091318	-1.0394	1.5563
863.0	-0.058735	39.0	0.001245	-0.057489	-0.018349	0.181953	0.091607	-1.0381	1.5911
863.2	-0.058787	42.0	0.001246	-0.057542	-0.018401	0.181941	0.091870	-1.0368	1.6232
863.0	-0.058811	45.0	0.001245	-0.057566	-0.018425	0.181917	0.091988	-1.0363	1.6532
862.6	-0.058805	48.0	0.001245	-0.057560	-0.018420	0.181922	0.091962	-1.0364	1.6812
862.6	-0.058817	51.0	0.001245	-0.057572	-0.018432	0.181910	0.092021	-1.0361	1.7076
863.2	-0.058834	54.0	0.001246	-0.057589	-0.018448	0.181894	0.092104	-1.0357	1.7324
864.0	-0.058829	57.0	0.001247	-0.057582	-0.018441	0.181902	0.092069	-1.0359	1.7559
863.2	-0.058829	60.0	0.001246	-0.057583	-0.018443	0.181900	0.092074	-1.0359	1.7782

Table 51. Isothermal Shrinkage Data for Region D,

II. ABS.2 Sample 10, Lo = 0.2044 inches, 864 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
861.3	-0.036820	3.0	0.001064	-0.033756	-0.004247	0.200013	0.020777	-1.6824	0.4771
861.4	-0.040058	6.0	0.001064	-0.038993	-0.007484	0.196776	0.036615	-1.4363	0.7702
862.2	-0.042649	9.0	0.001065	-0.041583	-0.010074	0.194186	0.049288	-1.3073	0.9542
862.9	-0.044829	12.0	0.001066	-0.043762	-0.012253	0.192008	0.059948	-1.2222	1.0792
862.8	-0.046738	15.0	0.001066	-0.045672	-0.014163	0.190098	0.069291	-1.1593	1.1761
862.4	-0.048336	18.0	0.001066	-0.047271	-0.015762	0.188499	0.077113	-1.1129	1.2553
863.3	-0.049723	21.0	0.001067	-0.048656	-0.017147	0.187115	0.083891	-1.0763	1.3222
863.1	-0.050781	24.0	0.001066	-0.049714	-0.018285	0.186057	0.089066	-1.0503	1.3802
864.0	-0.051315	27.0	0.001068	-0.050248	-0.018739	0.185224	0.091676	-1.0377	1.4314
864.1	-0.051826	30.0	0.001068	-0.050759	-0.019250	0.185013	0.094176	-1.0261	1.4771
864.9	-0.052167	33.0	0.001069	-0.051098	-0.019589	0.184674	0.095838	-1.0185	1.5185
864.8	-0.052461	36.0	0.001069	-0.051392	-0.019883	0.184388	0.097275	-1.0120	1.5563
864.2	-0.052473	39.0	0.001068	-0.051405	-0.019896	0.184367	0.097337	-1.0117	1.5911
864.0	-0.052420	42.0	0.001068	-0.051352	-0.019843	0.184419	0.097080	-1.0129	1.6232
864.1	-0.052290	45.0	0.001068	-0.051223	-0.019714	0.184549	0.096447	-1.0157	1.6532
864.3	-0.052214	48.0	0.001068	-0.051146	-0.019637	0.184626	0.096072	-1.0174	1.6812
864.8	-0.052220	51.0	0.001069	-0.051151	-0.019642	0.184621	0.095697	-1.0173	1.7076
864.3	-0.052167	54.0	0.001068	-0.051099	-0.019590	0.184673	0.095842	-1.0184	1.7324
864.9	-0.052114	57.0	0.001069	-0.051045	-0.019535	0.184727	0.095579	-1.0196	1.7559
864.1	-0.052126	60.0	0.001068	-0.051058	-0.019549	0.184713	0.095642	-1.0194	1.7702

Table 52. Isothermal Shrinkage Data for Region E,

I.AB8.1 Sample 8, $L_0 = 0.1878$ inches, 950 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
947.9	-0.053900	6.0	0.001080	-0.052820	0.000000	0.187543	-0.000002		0.7782
948.7	-0.053883	9.0	0.001081	-0.052801	0.000019	0.187562	-0.000101		0.9542
948.4	-0.053894	10.0	0.001081	-0.052814	0.000007	0.187550	-0.000037		1.0000
948.9	-0.053930	12.0	0.001081	-0.052848	-0.000028	0.187515	0.000148	-3.8311	1.0792
948.9	-0.053912	15.0	0.001081	-0.052831	-0.000010	0.187533	0.000054	-4.2676	1.1761
949.7	-0.053900	18.0	0.001082	-0.052818	0.000003	0.187547	-0.000014		1.2553
949.4	-0.053906	21.0	0.001082	-0.052824	-0.000004	0.187540	0.000019	-4.7169	1.3222
949.4	-0.053894	24.0	0.001082	-0.052812	0.000008	0.187532	-0.000043		1.3802
950.0	-0.053894	27.0	0.001083	-0.052812	0.000009	0.187533	-0.000047		1.4314
950.2	-0.053924	30.0	0.001083	-0.052841	-0.000020	0.187524	0.000108	-3.9656	1.4771
950.2	-0.053906	33.0	0.001083	-0.052823	-0.000003	0.187542	0.000014	-4.8400	1.5185
950.9	-0.053924	36.0	0.001084	-0.052840	-0.000019	0.187526	0.000104	-3.9848	1.5563
951.1	-0.053959	39.0	0.001084	-0.052875	-0.000054	0.187491	0.000290	-3.5375	1.5911
950.6	-0.053930	42.0	0.001083	-0.052846	-0.000026	0.187519	0.000137	-3.8646	1.6232
950.8	-0.053935	45.0	0.001084	-0.052852	-0.000031	0.187513	0.000167	-3.7773	1.6532
951.3	-0.053924	48.0	0.001084	-0.052839	-0.000019	0.187526	0.000101	-3.9949	1.6812
950.5	-0.053912	51.0	0.001083	-0.052829	-0.000008	0.187536	0.000043	-4.3631	1.7076
951.2	-0.053930	54.0	0.001084	-0.052845	-0.000025	0.187520	0.000133	-3.8760	1.7324
951.2	-0.053924	57.0	0.001084	-0.052840	-0.000019	0.187526	0.000102	-3.9923	1.7559
950.7	-0.053918	59.5	0.001084	-0.052834	-0.000014	0.187531	0.000073	-4.1338	1.7745

Table 53. Isothermal Shrinkage Data for Region E,

I. ABS. 1 Sample 13, Lo = 0.1934 inches, 1049 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1046.5	-0.043530	6.0	0.001232	-0.042298	-0.000028	0.193135	0.000147	-3.8332	0.7782
1046.6	-0.043524	9.0	0.001233	-0.042292	-0.000022	0.193141	0.000115	-3.9383	0.9542
1047.0	-0.043530	10.0	0.001233	-0.042297	-0.000028	0.193136	0.000144	-3.8426	1.0000
1047.5	-0.043534	12.0	0.001234	-0.042320	-0.000051	0.193114	0.000262	-3.5821	1.0792
1048.0	-0.043530	15.0	0.001234	-0.042296	-0.000026	0.193138	0.000137	-3.8638	1.1761
1048.4	-0.043542	18.0	0.001235	-0.042307	-0.000038	0.193127	0.000196	-3.7086	1.2553
1048.0	-0.043548	21.0	0.001235	-0.042313	-0.000044	0.193121	0.000227	-3.6437	1.3222
1048.2	-0.043607	24.0	0.001234	-0.042372	-0.000103	0.193062	0.000532	-3.2740	1.3802
1049.5	-0.043589	27.0	0.001236	-0.042353	-0.000083	0.193082	0.000432	-3.3650	1.4314
1049.1	-0.043601	30.0	0.001236	-0.042365	-0.000096	0.193070	0.000495	-3.3057	1.4771
1048.5	-0.043589	33.0	0.001235	-0.042354	-0.000085	0.193080	0.000438	-3.3587	1.5185
1048.8	-0.043618	36.0	0.001235	-0.042383	-0.000114	0.193052	0.000588	-3.2306	1.5563
1048.8	-0.043607	39.0	0.001235	-0.042371	-0.000102	0.193063	0.000527	-3.2780	1.5911
1049.1	-0.043642	42.0	0.001236	-0.042406	-0.000137	0.193029	0.000707	-3.1505	1.6232
1049.1	-0.043671	45.0	0.001236	-0.042435	-0.000166	0.192999	0.000859	-3.0658	1.6532
1048.9	-0.043559	48.0	0.001235	-0.042424	-0.000155	0.193011	0.000800	-3.0970	1.6812
1049.3	-0.043636	51.0	0.001236	-0.042400	-0.000131	0.193035	0.000676	-3.1702	1.7076
1048.9	-0.043671	54.0	0.001235	-0.042436	-0.000166	0.192999	0.000861	-3.0651	1.7324
1048.9	-0.043677	57.0	0.001236	-0.042442	-0.000172	0.192993	0.000891	-3.0503	1.7559
1048.8	-0.043677	60.0	0.001235	-0.042442	-0.000172	0.192993	0.000892	-3.0499	1.7782

$n = 0.98 \pm 0.09$, $\log(K) = -4.79 \pm 0.11$, $R \text{ Squared} = 0.880$

Table 54. Isothermal Shrinkage Data for Region E,

I.088.1 Sample 9, Lo = 0.1954 inches, 1146 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1144.0	-0.046456	6.0	0.001365	-0.045091	-0.000104	0.195009	0.000534	-3.2723	0.7782
1145.0	-0.046503	9.0	0.001367	-0.045137	-0.000150	0.194963	0.000768	-3.1144	0.9542
1144.6	-0.046527	10.0	0.001366	-0.045161	-0.000174	0.194939	0.000891	-3.0500	1.0000
1145.0	-0.046544	12.0	0.001367	-0.045178	-0.000191	0.194922	0.000979	-3.0093	1.0792
1146.3	-0.046562	13.0	0.001368	-0.045194	-0.000207	0.194906	0.001061	-2.9743	1.1761
1146.6	-0.046609	18.0	0.001368	-0.045241	-0.000254	0.194899	0.001300	-2.8861	1.2553
1146.4	-0.046638	21.0	0.001368	-0.045270	-0.000284	0.194830	0.001451	-2.8383	1.3222
1146.9	-0.046627	24.0	0.001369	-0.045258	-0.000271	0.194842	0.001388	-2.8576	1.3802
1146.5	-0.046697	27.0	0.001368	-0.045329	-0.000342	0.194771	0.001751	-2.7566	1.4314
1146.9	-0.046715	30.0	0.001369	-0.045346	-0.000359	0.194754	0.001839	-2.7354	1.4771
1146.9	-0.046703	33.0	0.001369	-0.045334	-0.000348	0.194766	0.001779	-2.7499	1.5185
1147.4	-0.046715	36.0	0.001369	-0.045345	-0.000359	0.194755	0.001836	-2.7361	1.5563
1147.6	-0.046738	39.0	0.001370	-0.045369	-0.000382	0.194731	0.001955	-2.7088	1.5911
1147.2	-0.046750	42.0	0.001369	-0.045381	-0.000394	0.194719	0.002018	-2.6952	1.6232
1147.9	-0.046768	45.0	0.001370	-0.045398	-0.000411	0.194702	0.002103	-2.6771	1.6532
1147.2	-0.046779	48.0	0.001369	-0.045410	-0.000424	0.194690	0.002168	-2.6640	1.6812
1147.0	-0.046809	51.0	0.001369	-0.045440	-0.000453	0.194660	0.002319	-2.6346	1.7076
1147.7	-0.046821	54.0	0.001370	-0.045451	-0.000464	0.194649	0.002376	-2.6242	1.7324
1147.1	-0.046815	57.0	0.001369	-0.045446	-0.000459	0.194654	0.002349	-2.6291	1.7539
1146.5	-0.046821	60.0	0.001368	-0.045452	-0.000466	0.194648	0.002383	-2.6229	1.7782

n = 0.62 ± 0.02, Log(K) = -3.69 ± 0.03, R Squared = 0.979

Table 55. Isothermal Shrinkage Data for Region E,

1. ABS.1 Sample 2, $L_0 = 0.1868$ inches, 1184 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1182.3	-0.054643	5.0	0.001350	-0.053293	-0.000042	0.186379	0.000223	-3.6824	0.6990
1182.6	-0.054690	8.0	0.001351	-0.053339	-0.000088	0.186333	0.000473	-3.3255	0.9031
1183.6	-0.054719	10.0	0.001352	-0.053368	-0.000116	0.186306	0.000623	-3.2054	1.0000
1183.1	-0.054684	11.0	0.001351	-0.053333	-0.000082	0.186340	0.000438	-3.3590	1.0414
1182.7	-0.054737	14.0	0.001351	-0.053386	-0.000135	0.186286	0.000723	-3.1408	1.1461
1183.8	-0.054784	17.0	0.001352	-0.053432	-0.000181	0.186241	0.000968	-3.0143	1.2304
1183.1	-0.054761	20.0	0.001351	-0.053409	-0.000158	0.186263	0.000846	-3.0724	1.3010
1183.9	-0.054784	23.0	0.001352	-0.053432	-0.000181	0.186242	0.000967	-3.0145	1.3617
1184.6	-0.054784	26.0	0.001353	-0.053431	-0.000180	0.186243	0.000963	-3.0165	1.4150
1184.9	-0.054819	29.0	0.001353	-0.053466	-0.000215	0.186208	0.001150	-2.9394	1.4624
1184.8	-0.054860	30.0	0.001353	-0.053507	-0.000256	0.186167	0.001370	-2.8631	1.4771
1183.7	-0.054854	32.0	0.001352	-0.053503	-0.000251	0.186167	0.001346	-2.8709	1.5051
1184.8	-0.054860	35.0	0.001353	-0.053507	-0.000256	0.186167	0.001371	-2.8631	1.5441
1183.9	-0.054901	38.0	0.001352	-0.053549	-0.000298	0.186124	0.001596	-2.7969	1.5798
1183.7	-0.054866	40.0	0.001352	-0.053514	-0.000263	0.186159	0.001409	-2.8512	1.6021
1183.3	-0.054919	41.0	0.001351	-0.053568	-0.000316	0.186105	0.001694	-2.7710	1.6128
1185.2	-0.054931	44.0	0.001354	-0.053577	-0.000326	0.186098	0.001745	-2.7582	1.6435
1184.0	-0.054960	47.0	0.001352	-0.053608	-0.000357	0.186066	0.001910	-2.7190	1.6721
1183.8	-0.054954	50.0	0.001352	-0.053602	-0.000351	0.186071	0.001880	-2.7259	1.6990
1184.0	-0.054937	53.0	0.001352	-0.053584	-0.000333	0.186089	0.001785	-2.7485	1.7243

$n = 0.83 \pm 0.04$, $\text{Log}(K) = -4.13 \pm 0.06$, $R \text{ Squared} = 0.953$

Table 56. Isothermal Shrinkage Data for Region E,

1. ABS. 2 Sample 1, $L_0 = 0.1881$ inches, 950 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
949.7	-0.051286	6.0	0.001084	-0.050202	-0.000045	0.187754	0.000239	-3.6212	0.7782
949.4	-0.051280	9.0	0.001084	-0.050196	-0.000039	0.187759	0.000210	-3.6784	0.9542
950.2	-0.051286	10.0	0.001085	-0.050201	-0.000044	0.187755	0.000236	-3.6272	1.0000
949.3	-0.051286	12.0	0.001084	-0.050202	-0.000045	0.187753	0.000242	-3.6159	1.0792
950.0	-0.051280	15.0	0.001084	-0.050196	-0.000039	0.187760	0.000206	-3.6858	1.1761
950.6	-0.051333	18.0	0.001085	-0.050248	-0.000091	0.187709	0.000484	-3.3153	1.2553
951.2	-0.051345	21.0	0.001086	-0.050259	-0.000102	0.187598	0.000542	-3.2657	1.3222
951.4	-0.051339	24.0	0.001086	-0.050253	-0.000096	0.187705	0.000510	-3.2927	1.3802
951.7	-0.051356	27.0	0.001086	-0.050270	-0.000113	0.187687	0.000602	-3.2207	1.4314
951.4	-0.051403	30.0	0.001086	-0.050317	-0.000161	0.187640	0.000854	-3.0688	1.4771
951.8	-0.051392	33.0	0.001087	-0.050305	-0.000148	0.187553	0.000788	-3.1034	1.5185
952.3	-0.051392	36.0	0.001087	-0.050304	-0.000148	0.187654	0.000785	-3.1050	1.5563
952.3	-0.051409	39.0	0.001087	-0.050322	-0.000165	0.187636	0.000879	-3.0562	1.5911
952.5	-0.051397	42.0	0.001087	-0.050310	-0.000153	0.187648	0.000815	-3.0889	1.6232
952.3	-0.051409	45.0	0.001087	-0.050322	-0.000165	0.187636	0.000879	-3.0561	1.6532
952.6	-0.051409	48.0	0.001088	-0.050322	-0.000165	0.187637	0.000877	-3.0571	1.6812
952.0	-0.051415	51.0	0.001087	-0.050328	-0.000172	0.187629	0.000912	-3.0400	1.7076
952.3	-0.051403	54.0	0.001087	-0.050316	-0.000159	0.187642	0.000848	-3.0716	1.7324
952.1	-0.051439	57.0	0.001087	-0.050352	-0.000195	0.187606	0.001036	-2.9846	1.7559
952.7	-0.051433	60.0	0.001088	-0.050345	-0.000188	0.187613	0.001001	-2.9994	1.7782

$n = 0.81 \pm 0.07$, $\log(K) = -4.39 \pm 0.09$, R Squared = 0.889

Table 57. Isothermal Shrinkage Data for Region E,

I. ABS.2 Sample 12, Lo = 0.2135 inches, 1049 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1046.1	-0.043383	6.0	0.001434	-0.041949	-0.000194	0.213060	0.000909	-3.0415	0.7782
1046.6	-0.043442	9.0	0.001434	-0.042008	-0.000252	0.213003	0.001181	-2.9278	0.9542
1046.8	-0.043436	10.0	0.001435	-0.042001	-0.000246	0.213009	0.001152	-2.9387	1.0000
1047.6	-0.043483	12.0	0.001436	-0.042047	-0.000292	0.212964	0.001367	-2.8642	1.0792
1047.3	-0.043536	15.0	0.001435	-0.042101	-0.000345	0.212910	0.001617	-2.7914	1.1761
1048.0	-0.043595	18.0	0.001437	-0.042158	-0.000403	0.212853	0.001887	-2.7243	1.2553
1048.0	-0.043630	21.0	0.001436	-0.042194	-0.000438	0.212818	0.002052	-2.6878	1.3222
1048.5	-0.043659	24.0	0.001437	-0.042222	-0.000467	0.212790	0.002187	-2.6602	1.3802
1048.5	-0.043724	27.0	0.001437	-0.042287	-0.000531	0.212725	0.002489	-2.6040	1.4314
1048.3	-0.043724	30.0	0.001437	-0.042287	-0.000532	0.212725	0.002491	-2.6037	1.4771
1048.4	-0.043771	33.0	0.001437	-0.042334	-0.000579	0.212678	0.002710	-2.5670	1.5185
1048.5	-0.043783	36.0	0.001437	-0.042346	-0.000590	0.212667	0.002764	-2.5584	1.5563
1048.8	-0.043830	39.0	0.001438	-0.042392	-0.000637	0.212620	0.002982	-2.5254	1.5911
1049.1	-0.043847	42.0	0.001438	-0.042409	-0.000654	0.212603	0.003063	-2.5138	1.6232
1048.8	-0.043894	45.0	0.001438	-0.042457	-0.000701	0.212555	0.003285	-2.4834	1.6532
1049.4	-0.043889	48.0	0.001438	-0.042450	-0.000695	0.212563	0.003254	-2.4876	1.6812
1049.3	-0.043912	51.0	0.001438	-0.042474	-0.000718	0.212539	0.003365	-2.4730	1.7076
1048.8	-0.043918	54.0	0.001438	-0.042480	-0.000725	0.212532	0.003395	-2.4691	1.7324
1049.4	-0.043971	57.0	0.001438	-0.042532	-0.000777	0.212481	0.003639	-2.4390	1.7559
1049.2	-0.043994	60.0	0.001438	-0.042556	-0.000801	0.212456	0.003751	-2.4259	1.7782

$n = 0.62 \pm 0.01$, $\log(K) = -3.53 \pm 0.01$, $R^2 = 0.994$

Table 58. Isothermal Shrinkage Data for Region E,

I. ABS.2 Sample 15, Lo = 0.2060 inches, 1145 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1145.2	-0.047614	6.0	0.001441	-0.046173	-0.000705	0.205016	0.003420	-2.4660	0.7782
1145.9	-0.047855	9.0	0.001442	-0.046413	-0.000945	0.204776	0.004585	-2.3387	0.9542
1145.9	-0.047943	10.0	0.001442	-0.046501	-0.001033	0.204688	0.005013	-2.2999	1.0000
1146.5	-0.048090	12.0	0.001443	-0.046647	-0.001179	0.204543	0.005722	-2.2424	1.0792
1146.1	-0.048260	15.0	0.001442	-0.046818	-0.001350	0.204371	0.006532	-2.1836	1.1761
1146.5	-0.048407	18.0	0.001443	-0.046964	-0.001496	0.204225	0.007263	-2.1389	1.2553
1146.2	-0.048577	21.0	0.001442	-0.047135	-0.001667	0.204054	0.008091	-2.0920	1.3222
1146.9	-0.048742	24.0	0.001443	-0.047299	-0.001830	0.203891	0.008886	-2.0513	1.3802
1146.9	-0.048871	27.0	0.001443	-0.047428	-0.001960	0.203762	0.009513	-2.0217	1.4314
1147.4	-0.049000	30.0	0.001444	-0.047557	-0.002088	0.203634	0.010137	-1.9941	1.4771
1147.3	-0.049112	33.0	0.001444	-0.047668	-0.002200	0.203522	0.010680	-1.9714	1.5185
1147.5	-0.049235	36.0	0.001444	-0.047791	-0.002323	0.203399	0.011278	-1.9478	1.5563
1147.1	-0.049318	39.0	0.001443	-0.047874	-0.002406	0.203316	0.011680	-1.9326	1.5911
1147.8	-0.049400	42.0	0.001444	-0.047956	-0.002487	0.203235	0.012074	-1.9181	1.6232
1148.0	-0.049500	45.0	0.001445	-0.048035	-0.002587	0.203136	0.012558	-1.9011	1.6532
1147.9	-0.049559	48.0	0.001444	-0.048114	-0.002646	0.203077	0.012844	-1.8913	1.6812
1147.8	-0.049629	51.0	0.001444	-0.048185	-0.002716	0.203006	0.013186	-1.8799	1.7076
1147.9	-0.049729	54.0	0.001444	-0.048284	-0.002816	0.202907	0.013671	-1.8642	1.7324
1147.9	-0.049747	57.0	0.001444	-0.048302	-0.002834	0.202889	0.013755	-1.8615	1.7559
1147.8	-0.049794	60.0	0.001444	-0.048349	-0.002881	0.202842	0.013985	-1.8543	1.7782

n = 0.61 ± 0.01, Log (K) = -2.91 ± 0.01, R Squared = 0.993

Table 59. Isothermal Shrinkage Data for Region E,

1. ABS.2 Sample 5, Lo = 0.1979 inches, 1184 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1183.0	-0.043092	5.0	0.001431	-0.041661	-0.000187	0.197409	0.000943	-3.0254	0.6990
1183.8	-0.043180	8.0	0.001432	-0.041748	-0.000274	0.197323	0.001383	-2.8992	0.9031
1183.0	-0.043227	10.0	0.001431	-0.041796	-0.000322	0.197274	0.001626	-2.7889	1.0000
1184.1	-0.043245	11.0	0.001433	-0.041812	-0.000338	0.197259	0.001708	-2.7676	1.0414
1183.8	-0.043286	14.0	0.001432	-0.041854	-0.000380	0.197217	0.001918	-2.7171	1.1461
1184.0	-0.043327	17.0	0.001433	-0.041895	-0.000420	0.197176	0.002124	-2.6727	1.2304
1183.3	-0.043392	20.0	0.001432	-0.041960	-0.000486	0.197110	0.002455	-2.6099	1.3010
1184.8	-0.043415	23.0	0.001434	-0.041982	-0.000508	0.197090	0.002565	-2.5910	1.3617
1184.6	-0.043486	26.0	0.001433	-0.042052	-0.000578	0.197019	0.002922	-2.5343	1.4150
1185.1	-0.043521	29.0	0.001434	-0.042087	-0.000613	0.196985	0.003097	-2.5090	1.4624
1184.0	-0.043533	30.0	0.001433	-0.042100	-0.000626	0.196971	0.003163	-2.4999	1.4771
1184.1	-0.043521	32.0	0.001433	-0.042088	-0.000614	0.196983	0.003104	-2.5081	1.5051
1185.3	-0.043586	35.0	0.001434	-0.042151	-0.000677	0.196921	0.003423	-2.4657	1.5441
1184.7	-0.043609	38.0	0.001434	-0.042176	-0.000702	0.196896	0.003545	-2.4504	1.5798
1184.8	-0.043662	40.0	0.001434	-0.042228	-0.000754	0.196843	0.003812	-2.4189	1.6021
1184.5	-0.043674	41.0	0.001433	-0.042241	-0.000767	0.196831	0.003873	-2.4119	1.6128
1184.7	-0.043680	44.0	0.001434	-0.042246	-0.000772	0.196825	0.003901	-2.4088	1.6435
1184.7	-0.043733	47.0	0.001434	-0.042299	-0.000825	0.196772	0.004168	-2.3800	1.6721
1184.8	-0.043762	50.0	0.001434	-0.042328	-0.000854	0.196743	0.004317	-2.3649	1.6990
1185.3	-0.043774	53.0	0.001434	-0.042339	-0.000865	0.196733	0.004373	-2.3593	1.7243

n = 0.63 ± 0.01, Log(K) = -3.44 ± 0.01, R Squared = 0.996

Table 60. Isothermal Shrinkage Data for Region E,

11.488.1 Sample 6, Lo = 0.1844 inches, 950 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
949.4	-0.053052	6.0	0.001062	-0.053989	0.000013	0.184067	-0.000069		0.7782
950.0	-0.053057	9.0	0.001063	-0.053994	0.000007	0.184062	-0.000040		0.9542
950.0	-0.053069	10.0	0.001063	-0.054006	-0.000004	0.184050	0.000023	-4.5325	1.0000
950.2	-0.053057	12.0	0.001063	-0.053994	0.000008	0.184062	-0.000042		1.0792
950.8	-0.053063	15.0	0.001064	-0.053999	0.000003	0.184058	-0.000014		1.1761
950.9	-0.053081	18.0	0.001064	-0.054017	-0.000015	0.184040	0.000081	-4.0897	1.2553
950.4	-0.053081	21.0	0.001064	-0.054017	-0.000016	0.184039	0.000085	-4.0725	1.3222
951.4	-0.053104	24.0	0.001065	-0.054040	-0.000038	0.184018	0.000206	-3.6865	1.3802
951.2	-0.053063	27.0	0.001064	-0.053999	0.000003	0.184059	-0.000016		1.4314
951.7	-0.053104	30.0	0.001065	-0.054039	-0.000038	0.184018	0.000204	-3.6903	1.4771
951.7	-0.053116	33.0	0.001065	-0.054051	-0.000049	0.184007	0.000268	-3.5722	1.5185
951.8	-0.053087	35.0	0.001065	-0.054022	-0.000020	0.184036	0.000108	-3.9684	1.5563
952.5	-0.053128	39.0	0.001066	-0.054062	-0.000060	0.183997	0.000386	-3.4870	1.5911
952.2	-0.053104	42.0	0.001066	-0.054039	-0.000037	0.184019	0.000201	-3.6972	1.6232
952.0	-0.053104	45.0	0.001065	-0.054039	-0.000037	0.184019	0.000202	-3.6947	1.6532
952.1	-0.053140	48.0	0.001066	-0.054074	-0.000072	0.183984	0.000392	-3.4064	1.6812
952.4	-0.053122	51.0	0.001066	-0.054056	-0.000054	0.184002	0.000295	-3.5299	1.7076
952.7	-0.053140	54.0	0.001066	-0.054073	-0.000072	0.183985	0.000388	-3.4107	1.7324
952.6	-0.053122	57.0	0.001066	-0.054056	-0.000054	0.184003	0.000293	-3.5326	1.7559
952.5	-0.053146	60.0	0.001066	-0.054080	-0.000078	0.183979	0.000421	-3.3753	1.7782

Table 61. Isothermal Shrinkage Data for Region E,

II. ABS. 1 Sample 3, $L_0 = 0.1855$ inches, 1049 deg. C.

Temperature, degrees C.	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1046.3	-0.053894	6.0	0.001182	-0.052712	0.000006	0.185230	-0.000034		0.7782
1046.4	-0.053894	9.0	0.001182	-0.052712	0.000006	0.185230	-0.000034		0.9542
1047.5	-0.053883	10.0	0.001183	-0.052699	0.000019	0.185244	-0.000105		1.0000
1047.1	-0.053900	12.0	0.001183	-0.052717	0.000001	0.185226	-0.000007		1.0792
1047.6	-0.053888	15.0	0.001184	-0.052705	0.000014	0.185239	-0.000074		1.1761
1047.2	-0.053912	18.0	0.001183	-0.052729	-0.000010	0.185214	0.000055	-4.2566	1.2577
1047.9	-0.053912	21.0	0.001184	-0.052728	-0.000009	0.185216	0.000051	-4.2963	1.3222
1048.4	-0.053906	24.0	0.001184	-0.052722	-0.000003	0.185223	0.000016	-4.8019	1.3802
1048.7	-0.053935	27.0	0.001185	-0.052751	-0.000032	0.185194	0.000172	-3.7635	1.4314
1048.6	-0.053906	30.0	0.001185	-0.052721	-0.000003	0.185223	0.000015	-4.8343	1.4771
1048.5	-0.053924	33.0	0.001185	-0.052739	-0.000020	0.185205	0.000110	-3.9567	1.5185
1048.8	-0.053924	36.0	0.001185	-0.052739	-0.000020	0.185206	0.000108	-3.9657	1.5563
1049.1	-0.053918	39.0	0.001185	-0.052733	-0.000014	0.185212	0.000075	-4.1257	1.5911
1049.4	-0.053924	42.0	0.001186	-0.052738	-0.000019	0.185207	0.000105	-3.9808	1.6232
1048.9	-0.053918	45.0	0.001185	-0.052733	-0.000014	0.185212	0.000076	-4.1176	1.6532
1049.0	-0.053924	48.0	0.001185	-0.052739	-0.000020	0.185206	0.000107	-3.9703	1.6812
1048.6	-0.053935	51.0	0.001185	-0.052751	-0.000032	0.185194	0.000173	-3.7620	1.7076
1049.8	-0.053947	54.0	0.001186	-0.052761	-0.000042	0.185184	0.000229	-3.6409	1.7324
1049.5	-0.053935	57.0	0.001186	-0.052750	-0.000031	0.185195	0.000167	-3.7766	1.7559
1050.2	-0.053959	60.0	0.001186	-0.052772	-0.000054	0.185173	0.000290	-3.5376	1.7782

Table 62. Isothermal Shrinkage Data for Region E,

II. ABS. I Sample 12, Lo = 0.1805 inches, 1043 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1048.1	-0.051832	6.0	0.001152	-0.050680	0.000019	0.180235	-0.000104		0.7782
1048.6	-0.051803	9.0	0.001153	-0.050650	0.000049	0.180266	-0.000270		0.9542
1048.4	-0.051768	10.0	0.001152	-0.050615	0.000064	0.180301	-0.000464		1.0000
1049.0	-0.051809	12.0	0.001153	-0.050656	0.000043	0.180261	-0.000240		1.0792
1048.4	-0.051773	15.0	0.001152	-0.050621	0.000078	0.180295	-0.000432		1.1761
1049.8	-0.051768	18.0	0.001154	-0.050614	0.000085	0.180304	-0.000473		1.2553
1049.3	-0.051779	21.0	0.001153	-0.050626	0.000073	0.180291	-0.000405		1.3222
1049.9	-0.051785	24.0	0.001154	-0.050631	0.000068	0.180287	-0.000376		1.3802
1049.6	-0.051791	27.0	0.001154	-0.050619	0.000079	0.180298	-0.000440		1.4314
1050.4	-0.051779	30.0	0.001155	-0.050637	0.000062	0.180280	-0.000342		1.4771
1050.2	-0.051756	33.0	0.001155	-0.050625	0.000074	0.180293	-0.000412		1.5185
1051.2	-0.051756	36.0	0.001155	-0.050601	0.000098	0.180317	-0.000541		1.5563
1050.0	-0.051762	39.0	0.001156	-0.050600	0.000099	0.180319	-0.000547		1.5911
1050.3	-0.051791	42.0	0.001155	-0.050607	0.000092	0.180310	-0.000507		1.6232
1050.7	-0.051773	45.0	0.001155	-0.050636	0.000062	0.180282	-0.000346		1.6532
1050.9	-0.051797	48.0	0.001155	-0.050618	0.000080	0.180300	-0.000446		1.6812
1050.5	-0.051809	51.0	0.001155	-0.050642	0.000057	0.180277	-0.000317		1.7076
1050.8	-0.051809	54.0	0.001155	-0.050654	0.000045	0.180264	-0.000249		1.7324
1050.6	-0.051797	57.0	0.001155	-0.050654	0.000045	0.180265	-0.000251		1.7559
1050.4	-0.051797	60.0	0.001155	-0.050642	0.000057	0.180276	-0.000314		1.7782

Table 63. Isothermal Shrinkage Data for Region E,

II.888.1 Sample 9, $L_0 = 0.1819$ inches, 1146 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected, Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1145.5	-0.054793	6.0	0.001273	-0.053520	-0.000016	0.181498	0.000089	-4.0506	0.7782
1145.7	-0.054787	9.0	0.001273	-0.053514	-0.000010	0.181505	0.000053	-4.2557	0.9542
1145.9	-0.054781	10.0	0.001273	-0.053508	-0.000004	0.181511	0.000021	-4.6759	1.0000
1146.3	-0.054799	12.0	0.001274	-0.053525	-0.000021	0.181494	0.000116	-3.9345	1.0792
1146.5	-0.054770	15.0	0.001274	-0.053496	0.000009	0.181524	0.000047	-3.5608	1.1761
1146.7	-0.054828	18.0	0.001274	-0.053554	-0.000030	0.181455	0.000275	-4.0848	1.2553
1146.5	-0.054793	21.0	0.001273	-0.053519	-0.000015	0.181500	0.000082	-3.8222	1.3222
1146.1	-0.054776	24.0	0.001273	-0.053502	0.000002	0.181517	-0.000012	-4.1302	1.3802
1146.9	-0.054781	27.0	0.001274	-0.053507	-0.000003	0.181513	0.000015	-4.1091	1.4314
1147.3	-0.054793	30.0	0.001275	-0.053518	-0.000014	0.181502	0.000078	-3.5900	1.4771
1147.7	-0.054817	33.0	0.001275	-0.053541	-0.000037	0.181479	0.000204	-3.6888	1.5185
1147.6	-0.054817	36.0	0.001275	-0.053542	-0.000037	0.181479	0.000205	-3.5154	1.5563
1147.0	-0.054834	39.0	0.001274	-0.053560	-0.000036	0.181460	0.000305	-3.8492	1.5911
1147.4	-0.054805	42.0	0.001275	-0.053530	-0.000026	0.181490	0.000142	-4.1108	1.6232
1147.3	-0.054793	45.0	0.001275	-0.053518	-0.000014	0.181502	0.000077	-3.4756	1.6812
1147.5	-0.054840	48.0	0.001275	-0.053565	-0.000051	0.181455	0.000334	-3.5230	1.7076
1147.9	-0.054834	51.0	0.001275	-0.053539	-0.000035	0.181462	0.000300	-3.4793	1.7324
1148.0	-0.054840	54.0	0.001275	-0.053565	-0.000050	0.181456	0.000332	-3.3402	1.7559
1148.6	-0.054864	57.0	0.001276	-0.053587	-0.000083	0.181434	0.000457	-3.4376	1.7782
1147.8	-0.054846	60.0	0.001275	-0.053571	-0.000056	0.181450	0.000355	-3.4376	1.7782

Table 64. Isothermal Shrinkage Data for Region E,

II. ABS. I Sample 1, $L_0 = 0.1900$ inches, 1184 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1183.5	-0.049814	6.0	0.001375	-0.048439	-0.000029	0.189627	0.000135	-3.8091	0.7782
1183.7	-0.049808	9.0	0.001375	-0.048433	-0.000023	0.189633	0.000123	-3.9086	0.9542
1183.6	-0.049843	10.0	0.001375	-0.048468	-0.000059	0.189598	0.000309	-3.5093	1.0000
1184.5	-0.049873	12.0	0.001376	-0.048497	-0.000087	0.189570	0.000458	-3.3388	1.0792
1184.8	-0.049902	15.0	0.001376	-0.048526	-0.000116	0.189542	0.000611	-3.2140	1.1761
1185.1	-0.049908	18.0	0.001377	-0.048531	-0.000122	0.189536	0.000640	-3.1938	1.2553
1184.8	-0.049908	21.0	0.001376	-0.048531	-0.000122	0.189536	0.000642	-3.1927	1.3222
1183.9	-0.049931	24.0	0.001375	-0.048536	-0.000147	0.189510	0.000771	-3.1129	1.3802
1185.8	-0.049955	27.0	0.001378	-0.048577	-0.000168	0.189491	0.000883	-3.0541	1.4314
1185.4	-0.049978	30.0	0.001377	-0.048601	-0.000192	0.189466	0.001009	-2.9959	1.4771
1186.1	-0.049990	33.0	0.001378	-0.048612	-0.000203	0.189456	0.001067	-2.9719	1.5185
1185.8	-0.049996	36.0	0.001378	-0.048618	-0.000209	0.189450	0.001099	-2.9589	1.5563
1185.3	-0.050019	39.0	0.001377	-0.048642	-0.000233	0.189425	0.001226	-2.9114	1.5911
1185.4	-0.050055	42.0	0.001377	-0.048678	-0.000268	0.189390	0.001411	-2.8504	1.6232
1185.7	-0.050061	45.0	0.001378	-0.048683	-0.000274	0.189385	0.001440	-2.8416	1.6532
1185.5	-0.050072	48.0	0.001377	-0.048695	-0.000286	0.189373	0.001503	-2.8230	1.6812
1185.8	-0.050084	51.0	0.001378	-0.048706	-0.000297	0.189361	0.001564	-2.8089	1.7076
1185.0	-0.050084	54.0	0.001377	-0.048707	-0.000298	0.189350	0.001568	-2.8046	1.7324
1185.1	-0.050119	57.0	0.001377	-0.048742	-0.000333	0.189325	0.001753	-2.7552	1.7559
1184.8	-0.050131	60.0	0.001376	-0.048755	-0.000345	0.189312	0.001817	-2.7406	1.7782

$n = 1.09 \pm 0.07$, $\log(K) = -4.64 \pm 0.09$, $R \text{ Squared} = 0.923$

Table 65. Isothermal Shrinkage Data for Region E,

11. ABS.2 Sample 8, $L_0 = 0.1820$ inches, 950 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected, Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
948.8	-0.056767	6.0	0.001048	-0.055719	-0.000017	0.181634	0.000092	-4.0370	0.7782
949.7	-0.056779	9.0	0.001049	-0.055730	-0.000027	0.181624	0.000151	-3.8217	0.9542
949.3	-0.056790	10.0	0.001048	-0.055742	-0.000040	0.181611	0.000218	-3.6617	1.0000
950.2	-0.056790	12.0	0.001050	-0.055741	-0.000039	0.181613	0.000212	-3.6742	1.0792
950.5	-0.056814	15.0	0.001050	-0.055764	-0.000056	0.181596	0.000339	-3.4697	1.1761
950.5	-0.056808	18.0	0.001050	-0.055758	-0.000056	0.181596	0.000307	-3.5128	1.2553
950.4	-0.056808	21.0	0.001050	-0.055758	-0.000056	0.181596	0.000307	-3.5124	1.3222
950.6	-0.056826	24.0	0.001050	-0.055776	-0.000073	0.181579	0.000403	-3.3943	1.3802
951.1	-0.056837	27.0	0.001050	-0.055787	-0.000085	0.181568	0.000465	-3.3329	1.4314
951.2	-0.056873	30.0	0.001051	-0.055822	-0.000120	0.181533	0.000658	-3.1820	1.4771
951.3	-0.056867	33.0	0.001051	-0.055816	-0.000114	0.181539	0.000625	-3.2045	1.5185
951.0	-0.056873	36.0	0.001050	-0.055822	-0.000120	0.181532	0.000659	-3.1812	1.5563
951.5	-0.056878	39.0	0.001051	-0.055828	-0.000125	0.181527	0.000688	-3.1623	1.5911
951.6	-0.056890	42.0	0.001051	-0.055827	-0.000125	0.181528	0.000688	-3.1627	1.6232
951.8	-0.056890	45.0	0.001051	-0.055839	-0.000137	0.181517	0.000750	-3.1247	1.6532
952.2	-0.056925	48.0	0.001052	-0.055874	-0.000171	0.181482	0.000942	-3.0261	1.6812
951.3	-0.056908	51.0	0.001051	-0.055857	-0.000155	0.181498	0.000850	-3.0704	1.7076
951.6	-0.056961	54.0	0.001051	-0.055910	-0.000207	0.181446	0.001139	-2.9434	1.7324
952.1	-0.056943	57.0	0.001052	-0.055892	-0.000189	0.181464	0.001039	-2.9832	1.7539
952.2	-0.056931	60.0	0.001052	-0.055880	-0.000177	0.181476	0.000974	-3.0114	1.7782

$n = 1.01 \pm 0.04$, $\text{Log}(K) = -4.76 \pm 0.05$, R Squared 0.970

Table 66. Isothermal Shrinkage Data for Region E,

II. ABS.2 Sample 11, Lo = 0.2216 inches, 1049 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1047.6	-0.015612	6.0	0.001414	-0.014198	-0.000232	0.221235	0.001135	-2.9450	0.7782
1047.3	-0.015671	9.0	0.001413	-0.014257	-0.000311	0.221176	0.001402	-2.8534	0.9542
1047.9	-0.015718	10.0	0.001414	-0.014383	-0.000357	0.221130	0.001610	-2.7932	1.0000
1047.7	-0.015759	12.0	0.001414	-0.014345	-0.000398	0.221089	0.001797	-2.7455	1.0792
1048.4	-0.015817	15.0	0.001415	-0.014482	-0.000456	0.221032	0.002057	-2.6968	1.1761
1048.0	-0.015853	18.0	0.001414	-0.014438	-0.000492	0.220996	0.002218	-2.6540	1.2553
1048.4	-0.015899	21.0	0.001415	-0.014485	-0.000538	0.220950	0.002428	-2.6148	1.3222
1048.6	-0.015958	24.0	0.001415	-0.014543	-0.000596	0.220891	0.002691	-2.5700	1.3902
1049.3	-0.015993	27.0	0.001416	-0.014577	-0.000631	0.220858	0.002846	-2.5458	1.4314
1050.3	-0.016029	30.0	0.001418	-0.014611	-0.000664	0.220825	0.002999	-2.5231	1.4771
1049.4	-0.016046	33.0	0.001416	-0.014630	-0.000683	0.220805	0.003084	-2.5109	1.5185
1049.1	-0.016123	36.0	0.001416	-0.014707	-0.000760	0.220728	0.003430	-2.4647	1.5563
1050.0	-0.016134	39.0	0.001417	-0.014717	-0.000771	0.220719	0.003477	-2.4588	1.5911
1050.7	-0.016205	42.0	0.001418	-0.014787	-0.000840	0.220650	0.003791	-2.4212	1.6232
1050.5	-0.016234	45.0	0.001418	-0.014816	-0.000870	0.220620	0.003925	-2.4062	1.6532
1050.2	-0.016275	48.0	0.001417	-0.014858	-0.000911	0.220578	0.004111	-2.3860	1.6912
1049.3	-0.016281	51.0	0.001416	-0.014865	-0.000918	0.220570	0.004144	-2.3826	1.7076
1049.0	-0.016305	54.0	0.001417	-0.014888	-0.000941	0.220548	0.004246	-2.3720	1.7324
1050.6	-0.016351	57.0	0.001418	-0.014934	-0.000987	0.220503	0.004454	-2.3513	1.7559
1050.3	-0.016375	60.0	0.001418	-0.014957	-0.001011	0.220479	0.004561	-2.3409	1.7782

n = 0.60 ± 0.01, Log(K) = -3.41 ± 0.01, R Squared = 0.997

Table 67. Isothermal Shrinkage Data for Region E,

11.088.2 Sample 2, Lo = 0.1966 inches, 1146 deg. C.

Temperature, degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1144.7	-0.045939	6.0	0.001375	-0.044565	-0.000468	0.195877	0.002381	-2.6232	0.7782
1144.7	-0.046104	9.0	0.001375	-0.044729	-0.000633	0.195712	0.003218	-2.4924	0.9542
1145.5	-0.046162	10.0	0.001376	-0.044787	-0.000690	0.195655	0.003512	-2.4544	1.0000
1145.8	-0.046239	12.0	0.001376	-0.044863	-0.000766	0.195579	0.003899	-2.4091	1.0792
1146.0	-0.046374	15.0	0.001376	-0.044998	-0.000901	0.195445	0.004585	-2.3387	1.1761
1146.3	-0.046474	18.0	0.001377	-0.045097	-0.001001	0.195345	0.005091	-2.2932	1.2553
1146.2	-0.046568	21.0	0.001376	-0.045191	-0.001095	0.195291	0.005569	-2.2542	1.3222
1146.3	-0.046597	24.0	0.001377	-0.045321	-0.001224	0.195122	0.006227	-2.2057	1.3802
1146.5	-0.046768	27.0	0.001377	-0.045391	-0.001294	0.195052	0.006584	-2.1771	1.4314
1146.6	-0.046856	30.0	0.001377	-0.045479	-0.001382	0.194964	0.007032	-2.1529	1.4771
1146.9	-0.046903	33.0	0.001377	-0.045526	-0.001429	0.194918	0.007259	-2.1385	1.5185
1146.9	-0.046979	36.0	0.001377	-0.045602	-0.001505	0.194841	0.007657	-2.1159	1.5563
1146.5	-0.047020	39.0	0.001377	-0.045644	-0.001547	0.194799	0.007859	-2.1041	1.5911
1147.0	-0.047056	42.0	0.001377	-0.045678	-0.001582	0.194765	0.008045	-2.0945	1.6232
1147.6	-0.047097	45.0	0.001378	-0.045719	-0.001622	0.194725	0.008251	-2.0835	1.6532
1146.5	-0.047173	48.0	0.001377	-0.045796	-0.001700	0.194647	0.008646	-2.0632	1.6812
1147.2	-0.047191	51.0	0.001378	-0.045813	-0.001717	0.194631	0.008731	-2.0589	1.7076
1147.3	-0.047267	54.0	0.001378	-0.045889	-0.001793	0.194594	0.009119	-2.0400	1.7324
1147.6	-0.047314	57.0	0.001378	-0.045936	-0.001839	0.194508	0.009357	-2.0289	1.7559
1147.7	-0.047343	60.0	0.001378	-0.045965	-0.001869	0.194479	0.009505	-2.0220	1.7782

n = 0.59 ± 0.01, Log(K) = -3.04, R Squared = 0.990

Table 68. Isothermal Shrinkage Data for Region E,

11.988.2 Sample 1, $L_0 = 0.1927$ inches, 1184 deg. C.

Temperature degrees C	Apparent Shrinkage, inches	Time, minutes	System Expansion, inches	Sample Shrinkage, inches	Isothermal Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Linear Shrinkage	Log Time
1183.7	-0.052214	6.0	0.001395	-0.050820	-0.000105	0.192259	0.000544	-3.2644	0.7782
1183.6	-0.052220	9.0	0.001394	-0.050825	-0.000111	0.192263	0.000575	-3.2403	0.9542
1184.3	-0.052249	10.0	0.001395	-0.050854	-0.000139	0.192235	0.000723	-3.1410	1.0000
1184.2	-0.052238	12.0	0.001395	-0.050842	-0.000128	0.192247	0.000663	-3.1787	1.0792
1184.8	-0.052261	15.0	0.001396	-0.050855	-0.000150	0.192224	0.000781	-3.1074	1.1751
1185.1	-0.052320	18.0	0.001396	-0.050924	-0.000209	0.192166	0.001004	-2.9651	1.2553
1185.9	-0.052332	21.0	0.001397	-0.050934	-0.000220	0.192156	0.001140	-2.9431	1.3222
1185.3	-0.052326	24.0	0.001398	-0.050928	-0.000213	0.192163	0.001107	-2.9538	1.3802
1185.9	-0.052337	27.0	0.001397	-0.050940	-0.000226	0.192150	0.001170	-2.9317	1.4314
1185.4	-0.052396	30.0	0.001398	-0.050998	-0.000284	0.192093	0.001472	-2.8322	1.4771
1186.1	-0.052431	33.0	0.001398	-0.051034	-0.000319	0.192057	0.001657	-2.7807	1.5185
1185.2	-0.052420	35.0	0.001396	-0.051023	-0.000309	0.192067	0.001601	-2.7955	1.5563
1185.8	-0.052449	39.0	0.001397	-0.051052	-0.000337	0.192039	0.001750	-2.7570	1.5911
1185.4	-0.052437	42.0	0.001398	-0.051039	-0.000325	0.192052	0.001685	-2.7734	1.6232
1185.4	-0.052473	45.0	0.001398	-0.051075	-0.000360	0.192016	0.001868	-2.7286	1.6532
1185.7	-0.052473	48.0	0.001397	-0.051076	-0.000361	0.192015	0.001873	-2.7276	1.6812
1185.6	-0.052496	51.0	0.001397	-0.051099	-0.000385	0.191991	0.001996	-2.6999	1.7076
1185.6	-0.052525	54.0	0.001397	-0.051128	-0.000414	0.191962	0.002147	-2.6681	1.7324
1185.7	-0.052561	57.0	0.001397	-0.051164	-0.000449	0.191927	0.002330	-2.6327	1.7559
1185.9	-0.052561	60.0	0.001397	-0.051163	-0.000449	0.191927	0.002329	-2.6329	1.7782

$n = 0.60 \pm 0.03$, $\log(K) = -3.86 \pm 0.03$, R Squared = 0.973

APPENDIX C

Figure 45. Isothermal Shrinkage Plots for II.ABS.2 Region B; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 46. Isothermal Shrinkage Plots for I.ABS.1 Region C; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 47. Isothermal Shrinkage Plots for I.ABS.2 Region C; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 48. Isothermal Shrinkage Plots for II.ABS.1 Region C; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 49. Isothermal Shrinkage Plots for II.ABS.2 Region C; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 50. Isothermal Shrinkage Plots for I.ABS.1 Region D; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 51. Isothermal Shrinkage Plots for I.ABS.2 Region D; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time

Figure 52. Isothermal Shrinkage Plots for II.ABS.1 Region D; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 53. Isothermal Shrinkage Plots for II.ABS.2 Region D; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 54. Isothermal Shrinkage Plots for I.ABS.1 Region E; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 55. Isothermal Shrinkage Plots for I.ABS.2 Region E; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 56. Isothermal Shrinkage Plots for II.ABS.1 Region E; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

Figure 57. Isothermal Shrinkage Plots for II.ABS.2 Region E; (a) Linear Shrinkage vs. Temperature, (b) Log Linear Shrinkage vs. Log Time.

APPENDIX D

Table 60. CHR Shrinkage Data for Region D,

I.ABS.1 Sample 2, $L_0 = 0.2257$ inches, $T(t) = 888$ deg. C.

Temperature, degrees C	$1/T_i$ 1/Kelvin	Apparent Shrinkage, inches	System Expansion, inches	Sample Shrinkage, inches	CHR Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Lin. Shrinkage $\times 1/(T+2)$	Log
819.7	0.000915	-0.016859	0.001116	-0.015743	-0.002074	0.223600	0.009188	-8.1139	
826.5	0.000909	-0.017986	0.001126	-0.016860	-0.003191	0.222489	0.014139	-7.9321	
834.3	0.000903	-0.019360	0.001137	-0.018223	-0.004554	0.221133	0.020177	-7.7838	
840.4	0.000898	-0.021045	0.001145	-0.019900	-0.006230	0.219462	0.027605	-7.6524	
848.3	0.000892	-0.023147	0.001157	-0.021991	-0.008321	0.217378	0.036869	-7.5329	
854.1	0.000887	-0.025731	0.001165	-0.024567	-0.010897	0.214808	0.048283	-7.4203	
861.6	0.000881	-0.028927	0.001176	-0.027751	-0.014082	0.211630	0.062392	-7.3149	
868.9	0.000876	-0.033585	0.001186	-0.032400	-0.018730	0.206988	0.082988	-7.1964	
875.7	0.000870	-0.040442	0.001195	-0.039247	-0.025577	0.200147	0.113325	-7.0662	
888.1	0.000861	-0.054114	0.001213	-0.052901	-0.039232	0.186504	0.173823	-6.8897	

$s = -22244 \pm 489$, $R \text{ Squared} = 0.996$

Table 70. CHR Shrinkage Data for Region D,

I. ABS.1 Sample 13, $L_0 = 0.2330$ inches, $T(t) = 888$ deg. C.

Temperature, degrees C	1/T, 1/Kelvin	Apparent Shrinkage, inches	System Expansion, inches	Sample Shrinkage, inches	CHR Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Lin. Shrinkage $\times 1/(T^{\circ}K^2)$
823.4	0.000912	-0.004770	0.001157	-0.003612	-0.001413	0.231522	0.006065	-8.2972
830.9	0.000906	-0.005297	0.001168	-0.004129	-0.001930	0.231111	0.008284	-8.1678
837.4	0.000900	-0.005884	0.001178	-0.004706	-0.002507	0.230940	0.010759	-8.0594
844.5	0.000895	-0.006271	0.001188	-0.005082	-0.002884	0.230170	0.012376	-8.0041
851.2	0.000889	-0.006300	0.001198	-0.005102	-0.002903	0.230157	0.012460	-8.0064
858.5	0.000884	-0.007813	0.001209	-0.006605	-0.004405	0.228650	0.018909	-7.8308
865.7	0.000878	-0.014626	0.001219	-0.013406	-0.011207	0.221855	0.048101	-7.4308
872.8	0.000873	-0.020778	0.001230	-0.019548	-0.017349	0.215729	0.074461	-7.2464
880.3	0.000867	-0.031527	0.001241	-0.030286	-0.028087	0.204999	0.120544	-7.0429
888.2	0.000861	-0.041756	0.001252	-0.040503	-0.038304	0.194788	0.164396	-6.9140

$s = -28462 \pm 2624$, R Squared = 0.936

Table 71. CHR Shrinkage Data for Region D,

I. ABS.2 Sample 1, $L_0 = 0.2255$ inches, $T(t) = 889$ deg. C.

Temperature, degrees C	$1/T,$ $1/\text{Kelvin}$	Apparent Shrinkage, inches	System Expansion, inches	Sample Shrinkage, inches	CHR Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Lin. Shrinkage $\times 1/(T^2)$
818.7	0.000916	-0.015189	0.001118	-0.014071	-0.002673	0.223767	0.011800	-8.0045
825.7	0.000910	-0.016745	0.001128	-0.015616	-0.004218	0.222228	0.018623	-7.8118
832.4	0.000904	-0.018653	0.001138	-0.017515	-0.006117	0.220335	0.027005	-7.6558
840.0	0.000898	-0.020931	0.001149	-0.019782	-0.008384	0.218075	0.037015	-7.5248
846.4	0.000893	-0.023773	0.001158	-0.022615	-0.011217	0.215248	0.049523	-7.4033
854.1	0.000887	-0.027039	0.001169	-0.025870	-0.014471	0.212000	0.063892	-7.2986
860.8	0.000882	-0.030921	0.001179	-0.029743	-0.018345	0.208133	0.080992	-7.2008
868.0	0.000876	-0.035533	0.001189	-0.034345	-0.022946	0.203537	0.101309	-7.1091
875.1	0.000871	-0.041186	0.001199	-0.039987	-0.028589	0.197902	0.126219	-7.0190
888.8	0.000861	-0.051104	0.001218	-0.049885	-0.038487	0.188016	0.169921	-6.9002

$s = -19012 \pm 1052$, $R \text{ Squared} = 0.978$

Table 72. CHR Shrinkage Data for Region D,

I. ABS.2 Sample 5, $L_0 = 0.2291$ inches, $T(t) = 887$ deg. C.

Temperature, degrees C	1/T, 1/Kelvin	Apparent Shrinkage, inches	System Expansion, inches	Sample Shrinkage, inches	CHR Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Lin. Shrinkage $\times 1/(T+2)$
820.0	0.000915	-0.012527	0.001133	-0.011394	-0.001691	0.227347	0.007381	-8.2092
826.2	0.000910	-0.013513	0.001142	-0.012371	-0.002668	0.226376	0.011645	-8.0161
833.4	0.000904	-0.014528	0.001152	-0.013775	-0.004072	0.224978	0.017774	-7.8382
841.7	0.000897	-0.015882	0.001155	-0.015718	-0.006015	0.223043	0.026253	-7.6753
847.3	0.000892	-0.016201	0.001173	-0.018029	-0.008326	0.220737	0.036340	-7.5384
853.7	0.000887	-0.021838	0.001182	-0.020655	-0.010953	0.218116	0.047808	-7.4243
861.1	0.000882	-0.025109	0.001192	-0.023916	-0.014213	0.214862	0.062040	-7.3168
868.2	0.000876	-0.029350	0.001203	-0.028147	-0.018444	0.210638	0.080505	-7.2091
876.2	0.000870	-0.034561	0.001214	-0.033346	-0.023643	0.205446	0.103201	-7.1073
887.0	0.000862	-0.040989	0.001230	-0.039759	-0.030056	0.199043	0.131190	-7.0111

$s = -22711 \pm 1223$, $R \text{ Squared} = 0.977$

Table 73. CHR Shrinkage Data for Region D,

11.A85.1 Sample 1, $L_0 = 0.2274$ inches, $T(t) = 895$ deg. C.

Temperature, degrees C	$1/T_1$ 1/Kelvin	Apparent Shrinkage, inches	System Expansion, inches	Sample Shrinkage, inches	CHR Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Lin. Shrinkage $\times 1(T+2)$
823.5	0.000912	-0.013854	0.001130	-0.012724	-0.002378	0.225018	0.010458	-8.0607
830.3	0.000906	-0.014887	0.001139	-0.013747	-0.003401	0.224001	0.014958	-7.9106
835.6	0.000901	-0.016201	0.001148	-0.015053	-0.004707	0.222700	0.020700	-7.7745
844.1	0.000895	-0.017745	0.001159	-0.016586	-0.006240	0.221174	0.027442	-7.6579
851.5	0.000889	-0.019665	0.001170	-0.018495	-0.008150	0.219272	0.035838	-7.5477
858.1	0.000884	-0.022108	0.001179	-0.020929	-0.010583	0.216944	0.045538	-7.4394
865.8	0.000878	-0.025038	0.001190	-0.023848	-0.013502	0.213932	0.059377	-7.3394
872.5	0.000873	-0.028873	0.001200	-0.028673	-0.018327	0.209113	0.080593	-7.2119
880.1	0.000867	-0.038192	0.001211	-0.036981	-0.026635	0.200812	0.117129	-7.0553
894.6	0.000856	-0.049820	0.001232	-0.048588	-0.038242	0.189218	0.168172	-6.9090

$s = -20741 \pm 492$, $R \text{ Squared} = 0.996$

Table 74. CHR Shrinkage Data for Region D,

II. ABS.1 Sample 9, $L_0 = 0.2264$ inches, $T(t) = 897$ deg. C.

Temperature, degrees C	1/T, 1/Kelvin	Apparent Shrinkage, inches	System Expansion, inches	Sample Shrinkage, inches	CHR Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Lin. Shrinkage $\times 1/(T+2)$
826.9	0.000909	-0.012660	0.001130	-0.011530	-0.003153	0.231583	0.013925	-7.9391
833.6	0.000903	-0.013939	0.001139	-0.012800	-0.004422	0.230319	0.019534	-7.7974
841.3	0.000897	-0.015624	0.001150	-0.014473	-0.006096	0.228652	0.026926	-7.6640
847.2	0.000893	-0.017819	0.001159	-0.016660	-0.008283	0.226470	0.036586	-7.5354
854.4	0.000887	-0.020872	0.001169	-0.019703	-0.011326	0.223434	0.050026	-7.4051
862.0	0.000881	-0.025441	0.001180	-0.024261	-0.015984	0.218882	0.070159	-7.2640
869.3	0.000875	-0.032008	0.001190	-0.030818	-0.022441	0.212332	0.099120	-7.1196
876.2	0.000870	-0.039746	0.001200	-0.038546	-0.030169	0.204610	0.133255	-6.9962
883.5	0.000865	-0.047955	0.001210	-0.046744	-0.038367	0.196419	0.169465	-6.8974
897.0	0.000855	-0.054699	0.001230	-0.053470	-0.045092	0.189705	0.199170	-6.8373

$s = -2177 \pm 1049$, R Squared = 0.982

Table 75. CHR Shrinkage Data for Region D,

11.085.2 Sample 8, $L_0 = 0.2281$ inches, $T(t) = 892$ deg. C.

Temperature, degrees C	1/T, 1/Kelvin	Apparent Shrinkage, inches	System Expansion, inches	Sample Shrinkage, inches	CHR Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Lin. Shrinkage $\times 1/(1+\epsilon)$
825.7	0.000909	-0.010495	0.001138	-0.009357	-0.002310	0.225780	0.010127	-8.0772
834.1	0.000903	-0.011457	0.001148	-0.010308	-0.003262	0.224835	0.014300	-7.9332
840.9	0.000898	-0.012724	0.001158	-0.011566	-0.004519	0.223583	0.019814	-7.7969
848.2	0.000892	-0.014297	0.001169	-0.013128	-0.006082	0.222027	0.026663	-7.6736
854.5	0.000887	-0.016504	0.001178	-0.015326	-0.008280	0.219835	0.036298	-7.5445
861.8	0.000881	-0.019933	0.001188	-0.018744	-0.011698	0.216423	0.051284	-7.4000
868.6	0.000876	-0.025588	0.001198	-0.024390	-0.017343	0.210784	0.076033	-7.2342
876.2	0.000870	-0.033448	0.001209	-0.032239	-0.025192	0.202942	0.110443	-7.0778
883.2	0.000865	-0.042467	0.001219	-0.041248	-0.034201	0.193939	0.149938	-6.9503
891.6	0.000859	-0.051950	0.001231	-0.050719	-0.043672	0.184475	0.191460	-6.8504

$s = -25082 \pm 441$, $R \text{ Squared} = 0.997$

Table 76. CHR Shrinkage Data for Region D,

II. ARS.2 Sample 1, $L_0 = 0.2326$ inches, $T(t) = 894$ deg. C.

Temperature, degrees C	$1/T,$ 1/Kelvin	Apparent Shrinkage, inches	System Expansion, inches	Sample Shrinkage, inches	CHR Shrinkage, inches	Corrected Sample Length, inches	Linear Shrinkage	Log Lin. Shrinkage $\times 1/(T+2)$
825.4	0.000910	-0.013910	0.001158	-0.012751	-0.002611	0.230008	0.011225	-8.0315
832.1	0.000905	-0.015060	0.001168	-0.013892	-0.003751	0.228873	0.016128	-7.8794
839.0	0.000899	-0.016557	0.001178	-0.015379	-0.005238	0.227393	0.022520	-7.7398
844.9	0.000894	-0.018430	0.001187	-0.017243	-0.007102	0.225534	0.030534	-7.6122
852.5	0.000888	-0.020719	0.001198	-0.019521	-0.009381	0.223262	0.040331	-7.4972
859.2	0.000883	-0.023438	0.001208	-0.022230	-0.012090	0.220560	0.051978	-7.3922
866.5	0.000877	-0.026774	0.001219	-0.025356	-0.015415	0.217241	0.066274	-7.2922
873.3	0.000872	-0.031509	0.001229	-0.030280	-0.020140	0.212523	0.086586	-7.1813
880.7	0.000867	-0.039070	0.001239	-0.037831	-0.027691	0.204979	0.119048	-7.0485
893.6	0.000857	-0.051615	0.001258	-0.050357	-0.040216	0.192465	0.172898	-6.8962

$s = -21189 \pm 544$, $R \text{ Squared} = 0.995$