STATISTICAL ANALYSIS OF COMPOSITION AND TEMPERATURE FOR POROUS ALUMINA FABRICATION

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Abstract

This investigation used statistical software to design and analyze the effects of dispersant, binder, and firing temperature (as independent factors) upon the apparent porosity and bulk density (as dependent factors) of porous alumina. Results show that all independent factors have significant effects on the dependent factors, but in different ways. In the first part of this work the dispersant (Darvan C) amount and the square of the dispersant amount were found to have significant effects on the apparent porosity and bulk density of porous alumina, while the firing temperature had important effects on the apparent porosity only. Additionally, in the second part the square of the binder (glue) amount and the square of the firing temperature were found to have large effects on both the apparent porosity and bulk density of porous alumina.

Keywords: Statistical analysis, bulk density, porous alumina, ANOVA

Introduction

Alumina or aluminum oxide (Al_2O_3) is an important raw material in ceramic industries owing to its hardness, high chemical stability, and high melting point. Pure alumina has a melting point of 2054ºC, a density equal to 3.97 g/cm^3, a modulus of rupture (MOR) of 410 MPa, a no-load shape stability at 1750ºC, and a hardness equal to 9 on the Mohs scale (Powpan, 2012). Much research has been done on porous alumina in recent years. This is because they can be used in many applications such as filters, thermal insulators, catalyst supports, and artificial bones (Tripkovic *et al*., 2006; Rahman and Yacob, 2010).

Several methods for fabrication of porous alumina have been proposed. The most common one is the polymeric sponge replica method. In this procedure, a polymeric sponge is immerged into alumina slurry followed by burning the polymer template away. In order to efficiently coat the polymeric sponge with alumina powder, the addition of a binder and dispersing agent to the alumina slurry is needed. Alumina slurry consists of 3 major components. These are alumina powder, a dispersant or deflocculant, and a binder.

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There are many types of commercially available alumina powder. The alumina powder used in this work was alumina A-5M (Suzhou Dexin Advanced Ceramics Co., Ltd., Jiangsu, China). Its purity was 95% with an average particle size of 5 μm. Darvan C® (R.T. Vanderbilt Co., Inc., Norwalk, CT, USA), a polymethacrylic acid, has been shown to be suitable for dispersing alumina slurry; thus Darvan C was chosen as the dispersant in this work (Srilomsak, 2006a, 2006b). Water glue, which contains mainly starch and water, was selected for use as the binder in this experiment because it is one of the simplest and most inexpensive binders available in the market. Two different sets of slurries were prepared. The first slurry set was made by varying the dispersant amounts while holding the binder content constant. The second set of slurries was prepared by keeping the dispersant amount constant and varying the binder content. The most important properties of porous materials are their apparent porosity and bulk density. Apparent porosity is the ratio of the open pore volume of the specimen to its exterior volume. Bulk density is represented by the specimen's dry mass divided by the exterior volume (ASTM, 1994). Generally, the goal in making porous materials is to fabricate materials that have high apparent porosity and low bulk density. The firing temperature also plays a significant role in determining the properties of porous alumina. Accordingly, this research also examined this temperature. A factorial design was employed for the experiments and analysis of variance (ANOVA) was used to analyze the resulting data. In order to simplify the calculations involved and to make this work as efficient as possible, Design of Experiment (DOE) software (Design-Expert® Version 8 of Stat-Ease, Inc. Minneapolis, MN, USA) was utilized in this research. The purpose of this study was to determine which process variables (Darvan C and binder amounts as well as the firing temperature) affect porous alumina's properties. Moreover a regression model representing an equation to predict the response was developed. A 3-dimensional (3D) response surface and contour plots were made. Finally, the optimal region of the important factors that yield the best possible response was identified.

Materials and Methods

The general factorial design in Design-Expert® was used in this experimental design. Since there were 2 sets of slurries, this experiment was separated into 2 parts. In part 1, the independent factors were the Darvan C amount (A) and the firing temperature (B). In part 2, the glue amount (A) and the firing temperature (B) were the independent factors. There were 3 levels of Darvan C (4, 7, and 9 g), glue amounts (30, 40, and 50 ml), and firing temperatures (1350, 1450, and 1550ºC). Each level of an independent factor represents 1 treatment combination. Thus, there are 3×3 or 9 combinations in each experimental part. Experimental errors may have been present. Therefore it was desirable to make 3 observations for each treatment combination. Therefore, there were 3×9 or 27 observations for each part of the experiment. These observations are shown in columns 1-4 of Tables 1 and 2. Table 1 represents part 1 experiments whereas Table 2 represents those of part 2. The first column in both Tables under the heading, Std, represents a standard number which is assigned according to the variation of independent factors. The second column under the heading, Run, is a run number which is the order in which data was collected. It is important to note that the run number was selected randomly. This means that the experiments defined by the standard number were performed in random order. This randomization is essential to minimize the effects of extraneous factors that may have been present. The third and fourth columns of Table 1 are the Darvan C amount and the firing temperature in each experimental observation,respectively, while those of Table 2 are the glue amount and the firing temperature, respectively. The fifth to last

columns of both tables are the dependent factors (i.e., apparent porosity and bulk density, respectively).

For the part 1 experiments, alumina powder (900 g), deionized water (200 cc), and Darvan C amounts 4, 7, or 9 g according to the run numbers in Table 1 were ball milled for 2 days. This was done in order to get mixtures which have Darvan C amounts of 0.36 wt% {= 4 ×100 ÷ (900 + 200)}wt%, 0.63 wt%{= 7 ×100 ÷ (900 + 200)}wt%, and 0.82 wt%, {= 9 ×100 ÷ (900 + 200)}wt%,

Table 1. Standard number (Std), Run number (Run), Darvan C amount (Darvan), Firing temperature (Temp), Apparent porosity (Porosity), and Bulk density (Density)

Std	Run	Factor 1 A:Darvan* (wt%)	Factor 2 B:Temp (°C)	Response 1 Porosity (%)	Response 2 Density (g/cm³)
1	12	0.36	1350	77.43	0.81
2	7	0.36	1350	73.92	1.00
3	17	0.36	1350	77.36	0.83
4	16	0.63	1350	57.55	1.57
5	10	0.63	1350	58.85	1.57
6	1	0.63	1350	59.53	1.56
7	26	0.90	1350	78.76	0.76
8	4	0.90	1350	81.01	0.69
9	23	0.90	1350	79.86	0.74
10	25	0.36	1450	77.54	0.82
11	3	0.36	1450	71.52	1.04
12	19	0.36	1450	74.13	1.00
13	15	0.63	1450	62.72	1.42
14	11	0.63	1450	60.72	1.40
15	22	0.63	1450	61.24	1.43
16	9	0.90	1450	78.29	0.80
17	8	0.90	1450	80.03	0.69
18	14	0.90	1450	79.07	0.75
19	24	0.36	1550	72.19	0.98
20	13	0.36	1550	70.30	1.08
21	6	0.36	1550	73.87	1.00
22	21	0.63	1550	54.39	1.70
23	27	0.63	1550	59.59	1.52
24	18	0.63	1550	59.30	1.54
25	5	0.90	1550	78.46	0.75
26	2	0.90	1550	79.62	0.70
27	20	0.90	1550	72.89	0.96

Note: The Darvan C amounts added into slurries were 4, 7, or 9 g in order to get Darvan C concentration 0.36, 0.63, and 0.90 wt%, respectively, in the slurries.

respectively. The mixtures were then passed through a 40 mesh sieve. Then 40 ml of water glue were added to the mixtures which were thoroughly stirred to get slurries according to Table 1. For the second part of the experiment, 900 g of alumina powder, 7 g of Darvan C, and 200 cc of deionized water were ball milled for 2 days. Next the mixtures were passed through a 40 mesh sieve (0.420 mm opening). Subsequently 30, 40, or 50 ml of glue (according to the third column of Table 2) were added to the mixtures and thoroughly stirred to yield slurries according to Table 2.

Table 2. Standard number (Std), Run number (Run), Glue amount (Glue), Firing temperature (Temp), Apparent porosity (Porosity), and Bulk density (Density)

Std	Run	Factor 1 A:Glue (ml)	Factor 2 B:Temp (^oC)	Response 1 Porosity (%)	Response 2 Density (g/cm^3)
1	27	30	1350	81.88	0.67
2	5	30	1350	82.21	0.68
3	13	30	1350	76.68	0.88
4	6	40	1350	57.55	1.57
5	1	40	1350	58.85	1.57
6	15	40	1350	59.53	1.56
7	14	50	1350	84.94	0.56
8	21	50	1350	77.73	0.84
9	3	50	1350	79.93	0.80
10	7	30	1450	81.89	0.64
11	20	30	1450	80.68	0.65
12	4	30	1450	80.40	0.75
13	25	40	1450	62.72	1.42
14	17	40	1450	60.72	1.40
15	19	40	1450	61.24	1.43
16	9	50	1450	85.93	0.58
17	10	50	1450	81.70	0.61
18	26	50	1450	76.50	0.86
19	18	30	1550	80.87	0.71
20	24	30	1550	78.72	0.79
21	16	30	1550	78.41	0.80
22	8	40	1550	54.39	1.70
23	23	40	1550	59.59	1.52
24	2	40	1550	59.30	1.54
25	12	50	1550	75.58	0.83
26	11	50	1550	75.84	0.88
27	22	50	1550	77.41	0.85

Next polymeric sponges with porosities of ~5-10 pores/cm were impregnated with the slurries of both experimental parts. The sponges were repeatedly compressed to remove air and immersed in slurry. Then they were allowed to expand several times to ensure that the slurries were maximally absorbed into the sponges. The saturated sponges were air dried for 2 h. During this time, the sponges were turned over several times to make sure that the alumina slurries were evenly distributed on both sides (top and bottom) of the sponges. Next the sponges were dried at 100ºC in an oven for 24 h. Subsequently, the dried sponges were fired at the temperatures specified in the fourth column of Tables 1 and 2. The following heating and cooling profile was used. First, the samples were heated from room temperature to 550ºC at a rate of 1ºC/min. Then the sample temperature was held at 550ºC for 3 h. Next samples were heated from 550ºC to the temperature specified in the fourth column of Tables 1 and 2. A heating rate of 2ºC/min was used. Upon reaching the specified temperature, the temperature was maintained for 2 h. After that the samples were cooled to room temperature under the cooling rate of 5ºC/min. Subsequently, the porous alumina specimens were removed from the furnace. Dependent factors (apparent porosity and bulk density) were determined according to ASTM C373-88 (ASTM, 1994). They were analyzed using the ANOVA in Design-Expert®. This was done to determine if the independent factors (Darvan C, glue amounts, and firing temperature) and their interactions had significant effects (>95% confidence) upon the dependent factors. Regression equations were developed to predict the effects of the Darvan C and glue amounts as well as the firing temperature on the apparent porosity and bulk density of the porous alumina. The ANOVA assumptions were verified with the normality and residual versus the predicted value plots. Finally, graphs of the 3D surface and contour plots of the predicted dependent factors as a function of the independent factors were developed.

Results and Discussion

Figures 1(a) and 1(b) show the dried infiltrated sponge and porous alumina after firing, respectively. The fifth through last columns of Tables 1 and 2 show the porous alumina's properties (i.e., apparent porosity and bulk density) that resulted from varying the Darvan C and binder amounts as well as the firing temperature. The results were separated into 2 major parts, each with 2 sub-divisions as follows:

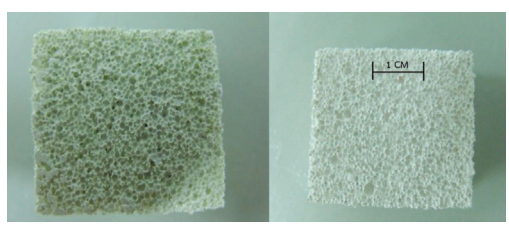
Part 1

a) Apparent porosity

Table 3 shows the ANOVA results for apparent porosity. The Darvan C amount (A), firing temperature (B), and square of the Darvan C amount (A^2) have a significant effect (>95% confidence) on the apparent porosity of the porous alumina. The resulting equation for predicting the apparent porosity is:

$$\text{Apparent porosity}(\%) = 166.5297 - 288.04 \times \text{Darvan}(\%) - 0.0131 \times \text{Temp}(^{\circ}\text{C}) + 235.0922 \times \text{Darvan}^2(\%^2)$$

Figure 2 is a normal plot of the residual values to check the ANOVA normality assumption. The plot slightly diverges from a straight line. However, this divergence is



(a) (b)

Figure 1. Alumina infiltrated sponge a) after drying in 100ºC oven, b) after firing at 1450ºC

small. Therefore the assumption that the residuals are normally distributed and have a mean ~0 is satified (Montgomery, 2001). Figure 3 shows the residual versus the predicted apparent porosity plot. This plot is used for checking the ANOVA assumption for the homoginety of variance. When the variance is homegeneous, the residual values are dispersed evenly around the zero line (Montgomery, 2001). Figure 3 has this characteristic implying that the homoginety of the variance assumption is met. 3D and contour plots of the predicted apparent porosity as a function of the Darvan C amount and the firing temperature are shown in Figures 4 and 5. From both graphs it is clear that the apparent porosity was quickly increased by using Darvan C in concentrations either higher or lower than 0.63 wt%. One possible reason for this is that 0.63 wt% may be the level of Darvan C which gives the highest amount of dispersion in the slurry. This, consequently, causes the alumina powder to be most closely packed in the sponges. As a result when the sponges were burned out, the porous alumina made with 0.63 wt% Darvan C had the lowest apparent porosity. In addition, one can see from Figures 4-5 that the apparent porosity of the porous alumina was slightly increased by firing the porous alumina at lower temperatures.

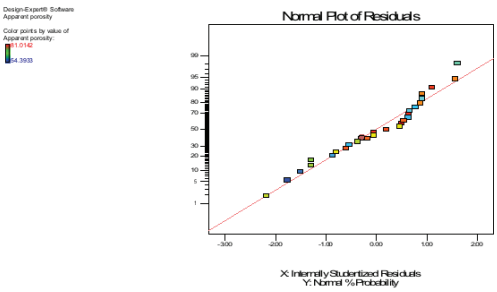


Figure 2. Normal probability plot of residuals for apparent porosity of porous alumina

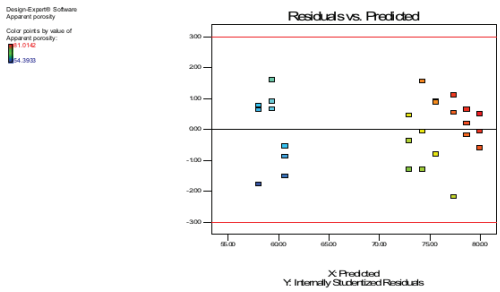


Figure 3. Plot of studentized residuals versus predicted apparent porosity

Table 3. ANOVA for apparent porosity data in part 1

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1881.12	3	627.04	124.81	< 0.0001	significant
A-Darvan	87.73	1	87.73	17.46	0.0004	
B-Temperature	31.07	1	31.07	6.19	0.0206	
A^2	1762.31	1	1762.31	350.79	< 0.0001	
Residual	115.55	23	5.02			
Lack of Fit	31.67	5	6.33	1.36	0.2854	not significant
Pure Error	83.88	18	4.66			
Cor Total	1996.67	26				

B) Bulk density

Table 4 shows the ANOVA results for the bulk density. The Darvan C amount (A) and the square of the Darvan C amount (A^2) have significant effects on the bulk density of the porous alumina. A regression equation for predicting bulk density is:

$$\text{Bulk density } (g/c^3) = 10.369 + 11.1754 \times \text{Darvan(wt\%)} - 0.0174 \times \text{Temp}(^oC) - 9.1475 \times \text{Darvan}^2 (wt\%^2) + 6.12E\text{-}06 \times \text{Temp}^2(^oC^2)$$

Athough not shown, there was no abnormallity in the normal probability and studentized residual versus the predicted bulk density plots. The ANOVA assumptions were satisfied. Consequently, the ANOVA results are acceptable. Figures 6 and 7 are 3D surface and contour plots of the predicted bulk density versus the Darvan C amount and the firing temperature. From both Figures it can concluded that in order to produce the lowest density porous alumina, the use of Darvan C in much higher or much lower concentrations than 0.63 wt% is required. Under these conditions, the firing temperature does not influence the bulk density of the porous alumina.

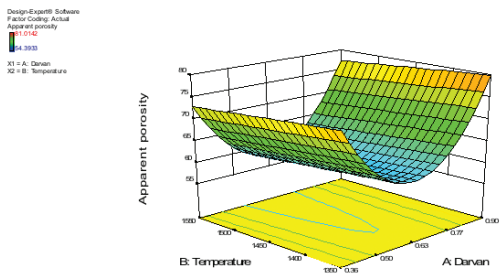


Figure 4. 3D surface plot of predicted apparent porosity as a function of the Darvan C amount and firing temperature

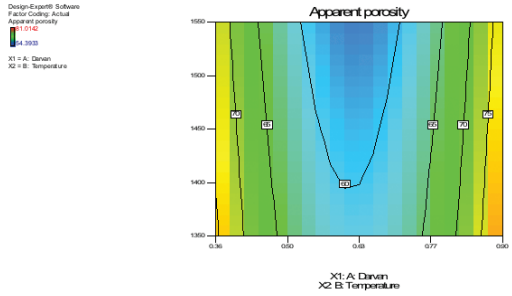


Figure 5. Contour plot of predicted apparent porosity as a function of the Darvan C amount and firing temperature

Table 4. ANOVA for bulk density data in part 1

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2.88	4	0.72	96.93	< 0.0001	significant
A-Darvan	0.16	1	0.16	21.69	0.0001	
B-Temperature	0.03	1	0.03	3.85	0.0625	
A^2	2.67	1	2.67	359.16	< 0.0001	
B^2	0.02	1	0.02	3.03	0.0958	
Residual	0.16	22	0.01			
Lack of Fit	0.04	4	0.01	1.52	0.2373	not significant
Pure Error	0.12	18	0.01			
Cor Total	3.04	26				

Part 2

a) Apparent porosity

Table 5 shows the ANOVA results for apparent porosity. The square of the glue amount (A^2) and the square of the firing temperature (B^2) have significant effects (>95% confidence) on the apparent porosity of the porous alumina. The equation developed for predicting apparent porosity is:

$$\text{Apparent porosity}(\%) = -109.843 - 16.4572\times \text{Glue(ml)} + 0.7012\times \text{Temp}(^{o}\text{C}) + 0.2053 \times \text{Glue}^2(\text{ml}^2) - 0.00025\times \text{Temp}^2(^{o}\text{C}^2)$$

The normal probability and residual versus the predicted apparent porosity were plotted, but are not presented. No abnormality was observed, hence the ANOVA results for the porosity data are acceptable. 3D and contour plots of the predicted apparent porosity as a function of the glue amount and the firing temperature are shown in Figures 8 and 9. From both graphs it is seen that the highest apparent porosity was obtained by using the glues at levels either higher or lower than 40 ml and the firing temperature at ~1450°C.

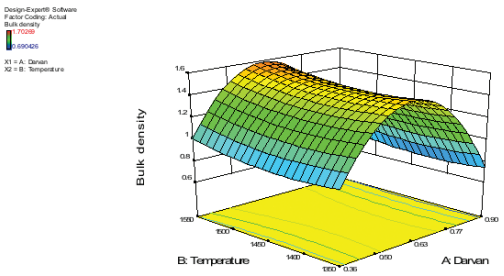


Figure 6. 3D surface plot of predicted bulk density as a function of the Darvan C amount and firing temperature

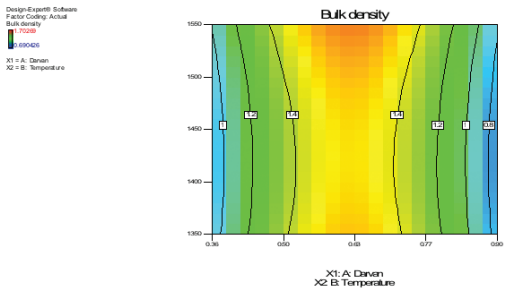


Figure 7. Contour plot of predicted bulk density as a function of the Darvan C amount and firing temperature

Table 5. ANOVA for apparent porosity data in part 2

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2587.27	4	646.82	103.24	< 0.0001	significant
A-Glue	2.11	1	2.11	0.34	0.5679	
B-Temperature	20.45	1	20.45	3.26	0.0845	
A^2	2528.57	1	2528.57	403.59	< 0.0001	
B^2	36.15	1	36.15	5.77	0.0252	
Residual	137.83	22	6.27			
Lack of Fit	18.66	4	4.67	0.70	0.5990	not significant
Pure Error	119.17	18	6.62			
Cor Total	2725.11	26				

b) Bulk density

Table 6 shows the ANOVA results for bulk density. The squares of the glue amount and the firing temperature (A^2 and B^2) have significant effects on the bulk density of the porous alumina. A regression equation for predicting bulk density is:

$$\text{Bulk density}(g/cm^3) = 12.8796 + 0.6255\times \text{Glue}(ml) - 0.0334\times \text{Temp}(^oC) - 0.0078\times \text{Glue}^2(ml^2) + 1.16E\text{-}05\times \text{Temp}^2(^oC^2)$$

There is no abnormallity in the normal probability and studentized residual versus the predicted bulk density plots. The ANOVA assumptions were satisfied. Consequently, the ANOVA results are acceptable. Figures 10 and 11 are 3D surface and contour plots of the predicted bulk density versus the glue amount and the firing temperature. From both Figures it can be concluded that the optimun conditions to produce the lowest density porous alumina occurred when using the glues at much higher or lower levels than 40 ml and the firing temperature at ~1450ºC.

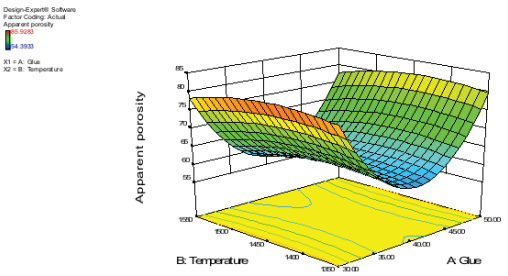


Figure 8. 3D surface plot of predicted apparent porosity as a function of the glue amount and firing temperature

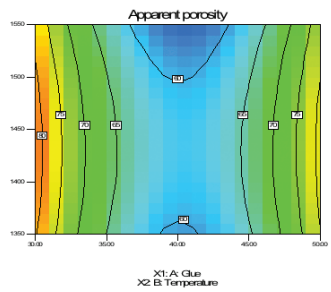


Figure 9. Contour plot of predicted apparent porosity as a function of the glue amount and firing temperature

Table 6. ANOVA for bulk density data in part 2

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	3.75	4	0.94	122.00	< 0.0001	significant
A-Glue	0.00	1	0.00	0.44	0.5141	
B-Temperature	0.01	1	0.01	1.89	0.1829	
A^2	3.65	1	3.65	475.16	< 0.0001	
B^2	0.08	1	0.08	10.50	0.0038	
Residual	0.17	22	0.01			
Lack of Fit	0.02	4	0.00	0.51	0.7319	not significant
Pure Error	0.15	18	0.01			
Cor Total	3.92	26				

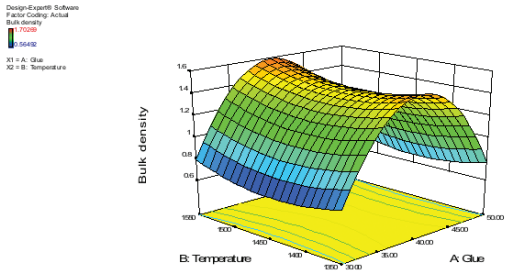


Figure 10. 3D surface plot of predicted bulk density as a function of the glue amount and firing temperature

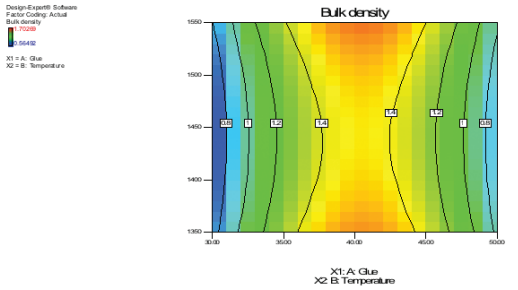


Figure 11. Contour plot of predicted bulk density as a function of the glue amount and firing temperature

Conclusions

From part 1 this research provides evidence that both the Darvan C amount and the square of the Darvan C amount have significant effects on the apparent porosity and bulk density of the porous alumina. The firing temperature has important effects on the apparent porosity only. Regression equations to predict the apparent porosity and bulk density of the porous alumina as a function of the Darvan C amount and the firing temperature are provided. An optimum condition to obtain the highest porosity is by using Darvan C in concentrations either much higher or lower than 0.63 wt% followed by firing the porous alumina at 1350ºC.

Part 2 of this work suggests that the square of the glue amount and the firing temperature have significant effects on the apparent porosity and bulk density of the porous alumina with (>95% confidence). Equations to predict the porous alumina's properties are presented. An optimum condition to produce the highest apparent porosity and lowest bulk density of the porous alumina involves the preparation of alumina slurry by mixing 900 g of alumina powder with 200 cc of deionized water and 7 g of Darvan C and adding glue at either much higher or lower levels than 40 ml and firing the porous samples at ~1450ºC.

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