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Preparation and Characterization of Peptizable Alumina

Chong Mok Lee and Youn Soo Sohn[†]

Inorganic Chemistry Lab, Korea Advanced Institute of Science & Technology, P.O. Box 150 Chongyangni, Seoul 131, Korea (Received June 4, 1985)

A procedure for the preparation of peptizable pseudoboehmite has been described in detail based upon a process of neutralization of an aqueous aluminum sulfate or chloride solution with aqueous ammonia. In order to obtain peptizable pseudoboehmite products, carefully controlled conditions were required in the whole processes of neutralization, aging, washing, and drying. The optimum conditions experimentally found are the following. The aluminum salt solution is neutralized with aqueous ammonia until the final pH of the solution reaches 10.0 to 10.8 or 9.0 to 9.3 for the sulfate or chloride, respectively. The alumina gel formed is subjected to aging at 80°C for about 3 hours and washed with water more than 5 times to reduce the residual sulfate or chloride ion in the final products to less than 4%. The pseudoboehmite gel thus obtained should be dried in oven at 80 to 100°C for a few to several hours depending on the selected temperatures.

Introduction

Alumina, $\text{Al}_2\text{O}_3 \cdot X\text{H}_2\text{O}$, is known to have many different forms depending on the water content such as aluminum trihydroxide ($X=3$), aluminum oxide hydroxide ($X=1$), transition alumina ($0 < X < 1$), aluminum oxide ($X=0$), and gel alumina.¹ Among the structurally different types of gel alumina, only pseudoboehmite has peptizable properties. Peptization refers to the returning of the alumina powder to a gel-like form using water or acid in aqueous solution during a mixing step. Such peptizable pseudoboehmite is suitable for active washcoat on honeycomb monolith, which turns into $\gamma\text{-Al}_2\text{O}_3$ form by calcining at 550°C for a few hours.

There are several reports on the formation of pseudoboehmite by different reactions such as base hydrolysis of aluminum cation,^{2,3} neutralization of aluminate with carbon dioxide,⁴ hydrolysis of amalgamated aluminum,⁵ and hydrolysis of aluminum alkoxide.⁶ Although pseudoboehmite is commercially available only as a byproduct called Catapal-SB from the process for the production of long chain aliphatic alcohols employing the hydrolysis reaction of aluminum alkoxides, details of the whole procedure for the isolation of pseudoboehmite as an end product have rarely been described yet.

Thus in this study a practical procedure for the preparation of peptizable pseudoboehmite will be described in detail based

upon a neutralization process of strong acid salts of aluminum with ammonia, and in particular, the important factors governing peptizability of the product will be quantitatively examined along with the optimum reaction conditions. Two aluminum salts, sulfate and chloride, were used to compare anion effect on the properties of peptization.

Experimental

Preparation of Pseudoboehmite. Neutralization reaction was performed in a 2l 3-neck round-bottom flask with a mechanical stirrer and a pH electrode. An aqueous solution of aluminum salt (900g) containing 7.0 wt % aluminum was made in the flask from reagent grade $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$ (Shinyo) or $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako). To this solution an aqueous ammonia solution (25% NH_3 , Merck) was slowly added with vigorous stirring in 40–50% excess of the equivalents necessary to neutralize the total aluminum. While neutralization was proceeding, the viscosity of the reaction mixture was increasing, but beyond the neutralization point, the viscosity was decreasing. This basic slurry of the neutralized alumina was stirred further for approximately 20 min. The final pH's of the neutralized sulfate and chloride solutions were 10.0–10.8 and 9.0–9.3, respectively. After the stirrer and pH electrode of the reaction flask were replaced with a condenser and a thermometer, the reaction

mixture was moved into a water bath for aging, and the aging temperature and time were varied from 40 to 90°C and 0 to 24 hours, respectively. The gel alumina product in the aged slurry mixture was separated from the mother liquor by vacuum filter or by centrifuge (IEC Model K), and then washed by repulping the filter-cake in distilled water amounting up to approximately 2-4 times of the cake volume. The amounts of residual sulfate or chloride ion in the final solid products were quantitatively measured depending on the number of washings. The finally washed and filtered cake was dried in an electric oven with forced air circulation in uniformly spread thin film. The drying temperature and period of time were also varied to see their effects on the peptizability of the product.

Characterization and Measurements. The dried alumina products were characterized by various chemical and physical methods. X-ray diffraction patterns were obtained from Norelco X-ray Diffractometer. In general, the XRD patterns of pseudoboehmite and boehmite exhibit almost the same peak positions but more broad peaks are observed with lower intensity in the former.⁷ From the peak position and broadening the average crystal size of the product could be calculated.⁸ Infrared spectra of the products in KBr wafer were recorded on an Analet FX Model 6160 FT-IR Spectrometer.

Finally, the peptizability of the products was measured and represented by "Peptization Index" as in the following.³ To an aqueous slurry of approximately 10 wt % solid product based on Al₂O₃ was added formic acid solution corresponding to 2.0 × 10⁻³ mole H⁺/g Al₂O₃, and then time was measured until the viscosity of the solution reached 5000 centipoises using Brookfield Viscometer.

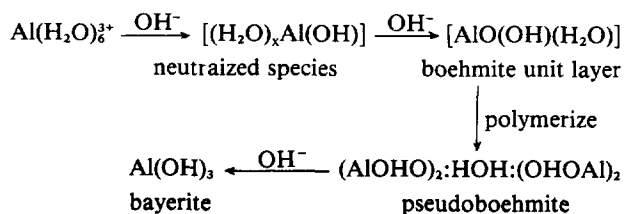
Results and Discussion

The procedure for the preparation of pseudoboehmite consists of four important consecutive steps of neutralization, aging, washing, and drying. In each step optimum conditions are required to obtain peptizable pseudoboehmite.

Since the neutralized solution containing ammonium sulfate or chloride and a large excess of ammonia in addition to the colloidal alumina precipitate is a buffer mixture the final pH of the solution is maintained throughout the aging period. Therefore, the degree of neutralization of the aluminum sulfate or chloride solution seems to affect the formation of pseudoboehmite from the colloidal alumina during the aging period. For instance, no pseudoboehmite could be obtained from a neutralized solution with pH less than 9, and on the hand at pH > 11, a gel mixture of gibbsite and bayerite was resulted.

The mechanism of the formation of pseudoboehmite has not been fully understood yet, although extensive studies⁹⁻¹³ were made on the base hydrolysis of aluminum ion. However, it is now understood that the amorphous gel alumina initially formed by adding a base to the aqueous solution of Al ions is not a hydroxide but a cluster form holding OH⁻ ions and H₂O molecules around Al ions. This gel alumina is transformed to crystalline hydroxide by replacement of H₂O by OH⁻ ions during the aging process. The final product of the aging process is crystalline Al(OH)₃, if the OH⁻ concentration is

sufficiently high, but usually the first X-ray crystalline form occurring in the aging sequence is a seed layer of boehmite composing of an aluminum oxide hydroxide (AlOOH). It was assumed that pseudoboehmite is formed from this crystal unit of boehmite and water molecules, which are situated between the structural layers.¹⁰ This explains why the XRD pattern of pseudoboehmite is closely resembled to that of boehmite. The above reactions occurring in the neutralization and aging sequence may be represented as follows:



As expected from the above reaction scheme careful reaction controls are necessary to obtain pseudoboehmite in pure form. The optimum reaction conditions experimentally found in this study will be given step by step.

Aging. As was mentioned in the above the optimum pH range of the neutralized solution seems to be in the range between 9 and 11. Therefore, with the pH maintained at this range the aging temperature was varied from 40° to 90°C and aging time from 0 to 24 hours. A preliminary study on the variation of the aging temperature revealed that at above 90°C ammonia gas was bubbling out disturbing the quiescent aging condition whereas at temperatures lower than 80°C the rate of formation of pseudoboehmite was noticeably low. Consequently, the best aging temperature turned out to be around 80°C. In Table 1 are listed the results of variation of the aging time for the neutralized solution of aluminum sulfate at the optimum aging temperature and at pH = 10.0. The results in the table indicate that all the products aged for more than two hours are peptizable in minutes. In fact, all these peptizable alumina products have shown almost exactly the same XRD pattern.⁷ From the major peak at 2θ = 13.2° corresponding to 020 reflection plane of boehmite the average crystal size of the products, for instance, batch No. 1 to 4, could be estimated to be approximately 28 Å and that of the commercial Catapal-SB to be 32 Å.⁸ In the experiment of batch No. 7, parts of the neutraliz-

TABLE 1: Effect of Aging Time on the Properties of the Product from a Neutralized Al Sulfate Solution

Batch No.	Aging Conditions			PI ^a /min	residual SO ₄ (%)
	Temp/°C	pH	Time/hr.		
1	r.t.	10.1	0	(-)	
2	80 ± 1	10.2	1	(-)	
3	80 ± 1	10.0	3	<2	
4	79 ± 1	10.0	5	<2	
5	77 ± 1	10.2	12	<2	
6	78 ± 2	10.2	24	<2	
7-1	r.t.	10.1	0	(-)	12.7
7-2	75 ± 2	10.1	0.5	(-)	4.7
7-3	75 ± 2	10.1	2.0	<2	3.0

^a Peptization Index. (-) indicates no or substantially no viscosity increase in 60 minutes.

ed slurry were sampled during aging process successively after the aging period indicated in the table, filtered, washed with the same amount of water corresponding to 400ml/g Al_2O_3 and finally dried in oven at 90°C. The results of the residual SO_4 analysis given in the table indicate that the SO_4 ions are strongly adsorbed on and not easily washed out from the solid product which is not aged long enough. The infrared spectra of the samples with different aging time from the same batch No. 7 are compared in Figure 1 with that of Catapal-SB. The initial precipitate does not clearly show the characteristic bands of pseudoboehmite¹⁴ appearing at 3096 cm^{-1} , 1160 cm^{-1} and 1073 cm^{-1} , corresponding to a OH stretching mode, $\nu\text{OH}(\text{A}_1)$, and two OH bending modes, $\delta\text{OH}(\text{B}_2)$ and $\delta\text{OH}(\text{A}_1)$, respectively. All these bands are hidden by strong absorptions due to the residual SO_4 and H_2O in the sample. However, the product aged for 2 hours exhibits clearly these characteristic bands proximate to those of Catapal-SB. The broadening of the two δOH modes is probably ascribed to the residual SO_4 in the sample. The other three strong bands at 743, 626 and 483 cm^{-1} assignable to O^{2-} lattice vibration are also observed clearly only in this aged sample.

When aluminum chloride, instead of sulfate, was neutralized with ammonia, almost the same results were obtained as far

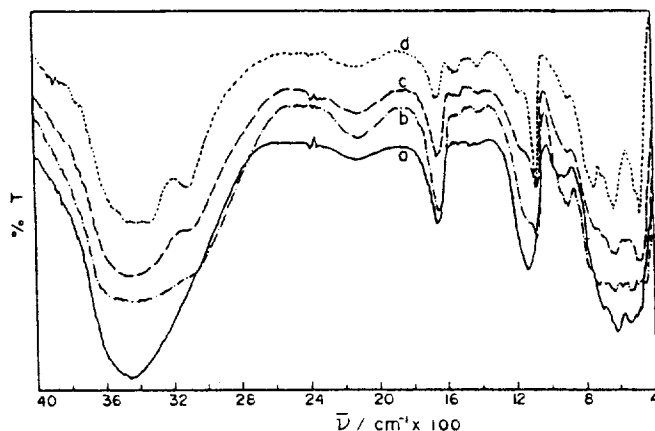


Figure 1. Infrared spectra of alumina products from neutralized Al-sulfate depending on aging time. a, initial ppt; b, aged for 30min.; c, aged for 2 hours; d, Catapal-SB.

TABLE 2: Effect of Washing Condition on the Peptizability of the Product from a Neutralized Al Sulfate Solution

No. of washings	Dilution ratio ^a	Accumulated dilution ratio ^b	Residual SO_4 (%)	PI ^c /min.
1	0.034	3.4×10^{-2}	16.4	(-)
2	0.406	1.38×10^{-2}	10.3	(-)
3	0.483	6.67×10^{-3}	6.5	(-)
4	0.533	3.55×10^{-3}	5.0	(-)
5	0.405	1.44×10^{-3}	3.7	1.0
6	0.352	5.07×10^{-4}	3.1	1.5
7	0.321	1.63×10^{-4}	2.7	1.3
8	0.257	4.17×10^{-5}	2.6	1.2
9	0.037	1.54×10^{-6}	2.6	1.8
9 ^d	0.056	2.34×10^{-6}	1.1	3.0

^a Dilution ratio(w/w) in each washing step represented by (filter cake)/(washing solvent + f.c.). ^b Product of dilution ratios. ^c Peptization index. ^d Washed with 0.13 % aqueous ammonia after washing 8 times with distilled water.

as aging conditions are concerned. The infrared spectrum of the product obtained from the above neutralized aluminum chloride after aging for more than two hours was nearly identical to that of the authentic Catapal-SB.

Washing. Although pure pseudoboehmite is formed under controlled conditions in the aging process, peptizable pseudoboehmite can not be obtained unless the product is not thoroughly washed. Since neutralization reaction yields 3 moles of $(\text{NH}_4)_2\text{SO}_4$ or 6 moles of NH_4Cl for each mole of Al_2O_3 and particularly the acid anions are strongly adsorbed on the surface of the alumina product, it is difficult to wash out these chemical impurities from the gel alumina formed. In Table 2 are given the results of successive washings of the product obtained from a neutralized aluminum sulfate solution after aging for 3 hours. It is seen from the Table that in order to reduce the residual sulfate in the final product to less than 4 %, the aged precipitate should be washed at least 5 times successively and more than 1000 grams of water are required for each gram of the product filter cake. Furthermore, the data in the table show that the efficiency of washings with water to remove the residual sulfate further down below 4 % is extremely low, and washing more than 5 times with water is meaningless. Fortunately, the concentration limit of the residual sulfate allowed for peptizability of the final product seems to be around 4 % as shown in the table. If more than 5 % of sulfate remains in the product of pseudoboehmite, the peptization process seems to be critically interfered by sulfate ions for the reason being unexplained yet. It should also be pointed out in the table that in the low range of residual sulfate less than 4 % aqueous ammonia solution is more efficient washing solution than water. Thus, in order to compare the washing efficiencies of 0.25 % aqueous ammonia and water, the pseudoboehmite gel formed by neutralization of aluminum sulfate solution was washed 4 times in a consecutive way using the two solutions, and the results of the residual sulfate analysis were listed in Table 3. At the beginning steps washing efficiencies of the two solutions are not distinguished, but aqueous ammonia solution becomes more efficient when the sulfate concentration in the pseudoboehmite gel is low. The isoelectric point of alumina gel is known to be at a pH round 9.4,¹⁵ where the surface of the gel particles is positively charged and as such strongly adsorbs anions which are not easily removed by washing. Actually, the pH of the pseudoboehmite slurry was measured to be approximately 9 after 2nd washing with water whereas the pH of 0.25 % aqueous ammonia is higher than 10.

The same washing experiments have been performed for the pseudoboehmite gel prepared by neutralization of aqueous aluminum chloride solution with aqueous ammonia and their

TABLE 3: Comparative Washing Efficiency of Distilled Water and 0.25 % Aqueous Ammonia

No. of washings	Distilled water				Aqueous ammonia			
	1	2	3	4	1	2	3	4 ^a
Residual SO_4 (%)	30.2	12.8	6.67	4.75	33.4	13.1	5.06	2.34
SO_4 washed out in each step (%)	-	58.4	47.9	28.8	-	60.8	61.4	53.8

^a Washed with distilled water.

TABLE 4: Effect of Washing Condition on the Peptizability of the Product from a Neutralized Al Chloride Solution

No. of washings	Accumulated dilution ratio ^a	Residual Cl (%)	PI ^b /min
1	4.80×10^{-2}	10.9	0.1
2	3.89×10^{-2}	6.6	0.3
3	2.78×10^{-2}	4.2	0.5
4	1.66×10^{-2}	2.8	1.8
5	8.39×10^{-3}	1.3	4.5
6	7.80×10^{-4}	0.5	9.8

^a Product of dilution ratios (w/w) in each step represented by (filter cake)/(washing solvent + f.c.) ^b Peptization index.

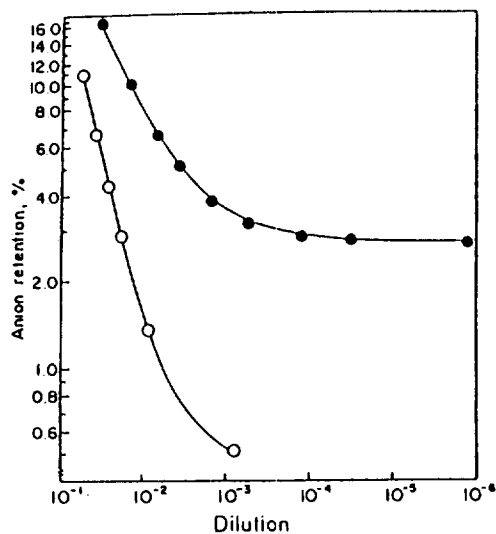


Figure 2. Decrease of the residual anion contents by stepwise washing. ○, chloride; ●, sulfate.

results are summarized in Table 4. The residual chloride content in the dried pseudoboehmite obtained after washing with water 5 times is only 1.3 % much lower than the residual sulfate (3.7 %) in the corresponding sample. It is also seen in the table that the chloride ions are generally more easily washed out than the sulfate ions. In order to compare washing efficiencies on the residual anions in the final product, the contents of anions retained in the products were plotted versus the accumulated dilution ratios in Figure 2 using the data given in Table 2 and 4. The residual chloride content in the product is decreasing almost linearly with the overall dilution ratio whereas the decrease of the residual sulfate content largely deviates from linearity as the dilution ratio increases. Such a result indicates that sulfate ions are much strongly adsorbed on the surface of the pseudoboehmite gel. It is generally known that sulfate ions are strongly adsorbed on alumina surface and it was proposed that the sulfate ion bridges across Al atom resulting in a 6-membered ring.¹⁶ However, the most surprising is that not only the pseudoboehmite sample containing more than 10 % of chloride maintains peptizable properties but also the peptization index is decreasing as the residual chloride content is increasing in the pseudoboehmite samples. Such results imply that contrary to sulfate ions chloride ions may contribute to the peptization process. Since chloride ions are not strongly adsorbed on the pseudoboehmite gel surface, chloride ions released into solution during the peptization process seem to act as strong

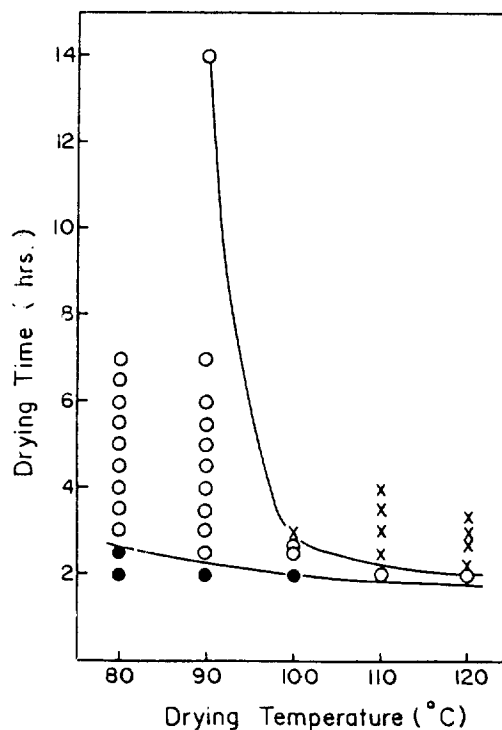


Figure 3. Peptizability depending on drying conditions for the alumina products from neutralized Al-sulfate. x, overdried and not peptizable; ○, peptizable; ●, too wet to test the peptizability.

acid which affect the peptization process.

Drying. Since pseudoboehmite is not thermodynamically a stable form, also controlled conditions are required in the drying process. The samples of pseudoboehmite gel prepared by neutralization of aluminum sulfate with aqueous ammonia followed by processes of 3 hours aging and thorough washings were dried in uniformly spread film in oven under varied drying conditions. The drying temperature was varied from 80 to 120°C and period of drying time up to 14 hours, and the results were plotted with peptizability in Figure 3. At 80 and 90°C, the minimum period of drying time required to yield peptizable pseudoboehmite turned out to be approximately 2.5 to 3 hours. Extension of the drying period up to 14 hours at these temperatures did not jeopardize their peptizability. However, at the temperatures above 100°C the period of drying time allowed for peptizable product is very narrow. For instance, the sample dried at 100°C for 2.5 hours was peptizable, but if the drying period was extended to 3 hours, peptizability of the sample was lost. At higher temperatures the allowed period of drying time becomes shorter and more careful control is needed. In conclusion, appropriate drying conditions for peptizable pseudoboehmite may be found in the zone between the two curves where the open circles are located in the figure.

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The Crystal and Molecular Structure of Cholesteryl Formate

Boo Kyung Kang, Myung Ja Chung and Young Ja Park†

Department of Chemistry, Sook Myung Women's University, Seoul 140, Korea (Received July 8, 1985)

Cholesteryl formate ($\text{HCOOC}_{27}\text{H}_{45}$) is monoclinic, space group $P2_1$, with $a = 15.757$ (1), $b = 6.073$ (1), $c = 13.592$ (2) Å, $\beta = 94.1$ (1)°, $Z = 2$. Intensities were measured, using an automatic diffractometer with graphite-monochromated $\text{Cu-K}\alpha$ radiation. The structure was solved by a direct method and refined by least-squares method. The final R factor was 0.087 for 1640 observed reflections. There are no unusual bond distances and angles. The molecules are arranged in antiparallel array forming monolayers of thickness $d_{100} = 15.757$ Å. Adjacent cholesteryl ring groups are related by the translation operation along the b axis.

Introduction

Cholesterol¹⁻³ is the most abundant steroid in the animal kingdom. In addition to being a primary metabolic precursor for many of the steroid hormones, it and some of its esters play an important role in the structural stabilization of membranes.⁴ The phase interactions of the cholesterol-phospholipid systems that comprise many membranes tend to be very complicated, and thus an important first step towards deriving detailed structural membrane models is a study of the stereochemistry and packing of cholesterol and its derivatives.

Though the crystal structures of cholesteryl chloroformate⁵ and many other cholesteryl esters⁶⁻¹⁶ were solved, the structure of cholesteryl formate has not yet been reported. From consideration of the crystal data of the cholesteryl formate it seems

interesting to study its crystal structure, because the different modes of cholesteryl-cholesteryl packing tend to be present in this compound.

Experimental

Cholesteryl formate from Tokyo Kasei Kogyo Co., Ltd. was crystallized by slow evaporation of an acetone solution. The resulting monoclinic lath-shaped crystals melted at 100.9°.

Preliminary crystal data obtained from X-ray Weissenberg photographs were agreement with those of Barnard and Lydon.¹⁷ Subsequent X-ray data collection was carried out at room temperature using a Rigaku AFC diffractometer with $\text{Cu-K}\alpha$ graphite-monochromated radiation. The crystal lattice parameters (Table 1) were obtained by a least-squares fit of 13 reflections with $15^\circ \leq \theta \leq 26^\circ \text{C}$. X-ray intensities with $2\theta \leq 120^\circ$ were collected by $\omega/2\theta$ scan, and 1640 reflections with $F_o > 3 \sigma(F_o)$ were used in structure determination. No absorption corrections were applied. The crystal density measured by the flotation method in a mixture of methanol and KI aqueous solution was 1.04 g cm^{-3} .

Determination and Refinement of the Structure

The structure amplitudes were converted to normalized structure factors and the structure was solved using MULTAN¹⁸ with 238 E values ($E \geq 1.40$).

Initial attempts to determine the structure from the E map computed with the set of the best figure of merit failed. Although the seventeen peaks selected from the E map were consistent with a chemically reasonable cholesterol fragment and the successive routine structure analyses gave a plausible

TABLE 1: Crystal Data

Cholesteryl formate	: $\text{HCOOC}_{27}\text{H}_{45}$
Mw	: 414.35
m.p.	: 100.9°C
Unit Cell Parameter	: a = 15.757(1) Å
	b = 6.073 (1) Å
	c = 13.592 (2) Å
	$\beta = 94.1$ (1)°
	V = 1297.3 (2) Å ³
	Z = 2

$\mu(\text{Cu-K}\alpha)$: 4.22 cm^{-1}

Crystal System : monoclinic

Space Group : $P2_1$

Density : $D_c = 1.061 \text{ g/cm}^3$

$D_m = 1.04 \text{ g/cm}^3$

$F(000)$: 460.00