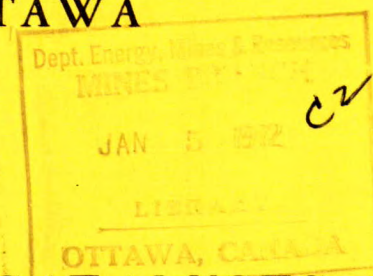


ser. 6 22(21)  
C 212 NN



DEPARTMENT OF  
ENERGY, MINES AND RESOURCES  
MINES BRANCH

OTTAWA



*LOW-DENSITY CATALYSTS AND  
CATALYST SUPPORTS  
PART I: THE PREPARATION OF  
HIGHLY POROUS ALUMINA*

G. T. SHAW AND B. I. PARSONS

FUELS RESEARCH CENTRE

DECEMBER 1968

© Crown Copyrights reserved

Available by mail from the Queen's Printer, Ottawa,  
and at the following Canadian Government bookshops:

HALIFAX

*1735 Barrington Street*

MONTREAL

*Æterna-Vie Building, 1182 St. Catherine St. West*

OTTAWA

*Daly Building, Corner Mackenzie and Rideau*

TORONTO

*221 Yonge Street*

WINNIPEG

*Mall Center Bldg., 499 Portage Avenue*

VANCOUVER

*657 Granville Street*

or through your bookseller

Price 75 cents      Catalogue No. M38-1/199

*Price subject to change without notice*

Queen's Printer and Controller of Stationery  
Ottawa, Canada

1969

## Mines Branch Research Report R 199

## LOW-DENSITY CATALYSTS AND CATALYST SUPPORTS.

## PART I: THE PREPARATION OF HIGHLY POROUS ALUMINA

by

G.T. Shaw\* and B.I. Parsons\*

---

ABSTRACT

A technique is described whereby highly porous, low-density alumina can be prepared by dehydrating hydrous aluminum hydroxide gel in thin layers or small-diameter extrusions at low temperatures until at least 25-30% of the water present has been removed, followed by conventional high-temperature drying and calcination. The procedure works well with any aluminum hydroxide gel which has been precipitated with a carbonate. The maximum allowable bulk gel temperature in the low-temperature drying step is 100°C. The preferred temperature is 75°C or less. Limited control of the pore size and pore volume (in the range 1000-20 Å radius and 0.5 to 2.2 ml/g) can be achieved by regulating the conditions affecting the bulk gel temperature in the low-temperature drying step, e.g., oven temperature, circulation of the air, thickness of gel layer, etc. The type of drying atmosphere and the age of the hydrous gel are not critical factors. The results of both laboratory-scale and pilot-plant-scale experiments are described.

---

\* Research Scientists, Fuels Research Centre, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Direction des mines

Rapport de recherches R 199

CATALYSEURS DE FAIBLE DENSITÉ ET SUPPORTS DE CATALYSEUR.  
PARTIE I: LA PRÉPARATION DE L'ALUMINE À FORTE POROSITÉ

par

G.T. Shaw\* et B.I. Parsons\*

----

RÉSUMÉ

Les auteurs décrivent une technique de préparation d'alumine à forte porosité et à faible densité par la déshydratation à basse température d'un gel d'hydroxyde d'aluminium hydraté en couches minces ou en profilés de petit diamètre, jusqu'à ce qu'au moins 25 à 30 p. 100 de l'eau présente ait été enlevée; cette déshydratation est suivie du séchage et de la calcination classiques à haute température. Cette technique donne d'excellents résultats avec n'importe quel gel d'hydroxyde d'aluminium qui a été précipité à l'aide d'un carbonate. La température maximale permise pour l'ensemble du gel au cours de l'étape du séchage à basse température est de 100°C. La température préférée est de 75°C ou moins. Il est possible de régulariser dans une certaine mesure les dimensions et le volume des pores (dans la gamme de 1000 à 20 Å de rayon et de 0.5 à 2.2 ml/g) en contrôlant les conditions qui affectent la température de l'ensemble du gel pendant l'étape du séchage à basse température, par exemple, la température du four, la circulation de l'air, l'épaisseur de la couche de gel, etc. Le type d'atmosphère de séchage et l'âge du gel hydraté ne sont pas des facteurs critiques. Les auteurs décrivent les résultats des expériences effectuées en laboratoire et en usine pilote.

---

\* Chercheurs scientifiques, Centre de recherches sur les combustibles,  
Direction des mines, ministère de l'Énergie, des Mines et des Ressources,  
Ottawa, Canada.

## CONTENTS

	<u>Page</u>
Abstract .....	i
Résumé .....	ii
Introduction .....	1
Surface Accessibility .....	2
Preparation of Low-Density Pellets .....	3
Impregnation and Preparation of Catalysts .....	3
Alumina for Liquid-Phase Fluidized Bed Applications .....	4
Apparatus and Procedures .....	4
Description of the Gel .....	5
Drying Procedure and Apparatus .....	5
The Measurement of the Pore Volume Distribution .....	7
The Measurement of the Apparent Bulk Density .....	7
Experimental Results and Discussion .....	8
The Extent of Dehydration Required at Low Temperatures .....	9
The Upper Temperature Limit .....	11
The Effect of the Drying Atmosphere .....	13
The Effect of Ageing the Gel .....	13
The Effect of Low-Temperature Drying on the Pore Volume Distribution .....	15
The Results of Experiments on a Pilot-Plant Scale .....	17
Summary .....	19
References .....	20

## FIGURES

<u>No.</u>		<u>Page</u>
1.	A photograph of the conveyor belt and tunnel used for continuous drying on a pilot-plant scale .....	6
2.	The effect of the thickness of the gel layer used in the drying process on the cumulative pore volume distribution .....	16
3.	The cumulative pore volume distribution in aluminas produced on a pilot-plant scale .....	18

## TABLES

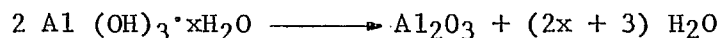
1.	Summary of Experiments Undertaken to Determine the Extent of Dehydration Required at Low Temperatures to Produce the Low-Density Form of Alumina .....	9
2.	Summary of Experiments in Which Partially Hydrated Alumina Powder was Added to the Hydrous Gel Prior to High-Temperature Drying .....	11
3.	Summary of Experiments Undertaken to Determine the Upper Temperature Limit of the Low-Temperature Drying Step .....	12
4.	Summary of Experiments Undertaken to Determine the Effect of the Atmosphere Used for Drying .....	13
5.	Summary of Experiments Undertaken to Determine the Effect of Ageing the Gel .....	14
6.	Summary of the Effect of Low-Temperature Drying on the Apparent Bulk Density and Pore Characteristics of Alumina .....	15
7.	Summary of the Physical Characteristics of the Aluminas Produced on a Pilot-Plant Scale .....	19

=====

## INTRODUCTION

The following report is the first in a series on the preparation and characterization of low-density catalysts and catalyst supports and their application to typical processes connected with the refining of low-grade oils and tars. The development of highly porous forms of catalysts has been the subject of considerable investigation at the Mines Branch. Most of the work to date has been on the characterization of porous catalysts (1,2,3) and the investigation of bench-scale techniques for controlling the pore volume distribution in support materials such as alumina and silica gels (4). In recent years, however, many interesting aspects of the potential use of such catalysts have become apparent during engineering studies on the hydrogenation of heavy crudes and gas oils. This has encouraged the development of techniques for preparing highly porous (low-density) catalyst supports on a pilot-plant scale. In the present report the results of an investigation of drying techniques for forming highly porous aluminas are described. It will be shown how, by combining chemical procedures and mechanical skills, aluminas containing 1 to 2.5 ml/g in pores 50 to 1000 Å radius can be formed with relative ease and at low cost.

Alumina containing a large surface area concentrated mainly in small pores, 200 Å diameter or less, is normally prepared by rapidly drying and calcining basic aluminum hydroxide gel at high temperatures. The hydroxide gel is usually prepared by adding an excess of an alkali, such as ammonium hydroxide, to an aqueous solution of a suitable salt of aluminum, such as aluminum nitrate. The water content of a typical aluminum hydroxide gel is in the range 85-95% by weight and the pH is about 9 to 11. The hydrous aluminum hydroxide is gradually converted to alumina in the course of dehydration. The conversion is not a sharply defined chemical transformation. The chemical composition of the gel gradually approaches that of alumina as more and more water is removed. The end point of the reaction is represented by the equation:



At intermediate stages, considerable chemically bonded water is associated with the alumina. The amount of water retained by the alumina depends primarily on the temperature, and also (to a much lesser extent) on the humidity of the air in the drying apparatus. A typical alumina product from the dehydration of aluminum hydroxide gel contains 10-15% water at 325°C and 2 to 5% at 500°C. The exact amount depends on the specific method used in the preparation of the gel and the technique used to dry it.

The porous nature of the alumina is created in the dehydration process. As drying proceeds, and water is removed, the mass of the gel shrinks in volume. Eventually, the inorganic skeleton of the structure sets (at some intermediate stage in the dehydration) and the space remaining when the last of the water is removed comprises the porous nature of the material. (Care must be taken not to expose porous alumina to high-temperature steam for any extended period of time. Steam promotes the sintering of small particles and surface imperfections and generally results in a drastic reduction in surface area.) The high-surface-area alumina so formed is frequently called "alumina gel" in industrial practice. It should be noted that the material is not truly a gel; it is a finely dispersed form of aluminum oxide produced from a hydrous gel of aluminum hydroxide.

There are a number of reasons, both theoretical and practical, why it is desirable to prepare alumina, intended for catalytic or adsorption applications, in a highly porous form. A few of these reasons are discussed briefly below to indicate a little of the background of the investigation.

#### Surface Accessibility

The rates at which many industrial separation or conversion processes using alumina proceed depend largely on the amount of surface available to the reagents. An ideal form of alumina would be one containing a large number of wide-diameter pores to provide easy access to the interior surfaces of the granule. All things being equal, the greater the surface area available to the reagents the greater the rate of adsorption or conversion; and the larger the pores, and the more accessible the surface, the less likelihood there is



of hold-up of gas or liquid within the alumina structure. The rate of undesirable side reactions is generally at a minimum under conditions of low hold-up.

#### Preparation of Low-Density Pellets

A large proportion of the alumina and alumina-supported catalysts manufactured commercially is prepared in the form of 1/8-inch to 1/4-inch diameter pellets for use in fixed-bed reaction systems. On an industrial scale it is desirable that the charge of catalyst in a reactor should weigh as little as possible commensurate with mechanical strength and attrition resistance. Highly porous alumina powders pellet easily (4), forming low-density pellets of moderate strength at low compacting pressures. Pellets of density 0.7 to 0.9 g/ml can be prepared using the highly porous aluminas, as compared with the conventional alumina pellets of density 1.2 to 1.5 g/ml.

#### Impregnation and the Preparation of Catalysts

Alumina is used widely as a support material in the preparation of many industrial adsorbents and catalysts. The procedure used in the preparation of such "supported" forms is generally one in which alumina is soaked in a solution of the appropriate metal salt(s), and then dried and treated (oxidized, reduced, sulphided, etc.) to produce the active species. The soaking process is frequently referred to, in the patent literature, as "solution-impregnation". The larger the pore volume present in the alumina the greater the volume of the impregnating solution it will take up. Under some circumstances this is desirable and eliminates the need for repetitive impregnation. Under other circumstances a large pore volume can be used as a means of concentrating the active salts at, or near, the surface of the granule . . . . by drying an alumina which has been saturated with a dilute solution of the active ingredients slowly, the solution and its salts can be drawn to the surface layer. Conversely, by using concentrated solutions, and rapid drying, the active ingredients can be dispersed uniformly throughout the structure of the alumina. With almost every impregnation procedure, more control and flexibility are possible with aluminas containing a large pore volume.

### Alumina for Liquid-Phase Fluidized Bed Applications

Considerable interest has developed recently in the liquid-phase hydrogenation of low-grade petroleum crudes and residual fuels. Two types of liquid-phase reaction systems are presently in industrial use on this problem. In Germany, a conventional liquid-phase reactor is in operation (5) using "small-particle" catalyst (iron dispersed on finely divided carbon black). On trial in the United States (6) is an ebullated bed reactor using 1/32-inch to 1/16-inch diameter extrusions of alumina-supported cobalt molybdate catalyst. In both arrangements the catalyst is expanded (suspended and circulated) by the upward flow of liquid. Catalysts of low density are more easily fluidized and require substantially lower liquid velocities and recirculation rates for successful operation. Particle strength and attrition resistance are not so critical in liquid-phase systems as in gas-phase fluidized beds. Development work on "small-particle" fluidized bed systems is in progress at the Fuels Research Centre (7).

#### APPARATUS AND PROCEDURES

There are many variables involved in the preparation of alumina from the hydroxide gel, and considerable care must be exercised in the selection and maintenance of uniform procedures and standard conditions. The character of the hydroxide gel itself is greatly affected by changes in the chemical procedure used to prepare it, i.e. the type and concentration of reagents used, pH, etc. The dehydration step is grossly affected by changes in the temperature and humidity of the drying atmosphere and by the amount of surface exposed. In the preliminary stages of the investigation, various combinations of equipment, gel and drying conditions were examined in a series of exploratory experiments. Prime consideration was given to simplicity and ease of operation. The procedure described below was settled upon as being a comparatively uncomplicated means of preparing low-density alumina (which was the ultimate purpose of the study), and also a means whereby, with only minor changes, the pore volume can be controlled in the range 0.5 to 2.5 ml/g.

### Description of the Gel

Dehydration experiments were made with hydrous aluminum hydroxide gel that had been prepared by precipitation from solutions of aluminum nitrate using ammonium hydroxide, sodium hydroxide and ammonium carbonate. It was found that the gels most sensitive to changes in the dehydration procedure (and hence most amenable to control) were those formed with ammonium carbonate or with ammonium carbonate combined with a small amount of ammonium hydroxide. The procedure used in most of the bench-scale development work was as follows:

Hydrous aluminum hydroxide gel was formed by adding a solution containing 750 g  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  dissolved in two liters of distilled water to a solution of 288 g  $(\text{NH}_4)_2 \text{CO}_3$  and 120 ml concentrated ammonium hydroxide (28% by weight  $\text{NH}_3$  in water) dissolved in four liters of distilled water. The aluminum nitrate solution was added to the base solution slowly, at room temperature, over a period of 5 to 10 minutes. The resultant mixture was slightly alkaline,  $\text{pH} = 7.5$ . The precipitate was allowed to settle overnight. As much as possible of the supernatant liquid was then decanted off and the remaining liquid removed in a stainless-steel pressure filter. The concentration of soluble salts in the gel was reduced by washing it twice with small quantities of distilled water (made slightly alkaline by adding 1 to 2 drops of concentrated ammonium hydroxide). The water content of the washed, filtered gel was 92% by weight.

Experiments on a pilot-plant scale were made with a commercially available aluminum hydroxide gel manufactured by the Reheis Company of Berkeley Heights, New Jersey. Essentially identical results were obtained with this Reheis "Type F" compressed gel as were obtained with the gel prepared using the procedure described above. The initial water content of the "Type F" gel was 90%.

### Drying Procedure and Apparatus

In the bench-scale investigation of the drying process, small portions of hydrous gel (precipitated with carbonate) were formed into thin layers or small-diameter extrusions on aluminum sheet and dried for varying periods of time at selected temperatures in an air oven or in a vacuum drying oven. The

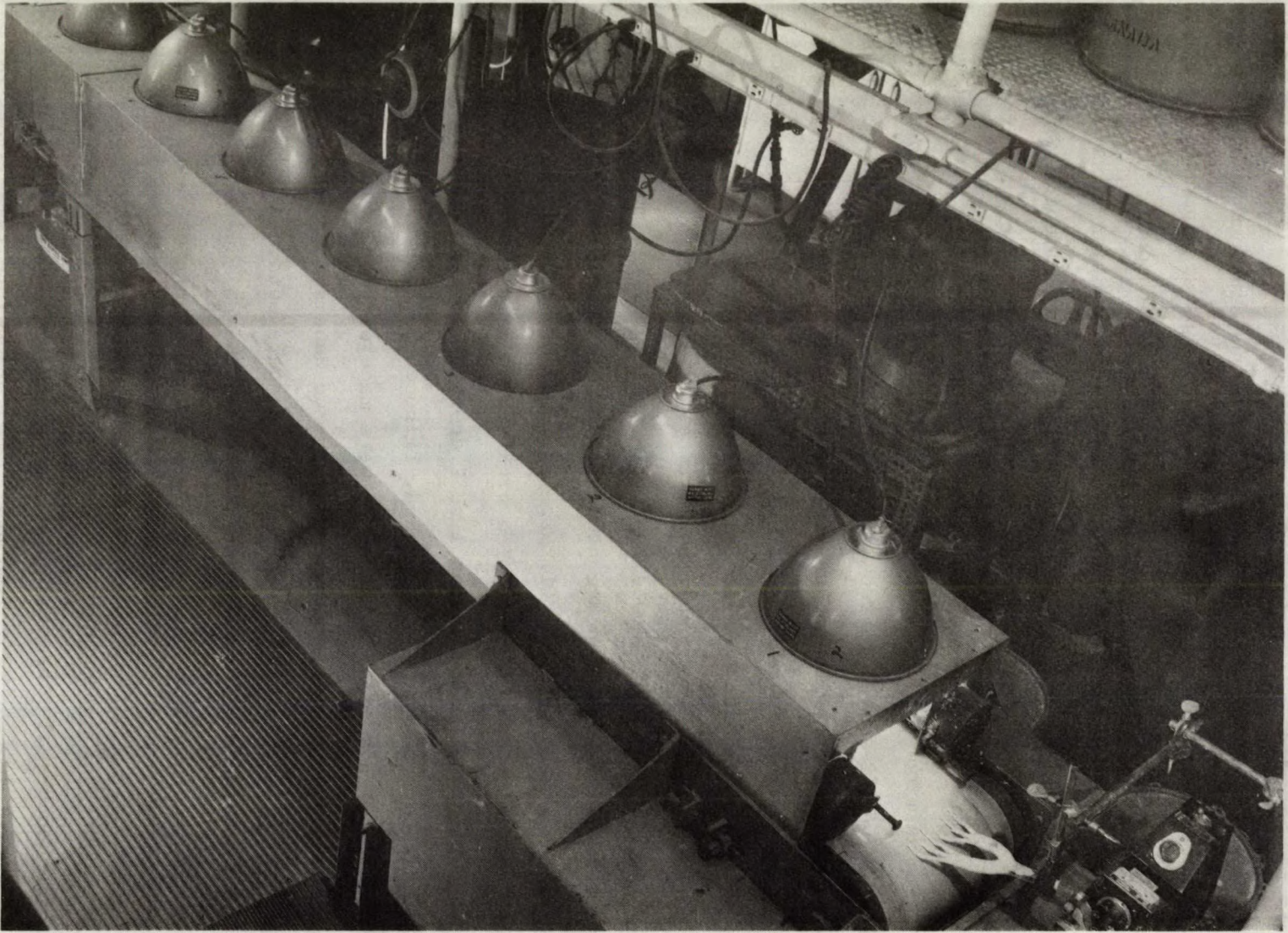


Figure 1 - A photograph of the conveyor belt and tunnel used for continuous drying on a pilot-plant scale.

layers of the gel were prepared using a flat spatula, and the extrusions were made with a hand-operated piston and barrel arrangement similar to a caulking gun. For the experiments at very low temperatures, the layers or extrusions were allowed to dry in the open air at room temperature. After drying, the samples were crushed lightly to pass a 10-mesh screen (U.S. Standard Sieve Size) and calcined overnight at 400-425°C.

Experiments on a pilot-plant scale were run, using a neoprene conveyor belt and drying tunnel. A photograph of this apparatus is shown in Figure 1. Extrusions of the hydrous gel were formed on to the conveyor belt and carried into the drying tunnel where they were exposed to infra-red heat from overhead lamps and to warm forced air from ducts along the side. The gel was shaped into extrusions approximately 1/8-inch diameter by forcing it through Tygon tubing (1/8-inch nominal diameter) with rollers working in a peristaltic manner. The drying tunnel was 10 feet long and the rate of travel of the belt was 1 foot per minute. The surface temperature of the belt rose to nearly 100°C at the discharge end, but the temperature of the gel did not exceed 50°C because of the cooling effect associated with evaporation. The water content of the extrusions was reduced by 40-45% as they passed through the drying hood. On discharge, the extrusions were dry enough so that they did not lose their shape, or run together, as they piled up in trays. The trays of the extrusions were then dried in an air oven at 200°C, coarsely ground to pass a 10-mesh screen, and calcined at 300-400°C as required.

#### The Measurement of the Pore Volume Distribution

The pore volume distribution measurements were made by the method of high-pressure mercury porosimetry. The apparatus and techniques used in these measurements have been described previously by the authors (3).

#### The Measurement of the Apparent Bulk Density

The portion of the gels used for the bulk density measurements was the -14 +30 mesh U.S. Standard Sieve fraction. The sample was poured slowly through a funnel into a weighed 10-ml graduated cylinder. The cylinder plus 10 ml of sample was then weighed, and the weight and apparent bulk density of

the powder were determined.

The accuracy and reproducibility of the method were affected by any factor, such as vibration or tamping, that interfered with the packing characteristics of the granules. To reduce the handling and vibration of the graduated cylinder to a minimum, the graduate was cut off and ground square at the 10-ml mark. The excess of granules over the top of the cylinder was removed with a straight-edge, taking care not to shake or tap the cylinder. The funnel used to feed the sample into the graduated cylinder was a standard 50-ml, 60° analytical funnel with a stem length of 1 inch. The funnel was set up in such a way that the tip of the stem was 1/2 inch above the top of the cylinder. The sample was poured through the funnel as uniformly as possible, usually over a period of approximately 10 seconds.

#### EXPERIMENTAL RESULTS AND DISCUSSION

The results of preliminary experiments indicated that highly porous, low-density alumina could be prepared by dehydrating aluminum hydroxide gel (which had been prepared by precipitation with carbonate) slowly, in thin layers, at low temperature followed by calcination. The present report is primarily a description of the investigation following this experimental observation. A number of variables and physical properties were involved and the results and discussions are listed under six headings:

1. The extent of dehydration required at low temperatures  
( - before high-temperature drying can be applied)
2. The upper temperature limit  
( - maximum temperature allowable in the preliminary drying step)
3. The effect of the drying atmosphere  
( - was oxygen critical to the process)
4. The effect of ageing the gel  
( - growth of particle size in the wet precipitate)
5. The effect of low-temperature drying on the pore volume distribution
6. The results of experiments on a pilot-plant scale.

The Extent of Dehydration Required at Low Temperatures

To determine the extent of dehydration required at low temperatures to produce the low-density form of alumina, small weighed batches of 1/4-inch diameter extrusions of hydrous gel (approximately 300 grams each) were placed on trays and allowed to dry for varying periods of time. The samples were dried either in the open air at room temperature for periods ranging from 3 to 24 hours, or in a vacuum oven at 1.0 psia and 75°C\* for periods ranging from 30 minutes to 3 hours. At the end of each drying test the extrusions were re-weighed (the amount of water lost from the batch was calculated by difference) and then placed in a preheated muffle furnace at 425°C to complete the dehydration process and calcine the sample. After calcination the samples were crushed and the -14+30 mesh fraction was separated for apparent bulk density measurements. Two batches of extrusions were prepared and placed in the calcining furnace immediately as control specimens. The results of the experiments are summarized in Table 1.

TABLE 1

Summary of Experiments Undertaken to Determine the  
Extent of Dehydration Required at Low Temperatures  
to Produce the Low-Density Form of Alumina

Treatment of Wet Gel	Water Removed from Gel Prior to Calcination at 425°C (wt %)	Apparent Bulk Density (g/ml) of -14+30 Mesh Fraction
Immediate calcination	0	0.54
	0	0.56
Air-dried at room temperature	13.3	0.43
	16.1	0.42
	19.2	0.44
	25.9	0.23
	29.0	0.22
	54.2	0.21
Vacuum-dried at 75°C	79.7	0.22
	14.0	0.47
	26.6	0.25
	32.7	0.22
	44.5	0.19
	64.1	0.20

\* Normal operating temperature.

The apparent bulk density of the calcined alumina gel decreased rapidly as the exposure time was lengthened and the water content decreased, prior to the application of high-temperature drying conditions. The experiments indicate that the hydrous gel need only be exposed to the drying atmosphere at low temperatures until the water content is reduced by 25-30% to obtain the highly porous form. Reducing the water content more than 30%, to say 50-60%, greatly facilitates handling and ensures a more uniform shape of product in the case of extrusions, but does not affect the porosity of the alumina finally produced.

The above experiments suggested that it might be possible to eliminate the low-temperature drying step by adding partially dehydrated alumina to the hydrous gel to lower the (apparent) water content by the 25-30% required. It was appreciated that the "gel" would then be a heterogeneous mixture rather than homogeneous, but it was felt that the point was worth exploring.

A quantity of 1/8-inch diameter extrusions were prepared and air-dried at room temperature for 24 hours. The water content of the hydrated alumina so formed was 67%. The extrusions were then crushed to pass a 40-mesh screen and small amounts were blended into batches of hydrous gel using a Mixmaster beater-type stirrer. The mixtures of hydrous gel and hydrated alumina were spread in thin layers on aluminum sheet and dried quickly at 425°C. Similar experiments were also made adding highly porous alumina which had been calcined at 320°C (i.e., the water content reduced to 10% by weight). The results of the tests are shown in Table 2.



TABLE 2

Summary of Experiments in Which Partially Hydrated  
Alumina Powder was Added to the Hydrous Gel  
Prior to High-Temperature Drying

Water Content of Hydrated Alumina Powder (wt %)	Amount of Hydrated Alumina Added to the Hydrous Gel (wt %)	Calculated Dehydration by Addition of Powder (wt %)	Apparent Bulk Density (g/ml) of -14+30 Mesh Fraction
Control (blank)	0	0	0.56
67	33(-100 mesh)	50	0.29
67	33( -40 mesh)	50	0.30
10	1.3( -40 mesh)	11	0.43
10	4.5 "	31	0.36
10	6.3 "	40	0.33

The aluminas formed were lower in density than the control sample (blank) but not as low in density, or as evenly textured, as were those prepared by the low-temperature drying technique. Repeated tests, taking special care to ensure thorough blending of the powder into the hydrous gel, did not bring about any significant improvement in homogeneity and this avenue of study was dropped.

The Upper Temperature Limit

It was only possible to make a qualitative estimate of the maximum temperature allowable in the low-temperature drying step. In a number of experiments, thermocouples were buried in the gel and monitored in the course of the drying process to determine the bulk-gel temperature. Where the hydrous gel was dried in thin layers or extrusions, quite large (and erratic) differences between the "nominal" oven temperature and the temperature of the gel were observed, as the result of the cooling effect associated with the evaporation of the water. Relatively stable temperature measurements, with values at (or near) the nominal oven setting, were only obtained after 1/2 to 2/3 of the water had been removed. Any factor which affected the number of air changes

around the extrusions or thin layers had a tremendous influence on the rate of evaporation and the bulk temperature, particularly in the initial stages of the drying process.

There were also problems as the result of shrinkage. The gel shrinks considerably in the drying process and the cracking and breaking which took place in the samples almost invariably occurred at the thermocouple .... exposing it and invalidating the test. This problem was greatest with the experiments in which the gel was shaped in thin layers or small-diameter extrusions, but was also present even in the experiments in which the gel was dried in thick layers.

After numerous trials it became evident that the practical upper temperature limit for the initial drying step was 100°C, and that for good reproducibility and sample uniformity the bulk gel temperature should not exceed 75°C. Typical results, indicating the general difficulties encountered in the temperature measurements, are shown in Table 3.

TABLE 3  
Summary of Experiments Undertaken to Determine the  
Upper Temperature Limit of the Low-Temperature  
Drying Step

Form in Which Gel Dried	Nominal Oven Temperature (°C)	Estimated Bulk Gel Temperature (°C)	Apparent Bulk Density (g/ml) of -40+30 Mesh Fraction
1/8-inch layer	200	< 50	0.22
1/4- " "	200	≈ 100	0.28
1/2- " "	200	> 100	0.39
3/4- " "	200	> 100	0.57
1/8-inch dia. extrusions	R.T.	R.T.	0.22
1/8- " " "	200	< 50	0.21
1/8- " " "	300	≈ 100	0.38
7/16-" " "	100	≈ 50	0.22
7/16-" " "	200	≈ 100	0.28
7/16-" " "	300	> 100	0.60

### The Effect of the Drying Atmosphere

In the course of the investigation, the question was raised as to whether the presence of oxygen (air) was critical to the dehydration process. The chemistry of the dehydration of aluminum hydroxide gel (see equation on page 2) did not suggest that it would be, but there were so many unknowns involved that it was thought that the point should be clarified.

Experiments were made in which small, weighed lots of 1/4-inch diameter extrusions were placed in enclosed trays and dried by passing nitrogen and carbon dioxide (from commercial cylinders) over the gel for approximately 8 hours at room temperature. The extrusions were then re-weighed, to determine the extent of dehydration which had occurred, and finally calcined at 400°C overnight. A similar experiment was run for comparison purposes, using compressed air as the source of drying gas. The results are shown in Table 4.

TABLE 4

#### Summary of Experiments Undertaken to Determine the Effect of the Atmosphere Used for Drying

Gas Used for Drying	Water Removed from Gel Prior to Calcination at 400°C (wt %)	Apparent Bulk Density (g/ml) of -14+30 Mesh Fraction
Air	55.5	0.21
Nitrogen	57.8	0.21
Carbon dioxide	59.0	0.21

There was no significant difference in the apparent bulk density of the aluminas formed using air, nitrogen, or carbon dioxide, and it was concluded that the drying atmosphere (either of itself, or by the exclusion of oxygen) was not critical to the process.

### The Effect of Ageing the Gel

Hydrous aluminum hydroxide gel is essentially a precipitated hydroxide,  $\text{Al}(\text{OH})_3$ , in contact with its supernatant,  $\text{H}_2\text{O}$ . Such a condition is conducive to change in both the size and shape of the precipitated particles. It was

decided, therefore, to establish whether any significant changes (relative to the drying process and the formation of low-density alumina) occurred within the first few hours of the formation of the precipitate.

A batch of hydrous aluminum hydroxide was prepared according to the procedure described on page 5. Instead of allowing the precipitate to remain overnight in contact with the supernatant liquor, however, it was filtered immediately and washed. After being washed the batch was divided into two halves. The drying of the first half of the batch was begun within two hours of the precipitation step. The second half was wrapped tightly in a polyethylene bag and stored for a period of one week before beginning the drying process. In both instances the gel was dried in the shape of 1/4-inch diameter extrusions, laid in rows 1 inch apart on aluminum sheet. Part of each lot of extrusions was placed immediately in a calcining furnace operating at 400°C (no low-temperature drying), and the remainder was air-dried slowly at room temperature for 24 hours prior to calcination. After calcination the samples were crushed and the -14+30 mesh fraction was separated for apparent bulk density measurements. The results of the measurements are shown in Table 5.

TABLE 5

Summary of Experiments Undertaken to Determine the  
Effect of Ageing the Gel

Age of Gel	Method of Drying	Apparent Bulk Density (g/ml) of -14+30 Mesh Fraction
2 hours	Calcined immediately	0.64
2 hours	Air-dried slowly, then calcined	0.26
1 week	Calcined immediately	0.58
1 week	Air-dried slowly, then calcined	0.24

There was no significant difference observed in the effect of low-temperature drying with the age of the gel. The apparent bulk densities of both the fresh and the week-old gels dried at low temperatures were less than half of those dried at high temperature. There was also no measurable difference

in performance with a commercial lot of aluminum hydroxide gel (Reheis, type F compressed gel) over a nine-month period.

The Effect of Low-Temperature Drying on the Pore Volume Distribution

Pore volume distribution measurements were made on samples of gel which had been dried in layers 1/8, 1/4, 1/2 and 3/4-inch thick at 200°C\* (nominal oven temperature), then calcined at 400°C for 4 hours. The pore volume measurements were made on the -14+30 mesh fraction. The results are summarized in Table 6 and Figure 2.

TABLE 6

Summary of the Effect of Low-Temperature Drying on the Apparent Bulk Density and Pore Characteristics of Alumina

Thickness of Gel Layer (inches)	Estimated* Bulk Gel Temperature (°C)	Apparent Bulk Density (g/ml) of -14+30 Mesh Fraction	Range of Predominant Pore Sizes (Å radius)	Total Pore Volume (ml/g)
1/8	< 50	0.22	1000-300	2.0
1/4	≈ 100	0.28	1000-50	1.3
1/2	> 100	0.39	100-30	0.80
3/4	> 100	0.57	50-20	0.55

A marked increase was observed in both the size of the pores present and the total pore volume as the thickness of the gel layer (and the bulk gel temperature) decreased. A corresponding decrease occurred in the apparent bulk density. The majority of the pores present in the dense form of the alumina (the 3/4-inch layer) occurred in the range 50-20 Å radius, and the total pore volume was only 0.55 ml/g; whereas the size of the pores present in the low-density gel (the 1/8-inch layer) occurred, generally, in the range 1000-300 Å radius and the total pore volume was approximately 2.0 ml/g. The results of the measurements on the samples prepared from the 1/2- and 1/4-inch layers occupied intermediate positions.

\* See section on the determination of upper temperature limit and experimental results, listed in Table 3, page 12.

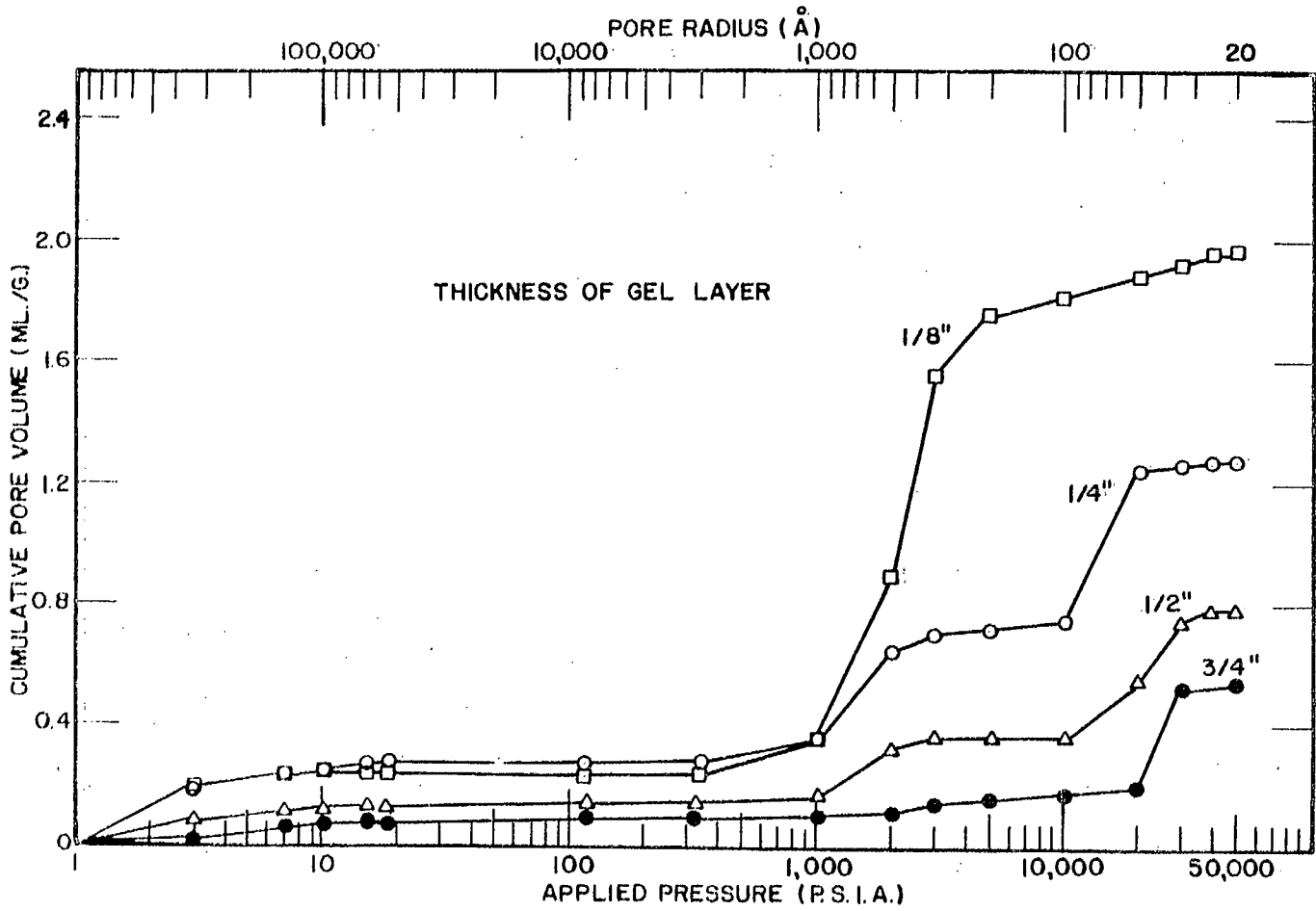


Figure 2 - The effect of the thickness of the gel layer used in the drying process on the cumulative pore volume distribution.

The above experiments illustrate a method whereby a limited measure of control over the pore volume distribution in alumina can be obtained. Under drying conditions where the cooling effect associated with evaporation is sufficient to maintain the bulk gel temperature in the range 50-150°C, the predominant pore size present in the alumina can be systematically increased by simply decreasing the thickness of the gel layer. Any factor which influences the rate of evaporation, i.e. the temperature, humidity, circulation, etc., will bring about a change in the effective bulk gel temperature. Anyone wishing to reproduce the aluminas described in Table 6 and Figure 2 is cautioned to remember this dependence, and is advised to run pilot tests with his own particular drying system, using the apparent bulk density of the products as a means of monitoring the changes achieved.

#### The Results of Experiments on a Pilot-Plant Scale

Approximately 100 pounds of aluminum hydroxide gel was formed into 1/8-inch diameter extrusions and dried using the conveyor-belt drying tunnel described on page 7. The gel used in the larger-scale experiments was the Type F compressed aluminum hydroxide gel, manufactured by the Reheis Corporation of Berkeley Heights, New Jersey. Small-scale experiments indicated that this gel responded to low-temperature drying in the same way as did the gel prepared in the laboratory investigation using ammonium carbonate as the precipitating agent. Following the low-temperature drying step on the conveyor belt, the extrusions were dried in an air oven at 200°C, coarsely ground to pass a 10-mesh screen, then calcined at 310°C. For comparative purposes a portion of the same lot of hydrous gel was spread in a layer 1 inch thick over aluminum sheet and dried quickly at 200°C, then calcined. Both portions were ground and the -14+30 mesh fraction separated for bulk density and pore volume distribution measurements. The results of these measurements are shown in Figure 3 and Table 7.

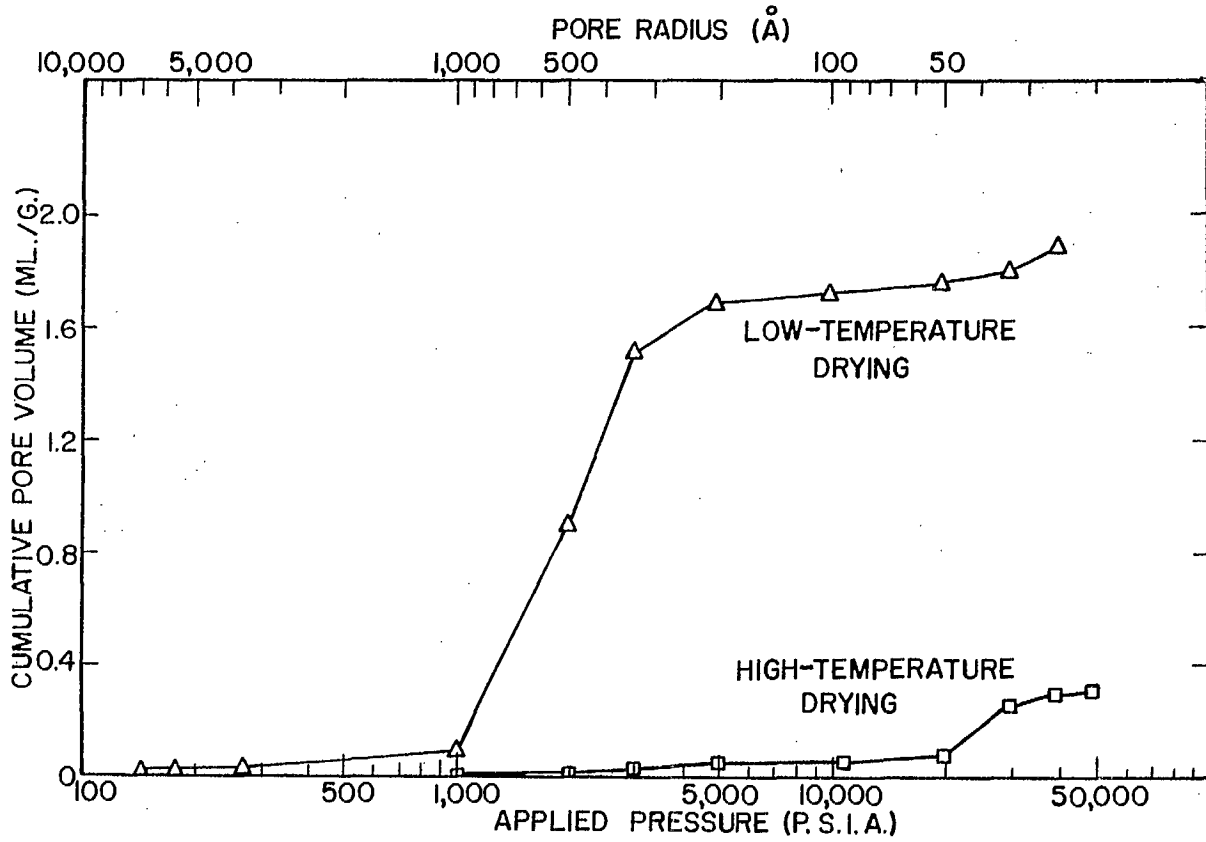


Figure 3 - The cumulative pore volume distribution in aluminas produced on a pilot-plant scale.



TABLE 7  
Summary of the Physical Characteristics of the Aluminas  
Produced on a Pilot-Plant Scale

Method of Drying	Apparent Bulk Density (g/ml) of -14+30 Mesh Fraction	Range of Predominant Pore Sizes (Å radius)	Total Pore Volume (ml/g)
1/8-inch dia. extrusions dried on conveyor belt at low temperature	0.21	1000-300	1.9
1-inch layer dried rapidly at high temperature	0.61	50-30	0.3

The aluminas formed using the continuous drying tunnel arrangement were essentially identical with those formed in the small-scale (batch) experiments. A little difficulty was encountered in priming the pump which fed the gel to the extrusion nozzles, but once started the system functioned well with a minimum of attention. In the present apparatus a white neoprene belt was used on the conveyor system ..... it is felt that a belt made of small-mesh stainless steel screen would improve the circulation around the extrusions (and the transfer of heat to the gel) and generally increase the degree of drying achieved. In exploratory tests, extrusions were formed on short lengths of stainless steel screen placed on top of the neoprene conveyor belt. There was a small improvement in the extent of drying which occurred, even in the presence of the belt. When the screening was flexed to simulate the bend around the roller on the conveyor, the dried extrusions broke away cleanly with very little adhesion or sticking.

#### SUMMARY

1. Highly porous, low-density alumina can be prepared by dehydrating hydrous aluminum hydroxide gel (which has been precipitated with carbonate) in thin layers, or small-diameter extrusions, at low temperatures.

2. To form the low-density alumina it is preferable that the bulk temperature of the hydrous gel should not exceed 75°C in the low-temperature drying step. The maximum allowable temperature is 100°C. At least 25-30% of the water present must be removed at low temperature before conventional high-temperature drying conditions can be applied.

3. The total pore volume contained in the aluminas prepared by this technique is in the range 1.0 to 2.2 ml/g. The predominant pore sizes present are 1000 to 300 Å radius. Limited control of the pore volume distribution can be obtained by regulating the conditions affecting the bulk gel temperature (oven temperature, air circulation, thickness of gel layer, etc.) in the low-temperature drying step.

4. The type of drying atmosphere (air, nitrogen, or carbon dioxide) and the age of the hydrous gel are not critical to the process.

5. The technique works well on both the laboratory and pilot-plant scale.

#### REFERENCES

1. W.D. Machin, B.I. Parsons and D.S. Montgomery - "Rapid Test Methods for Determination of the Approximate Average Pore Radius, Total Pore Volume and Surface Area Contained in Porous Materials", Mines Branch Technical Bulletin TB-16, Department of Energy, Mines and Resources, Ottawa (1960).
2. W.D. Machin, B.I. Parsons and D.S. Montgomery - "The Calculation of the Pore Size Distribution from the Nitrogen Desorption Isotherm", Mines Branch Technical Bulletin TB-26, Department of Energy, Mines and Resources, Ottawa (1961).
3. G.T. Shaw, B.I. Parsons and D.S. Montgomery - "Porosimetry by Mercury Injection", Mines Branch Technical Bulletin TB-45, Department of Energy, Mines and Resources, Ottawa (1963).
4. D. Basmadjian, G.N. Fulford, B.I. Parsons and D.S. Montgomery - Journal of Catalysis, 1, 547-563 (1962).
5. W. Urban - Erdöl and Kohle, 8, 780-782 (1955).

6. C.R. Griswold and R.P. VanDriesen - "Commercial Experience with H-Oil". Paper presented at the 31st Midyear Meeting of the American Petroleum Institute's Division of Refining (preprint 53-66), Houston, Texas (1966).
- K.C. Hellwig, M.C. Chervenak, E.S. Johanson and H.H. Stotler - "Convert Coal to Liquid Fuels with H-Coal". Paper presented at the 62nd National Meeting of the American Institute of Chemical Engineers (preprint 26C), Salt Lake City, Utah (1967).
- A.R. Johnson, S.B. Alpert and L.M. Lehman - Oilweek, 19, No.17, 54-67 (1968).
7. D.H. Quinsey and W.H. Merrill - "Combined Liquid and Vapour-Phase Hydrocracking of Heavy Oils", Proc. 17th Canadian Chemical Engineering Conference, sponsored by the Chemical Institute of Canada in Niagara Falls, Ontario, October 16-18, 1967.

= = = = =

BIP(PES)gdb

