

POLYELECTROLYTE REINFORCED AEROGELS OF CLAYS—APPLICATION AS CHROMATOGRAPHIC ADSORBENTS*

by

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ABSTRACT

AEROGELS of clays can be prepared by freeze-drying of clay water gels. The mechanical strength of the aerogels is improved by the addition of water-soluble polyelectrolytes to the hydrogels.

The porosity of the powdered aerogels can be adapted to the requirements for adsorbents in gas chromatography by compounding the hydrogels with suitable amounts of polyelectrolytes. Simultaneously, the surface of the clay may be modified by adsorption of polar or cationic organic compounds in order to achieve specific chromatographic separations.

Because of the toughness of the clay-polyelectrolyte aerogels, they can be rolled out to thin sheets which may be applied as chromatographic papers.

INTRODUCTION

THE solid character of gels in liquids ("lyogels" or "hydrogels") is commonly attributed to the presence of a continuous framework of submicroscopical particles or of macromolecules, extending throughout the total volume of the system.

When the liquid is removed from the gel by heating to a temperature above the boiling point of the liquid, the gel shrinks. Apparently the framework collapses or folds. When the gel is completely freed of the liquid, a coherent framework with a certain, though sometimes very low, porosity may still exist. For such systems, Freundlich coined the term "xerogel".

The shrinkage of the gel upon removal of the liquid has been attributed to the capillary pull of the receding meniscus in the capillaries of the gel. This interpretation is supported by the observation that shrinkage can be

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prevented if the liquid is removed under conditions at which no liquid meniscus exists. These conditions can be realized in two ways:

- (a) The gel is heated in an autoclave until the temperature and pressure are above the critical point for the liquid in the gel. Removal of the liquid by a sudden release of the pressure results in a dry gel which has practically the same volume as the original gel. This process is known as the Kistler process (Kistler, 1932). In this paper, however, we shall deal exclusively with the following method.
- (b) The gel is frozen, and the frozen liquid is removed by sublimation in a vacuum at freezing temperatures. This process is called "freeze-drying".

The highly porous xerogels obtained by applying these techniques are usually referred to as "aerogels".

Although shrinkage is largely prevented in the preparation of an aerogel, there is no guarantee that changes in the framework geometry are eliminated, nor is there a guarantee that the forces holding the framework together in the aerogel also existed in the original gel or that they are identical to any such forces in the lyogel. In principle, therefore, it is of doubtful value to consider the creation of an aerogel as direct proof of the existence of a framework in the original gel, as is sometimes argued, or to picture the framework in the lyogel as being identical to that in the aerogel. Actually, there are several indications that the structures of the aerogels and those of the liquid systems are entirely different.

Clay Aerogels

The occurrence of structural changes in the transfer of a hydrogel into an aerogel can be inferred when the differences in properties of hydrogels and aerogels of bentonite clay are analyzed.

Homogeneous gels of sodium bentonite in water can be prepared by concentrating a dilute suspension of the clay by ultracentrifugation and decanting the supernatant, particle-free liquid. A rigid gel of sodium bentonite is obtained at a clay concentration of about 2% or higher (van Olphen, 1956).

According to electron microscope studies, the sodium bentonite particles are thin, flat plates. Their average size in dilute suspensions has been determined by various indirect methods. There is evidence that the particles in the sodium bentonite gel are linked edge-to-face owing to the opposite double-layer charges on these two surfaces (van Olphen, 1951). Consequently, the framework in the hydrogel of sodium bentonite may be pictured as a cubic card-house structure. This is supported by the following observations. Assuming that the particle size does not change materially during concentration of the dilute suspension by ultracentrifugation, and knowing the average size of the "cards", we can compute the weight of sodium bentonite which is just sufficient to build a continuous cubic card house in a certain volume. The computed minimum clay content of a system required to create this framework agrees with the experimentally determined minimum clay content at

which a measurable yield stress develops in the system. When sodium bentonite is converted into calcium bentonite, the clay plates associate and become three to four times as thick; in accordance with this observation, the minimum clay content required to create a gel of calcium bentonite in water is three to four times higher than in the case of sodium bentonite (van Olphen, 1958).

An aerogel prepared from the transparent hydrogel of a small particle size fraction of sodium bentonite is opaque. The platy particles seem to have associated to form thicker plates during the freeze-drying process. Microscopically, the aerogel shows a layered structure. When the gel is freeze-dried in the form of a cylinder, a radial arrangement of the dry-clay layers can be observed in a cross section with the naked eye.

The presumed association of the plates to form thicker plates is corroborated by the measured nitrogen surface area of the freeze-dried gel material. If the 2-unit-layer-thick clay plates in the hydrogel had remained separated in the aerogel, the nitrogen area of the aerogel would have been of the order of 300–400 m²/g. Actually, the nitrogen surface area was much smaller—about 27 m²/g. Analogous observations have been reported by Call (1953), who found nitrogen surface areas of 70, 49, and 58 m²/g for freeze-dried sodium, calcium, and hydrogen bentonite, respectively.

According to the microscopic observation, the thickness of the sheets in the aerogel is in the micron range. However, a nitrogen surface area of 27 m²/g suggests a particle association of the order of 30 unit layers, which corresponds to a thickness of the order of 300 Å. Apparently the sheets observed microscopically still have a considerable fine-structure.

Since the basal spacing of the dried material is 9.8 Å, the strongly adsorbed interlayer water of the clay has been removed efficiently during the freeze-drying operation.

The radial structure of a freeze-dried cylinder of clay suggests that during the freezing step ice crystals have grown radially and that these ice crystals have pushed the clay aside, thus promoting parallel alignment of the clay particles. Hence the association of the particles to form thicker plates is probably induced during the freezing step.

Indications of the formation of thicker particles have also been obtained when clay suspensions were subjected to a freezing–thawing cycle under atmospheric conditions. The resulting particle association may be concluded from the observation that the specific viscosity of the suspensions was reduced 7%, 30%, and 60% for 0.25% suspensions of sodium, calcium, and potassium bentonite, respectively. In the last case, the originally transparent suspension had become slightly turbid after the freezing–thawing cycle. Also clay gels often lose some of their strength after a freezing–thawing cycle, indicating a reduction of the number of links; this may be partly a result of a reduction of the number of particles by association. The well-known frost heaving of soils is probably also partly a result of the reduction of the number of structure building units due to parallel association.

PREPARATION AND PROPERTIES OF AEROGELS

Aerogel Preparation

The samples were quickly frozen in a glass container, the "drying flask", by submersion in a dry ice-alcohol mixture. The drying flask was a round tube with a round bottom. When solutions or suspensions were being frozen, a small amount of the liquid was poured in the drying flask. A film of the solution was formed on the wall by rotating the flask. The flask was then submersed in the coolant and was rotated until the film was frozen. This procedure was repeated with a second quantity of liquid, and so forth, until a frozen layer about $\frac{3}{8}$ in. thick was built up. When a gel was being frozen, it was simply smeared in a thin layer on the walls of the drying flask.

Alternatively, cylinders of aerogel were prepared as follows. The solution or gel was frozen in a glass tube of the desired dimensions, and the frozen cylinder was removed from the tube and was placed in the precooled drying flask.

The drying step of the operation was performed in a "VirTis" freeze-drying apparatus, which consists of an evacuated stainless-steel cooling chamber with cylindrical walls, the inner wall of which is cooled with a dry ice-alcohol mixture. The evacuated chamber has several connections to which drying flasks can be attached. The vacuum is maintained at a few millimeters during evaporation, and at a few tenths of a millimeter toward the end of the process. The drying flasks are exposed to room temperature, but the heat extraction due to evaporation of the ice keeps the contents frozen during the drying process. The freeze-drying process takes about 8 hr for a layer $\frac{3}{8}$ in. thick, and about 24-36 hr for a cylinder 2 cm in diameter and several centimeters long.

Properties of Aerogels

The most striking property of aerogels is that they are coherent despite their large porosity, particularly if they are prepared from low-concentration hydrous systems. For example, a freeze-dried cylinder of Wyoming bentonite was prepared from a 3% suspension of bentonite. Shrinkage was very small, so that the solid content of the aerogel is about 0.03 g clay/cc, or about 0.01 cc clay/cc, which amounts to a porosity of about 99%.

Aerogels vary in appearance, shrinkage, strength, and coherence. In order to compare them on a quantitative basis, we have adopted the following simple, rather rough test procedures.

The hydrous system was frozen in the shape of a cylinder 1.9 cm in diameter and several centimeters long. After freeze-drying the ends of the cylinder were cut perpendicular to the axis.

The diameter and length of the cylinder were measured, and the weight was determined. An indication of the radial shrinkage was obtained from the reduction of the diameter of the cylinder. The volume shrinkage was determined from values of the calculated density of the cylinder and the original concentration of the hydrous system.

The strength of the aerogel cylinder was tested as follows. With the cylinder in a vertical position, loosely fitting in a glass tube, the top of the cylinder was loaded with successively increasing weights, and the linear compression of the cylinder was measured at each weight. Before the next heavier weight was put on, the recovery of length of the cylinder was measured after removal of the weight. Measurements of the length of the cylinder were made within a few minutes after application or removal of the load.

Another property of interest is the coherence of the aerogel, or its tendency to crumble when subjected to shear. When aerogels are sheared in a cutting-blade-type mixer, some yield a homogeneous, free-flowing, fluffy powder. Others yield a voluminous, slightly elastic, coherent mass. Such aerogels show easy cleavage along radial planes of the cylinder, yielding rather tough, thin sheets which may be torn by the cutting blades but which do not crumble.

In order to amplify these qualitative descriptions by a quantitative figure, we have determined the bulk density of the chopped aerogel according to the following procedure. The chopping was performed in an "Omni mixer" (Servall), in which the cutting blades rotate at 14,000 rev/min. The sample was chopped for 1 min, and the chopped mass was transferred to a graduated cylinder and was compacted by tapping of the cylinder. The volume and weight of the chopped mass were determined. As long as the bulk density of the chopped aerogel is of the same order as that of the aerogel cylinder, we can infer that the coherence has been preserved within the small pieces of chopped aerogel. In this respect, the data can be considered as a guide; otherwise not too much significance should be attached to small variations.

CLAY-POLYELECTROLYTE AEROGELS

In most potential applications of clay aerogels, reasonable strength and coherence are desirable. Aerogels of several clays, however, are rather fragile; some even disintegrate to a powder at the slightest touch. We have attempted to improve the strength of clay aerogels by incorporation of polyelectrolytes in the hydrogel. The thought behind this idea was that, in the hydrogel, the macromolecular chains of polyions might become adsorbed on several clay particles at the same time and might thus establish a strong bridge between the particles.

Indeed, clay aerogels do become stronger and tougher upon incorporation of certain polyelectrolytes. Polyelectrolyte solutions themselves also yield rather strong, tough aerogels. Therefore, their beneficial effect on clay aerogels may simply be due to a reinforcement of the clay aerogel by the polyelectrolyte skeleton and not necessarily to a bridging effect.

Aerogels of Polyelectrolytes

Aerogels prepared from polyelectrolyte solutions are often rather tough. Usually, shrinkage amounting to 10–20% radial linear shrinkage of the cylinders occurs during the freeze-drying process. Shrinkage was about 10%

for 1% and 2% CMC and 6.57% Daxad solutions, and about 20% for a 1.37% Lustrex solution. A film of a 1% Cypan solution yielded a shrunken gauze-type network with meshes of about $\frac{1}{2}$ mm.*

The results of strength tests on cylinders are presented in Fig. 1. In this and the following figures, the curves marked C are a plot of per cent linear compression versus the weight put on the cylinder. The curves marked R represent the same data after removal of the weight. The spread between the C and R curves measures the elastic recovery of the cylinders.

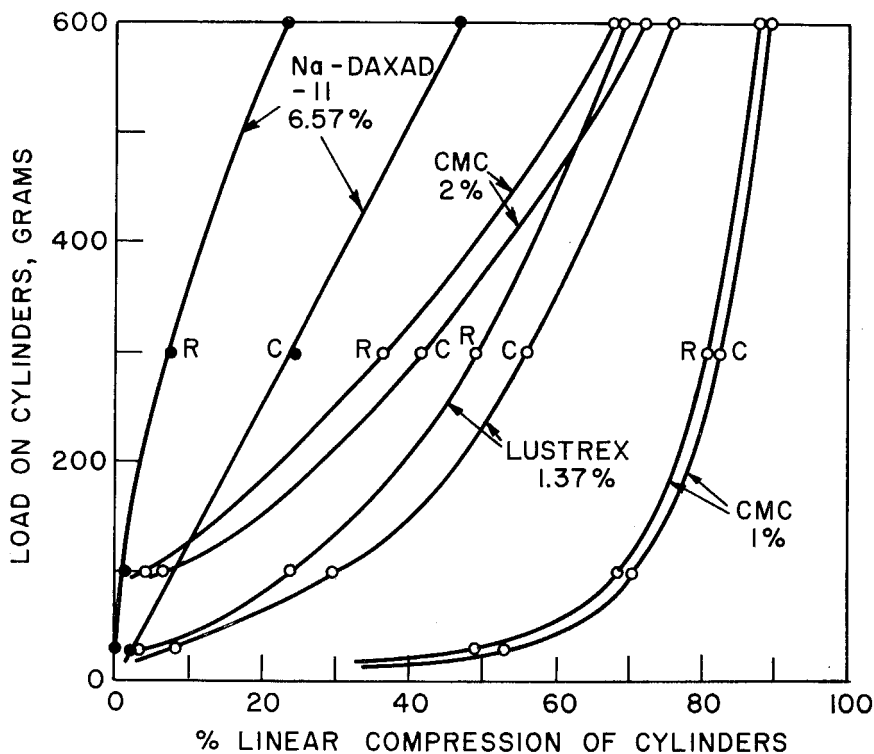


FIG. 1. Compression (C) and elastic recovery (R) of aerogel cylinders of poly-electrolytes.

Chopping of the cylinders leads to a voluminous, slightly elastic and coherent mass for CMC and Lustrex, but yields a homogeneous, flowing powder for Daxad. Densities of the chopped aerogels, together with the bulk

* CMC: sodium carboxymethylcellulose, Hercules 70 Premium-Low.

Na-Daxad 11: polymerized sodium salts of alkyl naphthalene sulfonic acids, Dewey and Almy Chemical Co.

Na-Lustrex X-770: sodium salt of polystyrene sulfonic acid, Monsanto Chemical Co.

Cypan: sodium polyacrylate, Magcobar.

densities of the cylinders, are plotted in Fig. 2 as a function of solids content of the original hydrous system. The dashed line represents the bulk density which the aerogel cylinder would have if no shrinkage had taken place. The points above this line for the bulk densities of the cylinders indicate that volume shrinkage occurred for all polyelectrolytes. The densities of the chopped aerogels are all lower than those of the cylinders, indicating the preservation of coherence.

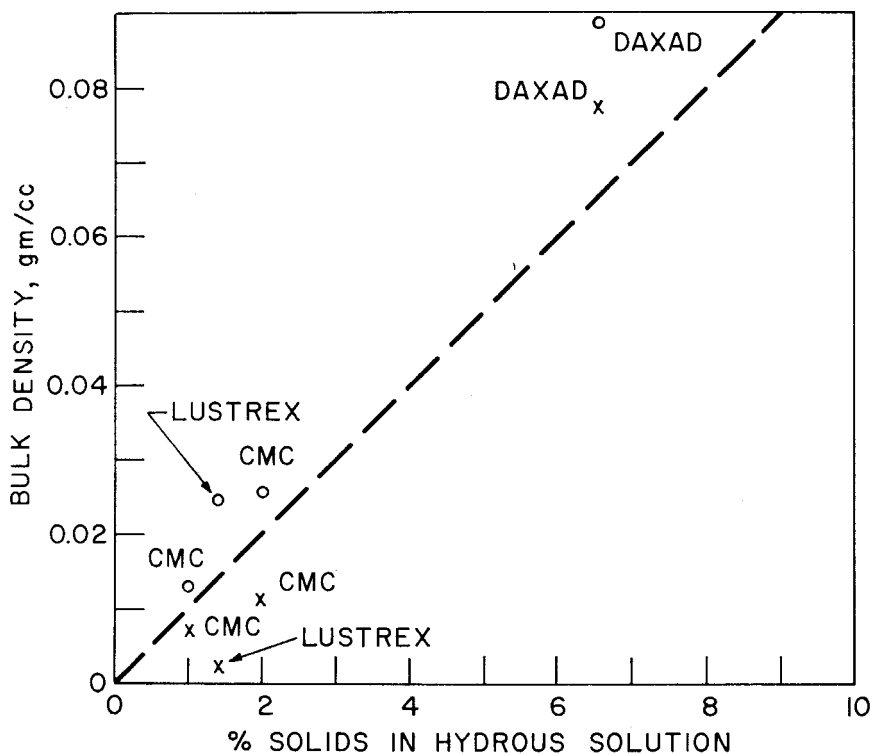


FIG. 2. Bulk density of aerogel cylinders (o) and of chopped aerogels (x) of polyelectrolytes.

The tough aerogels, particularly those of CMC, can be rolled out under pressure to yield a rather strong, paperlike sheet.

Bentonite and Bentonite/CMC Aerogels

Bentonites are among the best gel-forming clays, probably because the small thickness of the individual plates makes available a comparatively large number of frame-building units per gram of clay. Bentonite gels, as well as suspensions, give rather strong, tough aerogels, although they are

somewhat more fragile than the CMC aerogels. Very little shrinkage occurs during the freeze-drying process.

The addition of CMC to a bentonite gel or suspension yields a somewhat tougher, stronger aerogel, although the improvement is not as spectacular as with other clays. Figure 3 presents the results of strength tests on bentonite and bentonite/CMC aerogel cylinders. The strengths of a 1% bentonite gel* and a 1% CMC gel are comparable. The strength of a 1% bentonite/2% CMC

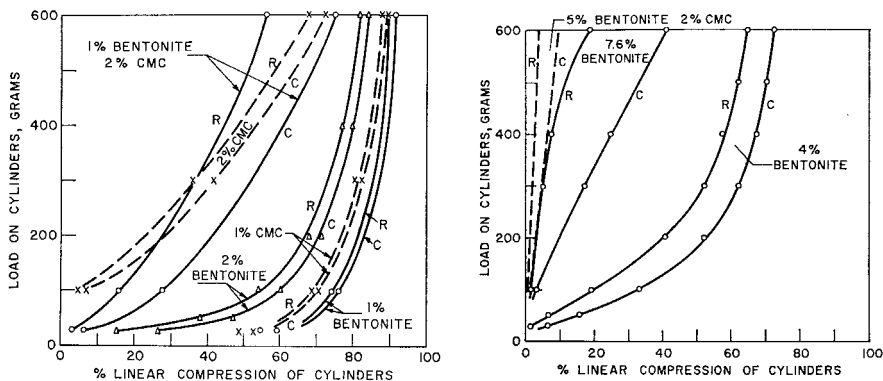


FIG. 3. Compression (C) and elastic recovery (R) of aerogel cylinders of bentonite and CMC.

gel is of the same order as that of a 2% CMC gel and is almost as great as that of a 5% bentonite aerogel. When 2% CMC is added to the latter, a very strong aerogel is obtained which is stronger than a bentonite gel with the same total solids content. The strength improvement by addition of CMC can be read from Fig. 4, in which per cent linear compression at a load of 600 g is plotted as a function of total solids content for bentonite, CMC, and bentonite/CMC aerogels. The strength of the aerogels increases more rapidly with total solids content for CMC and bentonite/CMC aerogels than for those made of bentonite alone.

In Fig. 5 the bulk densities of aerogel cylinders and of chopped aerogels are plotted as a function of total solids content for bentonite gels with and without CMC. Bentonite aerogels, both with and without CMC, yield chopped masses similar to that obtained with CMC alone. Still, the generally lower bulk densities of the chopped bentonite/CMC aerogels indicate a greater toughness of the aerogels which contain CMC. The position of the points representing the bulk densities of the cylinders with respect to the dashed line representing no shrinkage indicates that the CMC-containing gels shrink slightly more than the gels of bentonite alone.

* In these experiments we used raw bentonite, which is partly a calcium clay and contains many large particles. The suspensions in water do not show gel properties unless the concentration is about 6% or higher.

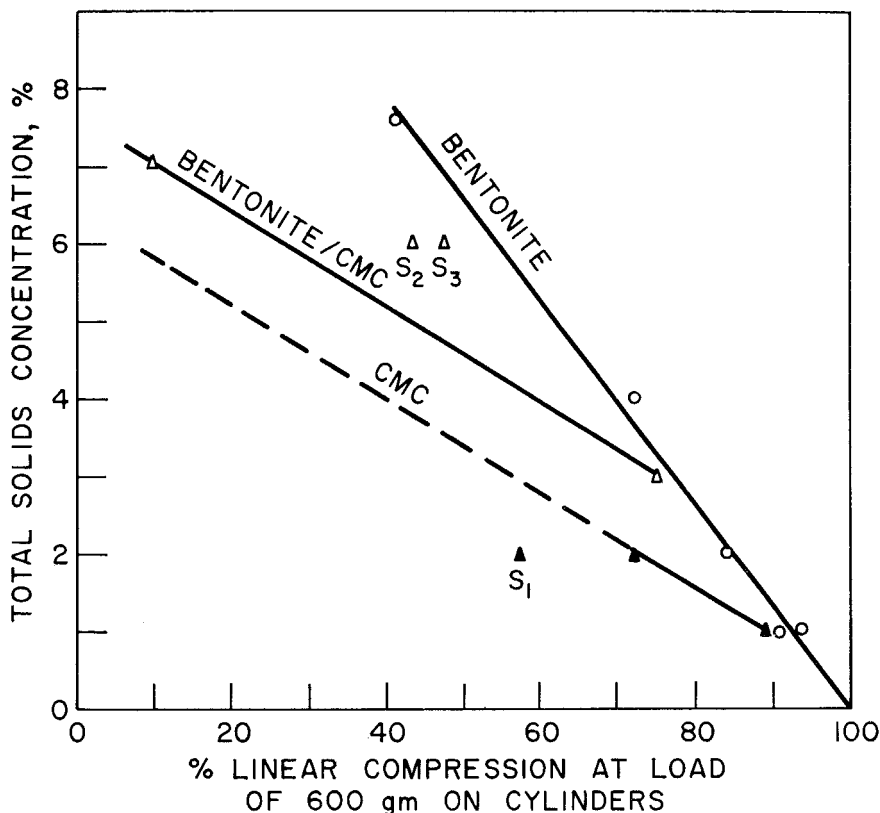


FIG. 4. Compression of aerogel cylinders at a load of 600 g as a function of total solids concentration for bentonite, CMC, and bentonite/CMC aerogels.

Effect of Salt

A few experiments were conducted to study the effect of salt on the strength of aerogels. An aerogel prepared from a 2% CMC solution containing NaCl in a concentration of 100 meq/l appeared to have become somewhat stronger, as indicated by the point marked S_1 in Fig. 4. Some loss of strength was observed in a 4% bentonite/2% CMC aerogel upon the addition of 100 meq/l of NaCl either to the bentonite gel before mixing with the CMC solution (point S_2) or to the CMC solution before blending with the bentonite gel (point S_3).

Kaolinite/CMC and Illite/CMC Aerogels

Because of larger particle size, the gel-building properties of illite and kaolinite are less pronounced than those of bentonite. Only at rather high

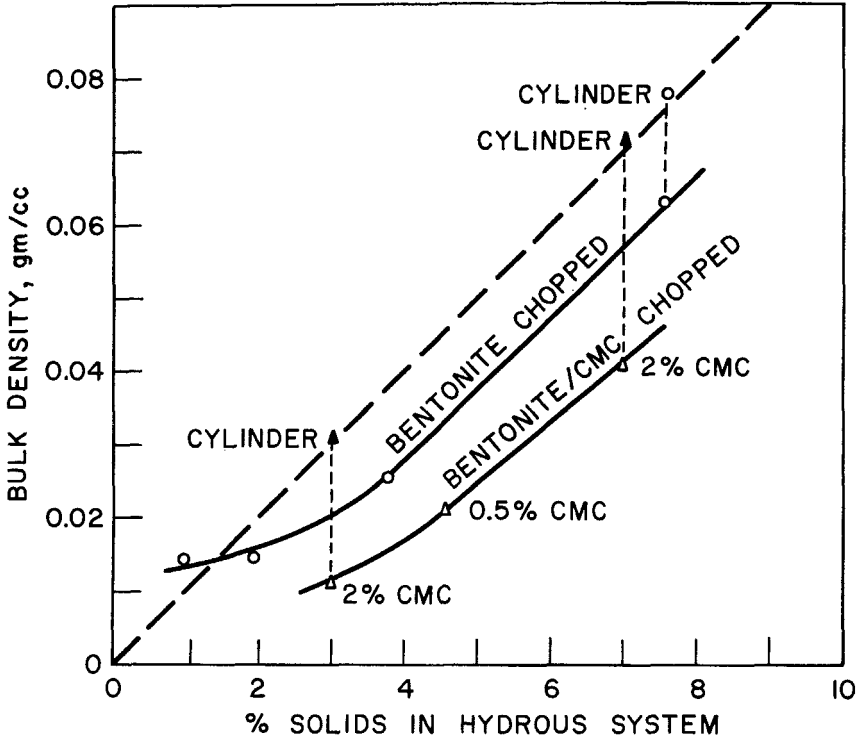


FIG. 5. Bulk densities of aerogel cylinders and chopped aerogels of bentonite and CMC.

clay concentrations are rigid systems obtained, and these have more the character of pastes than of gels. Freeze-drying of these pastes yields aerogels which crumble to a powder at the slightest touch. The incorporation of a small percentage of CMC in the concentrated clay pastes has a spectacular effect on the strength of the aerogels.

Whereas the aerogel prepared from a 27% paste of sodium Fithian illite crumbles when touched, the incorporation of 2% CMC yields a cylinder of aerogel which shows a linear compression of only 9% at a load of 3000 g and recovers to a compression of only 5% after removal of the load. The unsupported cylinder fractures when loaded with about 3500 g.

The bulk density of the chopped aerogel of illite is about 0.49 g/cc, and that of the illite/CMC aerogel is 0.34 g/cc.

The aerogel prepared from a 37% kaolinite paste crumbles easily, but the incorporation of 2% CMC yields a very hard aerogel which is compressed only 1% under a load of 4000 g. The unsupported cylinder can be loaded with 7300 g without a sign of fracture. The bulk density of the chopped

aerogel of kaolinite and CMC is, however, practically the same as that of the initial powdered material, i.e. about 0.65 g/cc.

POTENTIAL APPLICATIONS OF REINFORCED AEROGEL

Potential applications of the reinforced aerogel materials described in the preceding sections are as follows (van Olphen, 1965):

- (a) Heat insulators.
- (b) Gas-diffusion membranes.
- (c) Adsorbents and absorbents in filters for gases and smokes, and possibly for radiation by incorporating radiation-absorbing compounds or by such modifications as the use of clays in the cadmium form.
- (d) Adsorbents in gas and paper chromatography.

The use of clays in chromatography offers a wide variation of adsorbent properties by pretreatment of the clay surface with one of the many organic compounds known to form adsorption complexes with clays (e.g. see White and Cowan, 1958). The incorporation of polyelectrolytes, such as CMC, in these systems allows adjustment of the bulk powder density of the aerogels to suit the requirements of the gas-chromatographic techniques or to enable fabrication of suitable paperlike materials for paper chromatography.

One example from the field of gas chromatography has been worked out in this laboratory using a pyridine exchange complex of bentonite as the adsorbent in a gas-chromatographic column. Pyridine chloride is added to a colloidal suspension of bentonite. The pyridine-bentonite complex flocculates and is separated from the solution by filtration and washed. The product, however, is too compact for gas-chromatographic application. A somewhat more porous, but still not satisfactory packing is obtained by freeze-drying of the pyridine bentonite. The addition of sodium carboxymethylcellulose to the bentonite suspension prior to exchange with pyridine chloride yielded a much more voluminous product. Freeze-drying of this product gave a porous material with a resistance to gas flow which was less than that obtained with 60-80-mesh fire brick. A better temperature stability was achieved by using a sodium polyacrylate ("Lytron B", Monsanto Chemical Co.) instead of CMC.

An adsorbent packing with Lytron B is prepared as follows:

Suspend 20 g of Wyoming bentonite in 400 ml of water. Add 10 ml of a 3% Lytron B solution in water, and stir. Add 100 ml of a mixture composed of equal volumes of pyridine and 12N hydrochloric acid, stir, allow to settle, and decant. Repeat the additions of acid-pyridine mixtures four times. Wash free of excess reagent with water. Freeze mixture in a uniform layer on the walls of a drying flask, and freeze-dry.

The packing has been evaluated primarily for its ability to separate the xylene isomers. Figure 6 represents the separation of ortho-, meta-, and para-xylene with respective boiling points of 144°, 138.8°, and 138.5°C. The

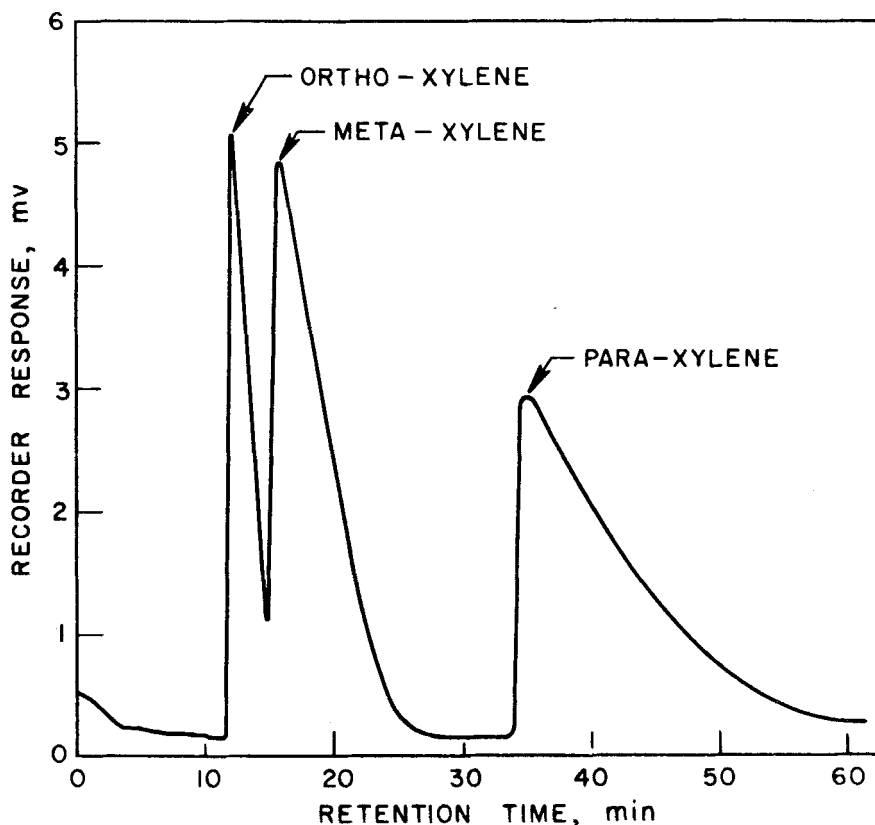


FIG. 6. Separation of xylenes on pyridine bentonite.

respective retention times of 11, 15, and 34 min were obtained under the following conditions:

Instrument: Perkin-Elmer 154 Vapor Fractometer.

Column dimensions: 2 m long \times 3 mm I.D.

Temperature: 97°C.

Carrier gas: helium.

Carrier-gas inlet pressure: 20 lb/in².

The observed order of elution was the reverse of that predicted from boiling-point considerations. Benzene was eluted after the higher-boiling xylenes, with toluene preceding them. Also, octane (boiling-point 126°C) was retarded and was eluted much later than the higher-boiling xylenes. With an instrument operating temperature of 142°C, the retention times were 2½ min for ortho- and meta-xylene, 5 min for para-xylene, and 25 min for normal octane.

A cylinder prepared from a precipitate of a pyridine bentonite exchange complex, which contained about 10% bentonite, was coherent but was extremely brittle. The density of the chopped aerogel was as high as 0.28 g/cc. On the other hand, a precipitate containing about 4% pyridine bentonite and about 2% CMC had a strength comparable to that of a bentonite/CMC aerogel of the same composition and had a bulk density of only 0.04 g/cc.

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