

# THE DEPENDENCE OF THE PERMEABILITY OF AN ASBESTOS DIAPHRAGM ON PRESSURE IN THE ABSENCE OF ELECTRIC CURRENT\*

L. I. Krishtalik

Translated from Zhurnal Prikladnoi Khimii, Vol. 36, No. 8,  
pp. 1776-1782, August, 1963

Original article submitted February 19, 1962

Industrial diaphragm baths for the electrolysis of brine are divided into two main types: with horizontal and vertical arrangement of the electrodes, the horizontal baths making it possible to obtain higher current efficiencies than most designs of vertical bath. In our opinion, the chief reason for this difference is the nonuniformity of the pressure of the vertical diaphragm and the resulting nonuniformity in permeability and alkali concentration along the height of the cathode. In this connection it was of interest to study the dependence of the permeability of the diaphragm on pressure in the absence of electric current and also while current was passing.

The dependence of the permeability of asbestos diaphragms on pressure was first studied by Stender and co-workers [1, 2], who established the fundamentally important fact that the permeability is independent of pressure.

Unfortunately these measurements were carried out for only 2-3 values of the hydrostatic pressure and therefore give an insufficiently complete picture of the dependence of permeability on pressure. In particular, no study was made of the low pressure range, in which a decrease in permeability with decrease in pressure might logically have been expected.

We carried out the experiments described below in order to obtain a more complete characterization of the existing relationships.

## EXPERIMENTAL

The permeability of the diaphragm at different pressures was determined by means of the following assembly (Fig. 1). A specimen of the diaphragm and a supporting gauze were fixed between two short glass tubes. The ends of the tubes facing the diaphragm were thickened slightly and polished. Before the application of the specimen these edges were moistened with polyvinyl chloride lacquer, which was also used to cover the point of contact of the two halves of the assembly, which were pulled together by means of elastic wound round lugs sealed to the tubes. The section of the assembly facing the diaphragm was filled with the appropriate liquid and joined by means of tubing to a branch piece connected to a Mariotte vessel.†

The experiments were carried out at room temperature. Simultaneous tests were carried out on a series of specimens both at identical pressures and at different pressures. The deviations from the mean value in parallel experiments did not generally exceed  $\pm 10\%$ . The duration of the experiments amounted to 15-140 days. In all the subsequent graphs showing the dependence of the permeability on pressure, the permeability values shown are those which remained practically constant for 5-20 days.

The data obtained are described and discussed below.

## DISCUSSION OF RESULTS

\*Paper I from a series of works on the study of the electrolytic preparation of chlorine and alkalies in vertical electrolyzers with diaphragms. The work was carried out in the period 1949-1952, and the principal results were presented at the VIIIth Mendeleev Congress.

†One of the arms of the branch piece was connected to an overflow vessel which protected the specimens from damage by accidental fluctuations in pressure.

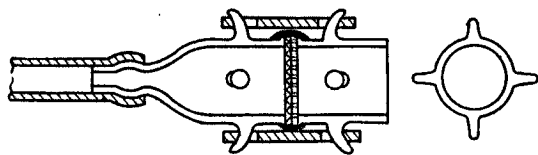


Fig. 1. Assembly for determining the permeability of the diaphragm. Area of specimen 4.5 cm<sup>2</sup>.

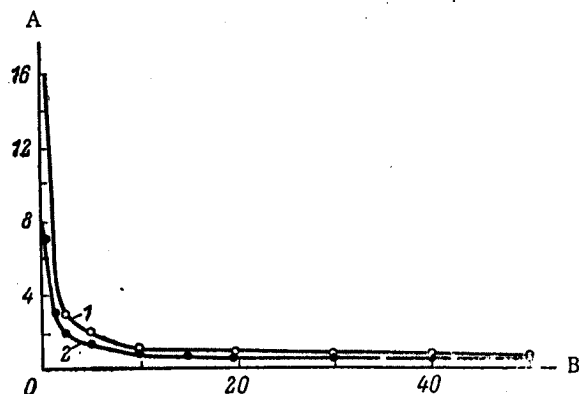


Fig. 2. Change in the permeability of the diaphragm with time; the diaphragm was shaped in water. A) Permeability (ml/h from one specimen); B) time (h). Pressure (mm water): 1) 1170; 2) 460.

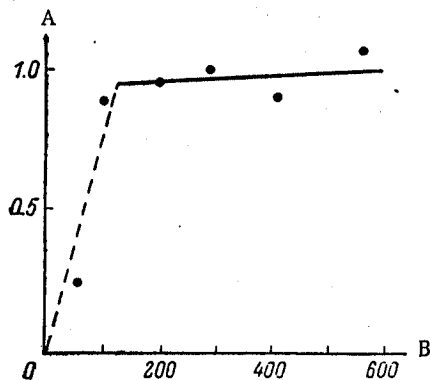


Fig. 3. Dependence of the stationary permeability of the diaphragm on the pressure; the diaphragm was shaped in water. A) Permeability (ml/h, from one specimen); B) pressure (mm of liquid); the same symbols are used for Figs. 4-6, 8 and 9.

Figure 2 shows the change in permeability with time for ordinary asbestos diaphragm paper manufactured by the Yaroslavl' asbestos factory; the diaphragm was shaped in water. As shown by Stender and co-workers [1], this decrease in the permeability of the diaphragm is due not to blockage by impurities but to a change in the diaphragm itself.

The dependence of the permeability of shaped diaphragms on pressure is shown in Fig. 3. It can be seen that from a pressure of approximately 10 cm of water, the permeability is almost independent of the pressure; increase in the pressure by factors of 2-3 increases the permeability by only a few percent.

Thus when the diaphragm is shaped in water the relationships observed (at a pressure greater than 10 cm of water are the same as those observed by Stender and co-workers [2] for brine and alkali solution. Stender attributed the fact that the permeability is independent of pressure to the mechanical action of pressure on the diaphragm, as a result of which the asbestos fibers are compressed slightly and the pores between them become narrower, the effect being greater, the greater the pressure. The decrease in the pore diameters, leading to a decrease in the permeability, compensates for the increase in permeability resulting from the increased pressure, as a result of which the permeability remains almost independent of pressure.

The change in permeability takes place throughout the whole period of operation of the diaphragm, a rapid decrease in permeability taking place initially, after which the permeability decreases extremely slowly (Fig. 2). This slow change appears to us to be due to a gradual change in the properties on the asbestos fibers as a result of the slow penetration of water between the very fine crystallites.\*

When the diaphragm is shaped in brine or electrolytic alkali solution, a slight increase in permeability is observed in the first few days and this is followed by a smooth decrease in permeability. The increase in the permeability is probably due to the gradual displacement of air bubbles from the pores of the diaphragm [1]. Some part in the increase in permeability is possibly played by an increase in the elasticity of the asbestos fibers on wetting [3, 4, 8], which may lead to uncoiling and "mutual repulsion" of the fibers, i.e. to an increase in the pore dimensions. When the diaphragm is shaped in water, these phenomena are masked by the marked decrease in permeability and are therefore not observed.

The dependence of the permeability on pressure for a diaphragm shaped in brine is shown in Fig. 4 and that for

\*A number of workers have established that the adsorption of various substances by asbestos and the swelling of asbestos in different media are accompanied by the introduction of water and other substances between the microscopic fibers of the asbestos [3-6]. At the same time the phenomena of adsorption and swelling in asbestos continue over a period of many days [7].

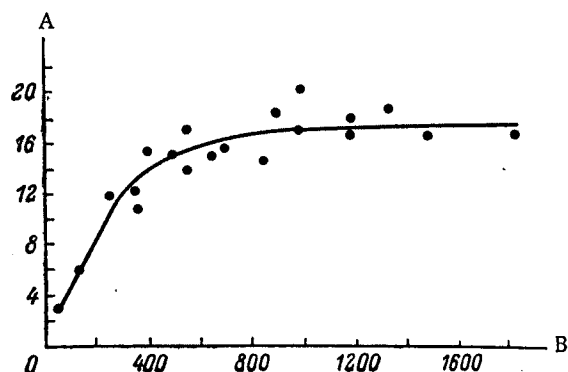


Fig. 4. Dependence of the stationary permeability of the diaphragm on pressure for a diaphragm shaped in brine.

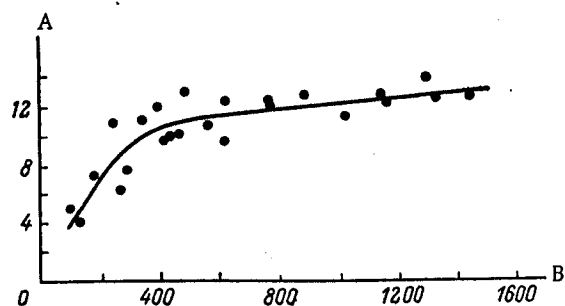


Fig. 5. Dependence of the stationary permeability of the diaphragm on pressure for a diaphragm shaped in electrolytic alkali solution with an NaOH concentration of approximately 100 g/liter.

sion of the diaphragm under a high pressure leads to a decrease in its permeability below the normal value. An analogous picture is obtained in brine.

Even more characteristic data are given in Fig. 7. A number of diaphragm specimens shaped under different pressures were then subjected to the same pressure of approximately 30 cm of alkali solution. The permeability was found to be lower, the higher the original pressure. In this experiment the specimens were under the same pressure and were therefore undergoing almost identical elastic deformation. The differences in the permeability can therefore be due only to irreversilbe deformation.

Here we may also have slight differences in elastic deformation as a result of differences in the structure of diaphragms shaped at low and high pressures. This factor also, however, is ultimately due to inelastic compression.

The part played by irreversible deformations in the operation of diaphragms may be illustrated by the following calculation. The permeability at a pressure of 150 cm is greater than the permeability at 50 cm by a factor of only 1.17, although the pressure is three times greater. This means that the permeability coefficient is smaller by a

the diaphragm shaped in electrolytic alkali solution with an NaOH concentration of approximately 100 g/liter is shown in Fig. 5. The Figures show clearly two regions in which the nature of the dependence of the permeability on pressure differs considerably.\*

At pressures up to 35 cm of brine (or alkali solution), the permeability increases rapidly with increase in pressure, although the rate is slightly less than that corresponding to direct proportionality. At higher pressures the permeability shows almost no increase, even for a 4-5-fold increase in pressure.

With increase in the pressure on a previously-shaped diaphragm, the permeability at first increases sharply and afterwards decreases with time, acquiring the normal value for the given pressure. This phenomenon is evidently related to further gradual compression of the diaphragm by the increasing pressure.

An interesting feature is that on going from an empty "cathode" compartment, i.e. the compartment beyond the diaphragm, to a compartment filled with electrolyte, the same change in permeability with time is observed.

Our experiments gave clear proof that the compression of the diaphragm is for the most part irreversible. If the compression were elastic, the stationary permeability of the diaphragm would depend only on the pressure applied to it at a given moment and would be independent of the pressure to which it was previously subjected. This is not the case, however.

Figure 6 shows the stationary permeability of several diaphragm specimens after their first shaping, after increase of the pressure on the diaphragms, and after return to the original pressure. It can be seen that preliminary compression of the diaphragm leads to a decrease in its permeability below the normal value.

\*The difference in the specific gravities of the brine (1.20) and the alkali solution (1.22) is neglected in the subsequent discussion, since the corresponding correction to the value of the pressure is much less than the error in the determination of the position of the point of inflection on the curves in Figs. 4 and 5.

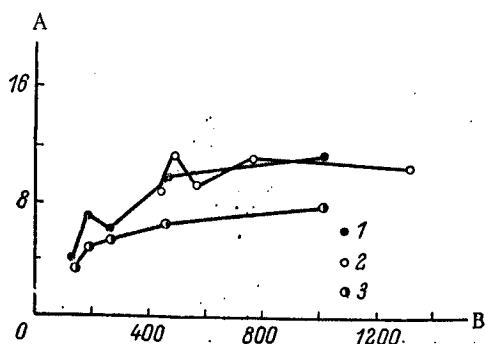


Fig. 6. Dependence of the stationary permeability of the diaphragm on pressure after initial shaping in electrolytic alkali solution (1), after increase in pressure on all the specimens (2), and after return to the original pressure (3).

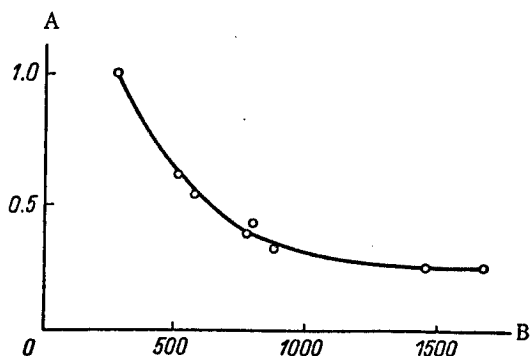


Fig. 7. Dependence of the stationary permeability of the diaphragm at a constant pressure of 300 mm of alkali solution on the pressure under which the diaphragm was shaped beforehand. A) Permeability (fraction of the normal permeability for a pressure of 300 mm); B) maximum pressure during the shaping of the given specimen (mm of alkali solution).

factor of 2.56 at high pressure. From the curve in Fig. 7 we find that the difference in the permeability coefficients due only to irreversible deformation amounts to 2.42, i.e. the elastic deformation changes the permeability coefficient by a factor of only 1.06. Thus the fact that the permeability is independent of pressure is due chiefly to irreversible changes in the diaphragm, elastic compression playing a subsidiary part.

The nature of these irreversible processes is not completely clear. It is most probable that in this case we have a change in the mutual orientation of some of the fibers and the production of more compact packing.

It should be noted that the data of some of the experiments of Stender and co-workers[1] indicate the existence of inelastic compression but no attention was previously paid to this.

The rate of filtration of brine in the high-pressure range is on the average 1.4 times greater than the rate of filtration of the alkali solution; this is almost entirely due to the greater viscosity of the alkali solution. This result shows some disagreement with the data obtained by Stender and co-workers[1], who obtained a lower permeability coefficient for diaphragms shaped in alkali. The reason for this apparently lies in the fact that these authors in their experiments used paper made from Canadian asbestos, some of whose physicochemical properties differ from those of the Urals asbestos from which our specimens were prepared.

The most difficult problem to explain is the difference previously observed in the GIPKh work, and shown even more clearly by the above data, in the results obtained when the asbestos paper is shaped in water and in concentrated electrolyte solutions—brine and alkali.

The permeability of the diaphragm in water, with a correction for the viscosity, is on the average smaller by a factor of 25 and the pressure at which the permeability becomes constant is smaller by a factor of 4.

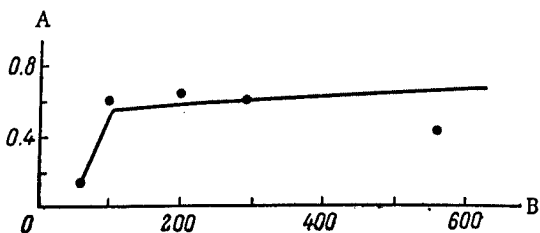


Fig. 8. Dependence of the stationary permeability of the diaphragm on pressure. Filtration of brine through a diaphragm previously shaped in water.

Stender [1, 2] states that this difference is probably due to the action of colloid-chemical factors. Our aim was not to determine the mechanism of these phenomena but it appears possible to put forward certain preliminary ideas regarding this mechanism.

The colloidal properties of asbestos [9, 10] are shown in particular by its ability to undergo swelling [10].

According to Deryagin [11-13], the swelling process is due to the so-called splitting action of the fine (of the order of  $10^{-3}$ - $10^{-1}$   $\mu$ ) elastic layers of liquid, which be observed. In dilute electrolyte solutions the splitting action

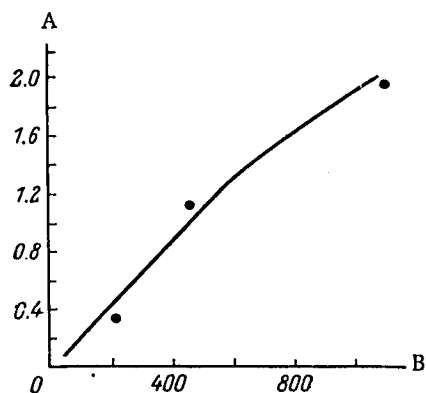


Fig. 9. Dependence of the stationary permeability of an asbolatex diaphragm on pressure for shaping in water.

In connection with the difference in the splitting action of water and concentrated solutions, another explanation for the observed phenomena may be put forward. It is known that the solvate layers on the surface of a solid may exhibit increased viscosity [14], as a result of which the effective radius of the pores decreases. This effect is appreciable for pores of very small radius, in particular for the filtration of water through clay soils.

If during the shaping of a diaphragm in water the solvate layers produced a significant change in the radius of the pores, the replacement of water by brine at the end of the shaping process would lead to an increase in the effective pore dimensions and hence to a considerable increase in the permeability coefficient. In actual fact the change to brine produced no change in the permeability coefficient.

The relevant data are shown in Fig. 8, in which the curve was calculated on the basis of the permeability coefficient values obtained for shaping in water. Thus the difference in the shaping of the diaphragm in water and in brine is due not to a decrease in the effective radii of the pores by the solvate layers but to the difference in the influence of the medium on the actual shaping process. The diaphragm shaped in water retains its structure and its characteristics even after the water has been replaced by brine. As a result of this, although the diaphragm is impregnated with brine, its permeability is smaller by a factor of approximately 25 and the inflection on the permeability curve lies at a pressure which is 25 cm lower than that for normal shaping in brine.†

Unlike the case of ordinary asbestos paper, the asbestos fibers in paper containing added latex are attached to one another by rubber-like films. These highly elastic films prevent the irreversible deformation of the diaphragm (experiments on the shaping of an asbolatex diaphragm with current passing showed that its deformation is completely elastic). Throughout the whole range of pressures studied, the permeability of this type of diaphragm increases with increase in pressure, although the permeability is not apparently directly proportional to the pressure (Fig. 9).

#### SUMMARY

The permeability of a diaphragm of ordinary asbestos paper shaped in the absence of current is almost independent of the pressure after the latter reaches a certain value. For the case of shaping in water this value is approximately 10 cm of water, but in brine and electrolytic alkali solution the value is approximately 35 cm of these liquids. The fact that the permeability is independent of pressure is due chiefly to irreversible changes in the diaphragm, increasing with increase in pressure. Inelastic deformations play a subsidiary role. The permeability of an asbolatex diaphragm depends on pressure through the whole range of pressures studied.

\*The use of purer water would have been pointless, in view of the unavoidable extraction of electrolytes from the asbestos paper [1, 3].

†The effect of preliminary shaping in water is not preserved after the current is switched on.

# LITERATURE CITED

1. V. V. Stender, M. I. Ravich, S. A. Mamulov, and I. G. Zhornitskii, Collection, Asbestos Diaphragms, Proceedings of the GIPKh [in Russian], 22 (1934).
2. V. V. Stender, The Electrolytic Production of Chlorine and Alkalies [in Russian], ONTI Khimteoret. L. (1935).
3. F. V. Syromyatnikov, Min. syr'e, 5, 99 (1930); D. N. Tarasenkov, Min. syr'e, 6, 76 (1931).
4. L. M. Pidgeon, and A. van Winsen, Canad. J. Research, 9, 153 (1933); 10, 1 (1934).
5. V. V. Shelyagin, Min. syr'e, 6, 52 (1931); Collection, Asbestos and its Application in Building [in Russian], Izd. VORS, 46 (1932).
6. N. E. Vedeneeva, Koll. zh., 12, 88 (1950).
7. E. N. Kitaev, Asbest, 3, 5 (1936); 10, (1), 28 (1937).
8. I. L. Rabinov, Asbest, 3/4, 16 (1935); R. I. Gringauz, Asbest, 52.
9. P. N. Shablykin, Min. syr'ev, 3, 695 (1928); 6, 47 (1931).
10. V. A. Naumov, and A. A. Avetisyan, Min. syr'e, 6, 66 (1931).
11. B. V. Deryagin, The Properties of Thin Liquid Films and Their Role in Disperse Systems [in Russian], 1. Izd. VSNITO, M. (1937).
12. B. V. Deryagin, Izv. AN SSSR, ser. khim., 741 (1936); 1113 (1937).
13. B. V. Deryagin, Friction and Lubricating Action [in Russian], Izd. Un-ta im. N. D. Zelinskogo. VKhO, M. (1938)
14. B. V. Deryagin, and E. F. Pichugin, DAN SSSR, 63, 53 (1948).

---

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

---