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**SILVER MIGRATION AND TRANSPORT MECHANISM
STUDIES IN SILVER OXIDE-ZINC BATTERIES**

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CALVIN COLLEGE

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FOREWORD

This report was prepared by Calvin College, Grand Rapids, Michigan, for the Aero Propulsion Laboratory at Wright-Patterson Air Force Base, Ohio, under Contract No. AF 33(615)-1236, Project No. 8173, Task No. 817304-16. Mr. J. E. Cooper is task engineer for this project.

This is a final report summing up the work performed under the above mentioned contract.

A B S T R A C T

Methods for testing the ability of separator materials to allow the diffusion of dissolved silver oxides, zincate ions, and hydroxide ions, have been checked to determine the reproducibility of the diffusion rates obtained by these methods. The results have also been studied to determine the applicability of Fick's first law of diffusion to these processes.

The use of surfactants in the electrolyte and in the zinc electrodes has been studied. The effect of these substances on cycle life and on various zinc electrode processes was measured. The greatest effects noted were those associated with the zinc electrode processes.

Various aspects of the decomposition of silver oxide in aqueous KOH were studied, particularly the effect of solid materials, some ions, and separator materials. A possible mechanism for these effects is given. This decomposition is very closely related to the deposition of silver on the separators in silver-alkaline batteries.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or conclusions contained herein. It is published for the exchange and stimulation of ideas.

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INTRODUCTION

The silver-zinc alkali battery has been of considerable interest as a power source because of its potentially high watt-hour per pound output. As yet this potential has not been realized. Part of the difficulty appears to be related to the separators that are used in such batteries, and part to the zinc electrode.

Studies of the separators taken from silver-zinc cells have shown that silver is deposited on the separators and that some passes through the separators. The amount of silver deposited on the separators varies with the type of material used. The silver which passes through can produce local cell action on the zinc electrode, thus promoting self-discharge. It has often been assumed that the silver which deposits on the separators may, in time, lead to electrical shorts between the positive and negative plates.

Thus the relationship of the separator to the transport of silver in a cell has come to be recognized as one of the problems requiring further study and solution before an improvement in the watt-hour per pound output of the silver-zinc cell can be realized.

Another problem area is the zinc electrode. During cycling the zinc tends to leave the electrode and become distributed throughout the cell. This also may lead to internal metallic shorts. Furthermore, this action decreases the capacity of the negative (zinc) electrodes.

These facts indicate certain desirable characteristics that any separator material must have: (a) ability to prevent transport of dissolved silver oxides; (b) ability to prevent the transport of zincate ions; (c) ability to allow hydroxide ions to diffuse freely from one electrode to the other for reaction. These characteristics can be tested outside a battery but the design of the experimental set-up and the reproducibility of the results need further study. These matters have been studied under this contract.

In recent years surfactants that are compatible with strongly alkaline solutions have become available. These materials do change some of the characteristics of the electrolyte, e.g., surface tension. Because of this, the availability of the KOH in the various parts of the cell may also change, and this could conceivably modify the cycle life of a silver-zinc cell. One of the main aims of the work being done under this contract was to investigate the effect of surfactants on the various processes taking place in the silver-zinc cell.

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SEPARATOR TESTING METHODS

In testing whether a given material can serve as a separator in a silver-zinc battery, attention must be given to the effect such a material has on the diffusion of zincate ions, dissolved silver oxide, and hydroxide ions. Ideally the first two of these should be prevented from diffusing while the third should be able to diffuse freely. Methods for testing the extent to which a given material allows these ions to diffuse through have been described (ref. 1). Further work has been carried out to refine and test these methods.

Zincate Ion Diffusion

The obvious method for testing this involves a device in which the separator to be tested is inserted between two solutions: one a zincate solution and the other a solution containing no zincate. The rate at which zincate diffuses into the latter can then be measured by a suitable analytical technique. This technique must be capable of quantitatively determining small concentrations of zincate. Two such methods which do not involve extensive sampling or the addition of reagents are available.

a. The first method, (ref. 1, p. 115) uses a measurement of $e m f$ to determine the concentration of zincate ion. In all our work cellophane was used as the membrane and 30% KOH was used on both sides of this membrane. ZnO was added to one of these solutions, and it will be called the zincate solution. The other will be called the KOH solution.

This $e m f$ method has the advantage of not disturbing the solution; it requires no sampling, and it is relatively rapid. However, at times there was a rapid voltage decrease at the beginning of the run and the voltage did not always recover to the approximate value before the run started. Figure 1 shows two voltage vs. time curves for similar solutions. No reasons for this difference have readily come to mind, and runs, in which the sharp voltage dip occurs, generally gave higher rates for the diffusion of zincate ions through the membrane. Taking all this into account, the reproducibility we have obtained with this method is about $\pm 20\%$.

b. The second method of analysis uses radioactive zinc as a tracer. Zn^{65} has a half-life of 246 days and so no correction need be made for normal decay in runs lasting a day or two. The cell case used is the same as that used in the $e m f$ method. One-half ml. samples of solution are removed for counting at various time intervals. The ratio of counts/minute to grams of zinc was determined by titrating a sample of the zincate solution with EDTA to determine zincate content. Another sample of the

same solution was counted for radioactivity. The energy spectrum of the gamma emission from Zn^{65} covers a narrow range and only this energy range was counted in a well-type scintillation counter. Because of this, the background was very low, about 5 counts/minute.

A typical set of results is shown on Figure 2. These were made on the same type of system as used to get the results of Figure 1. The decrease of zincate ion on one side and the increase on the other side vary linearly with time. Furthermore, the sum of the counts on both sides of the membrane add up to the total amount of radioactivity introduced into the system. The reproducibility we obtain for zincate diffusion rates determined this way is $\pm 10\%$.

The rate of zincate diffusion was calculated. First the number of counts on the KOH side was corrected for change in concentration gradient during the time elapsed. Because the count rate changes linearly with time, this can be done by multiplying the count rate by the following factor:

$$\frac{\text{Initial count rate of zincate solution}}{\text{Count rate of zincate solution at } 0.5t}$$

where t is the time at which the sample was taken. For more precise results the count rate of the KOH solution should be subtracted from the term in the denominator. This, however, would change the correction factor hardly at all.

The corrected count rate (CCR) was then used as follows:

$$\text{rate in moles/sq.in./min.} = \frac{\text{CCR} \times M \times .165}{\text{ICR} \times t \times A}$$

where ICR is the initial count rate of the zincate solution;

M is the molarity of the zincate solution;

.165 is the number of liters of KOH solution;

A is the area (sq.in.) of the membrane through which diffusion takes place.

In general, the results obtained using Zn^{65} are about twice those obtained by making e m f measurements. Part of the difference between the values calculated by these two methods is due to the method of calculation. In the e m f method, an initial voltage reading is obtained, and this is used to get an initial zincate concentration on the KOH side. This is generally of the order of $2 \times 10^{-4}M$, and is subtracted from the final zincate molarity on the KOH side when the diffusion rate is calculated. With the isotope method, an initial zincate concentration of zero is used for the KOH side. Using cellophane in 30% KOH this difference in calculation introduces a difference of about 15% in the diffusion rate values, with the isotope method giving the larger value.

The rest of the difference between the values calculated by these two methods relates to the potential of the zinc electrode. Several runs were made in which both types of measurements were used. From the count rate, the concentration of zincate in the KOH side was calculated. This was compared with the molarity calculated from e m f values using a table in ref. 1, p. 123. These comparisons showed that our electrode system was giving a voltage 10 mv. higher than it should have. This is not an unexpected difference. But it does point up the fact that in using the e m f method a calibration curve should first be made for a given electrode system. This needs to be done if one desires more precise absolute values. The relative values are substantially unchanged.

Another set of runs was made to see whether Fick's first law of diffusion does describe the behavior of these solutions. Solutions of different zincate concentrations in 30% KOH were used. The results, shown on Figure 3, were obtained using the e m f method. The raw data are linear, indicating that Fick's law is applicable to these systems. The corrected data were obtained by dividing the raw data by the zincate concentration gradient at the beginning of each run, thus giving results that correspond to an initial zincate concentration gradient of 1 molar. The circles are the average value, and the bars represent the high and low values obtained for each solution. The line through these values has a slight curvature, but it is very close to being linear, again indicating that Fick's law is applicable. The viscosity of these solutions is also shown but there appears to be no relationship between these values and the zincate diffusion rate, suggesting that viscosity is not a factor affecting the rate of zincate diffusion under these conditions.

The above methods describe tests for zincate diffusion through a membrane outside a battery. An attempt was also made to simulate battery behavior in determining zincate diffusion. Small cell cases such as shown in Figure 4 were used. A cellophane membrane was clamped between the two halves, and 20 ml. of 30% KOH were used as the electrolyte on each side. A zinc electrode was placed in one compartment and a cadmium electrode in the other. Both electrodes were 1.5" x 2". Such a cell was cycled four times at 50 ma. Each cycle consisted of a 2.75 hour charge and a 2.5 hour discharge. At the end of the cycling the electrolyte in the cadmium electrode compartment was titrated with EDTA to determine its zinc content. This would be the zinc that had diffused from the zinc electrode and through the cellophane. The results were not at all reproducible. Cellophane does allow zincate ions to diffuse through it, but the amounts found in the cadmium electrode compartment varied from 3.6 to 18.2 mg ZnO/ml. for eight different runs. This is due to several factors. The concentration gradient across the membrane varies throughout the cycling, and the zincate formed from the zinc electrode may settle downward giving different concentration gradients across various parts of the membrane.

These results seem to indicate that while diffusion rate tests may show that zincate ions diffuse more rapidly through one membrane than through another, this fact cannot necessarily serve as a basis for determining relative amounts of zincate that will diffuse through a membrane in a silver-zinc cell that is being cycled.

Silver Ion Diffusion

The method used for measuring the diffusion of dissolved silver oxide through a membrane has been described in ref. 1 (p. 103). However, several runs were made to determine the reproducibility of the results obtained by this method. The electrolyte was 45% KOH and the membrane was cellophane. Three separate runs were made and the results obtained for the rate of silver diffusion through the membrane were 0.9×10^{-7} , 2.1×10^{-7} , and 3.9×10^{-7} grams/sq.in./hr. This is an indication of the type of reproducibility that can be expected.

The cause of this lack of good reproducibility is not the method but the chemical nature of the system, and this must be taken into account whenever such measurements are made. The dissolved silver oxide undergoes a spontaneous decomposition in aqueous potassium hydroxide, and this decomposition is responsible for the lack of reproducibility. The manner of this decomposition is discussed later in this report, page 14.

Hydroxide Ion Diffusion

The method used is described in ref. 1 (p.93). Several runs were made to check whether Fick's first law of diffusion, that the rate of diffusion is proportional to the concentration gradient, is applicable to this process. Different concentrations of KOH were used, and the rate of diffusion of the hydroxide ion through various membranes into pure water was measured. At the same time, the viscosity of each KOH solution was also measured.

The data are presented on Figure 5 and Figure 6. The diffusion rates (raw data) are practically linear with KOH concentration. Furthermore, when the diffusion rates are divided by the KOH concentration to give, in effect, the diffusion rate assuming a concentration gradient of 1 molar for all solutions, the results are constant within experimental error, Figure 5. Both of these factors show that Fick's first law of diffusion does hold for these solutions. Furthermore, though the viscosity of the solutions increases markedly as the KOH concentration increases, the rate of diffusion of the hydroxide ions does not appear to be affected except perhaps at the highest KOH concentrations. The polyethylene material allowed the hydroxide ions to diffuse too readily for significant measurements to be made in KOH concentrations above 6 M.

USE OF SURFACTANTS

In recent years surfactants that are compatible with strongly alkaline solutions have become available. These materials do change some of the characteristics of the electrolyte, e.g., surface tension. Because of this, the availability of the KOH in the various parts of the cell may also change, and this could conceivably modify the cycle life of a silver-zinc cell.

Ten different surfactants were used in this work. These will be designated by number throughout this report. The chemical composition of these is given in Table I.

Effect of Surfactants on Cycle Life

To get some idea whether surfactants had any significant effect on the cycle life of silver-zinc cells, eleven small three-plate cells were prepared for cycling. Each cell contained one silver and two zinc electrodes. The size of these electrodes was 1.5 x 2 inches. One layer of fibrous sausage casing was used to separate the silver from the zinc plates. Lucite spacers were used to pack the plates tightly together, and 30% KOH was added to each cell in an amount sufficient to reach the tops of the plates. The separators extended about 1/4 inch above this electrolyte level. The cells were cycled in series. Each cycle consisted of a 1.5 hour charge at a constant potential of 2 volts per cell and a 1.5 hour discharge through a resistor. The average current during discharge was about 100 ma.

In one cell the electrolyte consisted of the 30% KOH with nothing added. To the 30% KOH in each of the other cells a different surfactant was added. The amount added was less than 1%. Solubility was a limiting factor.

Table II gives a summary of the results. Only one cell of each kind was tested. Consequently, the extent to which these results can be reproduced is unknown. However, there are some differences which seem to have significance. Thus surfactants 7-10 had definitely longer cycle life than the control. Because of these differences, it seems reasonable at this time to entertain the hope that surfactants may increase the cycle life of silver-zinc batteries.

The results in Table II were for cells in which the current density was about 5 ma./sq.cm. at the zinc electrode during discharge. This is a rather low current rate. Consequently, more cells were assembled in order to determine the effect of these surfactants at higher current densities.

The cells and cell cases were the same as those described above except that one zinc and two silver electrodes were used. The cells were charged for 85 minutes at a constant cell voltage

of 2 volts/cell with nine in a series and discharged through a resistor. The discharge current density was about 30 ma./sq.cm. Three cells of a kind were used. The results are given below.

<u>Surfactant</u>	<u>Ave. No. of Cycles</u>	<u>Range</u>
2	84	80-91
7	72	56-91
8	81	68-95
9	90	70-130
10	79	45-125
none	99	80-125

Considerable gassing was noted with surfactant No. 2. The other surfactants gave no improvement in cycle life. Reproducibility, shown in column 3, was not very good.

Because the use of surfactants did appear to improve cycle life at lower current densities, further studies were made of the effects these surfactants may have on various processes that take place in a silver-zinc battery.

Effect of Surfactants on the Amount of Silver Deposited on Cellophane

The cell case used in this work is shown on Figure 4. The membrane was cellophane. This has been chosen because it has been widely used as a separator material in silver-zinc batteries. Cellophane picks up most of the silver that gets into the electrolyte and allows very little to penetrate through it. Consequently, by using cellophane as a membrane in the test cells, it is possible to study the effect of various factors on the amount of silver that leaves the electrode merely by determining the amount of silver on the cellophane after such a run.

The electrodes were approximately 1.5 inches x 2 inches and each electrode compartment held 18 ml. of electrolyte. One electrode was a sintered silver and the other a cadmium electrode.

The amount of silver on the cellophane was determined by dissolving the silver from the cellophane in 2 M nitric acid and then titrating the dissolved silver with a KI solution that is approximately 10^{-3} molar. This is a potentiometric titration which uses a saturated calomel electrode as the reference and a silver wire as the indicating electrode. A stream of nitrogen is used to stir the solution and the cell case is painted black to avoid photo effects. The solution is made just slightly acid before titration. Three minutes are allowed to elapse between the additions of the KI solution. This is done to insure equilibrium at the silver electrode. Special care must be used to avoid the presence of chloride ions. These ions react also with the dissolved silver and cause the silver electrode to appear rather inert.

In order to determine the precision of this method, four

samples of a given silver nitrate solution were titrated with the following results:

Sample 1	$2.47 \times 10^{-4} \text{M}$
Sample 2	$2.47 \times 10^{-4} \text{M}$
Sample 3	$2.45 \times 10^{-4} \text{M}$
Sample 4	<u>$2.45 \times 10^{-4} \text{M}$</u>
Average-----	$2.46 \times 10^{-4} \text{M}$

The precision of the method thus is 0.4%.

Each time that a new variable was studied, such a cell was cycled in series with a control cell. The control cell contained 30% KOH as the electrolyte.

In order to judge the variation to be expected by this method of procedure, four control cells were cycled in series. Three cycles were completed consisting of a 2.75 hour charge at 40 ma. and a 2.75 hour discharge at 35 ma. At the end of this time the membranes were soaked in deionized water for 24 hours and then analyzed for silver content. The results were as follows:

No. 1	$10.1 \times 10^{-4} \text{ gms. Ag.}$
No. 2	$9.3 \times 10^{-4} \text{ gms. Ag.}$
No. 3	$8.0 \times 10^{-4} \text{ gms. Ag.}$
No. 4	<u>$8.2 \times 10^{-4} \text{ gms. Ag.}$</u>
Average---	$(8.9 \pm 0.8) \times 10^{-4} \text{ gms. Ag.}$

These results indicate that the reproducibility is good only to $\pm 10\%$. There are several reasons for this poor reproducibility. It may mean that the amount of silver that leaves the electrode and gets into the electrolyte depends on other variables than current density, KOH concentration, or temperature. It may also mean that the silver that is picked up by the cellophane is of a certain variety, e.g., larger than a minimum particle size, or of a certain ionic species. A companion assumption then is that the silver that gets into the electrolyte is not all of the same species and that the distribution of silver into the various species is dependent on factors other than those mentioned above.

There is another factor that is likely responsible for most of these deviations. Earlier work (ref. 2) has indicated that the amount of silver introduced into the electrolyte depends on the voltage level at which cycling occurs. This is borne out by results which will be presented later in this report.

Samples Nos. 1 and 2 as shown on the previous page were cycled only at the Ag/Ag₂O level while samples Nos. 3 and 4 were cycled to some extent on² the Ag₂O/AgO voltage level. This undoubtedly accounts for the differences shown on the preceding page. Because of individual differences between silver electrodes the amount of time which an electrode spends on each of the two silver oxide voltage levels is not always controllable. Where this behavior is similar, Nos. 1 and 2 or Nos. 3 and 4, the amount of silver picked up by the separator is reproducible to much better than 10%.

Very small amounts of the surfactants were added to the electrolyte. In many cases this was necessary because of their very limited solubility. When the surfactants were in the liquid form, 4 drops per 100 ml. of electrolyte were used. In these runs silver was always the positive electrode, cadmium the negative electrode, and 30% KOH the electrolyte. The current was about 40 ma. and each cell was cycled three times: 2.75 hours charge and 2.75 hours discharge. The results are given in Table III. A survey of the results indicates that the surfactants as used in these runs do not significantly alter the amount of silver deposited on the cellophane during cycling.

Effect of Surfactants on the Rate of Silver Diffusion Through a Membrane

The method used was the same as that referred to on page 5 of this report except that 30% KOH was used as the electrolyte. The surfactant was added to the KOH containing the dissolved silver oxide. The results are summarized in Table IV. The values in this table are adjusted for the concentration gradient of silver across the membrane. The actual rate values were divided by the silver concentration gradient at the beginning of the run. Consequently, these rate values are for a hypothetical initial silver concentration gradient of 1 molar.

There are some differences in the rate values given in Table IV, but they are within the limits of reproducibility. In fact, reproducibility is not too good as seen by comparing the two values for the solutions without surfactants. This lack of reproducibility is due to the decomposition of the dissolved silver oxide. This decomposition depends on several factors. Since these factors cannot be completely controlled during a silver-diffusion run, the extent of decomposition of Ag₂O, and hence the concentration of dissolved silver, is not precisely known at any time. However, since no large differences were noted in Table IV, it seems safe to conclude that the presence of surfactants has no great effect, beneficial or adverse, on the diffusion of dissolved silver through a cellophane membrane.

Effect of Surfactants on the Rate of Zincate Diffusion Through Cellophane

The method used in this work is the one described in ref. 1 (p. 115). The surfactants were added to the zincate solution. A summary of the results is given in Table V. When one considers that the reproducibility of this method is $\pm 20\%$, then it is evident that the surfactants have no significant effect on the diffusion of zincate ion through cellophane. Surfactants 5 and 6 give a slightly lower value but the difference is not great.

Effect of Surfactants on Hydroxide Ion Diffusion

The method used for this work is described in ref. 1 (p. 93). Two separator materials were used: cellophane and fibrous sausage casing. The electrolyte was 30% KOH and at this concentration the samples of polyethylenes which were available allowed the OH^- ions to diffuse too rapidly for precise rate measurements. A summary of the results is given in Table VI. Again the effect of surfactants is negligible.

Effect of Surfactants on Zinc Electrode Processes

1. Plating or Charging Process

A particularly serious problem of the silver-zinc alkaline cell is the apparent inability of the zinc to assume its former position on the negative plate during charge. On discharge a soluble zinc oxide or hydroxide is formed. This dissolves in the electrolyte. The charge process then may, as a first approximation, be considered as the plating of zinc from a zincate solution. The type of zinc plate obtained depends on several factors such as zincate concentration and current density. Ordinarily the zinc plate obtained from a zincate solution in 30% KOH is spongy and non-adherent. Often this can be remedied by the presence of small amounts of addition agents.

An ideal addition agent would be one which would give a good adherent zinc plate over a wide range of current densities and a wide range of zincate concentrations. In an operating silver-zinc battery the current density during charge may vary because of variations in charging current, but it may also vary from place to place on a given negative electrode. Furthermore, the zincate concentration in the electrolyte decreases as charging progresses, and it may vary from top to bottom in the cell. For these reasons an ideal additive should give an adherent plate over a range of current densities and zincate concentrations.

A common way of studying the effect of current density on the nature of a metal plate is by the use of a Hull cell. Because of the geometry of this cell, a given current rate covers a range of current densities on the electrode being plated.

A regular commercial Hull cell of 267 ml. capacity was used in this work. The range of current densities studied was 0.2 to 30 ma/sq.cm. The electrolyte was always 30% KOH. About 1% of surfactant was added to this, and the amount of zincate was varied. The latter was evaluated by titration with EDTA. Six surfactants were tried and with each one the zincate concentration was varied from about 0.15 to 0.7 molar. The presence of gassing was also noted during the plating process, and the plates were examined visually after the current had passed for one hour. A summary of the results is given on Table VII.

It is obvious that, of the surfactants tried, none meets the requirements of an ideal additive. Surfactants 7 and 8 most nearly meet the requirements but have the disadvantage of promoting hydrogen evolution. Surfactant 9 did not cause gassing but its plating characteristics were not much better than 30% KOH without additive. In general, all the surfactants used gave adherent zinc deposits over a wider range of current densities and zincate concentrations than did the 30% KOH solutions. This may be part of the reason why the addition of surfactants to the electrolyte may improve the cycle life of silver-zinc cells. However, they likely cannot be used in sealed cells unless some means is found to reduce the pressure caused by gassing at the zinc electrode on charge.

2. Additives to the Zinc Electrode

One of the disadvantages to the use of the zinc electrode is that with continued cycling the material tends to leave the grid. Attempts have been made to find a material which, when incorporated into the zinc electrode, will prevent this. Some polymeric materials have been tried with a bit of success. Because some of the surface active materials appear to improve some of the performance characteristics of the silver-zinc cell an attempt was also made to incorporate these in the zinc electrode.

The zinc electrodes were prepared by making a paste of ZnO and water and the surfactant. This paste was applied to a silver screen grid and the electrode was then inserted in a cell and formed.

The cell cases were the same as those referred to on page 6. The electrodes were 1.5 x 2". Three electrodes, two silver and one zinc, were used in each cell and the electrolyte was 30% KOH. One layer of fibrous sausage casing was used to separate the plates from each other. Lucite spacers were used to pack the electrodes tightly in the cell case.

The cells were cycled with 9 in a series. The charge lasted 85 minutes and was carried out at a constant cell voltage of 2 volts per cell. The discharge was through a 25 ohm resistor and lasted 35 minutes. In each series of 9 cells

there was one cell that served as control, i.e., its zinc electrode had no additive. Cells were removed from cycling when the voltage reversed on discharge. The surfactants were added in amounts of 1% and 2% of the amount of ZnO and duplicates were prepared in each case. The following surfactants were used: 2, 6, 7, 8, 9, 10. Some zinc plates to which molybdenum dioxide was added were also prepared.

In evaluating the results obtained, only those cells which gave a cycle life at least as great as the control were considered promising enough for further study. A summary of the results is given on Table VIII. In most instances a 1% addition of additive served better than a 2% addition.

These preliminary studies indicate that only surfactants 7, 8, and 9 offer enough promise for improving the zinc electrode to warrant further investigation.

3. Passivation Current Density

The purpose of this study was to determine whether surfactants have any effect on the limiting current density at which a zinc anode becomes passive. This is analogous to the limiting current density for the zinc electrode during discharge of a silver-zinc battery. The method used in this work was that described by Huber (ref. 3). The zinc anode in this case was a pure zinc rod, $\frac{1}{4}$ inch diam., encased in polystyrene. The cross section of the rod at the end of the polystyrene tube was polished and was the only surface exposed to the electrolyte. The electrolyte again was 30% KOH and the same surfactants as are listed in Table I were used. In each run the current was slowly raised and the potential of the zinc anode vs. a Hg/HgO reference electrode was measured. At the passivation point, both the current and the potential of the zinc anode dropped considerably. The results are given in Table IX. In general, the limiting current density is decreased when surfactants are present. The exceptions were surfactants 2, 9, 10. This means that, generally speaking, the use of surfactants may lower slightly the discharge current density of the zinc electrode. Generally, however, the difference is not great.

4. Polarography

Polarograms were also determined for alkaline zincate solutions containing surfactants. The solutions were about 10^{-3} M in ZnO in 30% KOH. While the reduction of zincate ions at a dropping mercury electrode is not the type of process that takes place in a silver-zinc cell, yet such polarograms may give information on whether or not surfactants change the electrode potential of the zinc electrode in the charging process in a silver-zinc cell. The polarograms were taken by a Sargent Model XXI Recording Polarograph and a Hg/HgO electrode was used as the reference. Each polarogram showed two reduction steps.

The first of these is the one associated with the reduction of zinc. The second has not been identified but may be related to the reduction of oxygen. Table X summarizes the results that were obtained. No great differences are observed although it appears that the presence of surfactants raises the reduction voltage by about 30 to 60 millivolts. If this is analogous to the charge of a silver-zinc cell, it would mean that the charge voltage would be raised a little if surfactants are present in the electrolyte. Whether this is beneficial or not will depend to some extent on what effect these surfactants have on the hydrogen overvoltage at the zinc electrode. This matter has not yet been studied.

5. Microscopic Examination

Small zinc sheet electrodes, about $\frac{1}{2}$ x 1 inch, were wrapped in cellophane, and placed in a petri dish. The electrodes were laid flat on the bottom of the dish. A small amount of electrolyte was added, and a current of about 12 milliamps was passed through the electrodes. The electrodes were then observed by means of a microscope. Special attention was paid to the means by which zinc penetrated the membrane. The electrolyte was 30% KOH in all cases but surfactants were also present in some of the runs. The electrolyte also contained zinc oxide, about 10 grams per liter. Only qualitative observations could be made but even then certain significant results were noted. First, the presence of surfactants increased the amount of gassing at the cathode. Foaming was often noted. Second, the zinc travels to the outside of the cellophane both by puncturing through weak spots and by growing into and through the membrane. Third, zinc embedded in the cellophane causes it to be electrically conductive.

A series of similar runs was made in which the electrolyte was the same. Different membranes were used to wrap the zinc cathode. The electrolyte in each case was 30% KOH containing zinc oxide to the extent of 8.5 grams per liter and a small amount of surfactant No. 7. The current was 10 milliamps in all runs. The membrane materials used were cellophane, an acrylonitrile, an irradiated polyethylene, fibrous sausage casing, and an irradiated cellophane. With both the acrylonitrile and the treated polyethylene, the zinc deposit on the cathode had broken through the entire membrane in about one hour. The zinc penetrated the treated cellophane less rapidly than the untreated material. The fibrous sausage casing was least readily penetrated by the zinc growth on the cathode.

SILVER DEPOSITION ON SEPARATORS

Studies of separators which have been removed from silver-zinc cells show heavy deposits of silver. Because this may lead to deterioration of the separators, to decreasing hydroxide ion mobility, and to possible metallic shorts, this is a serious matter in the operation of silver-zinc cells. Although this problem has been widely recognized, relatively little has been published about the factors affecting this silver deposition.

In order to get some factual information on this problem, small cells were set up containing one silver electrode and either a zinc or cadmium electrode. These cells were cycled and then the separator was examined to determine the amount of silver deposited. The procedure is described on page 7 of this report.

Effect of Palladium Additions to the Silver Electrode

Rather recent work (ref. 4) has indicated that the performance of silver-zinc batteries is improved when small amounts of palladium are added to the silver electrode. The precise nature of this improvement and the reasons for it are not yet clearly understood.

A series of tests was arranged to determine whether the palladium addition had any effect on the silver transport in a cell. To do this two cells were cycled in series. These cells were identical except that in the one cell a sintered silver electrode was used while in the other cell an electrode made of palladium-coated silver particles was used. Several pairs of cells were used to determine the effect of current density and the nature of the negative electrode. In one set of runs the cells were cycled at about 40 ma., 2.75 hrs. on charge and on discharge. With this current rate cycling took place on only the $\text{Ag}/\text{Ag}_2\text{O}$ voltage level. In another series the current was about 200 ma. and each cycle consisted of a 2.75 hour charge and a 2.75 hour discharge. Here the cells operated to a large extent during charge on the $\text{Ag}_2\text{O}/\text{AgO}$ voltage level. The results are given in Table XI.

Considering the first four runs, it is obvious that there is less pick-up of silver by the membrane when Ag-Pd electrodes are used. This is true in the early cycles. What the effect is after hundreds of cycles has not been tested. However, in the 4th, 6th, and 8th runs it appeared that the palladium leaves the silver electrode during cycling. In the 4th run the cellophane had only a trace of silver on it but there was some finely divided black deposit in the electrolyte. This was not observed in the 5th run. Furthermore, in the 6th and 8th runs the deposit on the cellophane dissolved only with difficulty and after a period of 8 or more hours. This was in marked contrast to the 5th and 7th runs in which the deposit on the cellophane dissolved in the nitric acid within 2 or 3 hours. It is suspected that part of the

dark deposit on the cellophane in the 6th and 8th runs was palladium, which dissolved so slowly. Then, too, in these runs very poor end points were obtained in the titration and the values given are at best guesses. It is possible that the dissolved palladium in solution reacted with the silver electrode thereby increasing the amount of silver in solution and giving a fleeting end point. These solutions, after titration, had a fine dark deposit in them, which likely was palladium. In other cases the only insoluble material is the somewhat yellowish silver iodide.

Thus, it appears from the above results, that during cycling of cells using silver-palladium electrodes, the palladium gradually leaches out of the silver electrode. If this is the case, then any decrease in silver pick-up by the separators when silver-palladium electrodes are used would be temporary and show up only during the early cycles. This suggests too that any improvement in cycle life of the silver-zinc battery when silver-palladium electrodes are used may be due to whatever effect the palladium has after it leaves the silver electrode rather than its effect on the silver electrode itself.

Effect of ZnO on the Silver Pick-up by Cellophane

One of the purposes of this work was to determine whether or not the nature of the negative electrode had an effect on the amount of silver picked up by the cellophane separator. Both zinc and cadmium electrodes were used. In some cases the electrolyte contained zinc oxide. The results are given in Table XII.

The results in Table XII seem to show that the use of Zn electrodes, or the introduction of zinc oxide into the electrolyte does reduce the amount of silver that deposits on the cellophane. Run 32 is the one exception to this. The presence of ZnO in the electrolyte with Cd electrodes reduced the silver deposit on the cellophane only to a small extent, probably less than the limits of reproducibility. The use of zinc electrodes, however, allowed less silver to deposit on the cellophane than the use of cadmium electrodes did, Runs 17-20. It should be pointed out, though, that at the end of Runs 17 and 20 there was a small dark deposit, probably silver, on the zinc electrodes. There may have been some of this on the cadmium electrodes also, but it was not observable with the unaided eye.

The above results and conclusions appear to be at odds with the generally held belief that during cycling less silver appears on the separators in silver-cadmium batteries than in those of silver-zinc batteries. Though this idea is quite prevalent, efforts to document it have proved fruitless. In any event, the comparison would be difficult to make because cycle-life is so different for the two systems and the separators used in the two systems are not always the same. Nonetheless, this matter was explored further and is dealt with later in this report.

Effect of Aluminum in the Electrolyte on the Amount of Silver Deposited on the Cellophane

Freshly precipitated aluminum hydroxide was dissolved in the 30% KOH, and this was used as the electrolyte in two cells. The results are given in Table XIII.

The results show that aluminum dissolved in the electrolyte increases the amount of silver picked up by the cellophane and this is accentuated when the silver electrode cycles at the Ag/Ag₂O voltage level.

In order to find out more about the effect of this silver deposit on the separator, several cells were cycled in series at a current of about 40 ma. during a 2.75 hour charge and 35 ma. during a 2.75 hour discharge. The cells were removed from cycling at different times. After a cell was removed from cycling, it was immediately taken apart and the cellophane was soaked in deionized water. Later each of these separators, and a piece of cellophane on which no silver had been deposited, were tested for the ability to allow the diffusion of hydroxide ions. The test procedure for this is described in reference (1) (p. 93). The same orifice and concentration of KOH (30%) were used in these runs, and two runs were made on each separator. Later these same membranes were analyzed for total silver content. The results are given on Figure 7. It is evident that the presence of silver on the separator does decrease the ability of the separator to allow hydroxide ions to diffuse through it. The highest silver value used, 40 mg/sq.in., is not very large compared to the silver deposits found in silver-zinc batteries that have cycled or been on charged stand for any length of time. However, even with this relatively small silver deposit the cellophane was very fragile and it was impossible to make hydroxide ion diffusion tests on cellophane separators having larger silver deposits. This observation also points up the fact that the cellophane separators become physically weaker with use in silver-zinc batteries.

The cellophane having about 6 mg. Ag/sq.in. was also tested for electrical conductivity. The dried separator was placed between two pieces of platinum foil and the resistance between the platinum foils was measured; and it was found to be infinite as measured by a volt-ohmmeter. This indicates that, at least at this stage of silver build up on the separator, the silver had not formed a conducting path through the separator. The X-ray diffraction pattern of another piece of cellophane with approximately the same amount of silver on it showed only lines found in the X-ray diffraction pattern of metallic silver.

The Nature of Solutions of Silver Oxide in Aqueous Potassium Hydroxide

In some work dealing with the solubility of silver oxides in potassium hydroxide solutions, ref. (5), it was noticed that such solutions appear to be unstable. The dissolved silver oxide undergoes a gradual decomposition to a finely-divided black substance which has been identified as metallic silver.

It has been assumed that the dissolved silver oxides were in the ionic form and that no colloidal material was present. This assumption was based on the fact that such solutions seem to be optically clear. This assumption, however, has on occasion been challenged. Consequently, a further investigation of such solutions was made.

Two approaches were used: (a) samples of such solutions were observed under a microscope using reflected rather than direct lighting; and (b) the turbidity of such solutions was measured using a nephelometric attachment with a Coleman Model 14 Spectrophotometer.

When viewed with a microscope these solutions did contain particles which could be observed with reflected light. Actually, the particles themselves were not observed but rather the light reflected from them. Consequently, the size of the particles could not be determined. However, light reflected from these particles had a diameter of about 10^{-5} cm. The particles were, no doubt, considerably smaller than this, likely in the range that is generally given for colloidal materials. Furthermore, upon filtering such solutions through a fine-pore Pyrex frit, the number of particles observed was considerably reduced. The chemical nature of these particles was not determined, but they were assumed to be metallic silver.

A more quantitative method of studying this phenomenon is to make nephelometric measurements. The reference substance in this work was distilled water or a solution of KOH. The instrument was set to read zero with either of these substances in the cuvettes. The cuvette was then filled with the solution to be studied and the scale reading was recorded. Increasing turbidity caused the scale reading to increase. In general, it was found that the turbidity of a solution increased, then levelled off, and finally decreased somewhat after a few days. The results for two such solutions are given on Figures 8 and 9.

The formation of colloidal particles, presumably silver, begins very shortly after a solution has been filtered to remove these particles. However, even at the point where the turbidity reaches its maximum value the solutions appear clear to the unaided eye. This maximum value appears to resemble an equilibrium. The best explanation at the moment is that this turbidity is due to the formation of small colloidal particles of silver. These come

from the decomposition of the dissolved silver oxide. The number of these particles increases with time. However, another process may occur simultaneously. This is the agglomeration of these small particles into larger particles which then precipitate and settle to the bottom of the solution.

Filtration of these solutions through a fine-pore Pyrex frit reduces the turbidity to zero or about 2% on the scale we were using. The rate of formation of these particles may depend on the concentration of the dissolved silver oxide. In Figures 8 and 9, for example, the rate of increase of turbidity becomes less as the amount of silver oxide in solution decreases. The same solution was used for all the runs in Figure 9, but it was filtered to remove all the colloidal and precipitated material before each run. With each succeeding run, then, there was less silver oxide in solution, and the rate of increase of turbidity also decreased.

This work presents the possibility that in a silver-alkaline battery, the separator picks up the larger, or colloidal, particles while allowing the silver oxide which is still in solution to pass through. This may or may not be accompanied by reaction between the separator material and the dissolved silver oxides.

Factors Affecting the Decomposition of Dissolved Silver Oxide

Using the preceding conclusion as a working hypothesis, the question then to be answered has to do with the factors that affect the rate of decomposition of silver oxide in the aqueous KOH. The factors of interest, of course, are those that prevail in silver-zinc cells. Those that hasten this silver oxide decomposition are, according to this hypothesis, responsible for the deposition of silver on the separator. This silver deposit, in turn, may be partly responsible for a weakening of the separator, and does lead to a restriction on the mobility of the hydroxide ions.

The rate of decomposition of Ag_2O in aqueous KOH is sensitive to several influences, e.g., light, temperature, and foreign substances. A small amount of extract from a rubber stopper has increased the rate of decomposition considerably. It is our opinion that this matter of the influence of these "foreign substances" may play a highly significant role in the deposition of silver on the separators in a battery. Consequently, this matter was studied further, especially the effect of zinc oxide or zincate ion.

The experimental techniques involved the use of a radioactive isotope of silver, $\text{Ag}^{110\text{m}}$, for analysis. Excess Ag_2O is added to the KOH solution and shaken, at intervals, for a day. The excess Ag_2O is then removed by filtration through a fine Pyrex frit. 2.5 microcuries of Ag is added to 5 ml. of a KOH solution containing no dissolved Ag_2O , and this solution is then added to 100 ml. of the KOH solution containing dissolved Ag_2O . The solution is filtered again and a 10 ml. sample is taken for silver

analysis by titration while a 0.5 ml. sample is taken for counting. The ratio of silver concentration to counting rate established in this way is used to determine the silver concentration of the solution at all later times.

The solution is then divided into two equal parts. One part serves as a control and the substance of interest is added to the other part. At intervals, 0.5 ml. samples are removed for counting. These samples are first filtered through a fine Pyrex frit before being counted. The instrument is set to register the gamma emission of 0.1 mev and above.

1. Effect of Zinc Oxide

Solid ZnO was added to KOH solutions which contained Ag_2O . The amount of ZnO added was sufficient to make the solutions about 0.03 M in zincate. Sampling was started after the ZnO had dissolved. In every solution the addition of the solid ZnO caused a definite drop in the dissolved-silver content of the solution and it appears that the silver was removed rapidly only during the time that the ZnO was dissolving. After the initial decrease, the rate of decomposition was about the same as in the control solutions. The results are summarized on Figure 10 and 11. Each point represents the average of three runs. All these were carried out at room temperature, approximately 25°C. The difference in silver content between the control and the zincate solution at zero time represents the amount of dissolved Ag_2O that was removed while the ZnO was dissolving. The fraction of the dissolved Ag_2O that was removed by the ZnO is greatest in the 10% KOH solution, and this is likely due to the fact that it took longer for the ZnO to dissolve in this KOH solution than in the others.

Because the results obtained were the average of several samples with a deviation of only $\pm 1.3\%$, the results were analyzed further to compare the rates of decomposition. The rates of decomposition were calculated on the basis of the results over the span of 190 to 400 hours. The rates are given in Table XIV, columns 2 and 3. These rates show that, except for 10% KOH, the rate of decomposition is increased somewhat by the presence of the zincate ion.

There is a further consideration, however. If the decomposition proceeds through the solute species, $\text{Ag}(\text{OH})_2^-$, then one would expect the rate of decomposition to be proportional to the concentration of the dissolved silver species. Consequently, a correction for this should be made before comparing results. This can be done by dividing the rates by the $\text{Ag}(\text{OH})_2^-$ concentration at the 190 hour point, the time from which the rate values were determined. This was done and these are the corrected rate values in columns 4 and 5. It is now evident that in each instance the presence of zincate ion does increase the rate of decomposition of the dissolved Ag_2O .

The results on Figures 10 and 11 appear to indicate that ZnO may have a two-fold effect on the decrease of Ag_2O dissolved in aqueous KOH. The zincate ion appears to increase the rate of decomposition of dissolved Ag_2O but a greater loss of dissolved Ag_2O was noted while the ZnO was dissolving, i.e., while solid ZnO was present. Thus a distinction must be made between the effect of solid ZnO and the effect of zincate.

One possibility is that the presence of zincate ion does lower the solubility of Ag_2O in KOH. This was checked in 30% KOH by making up zincate solutions and then dissolving Ag_2O in these solutions. The results are summarized in Table XV.

The concentration of zincate ion has little effect on the solubility of Ag_2O , but the presence of some zincate does reduce the solubility, though not greatly. However, this effect is far smaller than that noted earlier on Figure 10. Thus, while zincate ion does reduce the solubility of Ag_2O in KOH, it does so only slightly, and this is far from adequate to account for the loss of dissolved Ag_2O when ZnO is added to such solutions.

To determine more precisely the effect of zincate ion, several samples of 10% KOH were saturated with Ag_2O and then zincate ion was added to two samples, solid ZnO to a third, and the fourth was used as the control. The results are shown on Figure 12. It is obvious that while zincate ion does increase the rate of Ag_2O decomposition, the effect of solid ZnO is much greater. Moreover, in 10% KOH it is even possible that when the zincate solution was added small amounts of solid zinc oxide or hydroxide may have formed momentarily and influenced the rate of decomposition to some extent. For this reason the effect of zincate ion was next studied in more concentrated solutions.

A small amount of 0.4 M zincate in 30% KOH was added to solutions which had previously been saturated with Ag_2O . The final zincate concentration of the solutions was about 0.02M. In each case, three different samples were prepared as well as three different samples of control. The results on Figure 13 are the averages of these samples. According to these results (the results were similar in 20% KOH), the presence of zincate ion has little or no effect on the rate of decomposition of the dissolved Ag_2O .

The above results suggest that because the presence of the zincate ion has so little effect on the rate of decomposition of the dissolved Ag_2O , the solid ZnO must be largely responsible for the decomposition that was noted in connection with the results of Figures 10 and 11.

Solid ZnO was added to two solutions of dissolved Ag₂O in 20% KOH. These solutions had been standing for some time. One of these had zincate ion present, the other did not. In the former the dissolved Ag₂O content had dropped from 3.3×10^{-4} to 1.9×10^{-4} M during standing and before ZnO was added while the dissolved Ag₂O content of the second solution had dropped from 3.7×10^{-4} to 2.6×10^{-4} M during this same interval. As soon as the solid ZnO was added the dissolved Ag₂O content decreased rapidly and within 6 hours had decreased more than 30%. This emphasizes the effect of the solid ZnO on this process.

It appears, then, that this decomposition of Ag₂O is a process which takes place on the surface of the solid. If this is so, then there is the possibility that the ZnO may react somehow with the dissolved silver oxide. Because of this, an attempt was made to determine whether the black solid formed during this decomposition contained any zinc.

A 30% KOH solution was saturated with Ag₂O and then Zn⁶⁵ was added as a tracer. After the removal of samples for silver analysis and for Zn⁶⁵ activity determination, solid ZnO was added and mixed until it dissolved in the solution.

After several days the solution was filtered through a fine Pyrex frit to collect the decomposition product that had precipitated. The filtrate was analyzed for silver and for zinc content. The precipitate was washed with three 10 ml. portions of 30% KOH saturated with silver oxide. Then the precipitate was dissolved in 2 ml. of concentrated nitric acid, collected in a test tube, and counted for Zn⁶⁵ activity.

The two silver analyses established the amount of silver that was removed from the solution. Assuming that zinc is present in the precipitate in a 1:1 ratio with silver, the fraction of zinc removed from the solution can be calculated. This will lead to a certain amount of radioactivity (due to Zn⁶⁵) in the precipitate, and this can be calculated by multiplying the fraction of zinc removed by the total radioactivity of zinc in the original solution. This calculated radioactivity is then compared with the actual measured radioactivity of the precipitate. (Zn⁶⁵ was the only radioactive material present in this system.)

Three different solutions were used and the precipitates had 1/20, 1/26, and 1/12 the radioactivity calculated for 1:1 ratio of zinc to silver in the precipitate. From these results it seems safe to conclude that the precipitate does not contain zinc in combination with silver. In no case did the ratio approach anything that might be expected for a zinc-silver complex. The small amount of radioactivity that was

present in the precipitate in each case can readily be explained. The washing procedure did not remove all traces of zincate ion from the precipitate.

2. Effect of Calcium Carbonate and Silica

Because the presence of the solid ZnO was primarily responsible for the decomposition of the dissolved Ag_2O , other solids were also used to determine whether a specific solid or any solid will bring about this decomposition. Two solids chosen more or less at random were used: calcium carbonate and silica.

Five solutions of 30% KOH saturated with Ag_2O were prepared. The first served as a control. To the second a small excess of ZnO was added while a large excess of ZnO was added to the third. Calcium carbonate was added to the fourth and glass wool to the fifth. The results are shown on Figure 14. The removal of Ag_2O by the ZnO was very rapid. CaCO_3 and SiO_2 hastened the removal of silver compared with the control but did not remove the silver nearly as rapidly as the ZnO. After 48 hours, additional quantities of these materials were added and immediately the rate of removal of silver increased.

From these results it may be concluded that the decomposition of Ag_2O in KOH solutions takes place at a solid surface or at least is hastened at such a surface. Apparently there are certain sites on the solid at which reaction takes place. Thus, when additional CaCO_3 and SiO_2 were added, the rate of decomposition immediately increased. Not all solid surfaces, however, serve equally well for this. Solid ZnO serves especially well, and this may be the reason that silver deposits heavily on the separators in a silver-zinc battery. Any Ag_2O that gets into the electrolyte will be decomposed rapidly when it comes in contact with solid ZnO, the discharge product of the zinc electrode.

There is another possible interpretation of the above results, and that is that the surface of the CaCO_3 and the SiO_2 has on it some foreign materials that are oxidizable and these substances react with the dissolved Ag_2O . Only trace amounts would be sufficient for this. A 100 ml. sample of 30% KOH saturated with Ag_2O will contain only $0.1 \times 4 \times 10^{-4}$ or about 4×10^{-5} moles of dissolved Ag_2O . Consequently, about the same amount of foreign oxidizable material would be sufficient to reduce all the dissolved Ag_2O .

One gram samples of glass wool and of CaCO_3 were soaked in 50 ml. of 30% KOH for 4 to 6 days. This extracted solid material was then removed and placed in 25 ml. of 30% KOH that had been saturated with Ag_2O . At the same time fresh samples of glass wool and CaCO_3 were placed in other 25 ml.

portions of 30% KOH-Ag₂O solutions. A third 25 ml. sample of the 30% KOH-Ag₂O solution served as a control while to a fourth 25 ml. sample, 10 ml. of the solution in which the glass wool and CaCO₃ had been soaked were added. All of these solutions contained Ag^{110M} as a tracer. Duplicate runs were made in all cases.

The results of these runs are shown on Figures 15 and 16. It appears that there may be traces of oxidizable impurities on both the glass wool and the CaCO₃ because the solution in which these substances had been soaked does bring about some decrease in dissolved Ag₂O content. This decrease is completed in about 5 hours and after that the rate of decomposition is the same as that of the control.

The bulk of the decomposition, however, still appears to be a surface phenomenon. With CaCO₃ the unextracted materials cause a more rapid decrease in Ag₂O concentration during the first thirty hours or so than do the extracted materials. Thereafter the rates of decomposition are the same for the solids whether they had been previously soaked or not. This rate was greater than that for the controls.

With glass wool, the unsoaked material caused a faster decomposition of the dissolved Ag₂O than did the glass wool which had been soaked. Furthermore, the two samples of soaked glass wool did not give completely similar results. (With CaCO₃ the two samples gave results very close to each other.) This may be due to lack of uniformity of the material used. It may also be due to a reaction between the glass wool and the KOH. However, the results do allow for the interpretation that the decomposition of the Ag₂O is brought about by two factors: (a) the presence of traces of oxidizable materials on the surface of the CaCO₃ and the glass wool, or, perhaps the presence of Ca⁺⁺ and SiO₃⁼ ions in the solution; and (b) the surface of the solid materials present.

3. Effect of Cadmium Oxide

Cadmium oxide differs from ZnO in that the former is insoluble in KOH solutions. Consequently the only effect would be that of the presence of the solid CdO. No solute species would be involved.

Solutions of 30% KOH were saturated with Ag₂O and then divided into two groups. One group was used as a control and solid CdO was added to the other group. The presence of the solid CdO caused a drop in the dissolved-silver content from 5.15×10^{-4} to 4.75×10^{-4} M. Thereafter the silver oxide decomposed somewhat faster in the solutions containing the solid CdO. When corrected for dissolved-silver concentration, the rate in the control was 2.3×10^{-4} moles per hour while it was

6.4×10^{-4} moles per hour in the solutions to which CdO had been added. This latter rate is not nearly as large as that brought about by solid ZnO, see Figure 14.

If it is indeed true that the silver deposits on the separators of silver-zinc batteries is heavier than on the separators of silver-cadmium batteries, then the above results would seem to give a satisfactory explanation for this difference. Assuming that the bulk of the silver in the separators comes from the decomposition of dissolved silver oxide, then a cell in which solid ZnO is present would cause considerably more silver formation than would CdO. ZnO and CdO are the discharge products at the negative electrode in the silver-zinc and silver-cadmium cells, respectively.

4. Effect of Other Ions

For this purpose, three other ions were selected: Na^+ , Li^+ , and AlO_2^- . These were chosen because of the interest shown in them for silver-alkaline cells. Some work has been done in which these ions were present in the electrolyte.

Solutions of LiOH, NaOH, and KOH were prepared. These were all 4.4M, and were saturated with Ag_2O . It was found that the solubility of Ag_2O in KOH and NaOH was about the same: 4.75×10^{-4} and $5.05 \times 10^{-4}\text{M}$, respectively. However, the solubility in LiOH was $7.93 \times 10^{-4}\text{M}$. The rate at which the dissolved silver content decreased was about the same in all these solutions. Consequently, it appears that the main difference in these electrolytes is the amount of Ag_2O they will dissolve, but not the rate at which the dissolved Ag_2O decomposes. The rates of decomposition were as follows:

	moles/hour	
	<u>Uncorrected</u>	<u>Corrected for Ag concn.</u>
KOH	1.22×10^{-7}	2.77×10^{-4}
NaOH	1.28×10^{-7}	2.77×10^{-4}
LiOH	1.64×10^{-7}	2.18×10^{-4}

Another 30% KOH solution saturated with Ag_2O was divided into two parts. To one part was added some freshly prepared solid aluminum hydroxide. The other group served as a control. The effect of the solid $\text{Al}(\text{OH})_3$ was negligible on the amount of silver reduced compared to the control. From then on the silver oxide in the aluminate solution decomposed at a slightly faster rate, 2.5×10^{-7} moles/hour, compared to 1.5×10^{-7} moles/hour for the control. Thus the presence of aluminate ion in the electrolyte does not accelerate greatly the decomposition of dissolved Ag_2O .

5. Effect of Separator Materials

The work under the previous contract, ref. 2, showed that separator materials differ in the effect they have on the rate of decomposition of dissolved Ag_2O . The cellulosic materials all had about the same effect. The rate of Ag_2O decomposition was increased considerably by these substances. Some other materials, such as polyethylene, had hardly any effect on the rate of this decomposition. In the light of the foregoing results, (the effect of solid materials on the decomposition of dissolved Ag_2O), it was decided that these effects should be reviewed once again. This review was undertaken with two objects in mind: (a) to determine the effect that the presence of zincate ion has on these processes; and (b) to determine whether materials extracted from the separators are responsible for the decomposition.

- a. A tracer solution containing Ag_2O dissolved in 30% KOH was prepared and samples were removed for silver analysis and for Ag^{110} determination. The solution was divided into two parts of 100 ml. each and 0.8 gram of ZnO was added to one part. After the ZnO had dissolved, two 0.5 ml. samples were removed from each part for counting. The solutions were further divided into four parts of approximately 25 ml. each. A small piece of separator (cellophane or a polyethylene), 2 cm. on each side, was added to each of two of these solutions, the other two solutions serving as controls. The solutions used were:

two controls----- Ag_2O in 30% KOH

two of Ag_2O in 30% KOH + separator

two of Ag_2O in 30% KOH + zincate ion

two of Ag_2O in 30% KOH + zincate ion + separator

The change in dissolved silver content was determined by counting 0.5 ml. samples.

The results are summarized on Figures 17 and 18. In the case of cellophane, the presence of zincate ion makes little difference in the rate of Ag_2O decomposition. In general, this is true also with respect to the polyethylene. However, it appears that perhaps the presence of zincate ion does decrease the effect of the polyethylene slightly. There was no time left under this contract to check this matter further. A few preliminary runs were made but the results were inconclusive.

- b. The effect of any extract from the separator on the decomposition of the dissolved silver oxide was tested by soaking pieces of the material in 30% KOH for some time

and then adding part of this solution, after being filtered, to a solution of Ag_2O in 30% KOH. Again Ag^{110} was used as a tracer for analytical purposes.

First two pieces of cellophane, about one inch square, were soaked in 50 ml. of 30% KOH for 48 hours. Five ml. of this solution was added to 25 ml. of a Ag_2O -KOH solution. A control was prepared by adding 5 ml. of 30% KOH to another 25 ml. portion of the Ag_2O -KOH solution. The pieces of cellophane which had been soaked in the 30% KOH were also added to separate 25 ml. portions of the Ag_2O -KOH solution.

Within a few minutes of the time the 5 ml. of extract from the cellophane was added to the Ag_2O -KOH solution, the solution changed color and within 30 minutes was very dark. This indicates a rapid decomposition of the dissolved silver oxide. Further, this points out that the KOH does extract something from the cellophane which reduces the dissolved Ag_2O . However, the pieces of cellophane which had first been soaked in 30% KOH also reduced the dissolved silver oxide very rapidly.

It was possible that the amount of 30% KOH used was insufficient to extract from the cellophane all the material that reduces silver oxide. Consequently, two pieces of cellophane about 1 x 2 cm. were soaked in 200 ml. of 30% KOH for 60 hours. The cellophane was then removed and soaked in 50 ml. of deionized water for 20 hours.

A 200 ml. volume of 30% KOH saturated with Ag_2O was divided into eight 25 ml. portions and these were treated the following way.

2 samples served as controls;

to 2 samples 5 ml. of extract from the cellophane were added;

to 2 samples the cellophane which had been soaked was added;

to 2 samples the cellophane which was fresh was added.

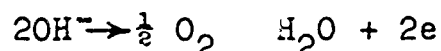
A similar series of runs was made in which polyethylene was used instead of the cellophane. In this case four square inches of the polyethylene were soaked in 50 ml. of 30% KOH for 84 hours and 10 ml. of the extract was added to the KOH- Ag_2O solution.

The results are given on Figures 19 and 20. The effect of the extract from the cellophane is very slight (Figure 19) because it is rather dilute. However, this same figure shows that the pre-soaked cellophane has practically the same effect on the silver oxide decomposition as does fresh cellophane. Therefore, although the 30% KOH will extract from the cellophane a material which reduces the dissolved silver oxide, yet there is an additional effect of cellophane apart from the extract. Pre-soaking does not appreciably alter the effect of cellophane on the decomposition of dissolved silver oxide.

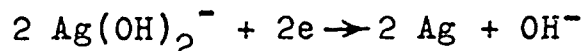
The results with polyethylene, Figure 20, are somewhat different. It appears here that the extracted material from the polyethylene is responsible for the reduction of the silver oxide. Pre-soaked polyethylene has but a slightly greater effect than does the control. The unsoaked polyethylene causes an increase in the rate of silver oxide decomposition and this effect continues over a week.

It appears then that the presence of solid substances affects the decomposition of dissolved silver oxide in two ways. In the first place, many of these substances have adsorbed oxidizable foreign materials, or else such materials can be extracted from them by the KOH. These materials then react with the dissolved silver oxide and reduce it to metallic silver.

The second mode may be called a surface effect. Tentatively it is suggested that solids which readily adsorb, e.g., OH^- ions bring about an increased rate of silver oxide decomposition. This adsorption may weaken the O-H bond to some extent and thus the following reaction can proceed more readily:

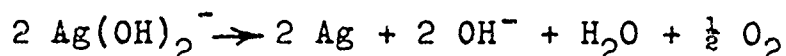


This is one-half of a local cell reaction, the other half being



These two reactions together describe the silver oxide decomposition.

Another possibility is that the $\text{Ag}(\text{OH})_2^-$ species is attracted to the surface of the solid material and is adsorbed there through the OH radicals in the ion. This adsorption can so weaken the bonds within the ion that the following decomposition takes place



In support of these alternatives it may be noted that

cellophane, which swells in KOH (due to adsorption), brings about a rapid rate of decomposition while polyethylene, which adsorbs very little KOH, has little effect on the rate of decomposition. Furthermore, zinc oxide increases the rate of decomposition considerably, in contrast to substances such as cadmium oxide and calcium carbonate. Zinc oxide also reacts readily with the KOH whereas the other substances do not.

The results presented here do not prove the above mechanism. However, they are consistent with it and further work should be done to check into the validity of this suggested mechanism.

CONCLUSIONS

The most significant conclusions to be drawn from this work are the following:

1. Fick's first law of diffusion does describe the diffusion of dissolved silver oxide, zincate ions, and hydroxide ions through separator materials.
2. Surfactants appear to increase the cycle life of silver-zinc cells when operating at low current densities.
3. Surfactants do modify some of the processes taking place at a zinc electrode. These processes are: hydrogen evolution, nature of the zinc deposit on charge, and limiting discharge current.
4. The decomposition of silver oxide in the KOH electrolyte is markedly affected by the presence of solid zinc oxide. This effect is much greater than the effect of solid cadmium oxide.
5. The effect of separator materials on the decomposition of dissolved silver oxide is due to materials which the KOH electrolyte can extract from the separators, and to the surface of the separator itself.

LIST OF REFERENCES

1. J. E. Cooper and A. Fleischer, "Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries," 1964, AF Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio.
2. T. P. Dirkse, "Silver Migration and Transport Mechanism Studies in Silver Oxide-Zinc Batteries," Technical Documentary Report No. ASD-TDR-63-863 of September 1963, Contract No. AF 33(657)-8689, Calvin College, Grand Rapids, Michigan.
3. K. Huber, "Anodic Formation of Coatings on Magnesium, Zinc, and Cadmium", J. Electrochem. Soc. 100, 376 (1953).
4. J. J. Lander, J. A. Keralle, "Silver-zinc Secondary Battery Investigation," Fourth Quarterly Technical Progress Report, 2 July 1963, Contract No. AF 33(657)-8943, Delco-Remy, Anderson, Indiana.
5. T. P. Dirkse, L. A. Vander Lugt, H. Schnyders, "Solubility and Stability of Silver Oxides in Alkaline Electrolytes.", J. Inorg. and Nuclear Chem., 25, 859 (1963)

APPENDIX I

FIGURES 1 THROUGH 20

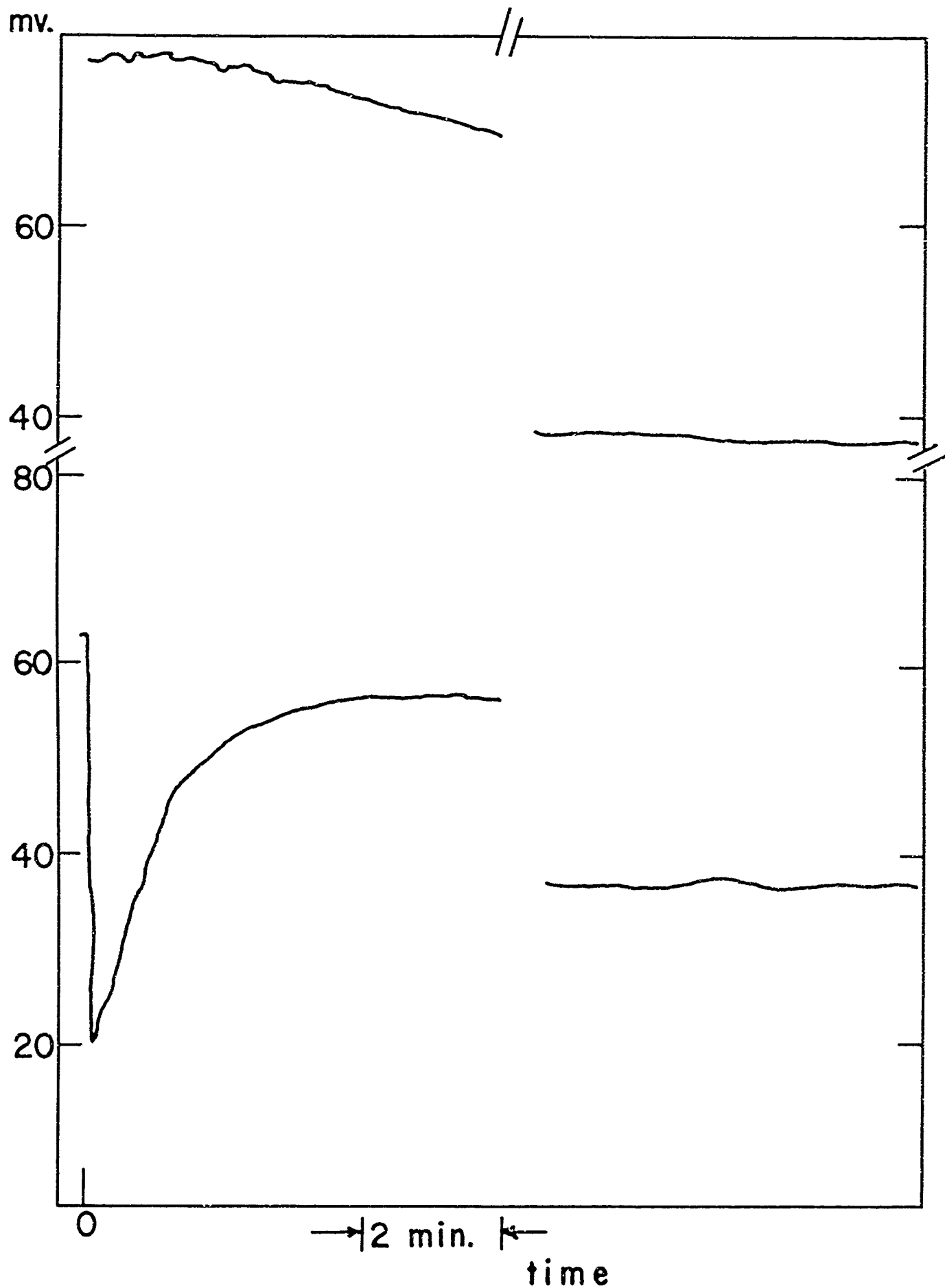


Figure 1 Change of emf with time in zincate diffusion run.
Both curves were obtained with the same system.

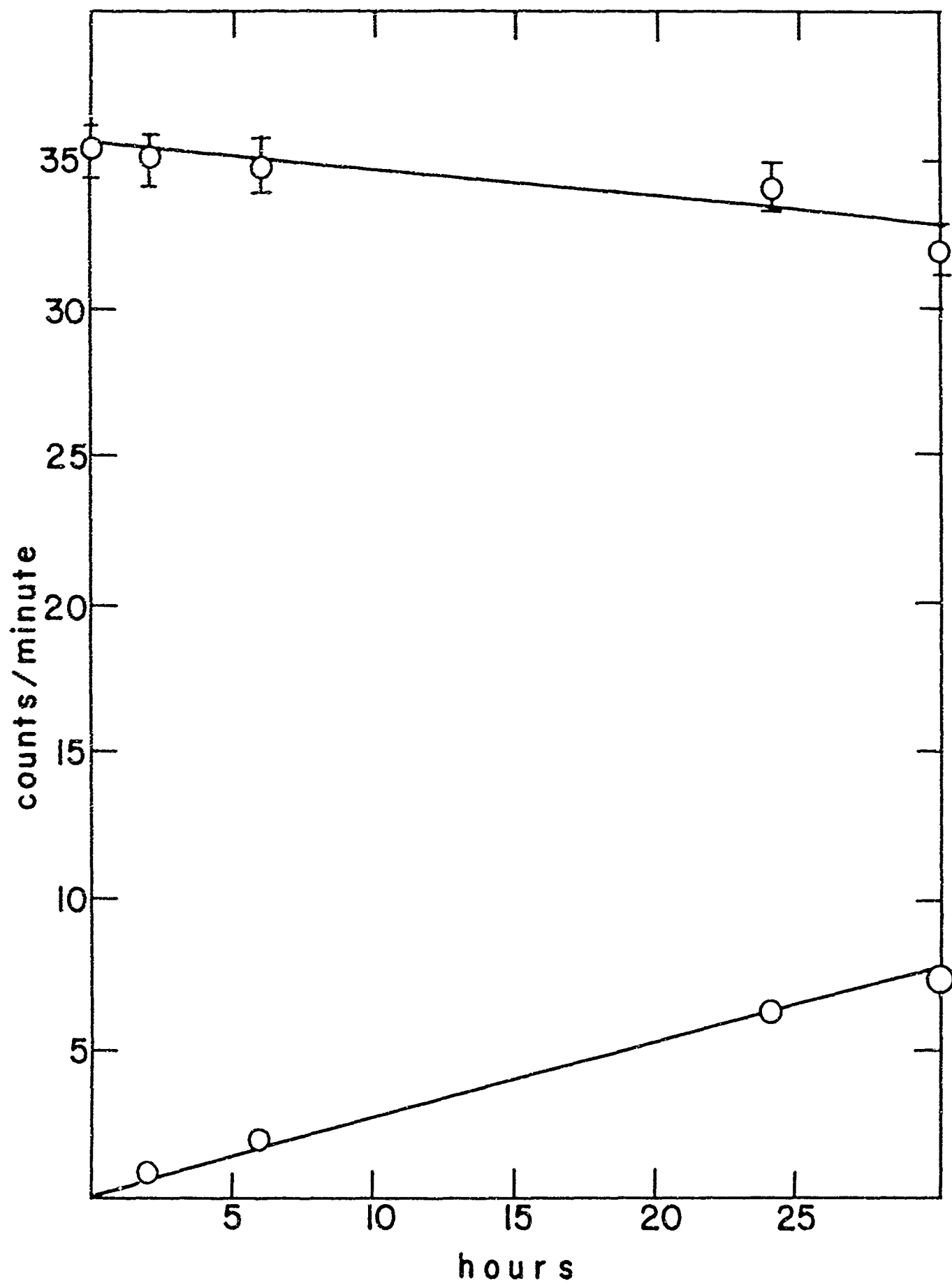


Figure 2 Change in radioactivity of solutions in the determination of the rate of zincate diffusion. The upper curve is for the zincate solution, the lower curve for the KOH solution.

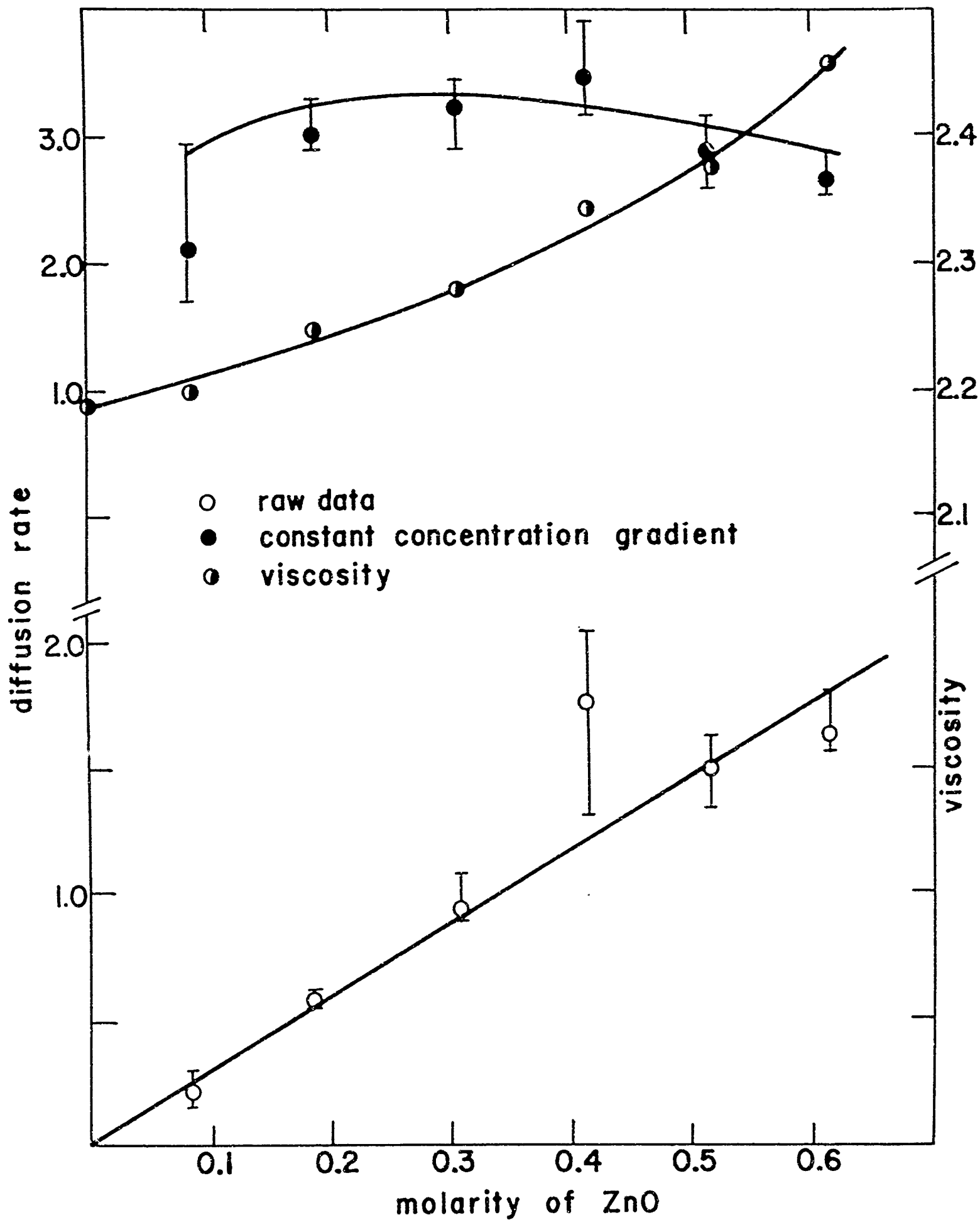


Figure 3 Variation of zincate diffusion rates with zincate concentration in 30% KOH. Diffusion rates are relative values; viscosity is in centipoises.

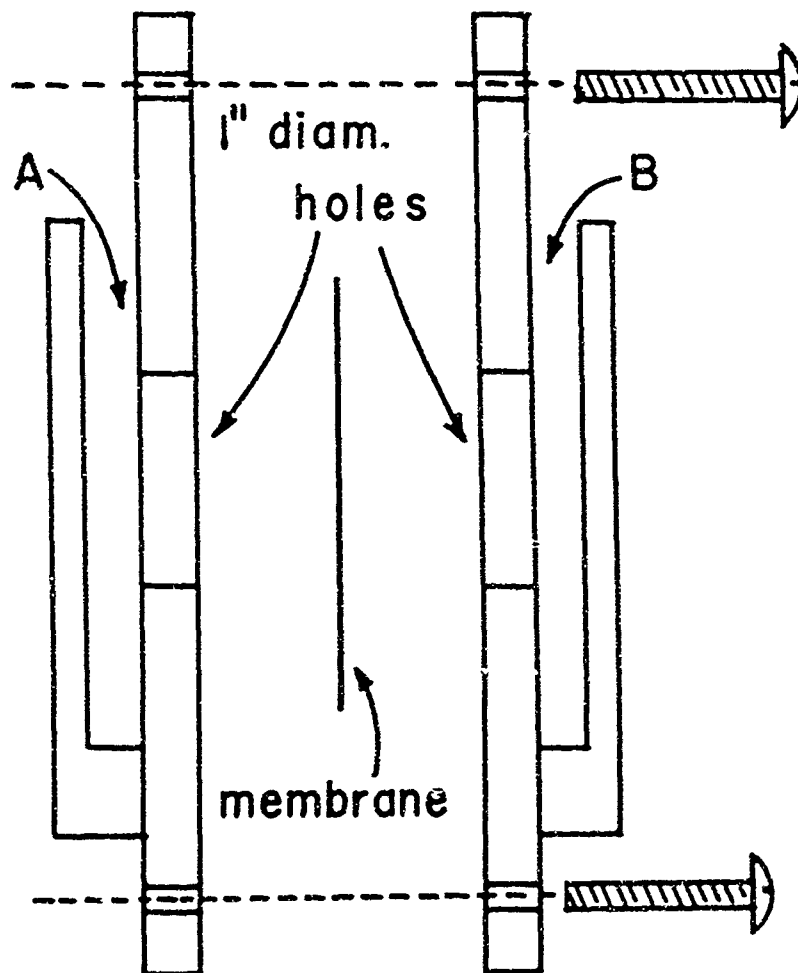


Figure 4 Cell case.

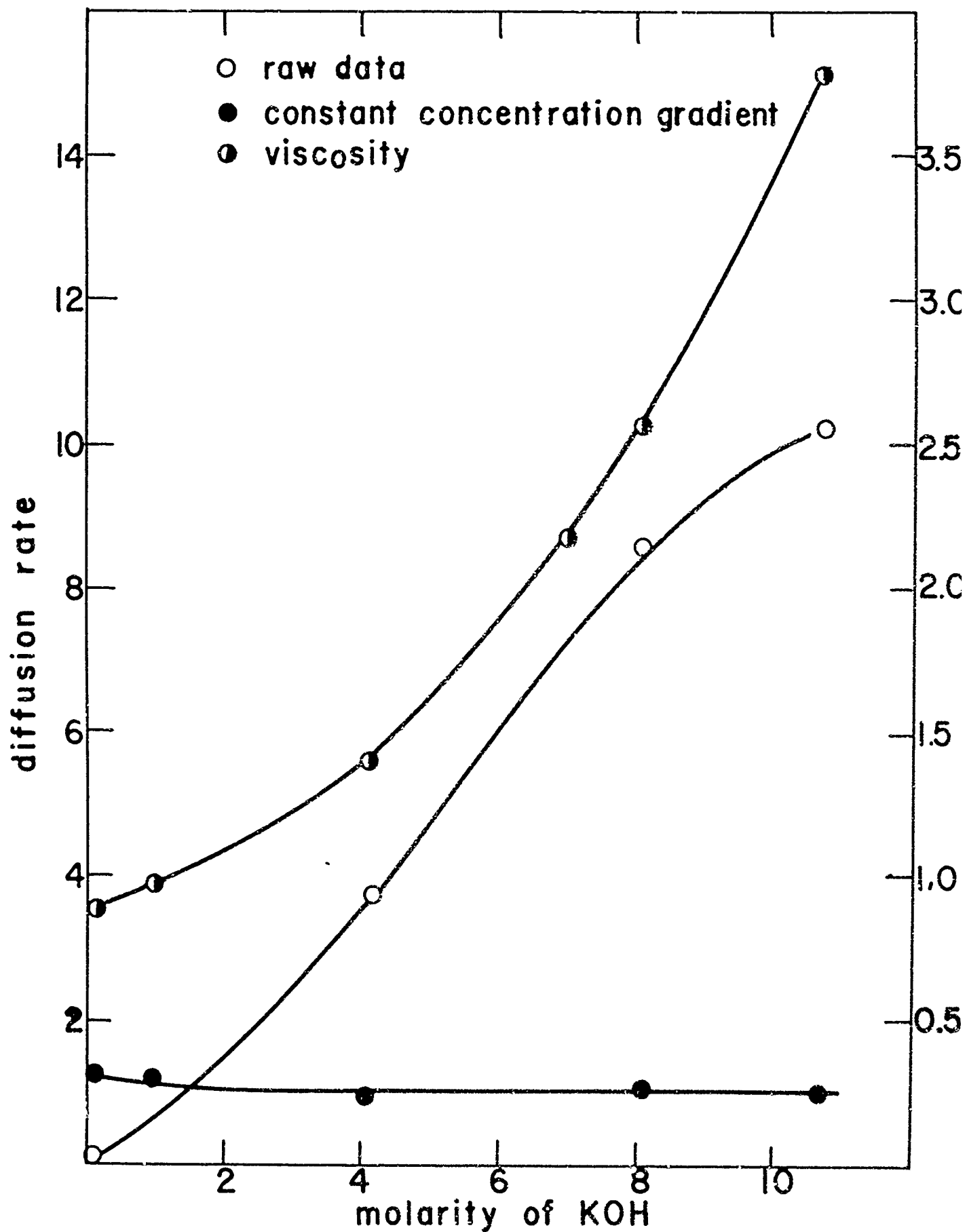


Figure 5 Rate of diffusion of OH^- ions through cellophane. The diffusion rate is $\text{moles/sq.in./min.} \times 10^3$ while viscosity is expressed in centipoises.

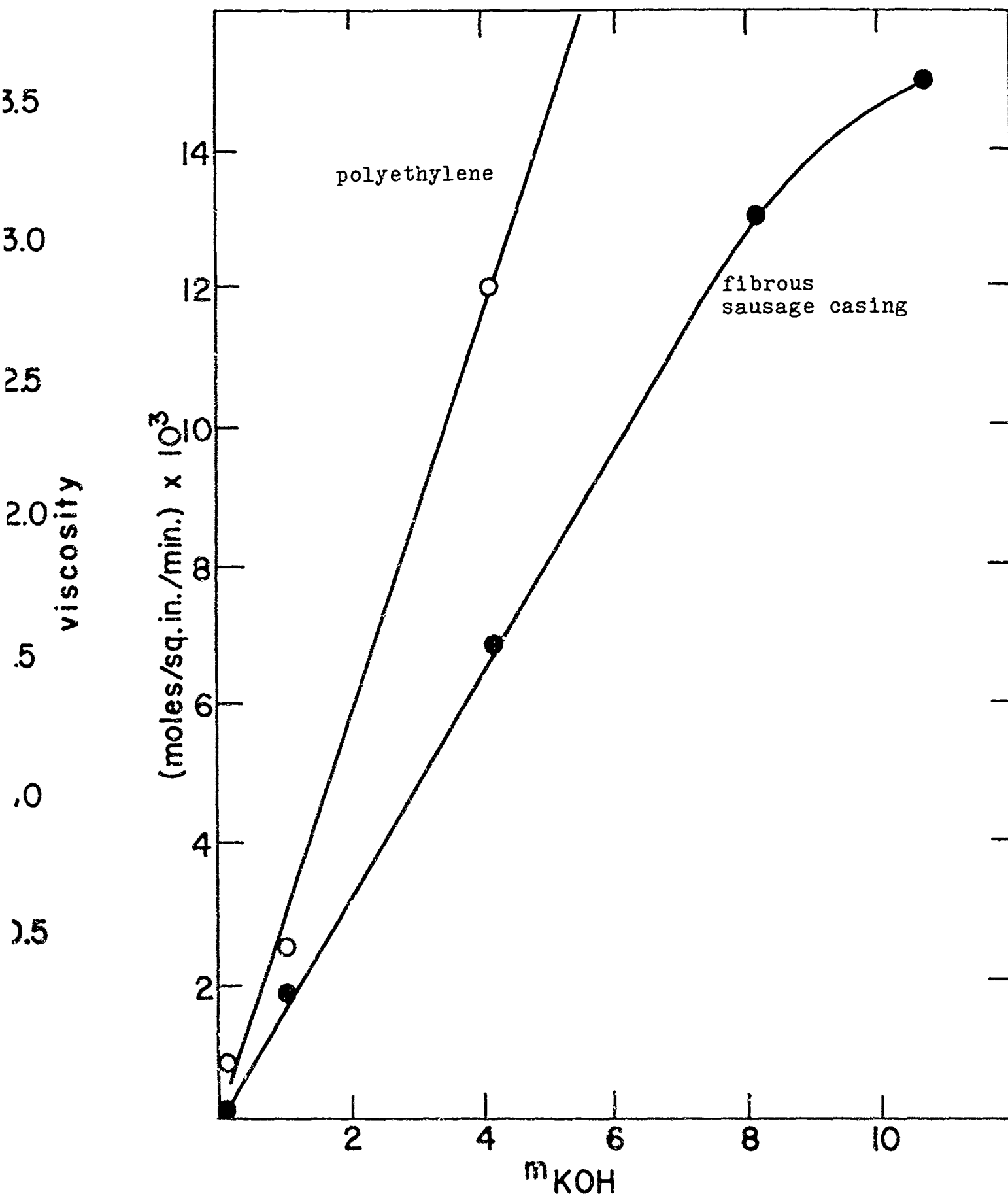


Figure 6 Rate of diffusion of OH^- ions through polyethylene and through fibrous sausage casing.

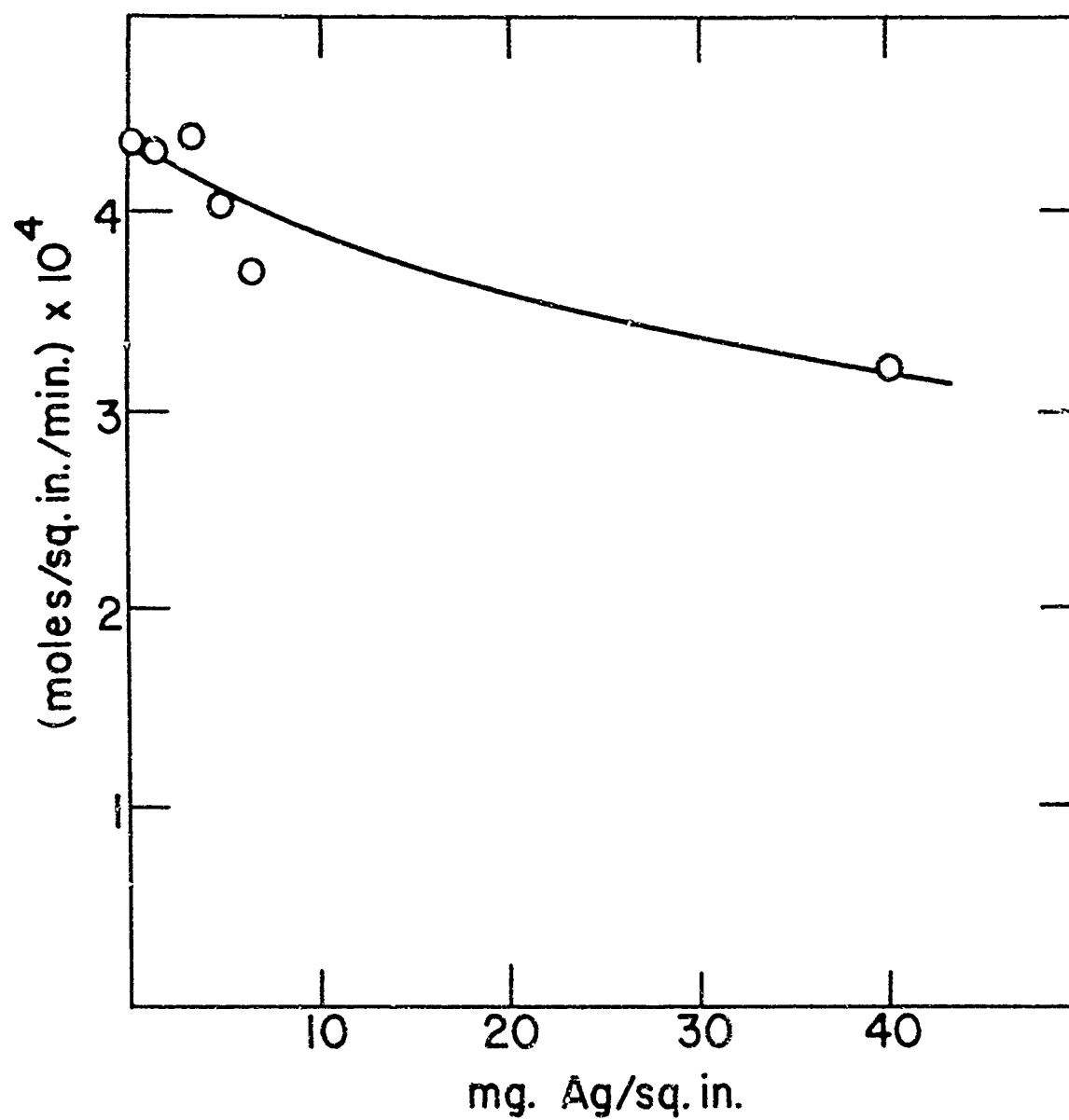


Figure 7 Hydroxide ion diffusion through cellophane.

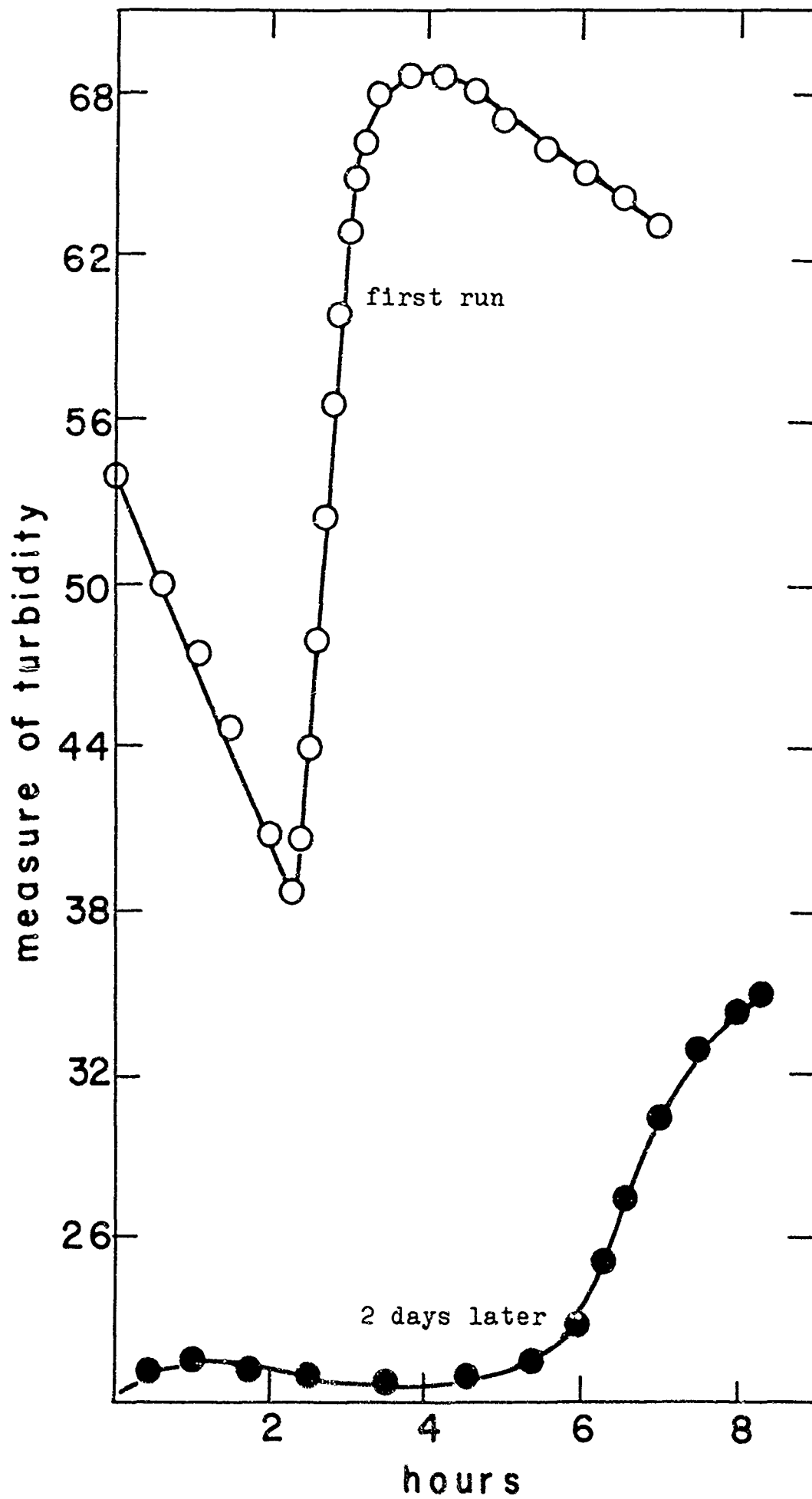


Figure 8 Turbidity of a solution of Ag_2O in 1 N KOH.

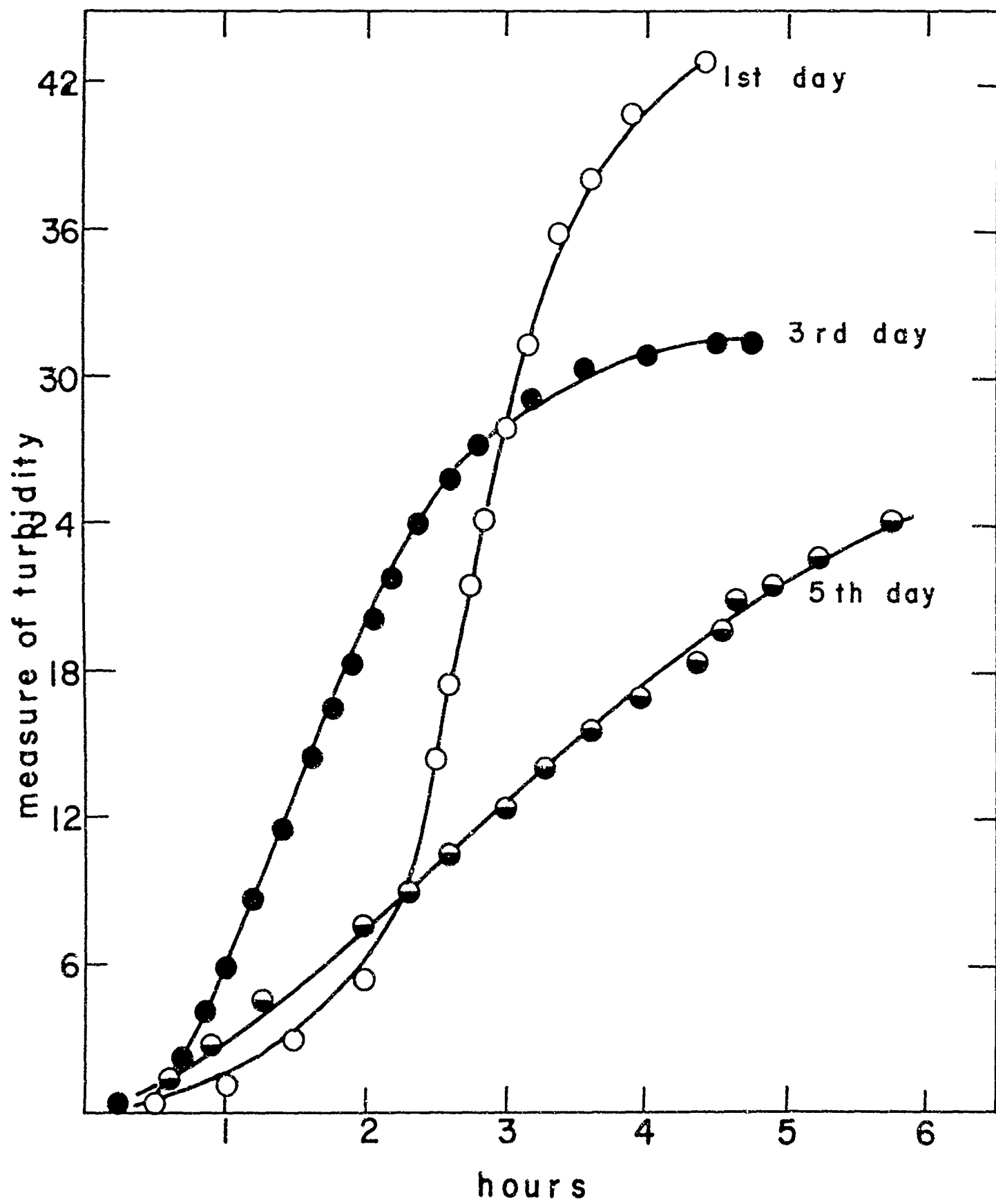


Figure 9 Turbidity of a solution of Ag_2O in 5 N KOH.

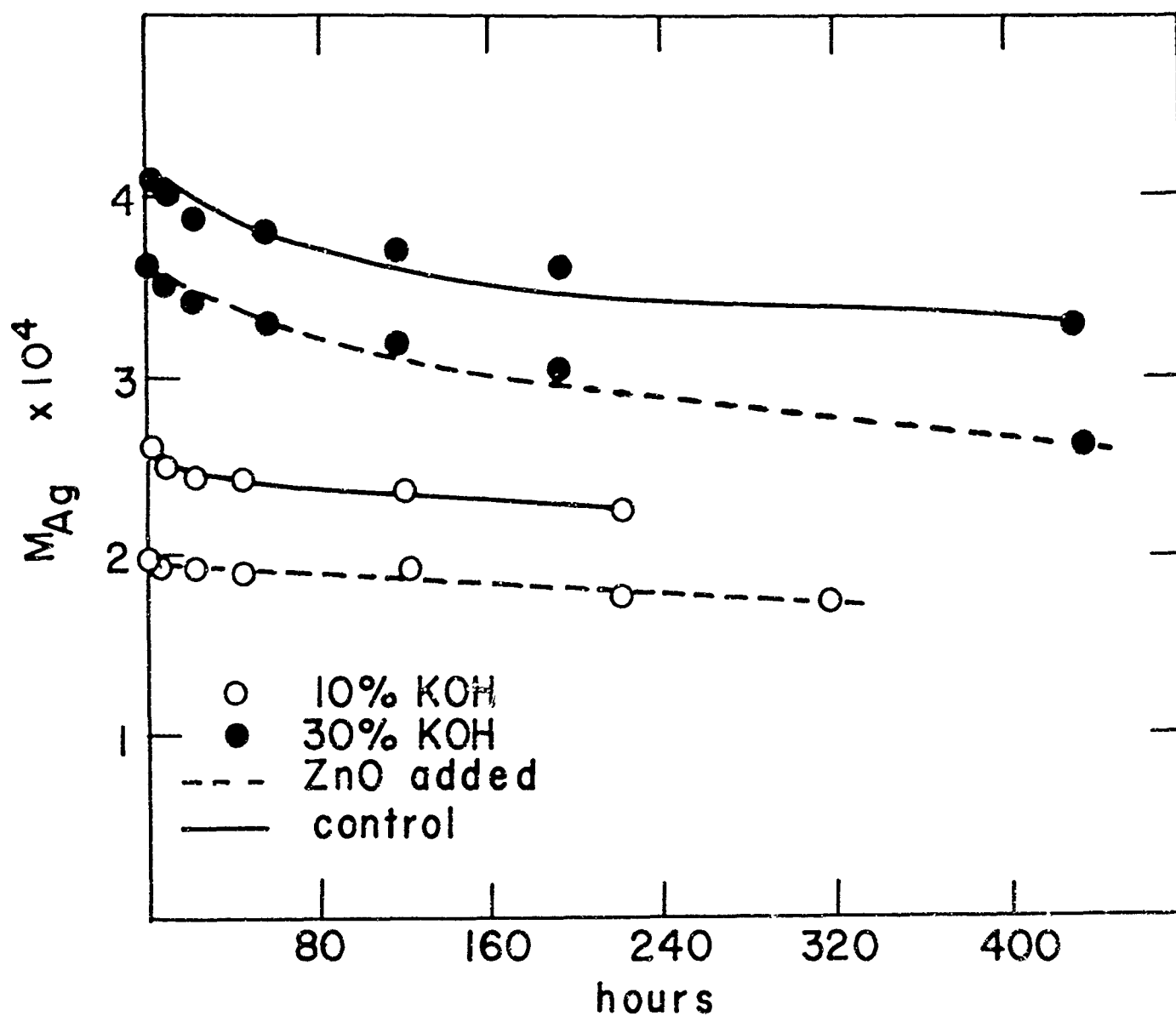


Figure 10 Effect of ZnO on rate of dissolved Ag_2O decomposition in 10% and 30% KOH at room temperature.

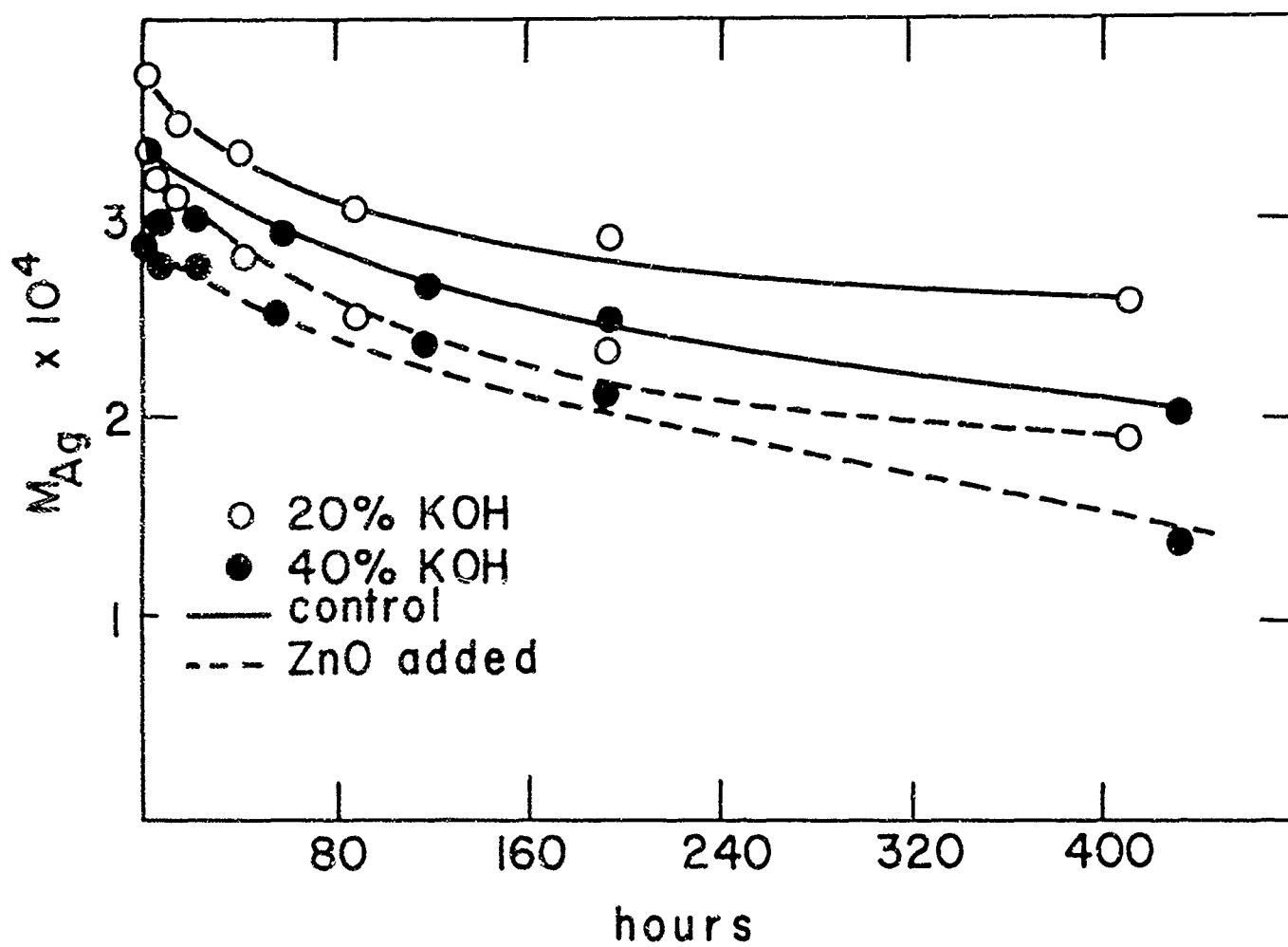


Figure 11 Effect of ZnO on rate of dissolved Ag_2O decomposition in 20% and 40% KOH at room temperature.

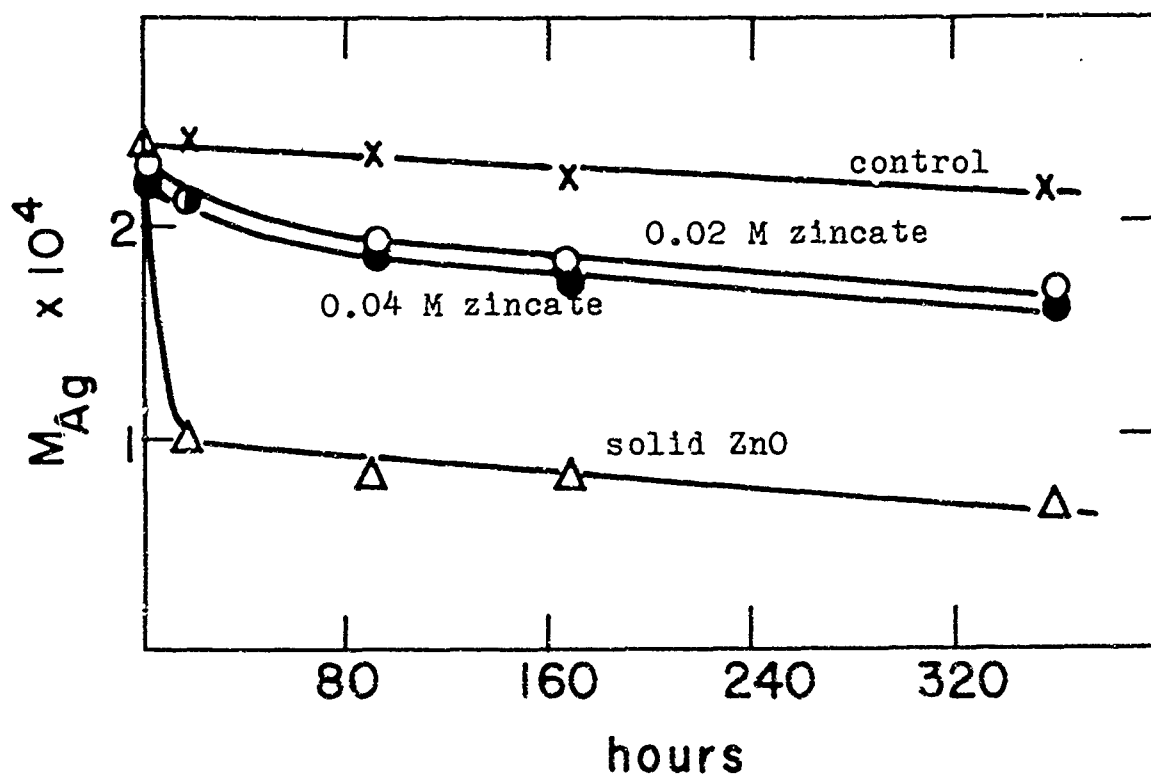


Figure 12 Effect of zincate ion and solid ZnO on the decomposition of Ag_2O in 10% KOH at room temperature.

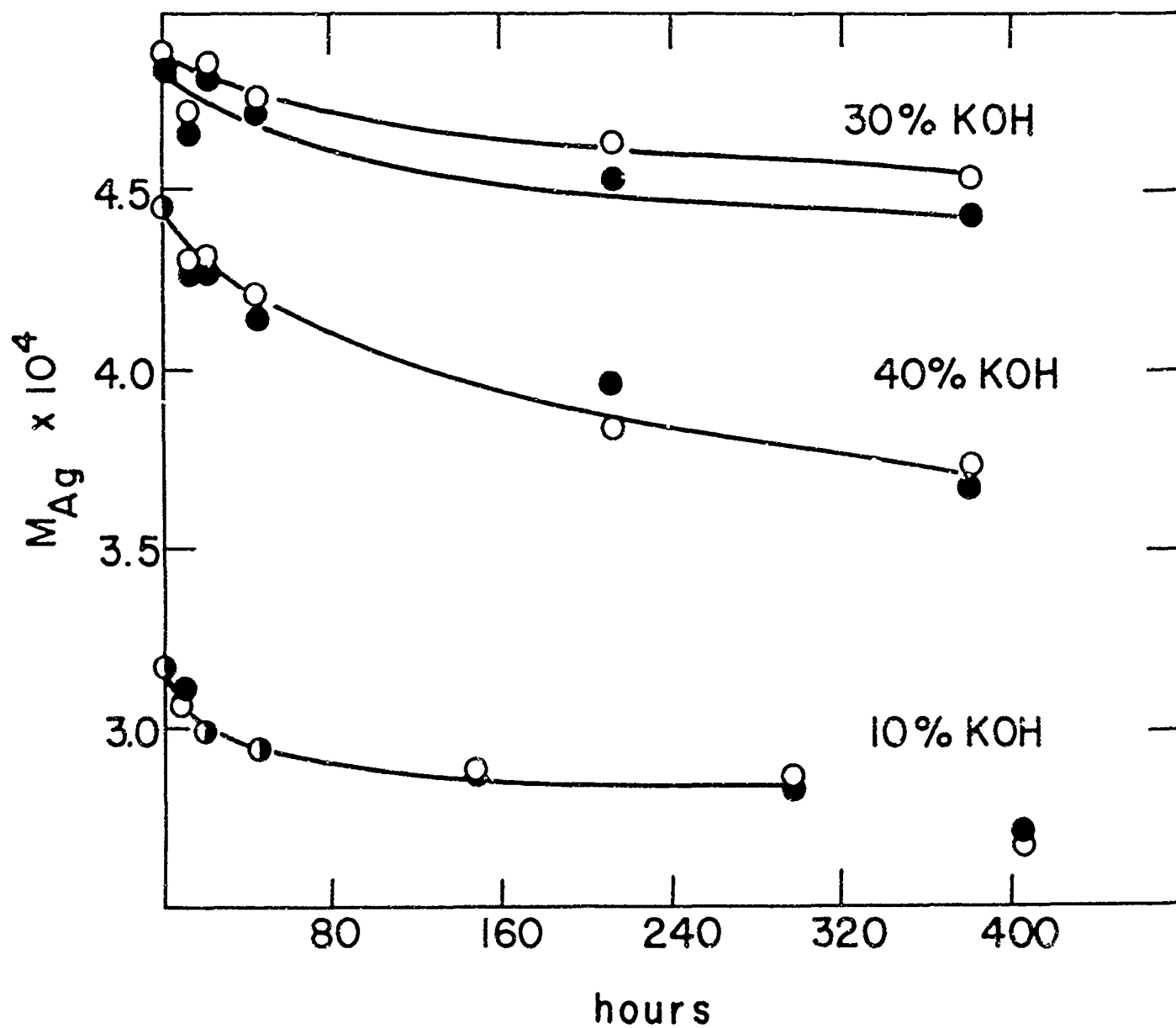


Figure 13 Effect of zincate ion on the decomposition of Ag_2O in aqueous KOH at room temperature. Open circles---controls; closed circles---zincate added.

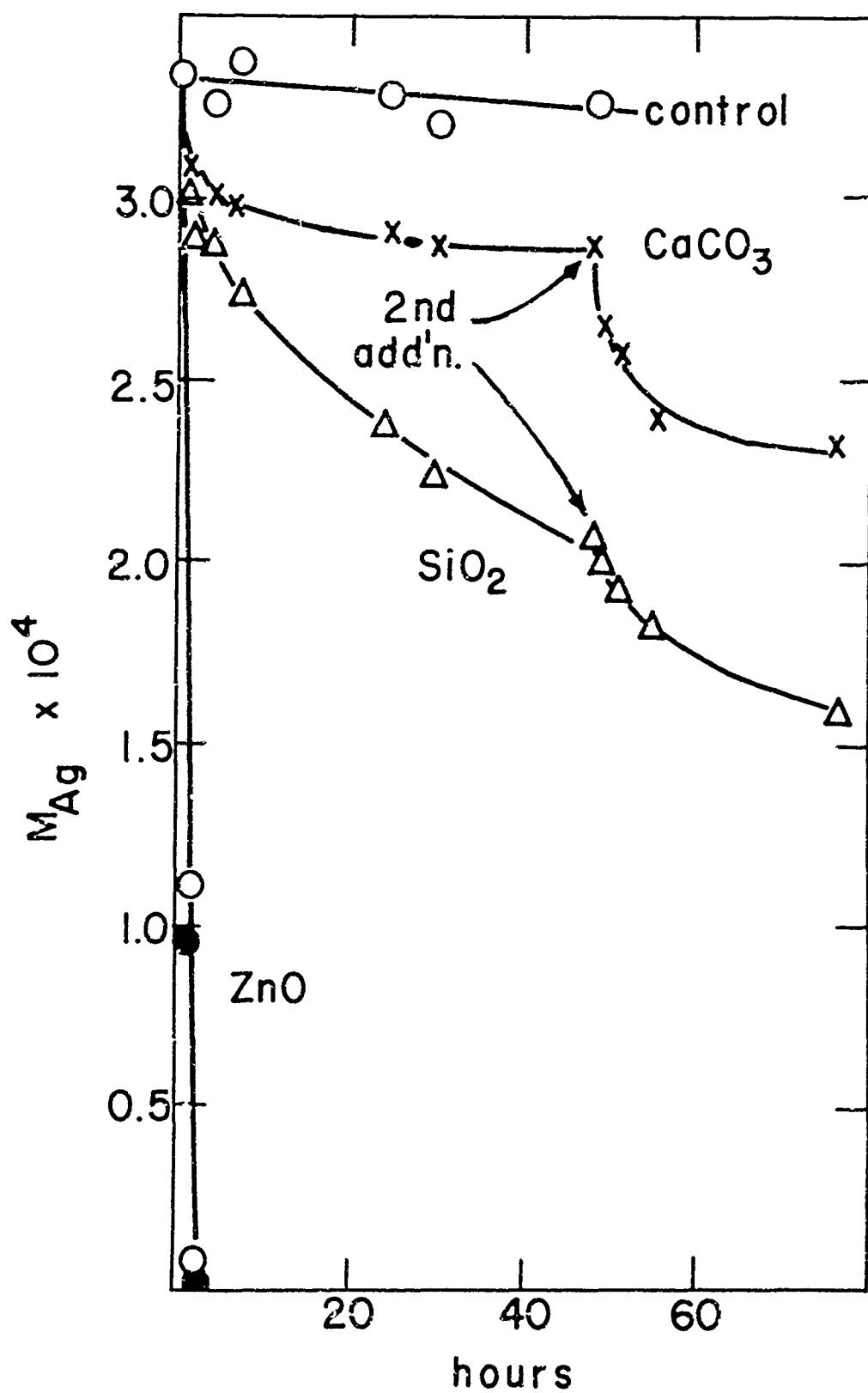


Figure 14 Effect of solid CaCO_3 and SiO_2 on the decomposition of Ag_2O in aqueous KOH at room temperature.

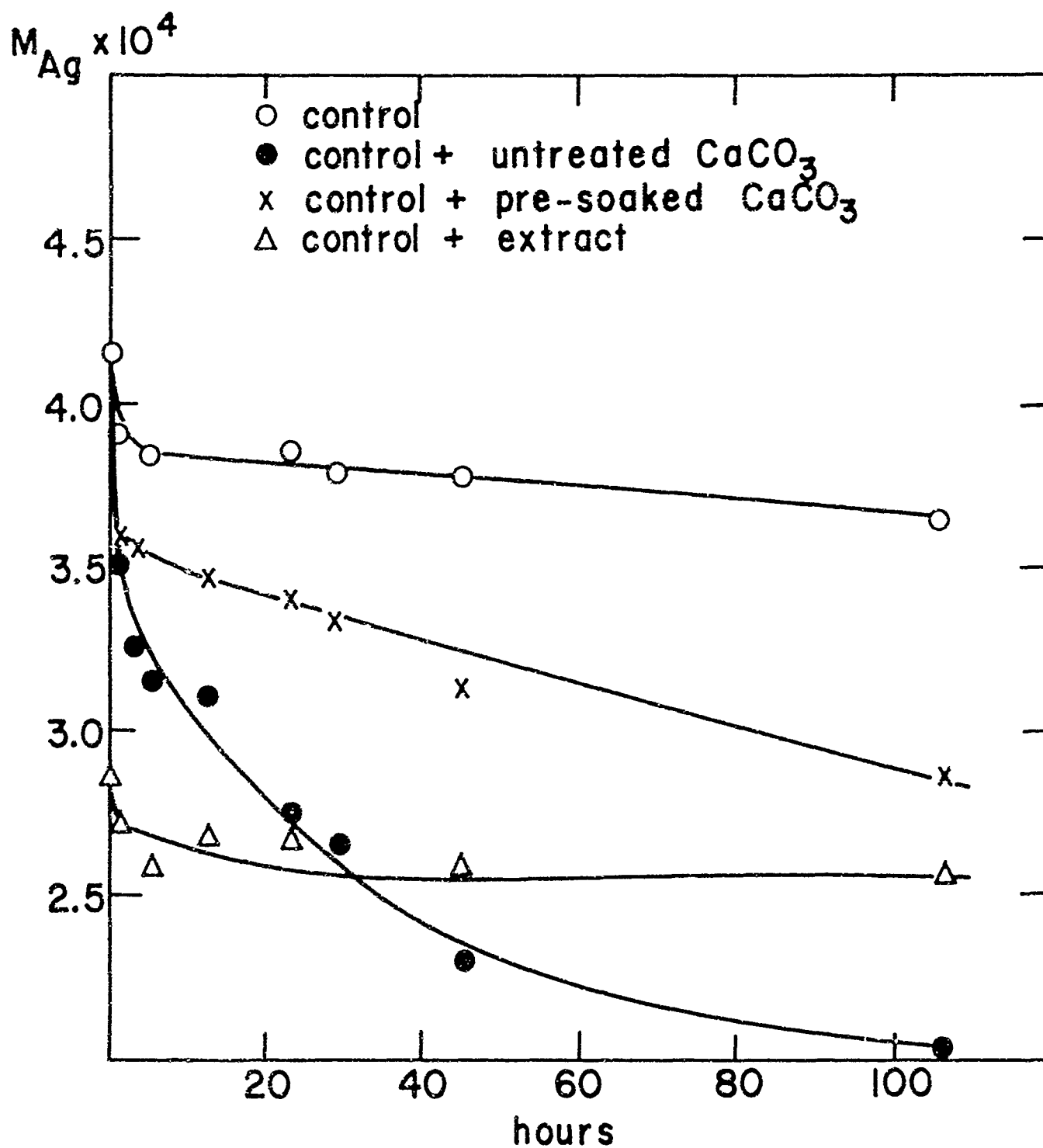


Figure 15 Effect of CaCO_3 and CaCO_3 extract on the decomposition of Ag_2O in 30% KOH .

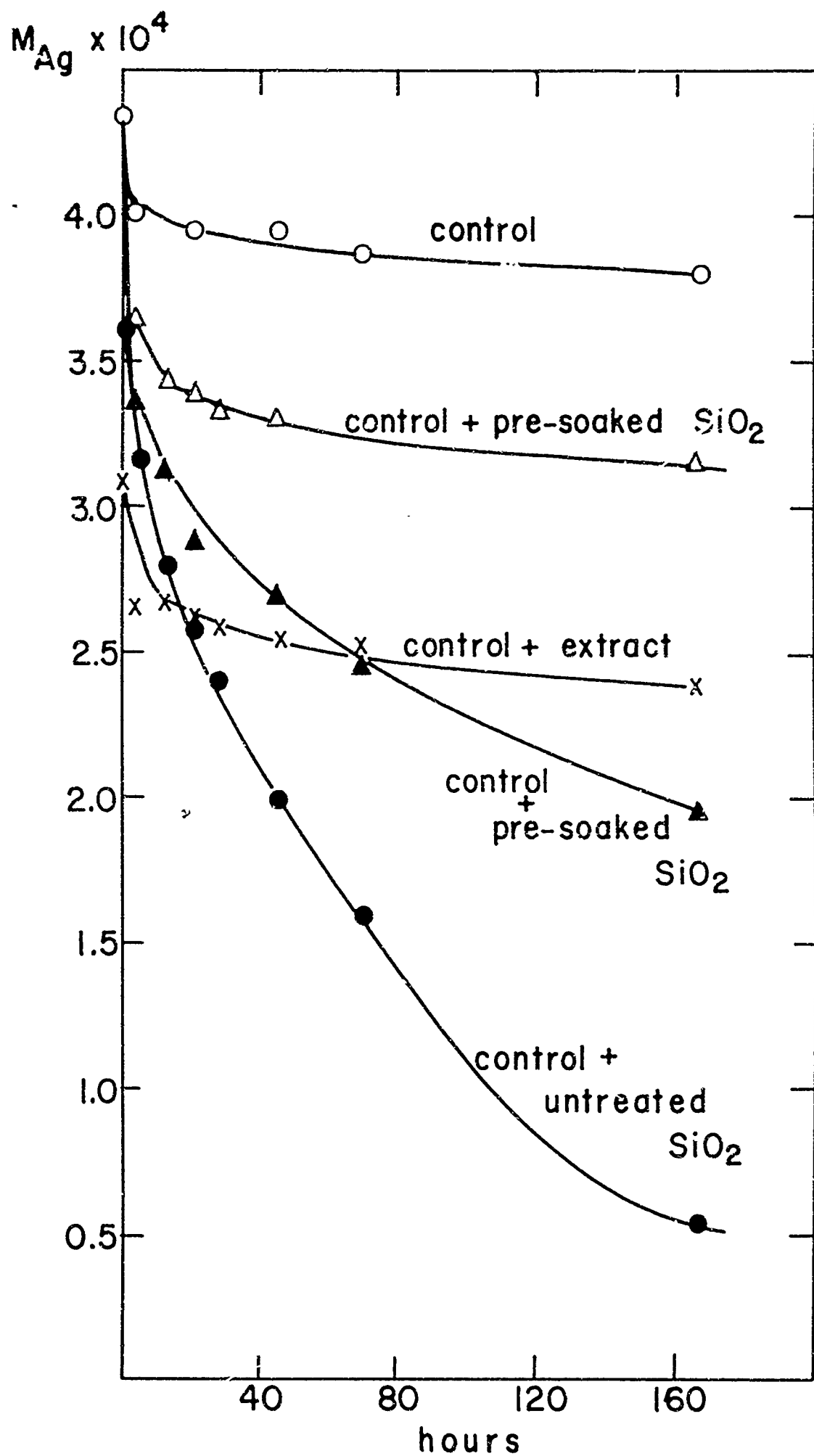


Figure 16 Effect of glass wool and glass wool extract on the decomposition of Ag_2O in 30% KOH.

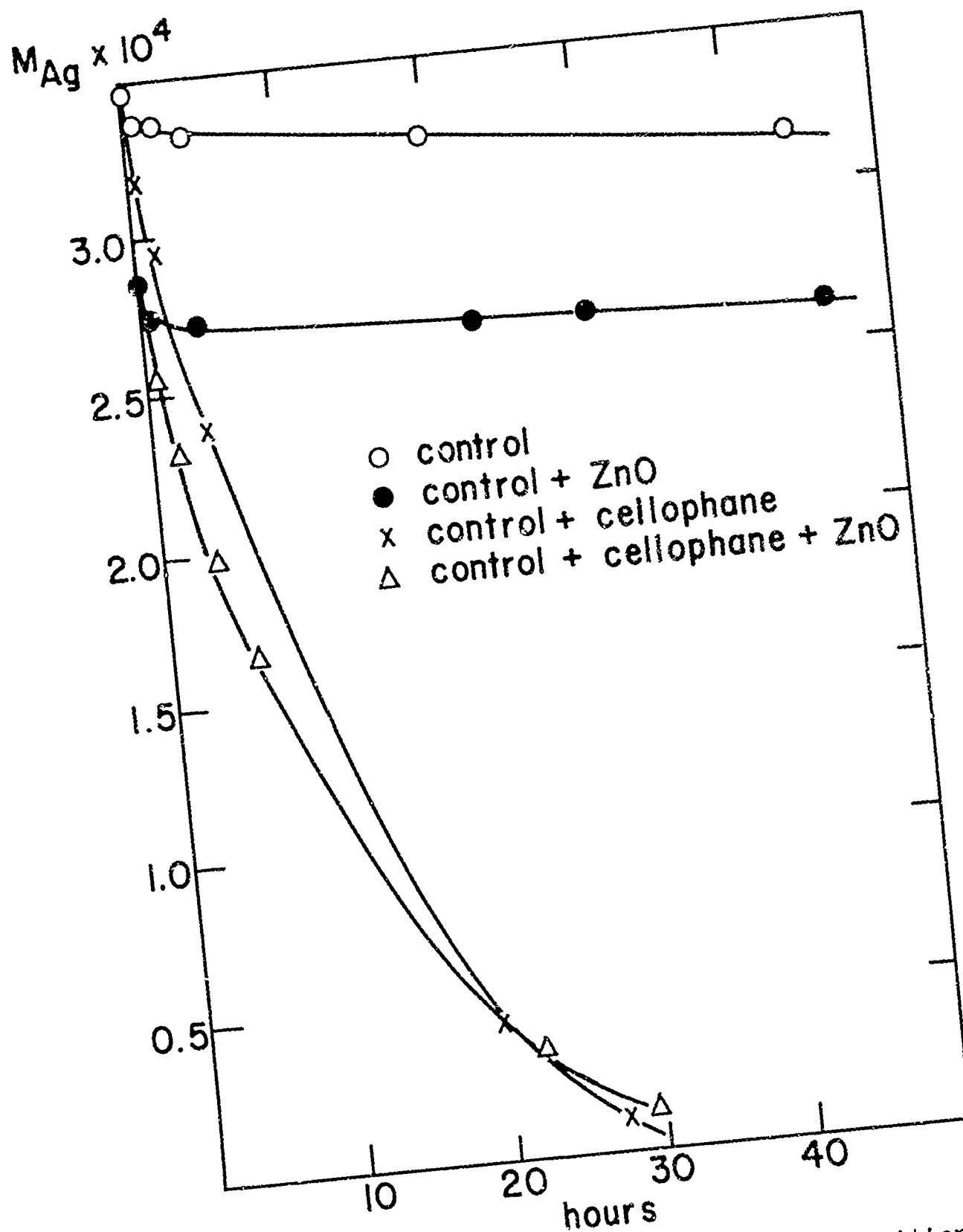


Figure 17 Effect of cellophane on Ag_2O decomposition.

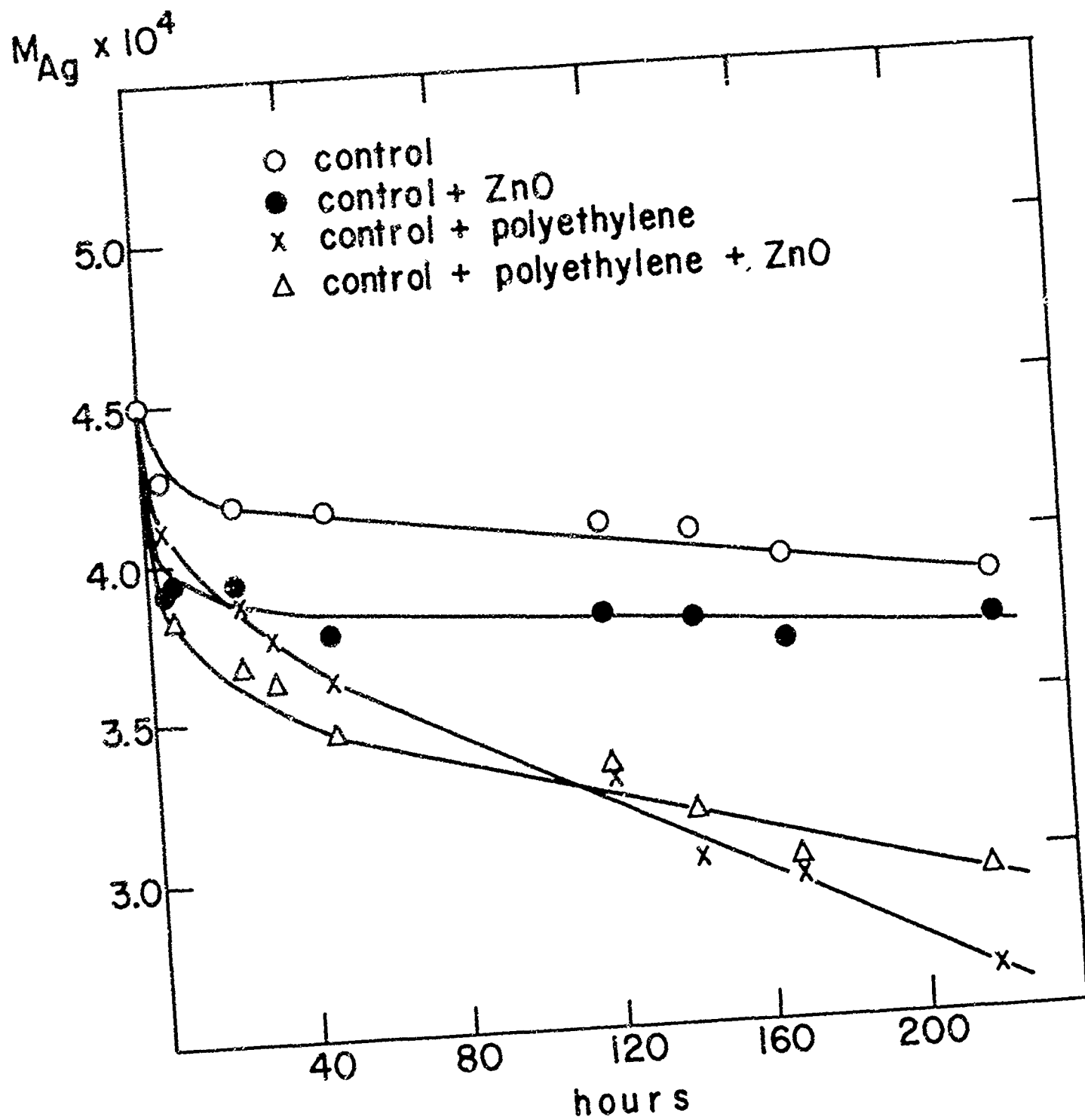


Figure 18 Effect of polyethylene on Ag_2O decomposition.

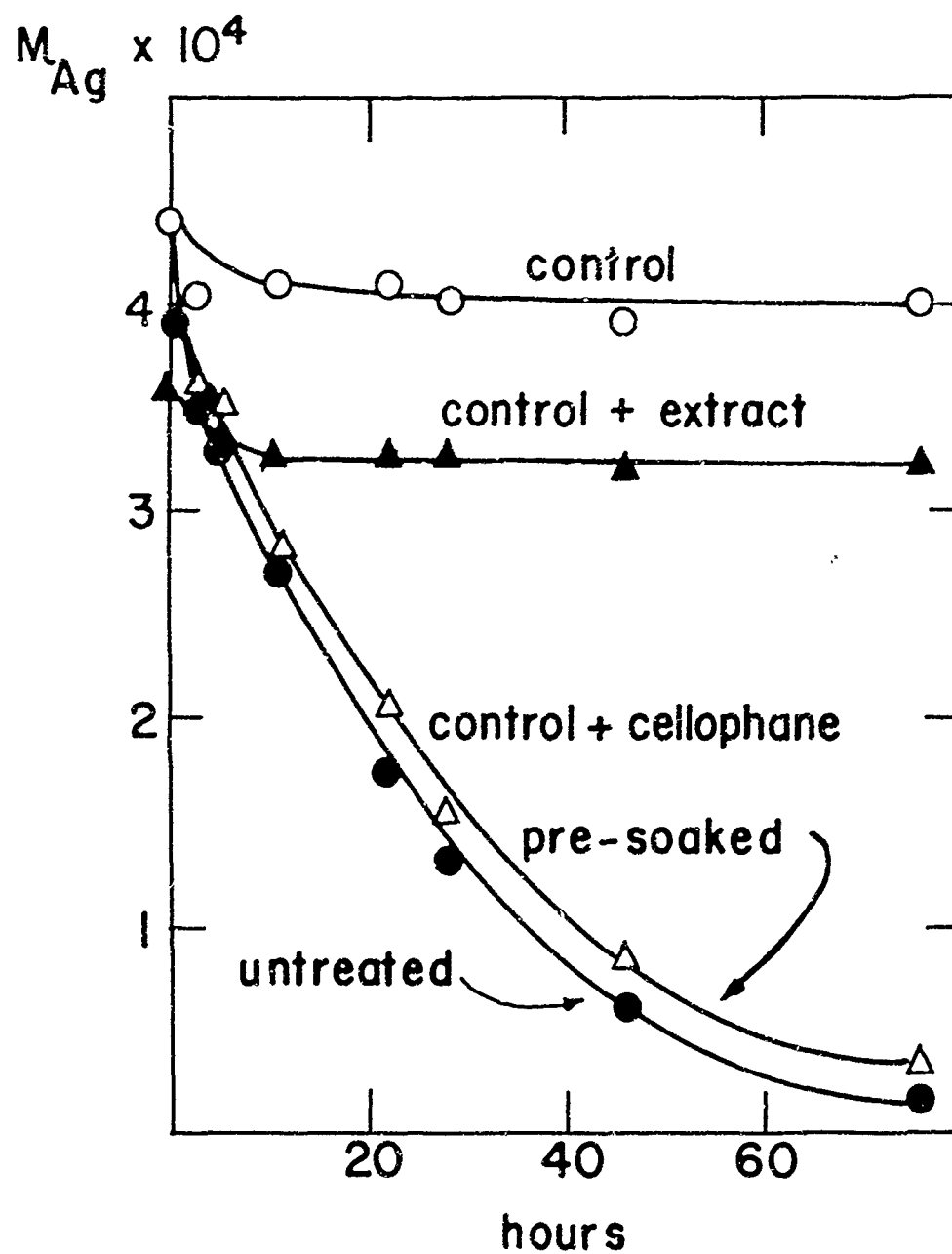


Figure 19 Effect of pre-soaked cellophane on the decomposition of dissolved Ag_2O .

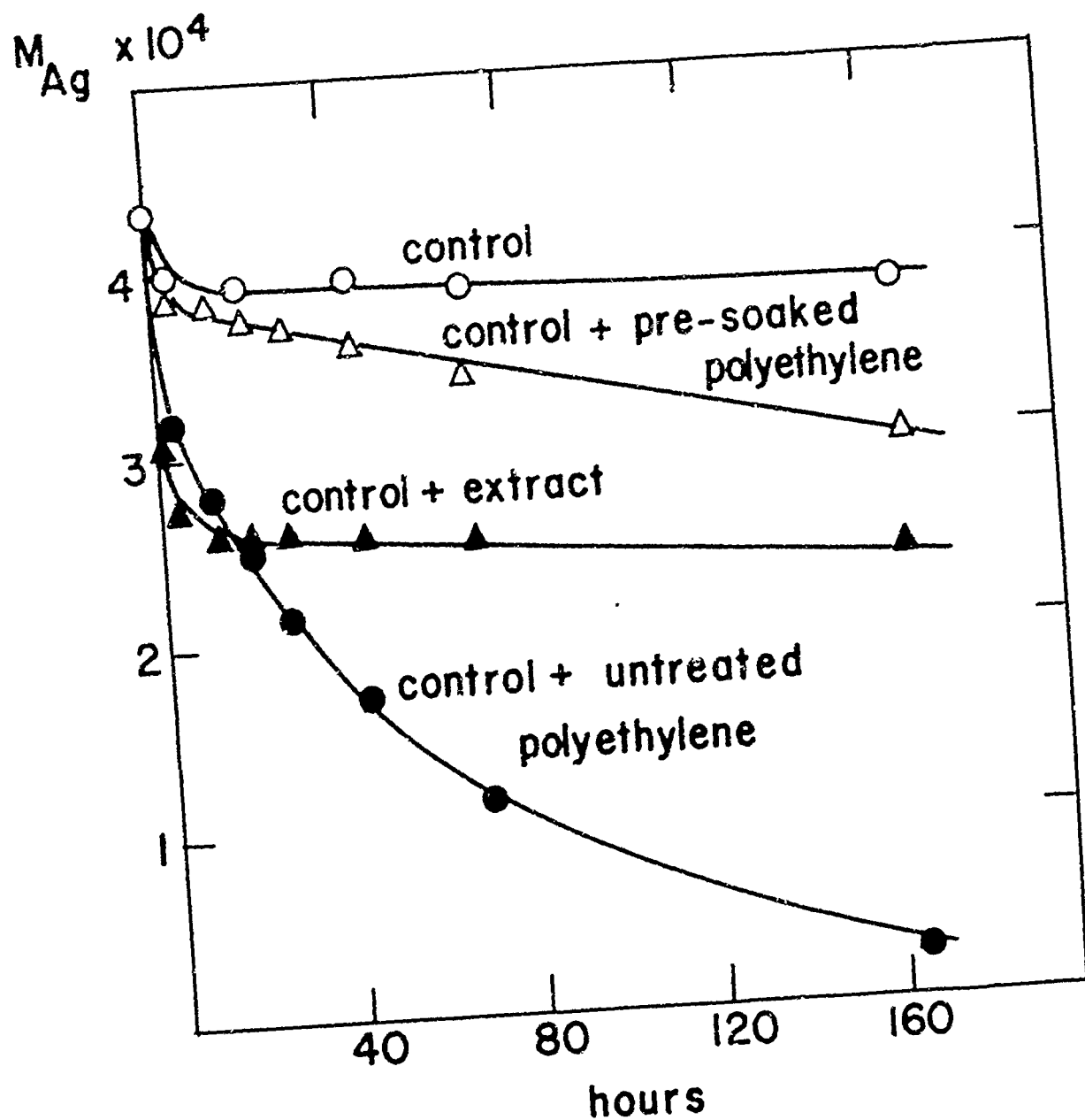


Figure 20 Effect of pre-soaked polyethylene on the decomposition of dissolved Ag_2O .

APPENDIX II

TABLES 1 THROUGH 15

TABLE I
SURFACTANTS USED IN THIS WORK

<u>Number</u>	<u>Nature</u>
1	anionic phosphate
2	sulfated fatty acid
3	anionic phosphate
4	alkanolamide
5	modified polyethoxy adduct
6	nonylphenoxypoly (ethelenoxy) ethanol
7	tridecyloxypoly (ethelenoxy) ethanol
8	similar to 7
9	poly(methyl vinyl ether/maleic anydride)
10	cellulose gum

TABLE II
EFFECT OF SURFACTANTS ON THE CYCLE-LIFE OF SILVER-ZINC
CELLS AT ROOM TEMPERATURE

<u>Surfactant</u>	<u>No. of Cycles</u>
1	78
2	348
3	174
4	186
5	186
6	320
7	421
8	561
9	561
10	473
None	165

Table III

EFFECT OF SURFACTANTS ON SILVER PICK-UP BY CELLOPHANE

<u>Surfactant</u>	<u>Ag pick-up gms x 10⁴</u>
none	6.8
1	6.5
none	5.8
2	7.7
none	4.0
3	4.5
none	4.5
4	2.5
none	5.8
5	6.5
none	5.6
6	5.6
none	2.9
7	3.4
none	3.4
8	3.4
none	5.7
9	5.6
none	6.1
10	5.0

TABLE IV

EFFECT OF SURFACTANTS ON THE RATE OF SILVER ION DIFFUSION
THROUGH CELLOPHANE IN 30% KOH AT ROOM TEMPERATURE

<u>Surfactant</u>	<u>Rate in gms. sq. in.⁻¹ hr.⁻¹ x 10³</u>
None	1.0
1	1.2
2	1.5
3	1.0
None	2.1
8	2.0
9	1.5
10	1.3

TABLE V

DIFFUSION RATE OF ZINCATE ION THROUGH CELLOPHANE IN 30%
KOH AT ROOM TEMPERATURE

<u>Surfactant</u>	<u>Diffusion Rate</u> <u>(moles/sq.in/min) x 10⁵</u>
1	3.4
2	4.1
3	3.6
5	2.8
6	2.8
7	3.9
8	3.7
9	3.7
10	3.8
None	4.1

TABLE VI

EFFECT OF SURFACTANTS ON THE RATE OF HYDROXIDE ION DIFFUSION
IN 30% KOH AT ROOM TEMPERATURE

<u>Surfactant</u>	(Moles/sq.in./minute) x 10 ²	
	<u>Cellophane</u>	<u>Sausage Casing</u>
2	1.7	1.2
6	1.5	1.1
7	1.5	1.1
8	1.5	1.0
9	1.5	1.0
10	1.5	1.0
None	1.6	1.1

TABLE VII

EFFECT OF ADDITIVES ON THE PLATING OF ZINC FROM ZINCATE SOLUTIONS

<u>Surfactant</u>	<u>Results</u>
None	Good plate at low current densities and low zincate concentration. Gassing at low zincate concentrations.
2	Gassing and foaming. ZnO or Zn(OH)_2 is precipitated during plating. Adherent plate except at high current densities and low zincate concentrations.
6	Some gassing. Adherent plate only at about 0.25 to 0.35M zincate.
7	Some gassing. Adherent plate except at high current densities and low zincate concentrations.
8	Some gassing. Adherence improves as both current density and zincate concentrations are lowered. Good plate over a wider range.
9	No gassing. No plate at low current densities and high zincate concentration. The plating improves as the zincate concentration decreases.
10	Some gassing. Very little plating at high zincate concentrations, but this improves as the current density increases and the zincate concentration decreases. No good at low zincate concentrations.

TABLE VIII
USE OF SURFACTANTS AS BINDERS IN ZINC ELECTRODES

<u>Surfactant</u>	<u>Results</u>
2	Considerable foaming but the zinc electrodes were in good condition.
6	Negatives were in poor condition. They did not seem to charge well.
7	Similar to No. 87, but cycled as long as the control.
8	Cycled as long as control, but active material was lost from the electrode.
9	Cycled longer than control; electrodes in good condition.
10	Poor cycle life; loss of active material from zinc electrode.
MoO ₂	Loss of active material from zinc electrode.

TABLE IX

EFFECT OF SURFACTANTS ON THE CURRENT DENSITY AT WHICH PASSIVATION OCCURS FOR A ZINC ANODE IN 30% KOH + 7 GRAMS/LITER OF ZnO AT ROOM TEMPERATURE

<u>Surfactant</u>	<u>Limiting C.D. amps/sq.in.</u>
1	1.66
2	3.16
3	1.54
4	1.30
5	2.60
6	2.40
7	2.66
8	2.66
9	2.80
10	3.06
None	2.76

TABLE X
 HALF-WAVE POTENTIALS FOR POLAROGRAPHIC REDUCTION OF ZINCATE IN
 30% KOH AT ROOM TEMPERATURE
 $E_{\frac{1}{2}}$ vs. Hg/HgO

<u>Surfactant</u>	<u>First Wave</u>	<u>Second Wave</u>
1	1.53	2.23
2	1.37	1.95
3	1.38	2.12
4	1.36	1.93
5	1.35	1.90
6	1.36	
7	1.34	1.90
8	1.39	1.95
9	1.36	1.91
10	1.34	1.89
None	1.32	1.86

TABLE XI
EFFECT OF PALLADIUM ON SILVER PICK-UP BY CELLOPHANE

<u>Positive Electrode</u>	<u>Current, ma.</u>	<u>Negative Electrode</u>	<u>No. of Cycles</u>	<u>Ag on separators gms x 10⁴</u>
Ag	40	Cd	13	17.4
Ag-Pd	40	Cd	13	12.2
Ag	200	Cd	13	15.1
Ag-Pd	200	Cd	13	0.2
Ag	40	Zn	13	9.1
Ag-Pd	40	Zn	13	± 15
Ag	200	Zn	5	9.2
Ag-Pd	200	Zn	1	± 6

TABLE XII
EFFECT OF ZnO ON SILVER PICK-UP BY CELLOPHANE

<u>Run No.</u>	<u>Positive Electrode</u>	<u>Negative Electrode</u>	<u>Electrolyte 30% KOH</u>	<u>Current, ma.</u>	<u>Ag Pick-up, gms $\times 10^4$</u>	<u>No. of Cycles</u>
17	Ag	Zn		200	6.3	5
19	Ag	Cd		200	30	13
20	Ag	Zn		40	12	13
18	Ag	Cd		40	34	13
25	Ag	Cd		40	14.6	5
26	Ag	Cd	+ZnO ^a	40	12.6	5
27	Ag	Cd		200	12.4	5
28	Ag	Cd	+ZnO ^a	200	11	5
29	Ag	Cd		40	16.8	5
30	Ag	Cd	+ZnO ^b	40	14.2	5
31	Ag	Cd		200	10.8	5
32	Ag	Cd	+ZnO ^b	200	13.2	5
33	Ag	Cd		40	7.4	3
34	Ag	Cd	+ZnO ^c	40	6.6	3
35	Ag	Cd		200	8.6	3
36	Ag	Cd	+ZnO ^c	200	4.7	3

a- ZnO added only to electrolyte in Cd compartment

b- ZnO added only to electrolyte in Ag compartment

c- ZnO added to all the electrolyte, 16 gm/liter

TABLE XIII
EFFECT OF ALUMINUM ON THE SILVER PICK-UP BY CELLOPHANE

<u>Positive Electrode</u>	<u>Negative Electrode</u>	<u>30% KOH</u>	<u>No. of Cycles</u>	<u>Current, ma.</u>	<u>Ag pick-up gms. x 10⁴</u>
Ag	Cd		3	40	6.3
Ag	Cd	+Al(OH) ₃	3	40	21
Ag	Cd		3	200	2.9
Ag	Cd	+Al(OH) ₃	3	200	4.8

TABLE XIV
EFFECT OF ZnO ON THE RATE OF DECOMPOSITION OF DISSOLVED Ag₂O IN
AQUEOUS KOH AT ROOM TEMPERATURE

<u>K O H</u> <u>concen.</u>	<u>Rate, moles/hr x 10⁷</u>		<u>Corrected rate,</u> <u>Moles/hr x 10³</u>	
	<u>Control</u>	<u>ZnO</u>	<u>Control</u>	<u>ZnO</u>
10%	1.4	1.3	0.7	2.3
20%	1.5	2.1	0.5	0.9
30%	1.3	1.9	0.36	0.6
40%	2.0	3.1	0.8	1.4

TABLE XV
SOLUBILITY OF Ag_2O IN 30% KOH CONTAINING ZINCATE AT ROOM TEMPERATURE

<u>Zincate Concen.</u>	<u>Molarity of $\text{Ag}_2\text{O} \times 10^4$</u>
0	4.1
0.04 M	3.9
0.20 M	3.8
0.22 M	3.6
0.40 M	3.7
0.60 M	3.9

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