

Investigation of the height and rate of capillary lift of electrolyte in the glass-mat separator of a sealed lead-acid battery

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Abstract

The height and rate of capillary lift of the electrolyte in the glass-mat separator of a sealed lead-acid battery was investigated. Dependence of the height and rate of rise of sulfuric acid on its density and separator compression degree was established. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Separator; AGM type; Lead-acid batteries; Capillary lift

1. Introduction

The height and rate of capillary lift of electrolyte in the separator are the important parameters for sealed lead-acid batteries. The first parameter in many respects predetermines the degree of electrolyte filling of the separator and the second the duration of the operation for filling the battery with electrolyte. Since sulfuric acid serves as active material in the lead-acid battery and participates in the main current formation reactions, its deficiency results in a decrease in capacity characteristics of the battery. So the ability of the separator to retain a certain volume of acid is a prerequisite for the operability of the sealed battery. In this work the investigation covered the effect of a number of factors, such as degree of compression of the separator and density of sulfuric acid on the height and rate of lift of electrolyte in the separator.

2. Experimental

As the object of investigation the use was made of the separator AXM300 with thickness of 2.03 mm (at 10 kPa), basis weight 300 g/cm², average pore size 3.2 μm, volume porosity >93%.

The diagram of the unit is shown in Fig. 1. The unit was fabricated out of Plexiglas. The strip of the separator of

width of 30 mm and length of 800 mm was inserted between the half-sections of the unit in a gap 3 mm wide. Both sections of the unit were compressed uniformly over the height with the help of bolts and nuts. The degree of compression of the separator was varied by means of vinyl plastic inserts with thickness of 0.4 mm fitted in the gap simultaneously with the separator. The assembled unit was positioned vertically and placed with the lower end in the tray with electrolyte tinted with copper sulfate in advance. The strip occupy all the volume when it is filled with electrolyte. The height of electrolyte was measured with the help of the ruler fitted on the unit.

3. Results and discussion

The maximum height of electrolyte in an individual capillary in principle can be easily determined as an equality of capillary (F_c) and gravitational (F_g) forces.

$$F_c = F_g \quad (1)$$

where $F_c = 2(\gamma S \cos \theta)/R$, $F_g = \rho H \beta S g$,

Having resolved (1) in respect to H , we get

$$H = \frac{2\gamma \cos \theta}{\rho \beta R g} \quad (2)$$

The similar equation, but without considering the tortuosity factor, is given in paper [1].

The Eq. (2) shows that in real conditions of the capillary rise of electrolyte in the separator, it is not possible to secure a clear-cut interface, as the separator contains capillaries of

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Nomenclature

d_{10}	thickness of separator mat under 10 kPa
d_P	thickness of separator mat under pressure P
F_c	capillary force
F_f	friction of liquid caused by flow
F_g	gravitational force
g	gravitational constant
H	height of electrolyte
P_c	capillary pressure
P_g	gravitational pressure
r	distance from the center of the capillary (pore)
R	capillary (pore) radius
S	cross-sectional area of capillary

Greek letters

β	tortuosity
γ	surface tension
η	viscosity
θ	contact angle
ρ	density of electrolyte
τ	time

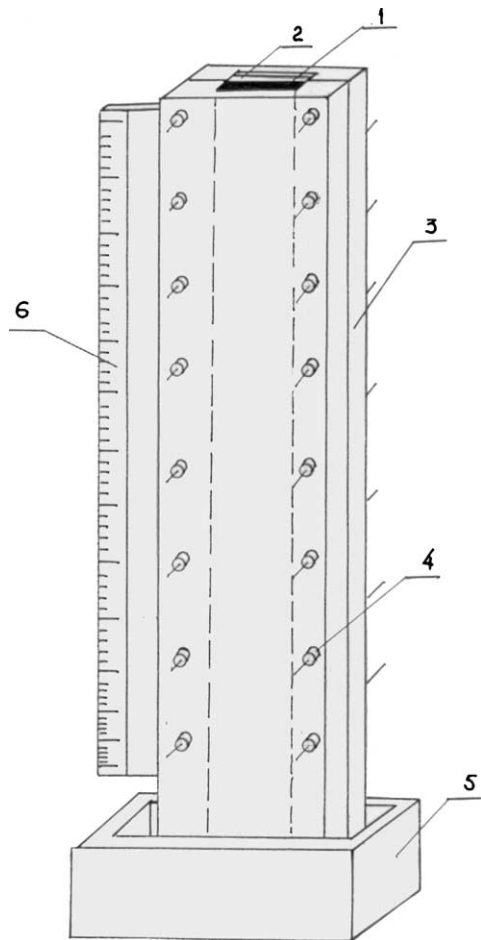


Fig. 1. Diagram of unit for determination of height and rate of capillary rise of electrolyte in separator: (1) separator; (2) insert; (3) body of unit; (4) fixing bolt; (5) tray filled with electrolyte and (6) ruler.

different diameter and tortuosity factor. In this case distribution of electrolyte over the height could be represented as:

$$F(H) = \frac{A}{F(R) F(\beta)} \quad (3)$$

where $A = (2\gamma \cos \theta) / \rho g$ and $F(H)$, $F(R)$, $F(\beta)$ are the functions of distribution of electrolyte over the height, radius and tortuosity of pores of the separator, respectively.

The tests run proved the above statement. As a result of the rise of electrolyte the coloring of the separator was non-uniform. In the lower section the separator was colored practically completely, but with an increase in height the intensity (density) of coloring reduced to zero. In this connection two parameters were proposed to describe the height of the of electrolyte rise:

1. The height of electrolyte interface below which the separator filling degree was more than 80% (H_{80}).
2. The height of the electrolyte interface at which the last traces of electrolyte were noted—the maximum height of the lift (H_{\max}).

It follows from Eq. (2) that the height of the capillary rise also depends on the density of the electrolyte, it drops with increase in density and degree of separator compression. The latter follows from dependence of the height of the electrolyte rise on the radius of the pores.

Fig. 2 shows the dependence of H_{80} and H_{\max} on the degree of separator compression (K) (determined out of the equation $K = (1 - d_P) / d_{10} \times 100\%$) for the specimens cut from the longitudinal and crosswise directions of the separator roll. The electrolyte used was 1.28 g/cm³ density acid.

Based on the magnitude of the gap of the unit modified by means of inserts, the following degrees of compression were obtained: 8.4% ($d_P > d_{10}$), 11% ($d_P < d_{10}$), and 30% ($d_P < d_{10}$). It is seen from the figure that H_{\max} practically independent of the separator compression, while H_{80} significantly increases with compression. For the range of change of K , 10–30%, H_{\max} varies between the limits of 52 and 56 mm and H_{80} in the range from 20 to 40 mm. The nature of these curves is understandable physically and is explained on the basis of the following model.

In the initial material in the direction Y (along the surface of the electrodes) there occurs a certain distribution of pore radius and the electrolyte distributes itself as a function of height in accordance with $F(R)$. Upon compression of the separator there takes place the spatial redistribution of the micro glass fibers in such a way as to diminish the fraction of large pores (area of the lower density of fibers), since it is much easier for fibers to fill these voids. At the same time fine pores (area of high density of fibers) remain unchanged, since they exhibit high resistance to ingress of fibers. As a result the normal function of distribution of pore radius shifts towards a decrease of radius of pores in such a way that the radius of small pores does not change, which is evidenced by the independence of the maximum electrolyte

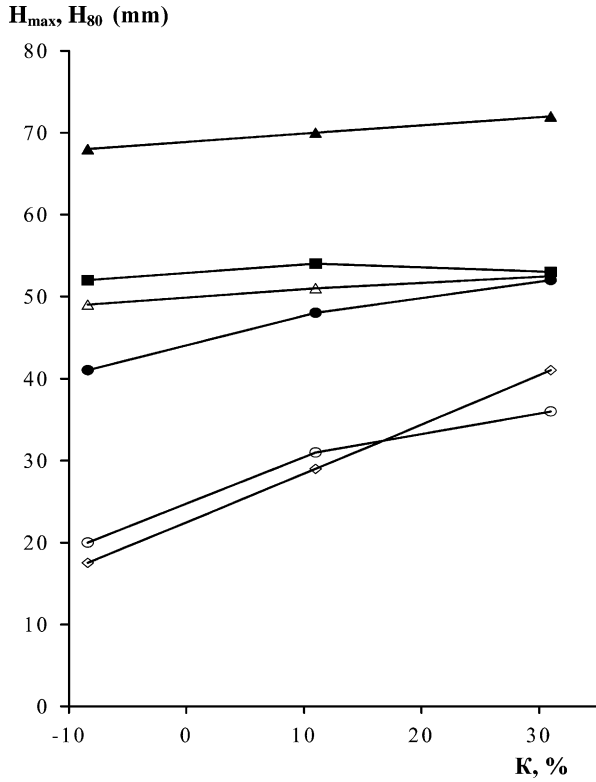


Fig. 2. Dependence of (○, ◇, ●) H_{80} and (△, ■, ▲) H_{max} on the separator compression (K) for the specimens cut out in the (◇, ●, ■, ▲) longitudinal and (○, △) crosswise directions of separator roll in solution acid (H_2SO_4) of density (○, ◇, △, ■) 1.28 and (●, ▲) 1.05 g/cm^3 .

rise (H_{max}) from degree of compression, but parameter H_{80} increases, since the average radius of pores goes down, which corresponds to the Eq. (2).

Fig. 2 shows the dependence of the height of electrolyte on acid density. It is seen that with a reduction in density the height of electrolyte increases, which is also consistent with Eq. (2).

In papers [1,2] the equation is shown which relates the height of lift of electrolyte and time. However, it was obtained without considering the gravitation forces, which affect the rate of rise of electrolyte in the capillaries of the porous body. In this work an attempt was made to derive the analytical dependence of the rate of rise of electrolyte on parameters characterizing the condition of the separator and its experimental verification.

The rise of liquid in capillaries is determined by the ratio of moving forces and movement braking forces. In stationary conditions we will have:

$$F_c = F_g + F_f \quad (4)$$

Friction between layers during flow emerges due to their different velocity. Thus, the further the layer of liquid is from the center of the capillary, the lower is its velocity. Then with consideration of the Newton equation for friction forces in

liquid flow, one can write for the overall friction force on a selected layer dr :

$$F_f = -\eta 2\pi d \left(\frac{r dW}{dr} \right) \quad (5)$$

Considering (4) and replacing forces by pressure we can write:

$$-\eta d \left(\frac{r dW}{dr} \right) = (P_c - P_g) r dr \quad (6)$$

From (6) we get,

$$\frac{d^2 W}{dr^2} + \frac{1}{r} \frac{dW}{dr} = -\frac{1}{\eta} (P_c - P_g) \quad (7)$$

Having resolved (7) we can write for the rate of the flow in the layer in question:

$$W = \frac{(P_c - P_g) (R^2 - r^2)}{4\eta} \quad (8)$$

With the rate of flow W per unit of time through the layer with thickness dr the following volume of electrolyte will be transferred (dV):

$$dV = (2\pi r dr) W \quad (9)$$

Having substituting (8) and (9) and integrating within the limits (0, R) we get

$$V = \frac{\pi (P_c - P_g) R^4}{4\eta} \quad (10)$$

The volume of liquid dV which passes for time $d\tau$:

$$dV = \frac{\pi (P_c - P_g) R^4 d\tau}{4\eta} \quad (11)$$

Having substituted $dV = \rho \pi R^2 \beta dH$ into (11), we get the equation for the rate of rise of the liquid in the capillary:

$$\frac{dH}{d\tau} = \frac{(P_c - P_g) R^2}{4\eta \rho \beta} \quad (12)$$

It follows from the Eq. (12) that the rate of rise of the liquid in the capillary increases with increase in radius and drops with increase in viscosity and density of electrolyte:

Having substituting $P_c = 2\gamma \cos \theta / R$ and $P_g = mg / \pi R^2 = \rho \beta g H$ into (12), we get

$$\frac{dH}{d\tau} = \frac{\gamma R \cos \theta}{2\eta \rho \beta} - \frac{g R^2 H}{4\eta} \quad (13)$$

Transforming (13) it is easy to derive:

$$\frac{dH}{(A_2 R - A_3 R^2 H)} = d\tau \quad (14)$$

$$A_2 \equiv \frac{\gamma \cos \theta}{2\eta \rho \beta}, \quad A_3 \equiv \frac{g}{4\eta}$$

Integrating with consideration of the initial conditions $\tau = 0, H = 0$, we get

$$\ln\left(1 - \frac{A_3RH}{A_2}\right) = -A_3R^2\tau \quad (15)$$

From (15) we get the dependence of the height of lift of electrolyte with time:

$$H = \frac{2\gamma \cos \theta}{\rho\beta gR} \left[1 - \exp\left(-\frac{gR^2}{4\eta} \tau\right)\right] \quad (16)$$

If τ is small, then the exponent in (16) could be expanded into the sequence limited by two first members of expansion. Then for small τ we will get

$$H = A_2R\tau = \frac{\gamma R\tau \cos \theta}{2\eta\rho\beta} \quad (17)$$

It follows from (17) that with small τ the height of electrolyte in the capillary should show linear dependence on time and increase with increase in radius of the capillary. With relatively large values of time one should expect a

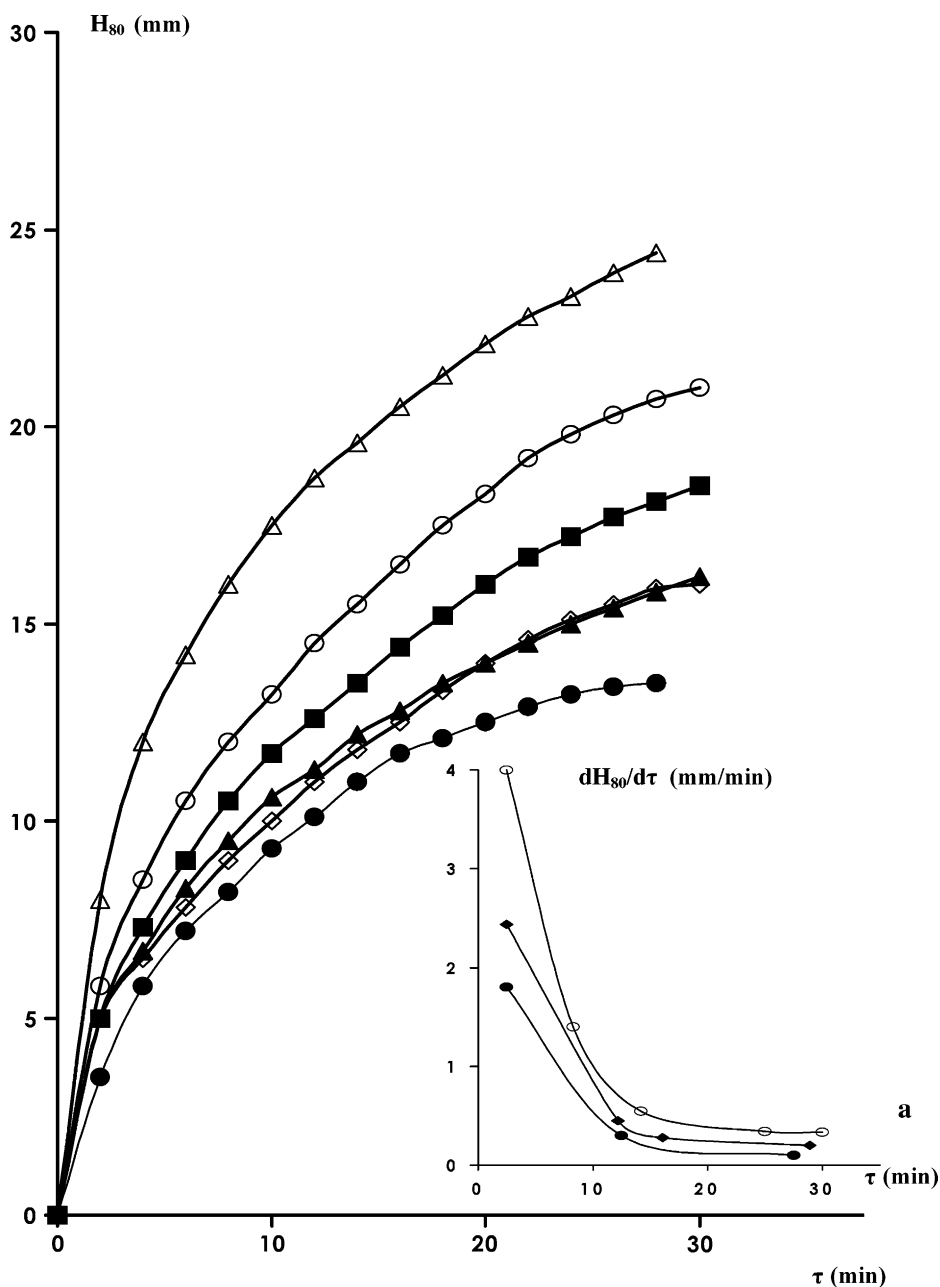


Fig. 3. Dependence of height of electrolyte (H_{80}) and rate of rise ($dH_{80}/d\tau$) (Fig. 3a) on time in solution acid of density (\circ, \diamond, \bullet) 1.28 and ($\triangle, \blacksquare, \blacktriangle$) 1.05 g/cm^3 . Symbols: (\circ, \triangle) freely suspended uncompressed separator; (\diamond, \blacksquare) separator fitted in gap 2.2 mm ($K = -8.4\%$); (\bullet, \blacktriangle) separator fitted in gap 1.4 mm ($K = 31\%$).

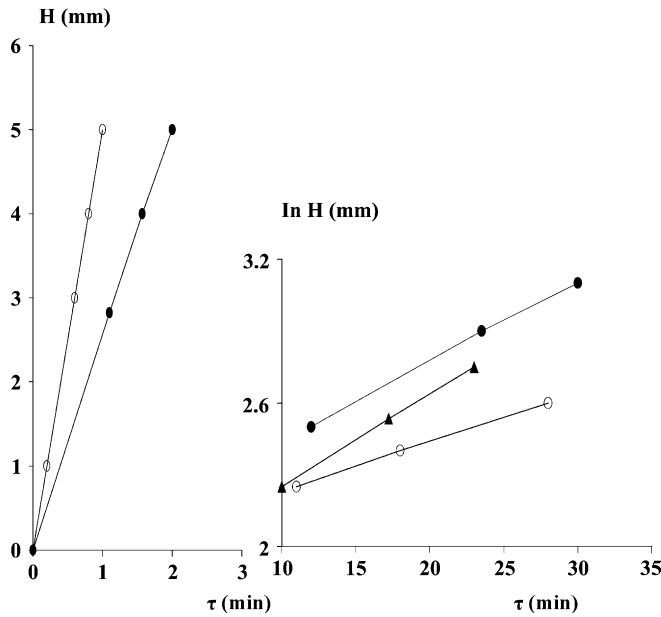


Fig. 4. Dependence of $H = F(\tau)$ for the initial period of wetting of the separator and dependence $\ln H = F(\tau)$ for subsequent stage. Symbol: (○) freely suspended uncompressed separator; (▲) separator fitted in gap 2.2 mm; (●) separator fitted in gap 1.4 mm.

linear dependence of $\ln H$ on τ in accordance with (16). For large values of τ with $\exp(2gR\tau/4\eta) \gg 1$ from (16) we get:

$$H_{\max} = \frac{2\gamma \cos \theta}{\rho\beta gR} \quad (18)$$

The Eq. (18) coincides with the earlier derived Eq. (2). It follows from (18) that the maximum height of electrolyte increases with higher γ and $\cos \theta$ and decreases with a reduction in ρ , β .

Fig. 3 shows the dependence of the height of electrolyte (H_{80}) and Fig. 3a rate of rise ($dH_{80}/d\tau$) on the duration of soaking. The density of the acid is 1.28 g/cm^3 . The tests were run at compressions of -8.4 and 31% .

It is seen from the figure that with an increase in compression (reduction of radius of pores) of the separator, the rate of rise as function of time drops. It was indicated earlier that this parameter ($dH/d\tau$) is important, since it determines the rate of wetting of the electrode block when filling the battery with electrolyte. It is evident that the higher compression of the separator will lead to a longer duration of this technological operation.

For verification of the earlier discussed mathematical model of the process of capillary rise we use the dependence $H = F(\tau)$ for the initial period of wetting and the dependence $\ln H = F(\tau)$ for the subsequent stage (Fig. 4). It is

seen from the figure that during the initial period of the process of capillary rise the dependence of the height of lift of electrolyte has a linear dependence on time, which corresponds to the Eq. (16) for small values of τ . For $\tau > 10 \text{ min}$ the dependence $\ln H = F(\tau)$ is linear, which also corresponds to the Eq. (16) for large τ . With extremely large τ the height of lift does not depend on time as shown by the Eq. (18).

Thus, the analytically derived model of the capillary lift of electrolyte in contrast to the paper [1] adequately describes the experimental data over the entire time interval while considering the gravitation forces.

Fig. 3 shows the dependence of the height on time for electrolyte with density 1.05 and 1.28 g/cm^3 , i.e. for the electrolyte of discharged and charged battery. The separators were tested in the following conditions:

- freely suspended uncompressed separator;
- separator fitted in gap 2.2 mm ($K = -8.4\%$);
- separator fitted in gap 1.4 mm ($K = 31\%$).

The resulting dependences $H = F(\tau)$ in acid solution of density 1.05 g/cm^3 are qualitatively consistent with the similar curves obtained for acid of density 1.28 g/cm^3 , i.e. with increase in time of wetting and degree of compression of the separator the rate of rise of electrolyte drops. It is also seen from the figure that the rate of electrolyte rise noticeably increases with decrease of density of acid.

4. Conclusions

The work investigated was the process of rise of electrolyte in the pores of AGM separator.

A model of the process allowing to evaluate the velocity and height of capillary rise of electrolyte has been suggested and also factors affecting these parameters have been determined. The correctness of the suggested model has been confirmed by the results of the experiments to determine the velocity and height of electrolyte rise versus time, separator compression and electrolyte density. The results received may be useful for selecting an optimal condition of filling of a large-sized valve-regulated lead-acid battery with electrolyte.

References

- [1] B. Culpin, J. Power Sources 53 (1995) 127–133.
- [2] G.C. Zguris, J. Power Sources 88 (2000) 36–43.