

FACTORS AFFECTING THE FORMATION OF LEAD/ACID TUBULAR POSITIVES

J. M. STEVENSON

Chloride Motive Power, P.O.Box 1, Salford Road, Bolton BL5 1DD (Gt. Britain)

A. T. KUHN

Bio-Materials Science Department, Institute of Dental Surgery, 256 Gray's Inn Road, London WC1X 8LD (Gt. Britain)

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Summary

The first-cycle discharge capacity of tubular ("gauntlet"), wet-filled, lead-acid traction positives is reported as a function of the formation parameters and fill density. Formation acid specific gravities from 1.060 to 1.300, temperatures from 10 to 50 °C, formation current densities from 0.53 to 0.84 A dm⁻² all at three paste densities, together with formation time (charge), are systematically varied. It is seen that very large variations in capacity can result, and the data point to optimum conditions for this important stage of battery manufacture.

Factors affecting the formation of lead/acid tubular positives

The capacity of the lead/acid battery is ultimately limited by three factors, namely, positive plate discharge, negative plate discharge, and acid starvation. In practice, the capacity of most automotive or traction batteries is limited by positive plate/acid volume factors. Positive plate capacity can be examined in isolation by using "infinite volume of acid" conditions, *i.e.*, ensuring sufficient volume of acid to avoid any significant change of acidity during the discharge process. If constant current and temperature conditions are employed then valid measurements of positive plate capacity can be made. This has been the procedure in the work reported here.

There is little published data relating the capacity of positive lead/acid plates to formation conditions. Almost all of these data relate to flat-plate (automotive type) positives, and whilst the electrochemistry of these is no different from that in tubular or gauntlet type (traction) positives, their configurational differences, with the far greater diffusion restrictions in the gauntlet types, means that formation behaviour for the two may well be quite different, and any suggestion [12] that they must be the same is erro-

neous. No published study relating to the formation of tubular plates has been found in the literature. Factors which are known to affect the formation (and, hence, the initial capacity) of positives are numerous, *e.g.*, paste composition, paste density (pore volume), concentration of forming electrolyte, temperature of forming electrolyte, current density during formation, current duration in formation, use of rest periods during formation.

An early study of flat positive plates [1] covered a wide range of temperatures but employed a single current density, paste density, and electrolyte concentration. Furthermore, the plates were formed as groups in excess acid and discharged in a restricted acid volume, *i.e.*, acid starvation would have been important. The work of Greenburg and Caldwell [2] has also been widely reported. Again, electrolyte temperature was the only variable. Although tank formation was used, it appears that the plates were assembled in cells and then discharged, again in a limited volume of acid. These workers focussed on rather specific aspects, in particular local action and its relation to the chemical composition of the formed plates.

In a more extensive study on SLI plates formed in excess electrolyte, Brumbaugh [3] investigated the relationships between the so-called "outer" parameters of current density, acid concentration and electrolyte temperature, and the so-called "inner" parameters of porosity, surface area, pore volume, and capacity. A relationship was also shown to exist between the surface area of the active material (PbO_2) and the particle size of the starting material (PbO) from which it is formed. The study also included a discussion of the effects of battery cycling on these relationships, but details of the conditions were not given. Closely following this work, Dobson [4] examined the outer forming parameters, including paste density, in relation to the total PbO_2 content, the ratio of $\alpha\text{-PbO}_2$ to $\beta\text{-PbO}_2$ and their effects on capacity. The work provided the first insight into the little known effects of formation on the two PbO_2 modifications.

Many studies have been carried out on the crystallography and morphology of lead dioxide in both formed and cycled SLI positive plates, *e.g.*, refs. 5 - 11. Most of these workers used a rigid set of conditions with little or no variation in forming parameters. However, in an attempt to optimise formation conditions, Simon and Jones [9] studied the size and shape of the formed crystals as a function of temperature, specific gravity of the electrolyte, and current density. As in the investigations of others, little attempt was made by these authors to correlate their findings to plate capacity.

More recently, Bode [10] studied a broad range of formation characteristics. He commented on the resulting chemical composition, ratio of $\alpha\text{-PbO}_2$ to $\beta\text{-PbO}_2$, porosity, pore distribution, internal surface area, crystal morphology and capacity. With particular reference to the latter, Bode examined the A h kg^{-1} after 6, 25, 50, and 75 cycles. The variables used were electrolyte temperature, forming acid concentration, and formation current density.

Considering all the above studies, we must first assess the methodology and secondly, summarise the findings. In respect of the first, it is clear that

many of the studies were not rigorous. Quite apart from lack of consideration shown towards possible effects from acid starvation, insufficient control was exercised on temperature. Recently the use of transistorised constant-current power sources has allowed a more precise control of this variable.

The findings of early workers can best be discussed in terms of trends. Thus, it can be said that [10] :-

(i) increase in formation temperature causes an increase in capacity, but a limit is reached at 40 - 50 °C;

(ii) increase in formation acidity causes an increased capacity;

(iii) initial capacity as a function of formation current density passes through a maximum;

(iv) paste density is inversely proportional to initial capacity (defined as $A \text{ h kg}^{-1}$) although a lower limit to this trend is determined by voids and packing density. Cycling affects low density pastes more drastically than denser mixtures.

In respect of the above trends, there are a number of conflicting factors, such as the proportion of $\alpha\text{-PbO}_2$ present (adverse), a high surface area (favourable) and a high pore size (adverse), which all affect the initial capacity.

Since a comprehensive examination of all of these variables would require a huge programme of work, we have attempted only to cover what we consider to be the major variables, (*i.e.*, acid concentration, temperature, current densities, paste density). A single paste composition was used for the whole of the programme to eliminate errors due to compositional variation. Capacity was measured as a function of the parameters listed above, discharging the plates at a single current density, although this too is potentially a variable.

In summary, while it is not claimed that the results reported here are in any way exhaustive, even though over 200 experiments were carried out, it is at least felt that the experimental conditions were much more rigorous than many previous studies, and that they can serve as a bench mark for extensions of the present work.

We have used two units to measure capacity, namely, capacity (or $A \text{ h}$) per plate and capacity per kg of paste. The latter, though it appears to be the more fundamental quantity, should not be over-rated as such. As long as the positive plate geometry and configuration are constant, it is meaningful, but it should be understood that tubes of greater or lesser diameter will give different capacities even when filled with the same paste.

Experimental

In order to eliminate processing variables, all plates were made up from the same bath of oxide slurry. The oxide for this slurry consisted of two parts red lead to one part Hardinge Mill type oxide (grey oxide). This oxide was then filled into non-woven tubular retainers which contained antimonial-lead spines (12% Sb). All plates were 15-tube traction type, with a geometric

surface area of 9.5 dm^2 . The density of the active material was in the range $3.8 - 5.2 \text{ g cm}^{-3}$. The plates were then sulphated (70 - 80%) in sulphuric acid of relative density 1.500 for 6 h, and then washed free from sulphuric acid, dried, and then stored. The acid used throughout the work was general purpose reagent-type quality.

The test rig consisted of three tanks connected through a centrifugal pump (Type Totton PC40/6) to a main reservoir. The circulation rate from the main tank (equally distributed to the three test tanks) was $15 - 20 \text{ l min}^{-1}$. The total volume of acid in the system was 50 - 60 l. The electrolyte in the main reservoir was thermostatted using glass heat exchanging coils connected to a (Churchill) temperature regulator unit. Measurements showed that the test tanks could be maintained to within $\pm 1 \text{ }^\circ\text{C}$ of the preset temperature. Current was supplied from a constant-current unit (max. rating 10 A) and measured with a Sangamo Weston ammeter. Plate and cell voltages were measured using a Chessell flat-bed, multi-channel recorder.

A cadmium stick or $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode was used in the formation acid. Capacity values were derived in the normal manner by measuring to the "knee" of the discharge curve. The discharge data were obtained by driving current through the positive plate and an unfilled 6% antimonial grid. This procedure avoided any effects due to negative plate variations.

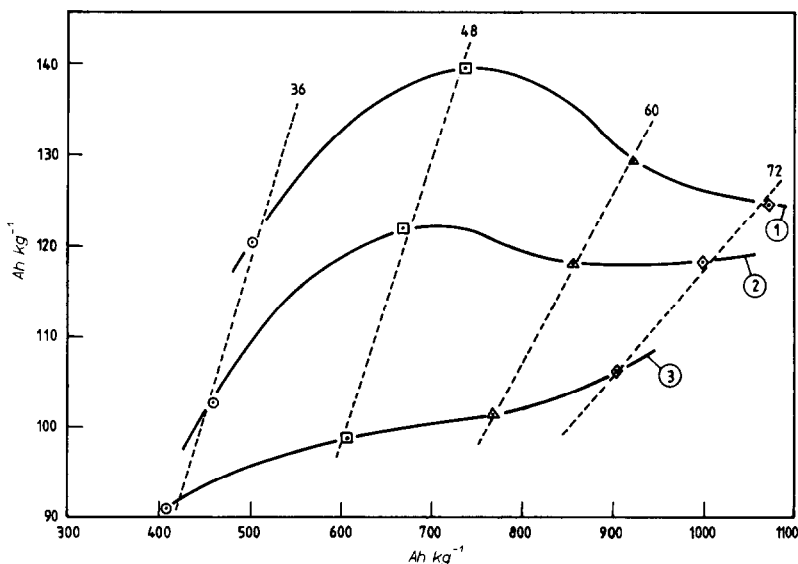


Fig. 1. Capacity of positive (after 1st discharge) vs. formation charge (both parameters expressed as Ah kg^{-1} active material). Formation conditions: $20 \text{ }^\circ\text{C}$; sp. gr. 1.060; current density 0.84 A dm^{-2} geometrical plate area. Paste density: 1, low; 2, medium; 3, high. Discharge current density 1.24 A dm^{-2} . The dashed lines are inserted to indicate points having the same formation times (marked in hours).

Results

Capacity is a multi-variate factor where the constituent parameters may or may not be interdependent, and analysis is an exceedingly difficult problem. The best approach is initially to seek dominant trends. To do so, we have taken the very large body of data and examined it in a number of ways (Figs. 1 - 9).

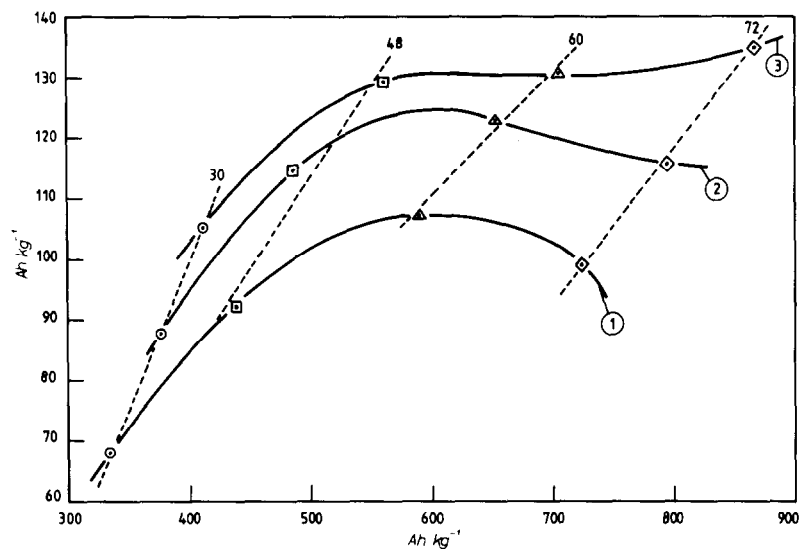


Fig. 2. As Fig. 1, but formation current density 0.63 A dm^{-2} . Paste density: 1, high; 2, medium; 3, low.

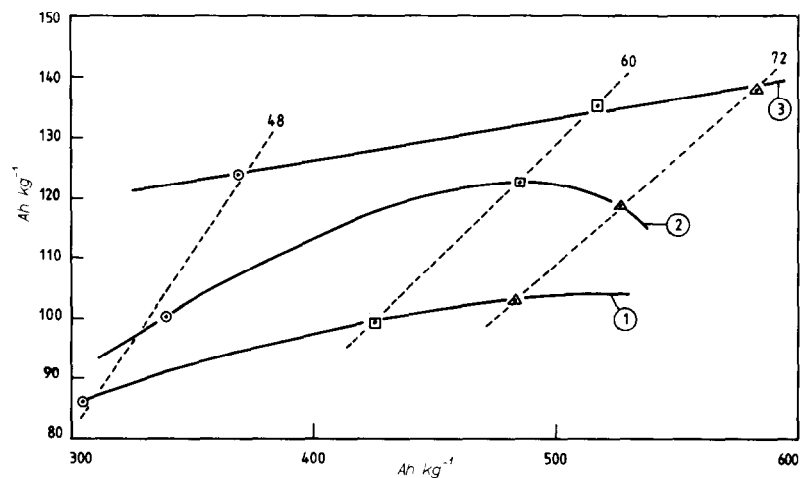


Fig. 3. As Fig. 1, but formation current density 0.42 A dm^{-2} . Paste densities as in Fig. 2.

An important first conclusion can be drawn from inspection of the graphs. Whilst one would predict that the rate of charge acceptance might vary as a function of temperature, specific gravity, and current density (though not fill density), at "infinite" time, it might be expected that a constant maximum possible capacity would be obtained. In fact, as can be seen, this is not so, and under a range of conditions excess charge input can lead to a decrease in capacity (*cf.* Figs. 1 - 3). This observation, which we have not seen reported elsewhere in the literature, has significance both in practical and theoretical terms. It thus emerges that the point in time at which the comparison is made (in terms of either formation time or charge input) is arbitrary. The reason for the decrease in capacity with excess charge is at present undetermined. A possible explanation may be that the gassing which occurs within the tube under these conditions allows a settling of the active material with a resultant increase in density, and this is currently being investigated.

Effect of electrolyte concentration

Considering the effects of electrolyte specific gravity, it seems (Figs. 4 - 6) that the capacity of the positive plate at the initial discharge is inversely proportional to specific gravity in the range 1.060 - 1.300 for all paste densities. The values converge at very long formation times or high charge inputs (quite beyond those that would be used in practice). Overall, the difference in capacity caused by change in formation acid gravity over the range investigated is very small by comparison with other parameters discussed below.

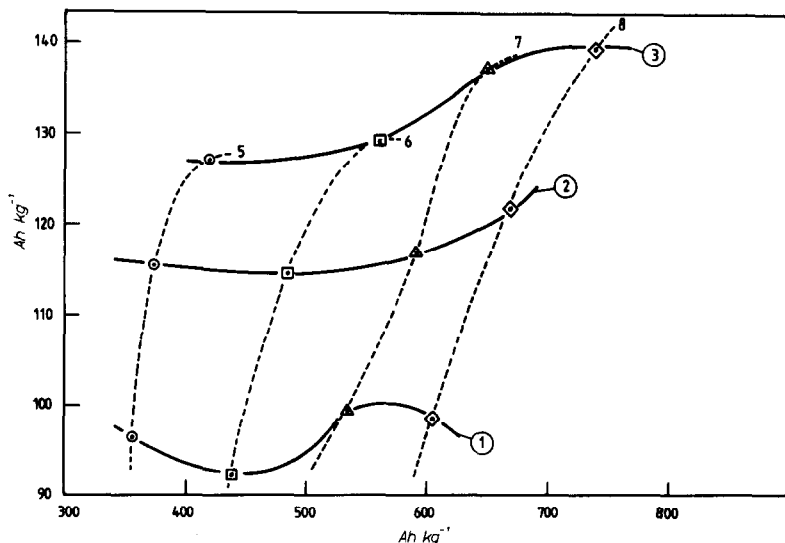


Fig. 4. As Fig. 1, but showing effect of electrolyte concentration at different formation current densities, 5, 6, 7 and 8 A (0.53, 0.63, 0.74 and 0.84 A dm⁻², respectively). Formation electrolyte 1.060 sp. gr. The dashed lines tie together points of equal formation current density. (Paste densities: 1, high; 2, medium; 3, low.)

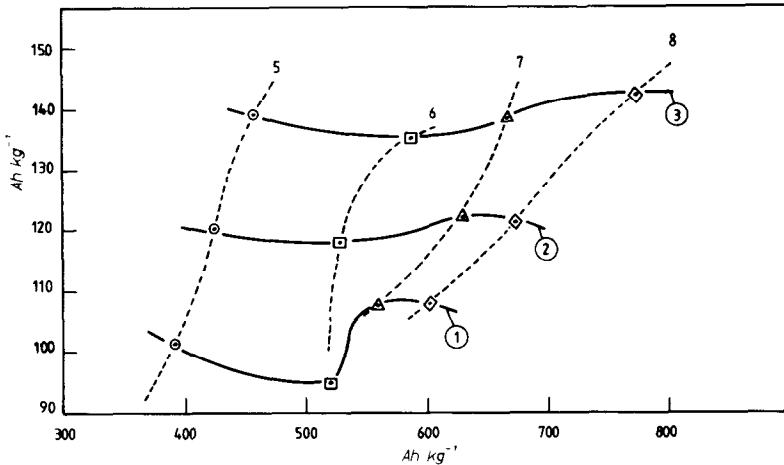


Fig. 5. As Fig. 1, but with formation electrolyte 1.120 sp. gr. Formation currents and paste densities as in Fig. 4.

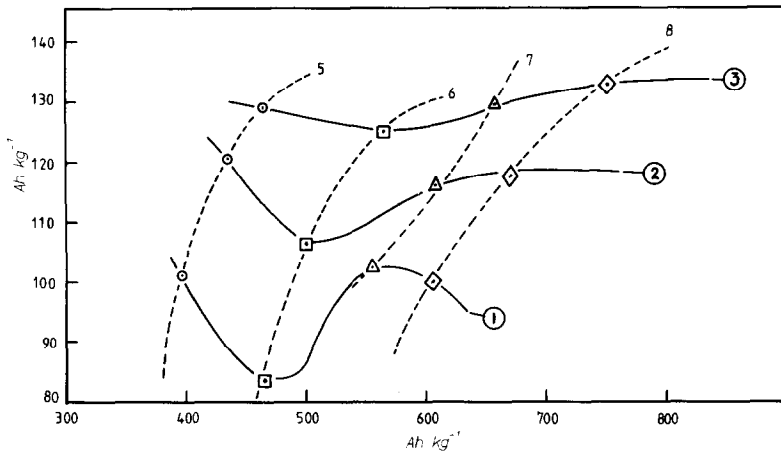


Fig. 6. As Fig. 1, but formation electrolyte 1.270 sp. gr. Formation currents and paste densities as in Fig. 4.

However, this observation has been made under conditions where the formation temperature has been held constant. This is not the case in practical situations. Reduction in acid conductivity will increase ohmic heating which, in turn, may cause undue rise in temperature, the effects of which are considered below. Using data given by Bode [10], it is seen that the ohmically generated heat for the 1.260 filled formation is virtually double that for the 1.060. Whether this is significant in the context of the other sources of heat, which include overvoltage heat losses at, and in, the tubes themselves, is not known.

Effect of temperature

Investigation of the influence of formation temperature (Figs. 7, 8) shows that formation at 15 and 20 °C is clearly disadvantageous. Increasing the temperature beyond 30 °C has little real benefit and intersection of the

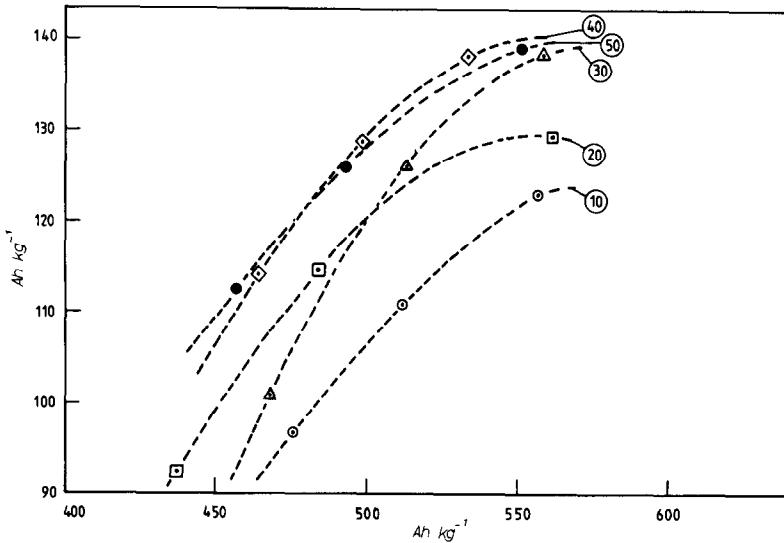


Fig. 7. As Fig. 1, but showing effect of formation temperature 10 - 50 °C, indicated by circled figures. Formation current density $0.63\ A\ dm^{-2}$. Formation electrolyte 1.060 sp. gr. Paste densities as in Fig. 4.

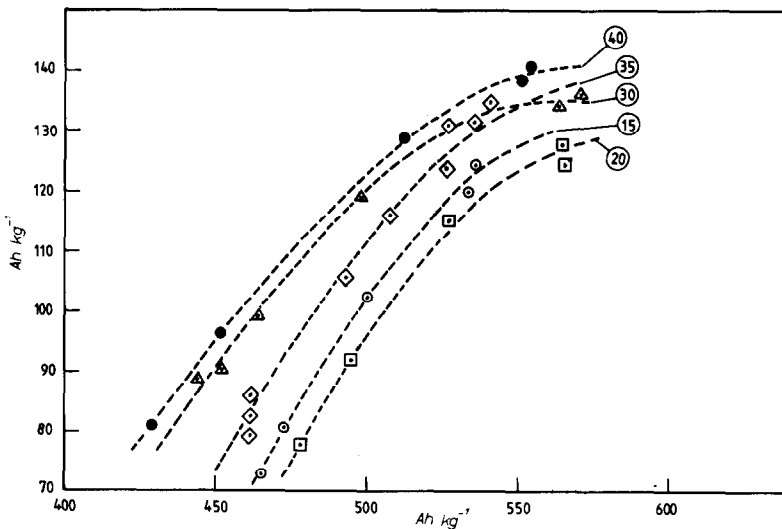


Fig. 8. As Fig. 7, but formation electrolyte 1.270 sp. gr.

capacity-formation charge curves makes it difficult to interpret results. However, plots of C_{\max} vs. temperature show a smooth progression. It is seen that C_{\max} is at all times proportional to formation temperature up to a maximum value of around 45 °C. This temperature is slightly higher than the 40 °C quoted by Bode [10]. Whether the discrepancy results from the fact that Bode's data refer to a flat plate or rather that they relate to the capacity at the sixth discharge cycle or perhaps to a "matrix" less comprehensive than our own, we cannot determine. The change in C_{\max} with temperature confirms that this is one of the more important parameters which can easily produce a 30% variation in initial capacity.

Effect of current density

The effect of charge current density is shown in Figs. 4 - 6. Current density is here defined as amperes per unit area, where area is the internal surface area of the tubular retainer, which is equated to the external surface area of the active mass it contains. In general, the capacity for each otherwise comparable run was the same, irrespective of the charge current density. Looking at the tie lines (which represent points of equal current density) in Figs. 4 - 6, it is seen that there is a general trend towards a limiting value of capacity as the lower paste densities are reached. In one or two cases, however, this is not so (*e.g.*, at *s.g.* 1.12, 0.74 A dm⁻²; 1.27, 0.74 A cm⁻²). However, at further times such a maximum might, indeed, have appeared. Here, in particular, the evidence of deterioration in performance caused by extended formation is seen. Formation time optima can also be seen in Figs. 1 - 3 and lie between 48 and 64 h in most cases.

The effect of paste density, Figs. 1 - 6, shows that the lowest fill density provides the greatest capacity (expressed as A h kg⁻¹). The construction of the tubular gauntlets allows a far wider range of densities to be explored than is possible with flat-plate construction.

However, factors other than purely electrochemical ones demand the use of more densely filled tubes than our data would suggest. This is due to a number of reasons, first, the much greater change in capacity with cycling of low-density tubes, second, that capacity per tube (or plate) rather than per kg is, in practice, a more important parameter.

Discussion

What are the physico-chemical origins of the effects reported here? We exclude fill density from this question since it is obviously very complex and relates to porosity, surface area, and other parameters not considered here. At higher temperatures (which are seen to be favourable to charge acceptance) the acid will be less viscous, thus explaining the *sp. gr.* effect. In respect of fill density, the effect of tortuosity and effective diffusion rates will be important.

In the present study, emphasis is laid on the most important formation parameters and the manner in which the first cycle is affected by these. We are well aware that first, second, and *n*th discharge cycles differ from one

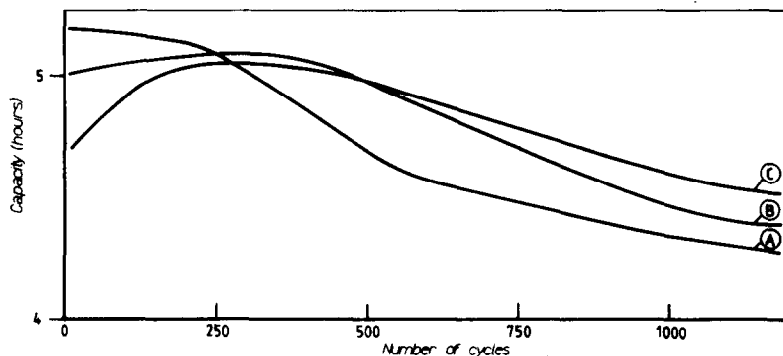


Fig. 9. Positive plates capacity (h) vs. number of cycles. Paste densities: A, low; B, medium; C, high.

another in a highly complex fashion. The capacity increases over the first 50 cycles and thereafter slowly decays. Studies of the way in which first and subsequent discharge capacities vary have been made by Bode [10] and other workers, but again on S.L.I. type plates.

As can be seen in Fig. 9, the plots for the three density fills of low (A), medium (B) and high (C), cross. Low-fill densities are susceptible to premature failure, whilst high densities have a more constant capacity over a prolonged cycle life if poor initial performance is neglected. In adopting the present approach, it is in no way suggested that it is more meaningful to study capacity at, say, the 50th cycle. However, in the almost complete absence of published data relating to this industrially important system, the 1st cycle data presented here are offered as a starting point for further studies which are undoubtedly called for.

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