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An Exploratory Study on Electrolyte Circulation as a Means of Achieving Faster Formation of Lead Acid Batteries

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In the present work, we studied “formation by electrolyte circulation” in relation to its efficiency and influence on battery performance. The electrolyte is circulated with the help of an external pump in order to reduce the temperature build up inside the cell during formation thereby providing an opportunity for fast charging. The behavior of critical formation parameters namely, “voltage and temperature” as well as battery electrical performance under two experimental conditions i.e. charge current density and acid gravity were studied as to understand the efficiency of the new formation process. The results show that when electrolyte is circulated within the cell, the average formation temperature is reduced by 10^{o}C, while the voltage profile is observed to be similar to that of regular. Reduced temperature due to electrolyte circulation provided an opportunity to increase the charge current density which eventually resulted in reducing formation duration by 25%. The results were reviewed in relation to the performance of batteries formed by conventional method. The plate morphology and electrical performance results reveal that new method can produce batteries of similar quality as in case of conventional formation but with an advantage of having better formation cycle time. However, appropriate selection of current density and acid flow control parameters are very much essential to achieve desired results.

Keywords: Lead acid battery, Formation, Electrolyte Circulation, Electrolyte Temperature, Voltage

1. INTRODUCTION

Formation is one of the critical steps in lead acid battery manufacturing process. The purpose of the formation step is to convert the cured pastes into electrochemically active porous materials i.e. PbO_2 and Pb in the positive and negative plates respectively.

The process of formation can be conducted via two basic schemes namely, tank formation and container formation. In the former case, cured positive and negative plates (50-200 no’s) are formed in large electrolytic tanks containing H_2SO_4 of 1.08-1.10 rel. dens. and then plates are assembled. Whereas in case of container formation, cured positive and negative plates are assembled into groups along with separator, which are then placed into the battery container and subjected to formation after filling with H_2SO_4. Generally two formation methods are applied in container formation, two shot and single shot formation. In the former case, the battery is filled with H_2SO_4 of rel dens. 1.08-1.15, after completion of formation the electrolyte is replaced with higher rel. dens. H_2SO_4 to achieve the required rel. dens. In single shot formation, the battery is filled with H_2SO_4 of rel dens. 1.24-1.25 and then subjected to formation [1-5].

In an endeavor to make formation process more efficient and environment friendly, various studies have been carried out earlier [2-6]. Pavlov et al studied various formation current algorithms to achieve efficient formation [2]. K. R. Bullock et al, reviewed various additives and also investigated the Ozone treatment that enhances conductivity of positive material and thereby reducing the formation cycle time [6]. Flamarion B. Diniz et al studied various pulse formation techniques and compared with constant current formation [7]. Further, chilled acid, forced air/water cooling and programmed multi step formation have been used as means of achieving lower formation duration [3]. Though, many of these techniques are being used, constant current formation technique is the most common and quite extensively used technique as on today. The main challenge of quick formation is still the goal of industry.

There is an emergence of new formation method in recent past wherein the electrolyte in multi cells is continuously circulated as to take away the heat from the battery thereby facilitating pumping of larger current input to accomplish the formation in shortest possible time down to 6-10h. But this electrolyte circulation system is fairly complex as it consists of numerous pipes, conduits, valves, pumps etc. [8].

The published information on this subject is scarce and very little is understood in terms of its impact on the plate quality and battery performance. Hence, the current study comprehensively reviews the performance of this new method.

2. EXPERIMENTATION

2.1 Formation

JIS (Japanese Industrial Standard) model automotive battery of 35 Ah (@ C20) was used for this experiment. The plates were produced using paste that is prepared out of ball mill oxide and pasted on to the standard automotive positive and negative grids of Pb-Ca-Sn and Pb-Ca-Al alloy respectively.

Standard recipe and curing program to obtain 3BS paste were used and subjected to plate preparation followed by battery assembly. The filling and formation was done through different methods as indicated in Table 1. The experimental set up was done as explained in Fig 1.

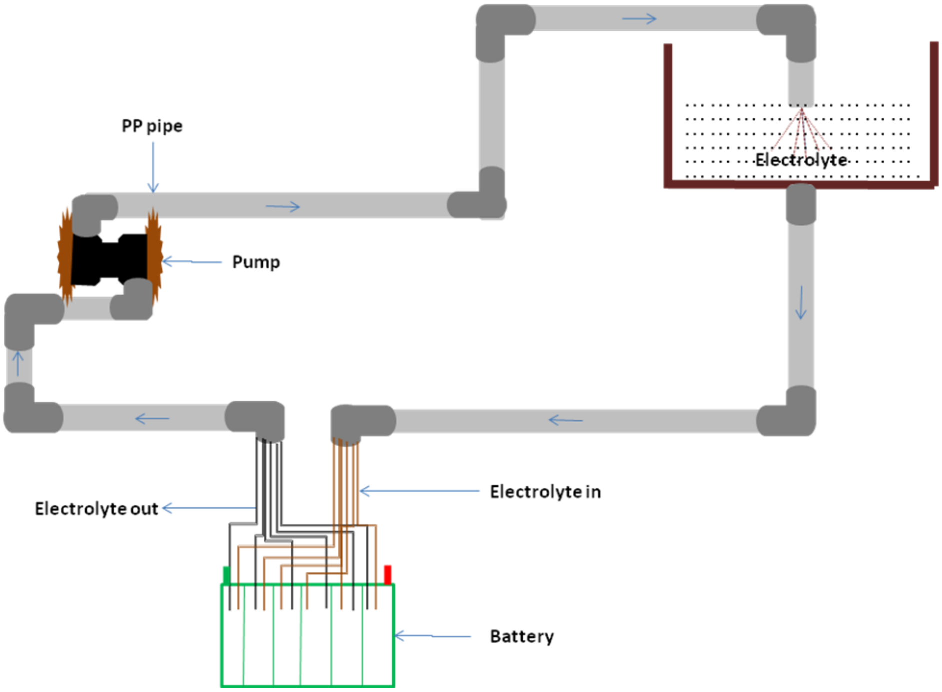


Figure 1. Pictorial representation of electrolyte circulation

Table1. Formation conditions

Sample	Rel. dens.	Formation Method	Current Density (mA/Sq. cm)	Charge time (hrs)
A	1.150	Two Shot without circulation	5-10	12.5
B	1.150	Two shot with circulation	5-10	12.5
C	1.150	-do-	5-15	9.2
D	1.245	Single shot with circulation	5-15	9.2

2.2. Analytical Methods

2.2.1 Formation Voltage

The battery “on charge voltage” during formation was monitored using LCN (Make: Bitrode, Model: LCN 36V25A) circuits. The formation voltage was recorded every 15 minutes and also during starting and ending of each step.

2.2.2 Electrolyte Temperature

The battery electrolyte temperature was monitored using a mercury thermometer (Make: Zeal) and data was recorded once in every 15 minutes and also during starting and ending of each step.

2.2.3 Paste Composition and Morphology

The positive paste composition was estimated by a gravimetric method. The morphology was analyzed using an SEM; Model S 3400 N (Hitachi). The porosity was estimated by water immersion method.

2.2.4 Plate Surface analysis

The surface topography of both positive plates was studied for crack width using stereo microscope, Model SKZ – 2, Make: Seiwa

2.2.5 Battery Electrical Performance

After formation, test samples were subjected to electrical performance tests such as initial capacity, cold cranking amps and charge acceptance as per the JIS D 5301:2006 Standard. The tests were carried out with the help of LCN and High rate discharger (Make: Bitrode, Model: 36V25A, DTN4000). The critical parameters namely, Voltage, Current, Time, Ah was recorded at periodical intervals.

3. RESULTS AND DISCUSSION

3.1 Formation Voltage

Formation voltage is one of the critical indicators of formation efficiency. As the formation progresses, lead sulfate present in the active material start getting converted to lead dioxide in case of positive and lead in case of negative electrode. Simultaneously, positive and negative electrodes begin to assert themselves in terms of reaching equilibrium potentials. This shows up initially as a fall in the measured charging voltage from its peak value. As time passes and once, appreciable portion of the active material is converted into lead dioxide and lead, the electrode potential rises steadily until significant gas evolution occurs and remains stable since then. At this stage, formation efficiency falls due to polarization of the electrodes i.e. lead/lead sulfate and lead dioxide/lead sulfate interfaces move away from the grid and thus increase the impedance to the passage of formation current for further conversion to happen [9]. Typically rest is incorporated and during this period, sufficient acid flow into the bulk of paste material helping towards efficient formation once formation is reinitiated. Further, continuous gassing at high voltage (particularly during initial stage) and high temperature are reported to be detrimental to plate quality by causing poor bonding between grid and active material [2]

The voltage behavior of test samples under different experimental conditions is depicted in Fig 2. As evident, the voltage of the battery rises initially and decreases and again increases for reasons mentioned above [9].

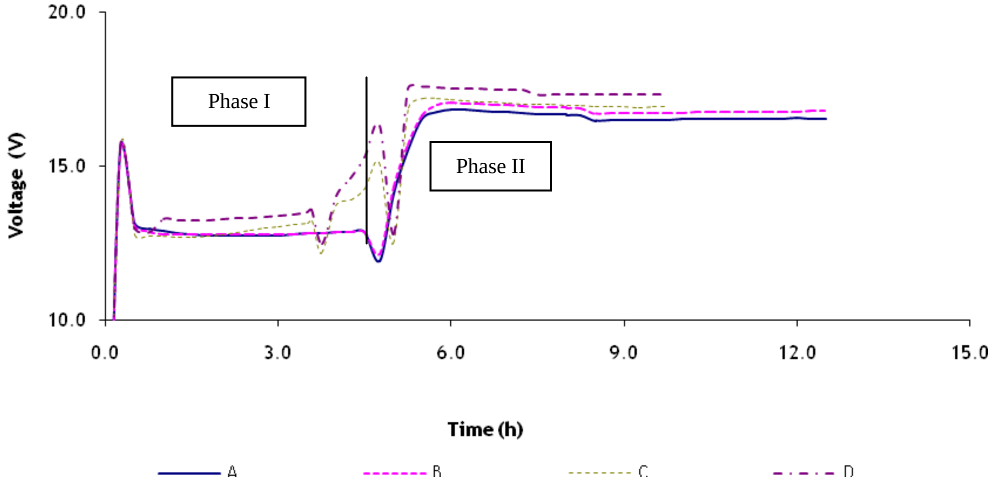


Figure 2. Formation charge voltage behavior with formation time

While the voltage trend remains same in all the experiments, the absolute formation charge voltage is impacted by the experimental conditions. For e.g. the formation charge voltage in phase I of formation, the average voltage is observed to be 2.15 VPC for samples A, B and C while sample D shows an average voltage of 2.22 VPC. Similarly, the average voltage of sample D during phase II formation observed to be 0.05 V higher than that of samples of A, B and C. The higher voltage in case of sample D can be attributed to the higher fill gravity. A similar nature of voltage profiles in three different cases, namely, A, B and C infer similar formation efficiency levels in all the cases. In other words, sample C despite formation being accomplished at high current rates, exhibited more or less similar efficiency of active material conversion as compared to sample A. This clearly infers that high level of formation efficiency can be achieved as long as formation voltage profiles are well managed.

3.2. Formation Electrolyte Temperature

Temperature is another vital performance indicator of formation process. It should neither too high as it destroys the active material nor too low as it dampens the rate of chemical reactions The extent of rise however depends upon the current density and the volume of electrolyte. Negative plates are claimed to exhibit superior cold cranking performance, when formed below 40°C, whilst positive plate exhibit improved performance when formed at 50°C. Often, temperature in excess of 60°C is avoided [9]. At 60°C, it has been found that α – PbO_2 to ß-PbO2 ratio is lower. Further, elevated temperature reduces the capacity of the negative plate too possibly due to expander degradation and hence high rate discharge ability of the battery declines [10]. Moreover, corrosion of positive grids shortens the life of battery [2]. It is from this context, formation schedules with multiple charge steps have been adopted as they can effectively control electrolyte temperature. The use of forced air or water cooling while charging the batteries facilitate higher charge current densities.

It is for this reason the influence of electrolyte circulation on this vital parameter is studied. The rise in temperature with formation time is depicted in Fig 3. Initially while filling, the acid was chilled, (< 5^{o}C) and the electrolyte temperature was monitored after the initial soaking period. There is a significant difference in the temperature peak of phase I between samples A and B, C, D. In sample A (No Circulation) the electrolyte temperature reached a peak temperature of 60^{o}C, whereas it is of interest to observe the peak temperate touching maximum of 45^{o}C only in other samples. A similar trend is evident during phase II formation as well. Although the temperature tends to be flat during this period, the average temperature of sample A is significantly high (53^{o}C) when compared to that of either B or C (43^{o}C) and D (47 ^{o}C). Obviously, the electrolyte when circulated in the cell acts as a good heat exchanger i.e. it takes away the heat from the cell, gets cooled during the cycling process and then enters the cell once again in ambient condition. Obviously, this provides an opportunity to increase the current density to the extent possible but not resulting in too high temperatures. Hence electrolyte circulation will help reduce formation time if optimized properly.

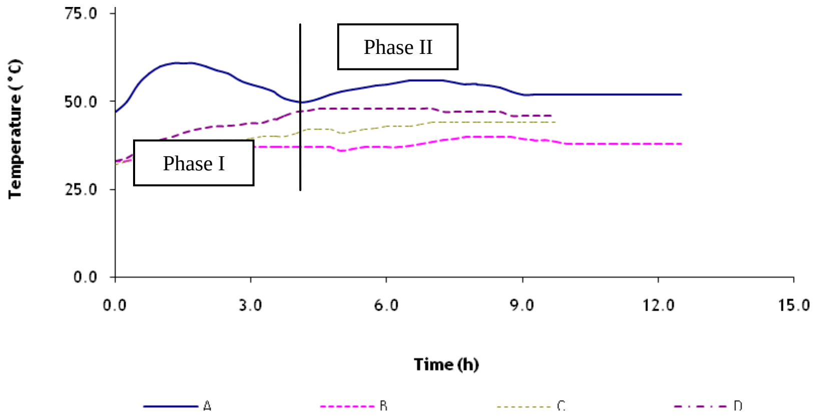
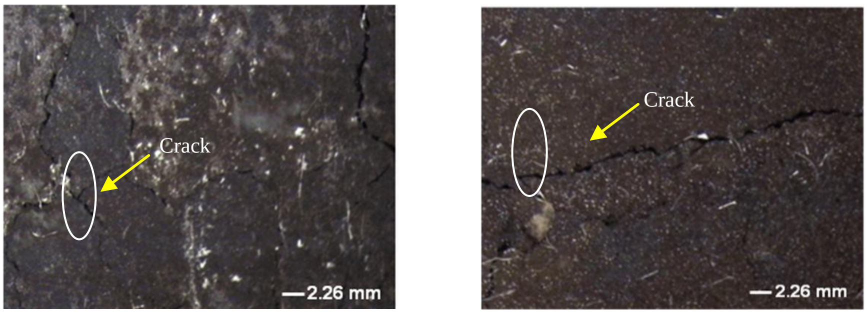


Figure 3. Formation Electrolyte Temperature

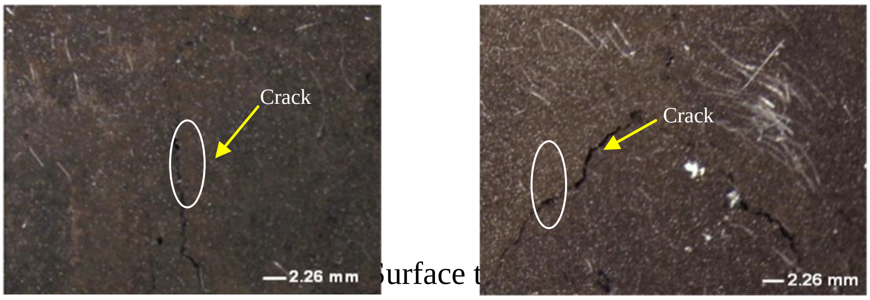
3.3. Formed Positive plate Quality

While the above two governing parameters indicate improved formation efficiency and faster formation in case of electrolyte circulation, it would be dangerous to conclude this based on these two parameters alone. These results have to be corroborated with plate quality and subsequently with battery electrical performance results as to gain confidence on the new method. The formed plate quality can be assessed in many different ways, namely active material conversion, paste adhesion, absence of blisters, absence of softening, lesser surface cracks etc. For example, formation profile and gassing rate would influence the cracks. The gas bubbles evolved on the grid surface exert sufficient pressure on the skeletal branches in the paste that connect it to the corrosion layer and it cracks the branches [2]. Therefore, an attempt is made to study and to find out the significance of new formation technology accordingly.

The formed plate surface is examined using a stereo microscope to analyze the surface cracks (Fig 4). The crack profile happens to be similar in all the cases, indicating electrolyte circulation does not influence the surface phenomena of positive plate.



Sample A Sample B



Sample C Sample D

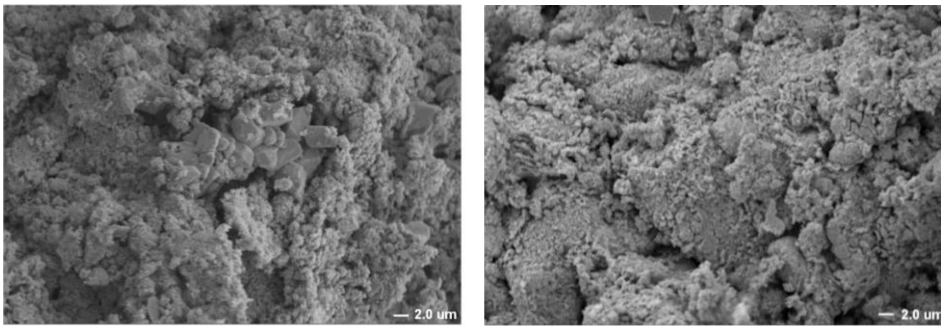
Figure 4. Surface topography of positive plate

3.4 Formed positive plate Morphology

The structural and textural features of PbO_2, which obviously depend on the formation mechanism, have strong influence the performance of the batteries [11]. The positive active material of lead acid battery plates consists of a mixture of two PbO_2 modifications; orthorhombic $\alpha - PbO_2$ and tetragonal β-PbO_2. Orthorhombic $\alpha - PbO_2$ is the product of cured battery plate electrochemical formation at higher pH and tetragonal β-PbO_2 is formed by oxidation of cured battery plate at lower pH. It has been found that the capacity of $\alpha - PbO_2$ is lower than that of β-PbO_2 [12].

Therefore, the plate composition at the end of formation is all the more important to achieve desired performance levels. While formation of the NAM is not so much complicated but this is not the case with formation of the positive plates [1].

The scanning electron microscope pictures (Fig 5) of sample A and D are more or less identical, reveals the uniform conversion throughout the material except few lead sulfate crystals seen in sample A. These results when correlated with the chemical analysis (Fig 6) infer positive plate exhibiting good conversion level i.e. as high as 85 % in both samples A and D. The porosity data shown in (Fig. 7) inline with the standard requirements of formed plate.



Sample A: Sample D:

Figure 5. Scanning Electron Microscope of formed positive active material

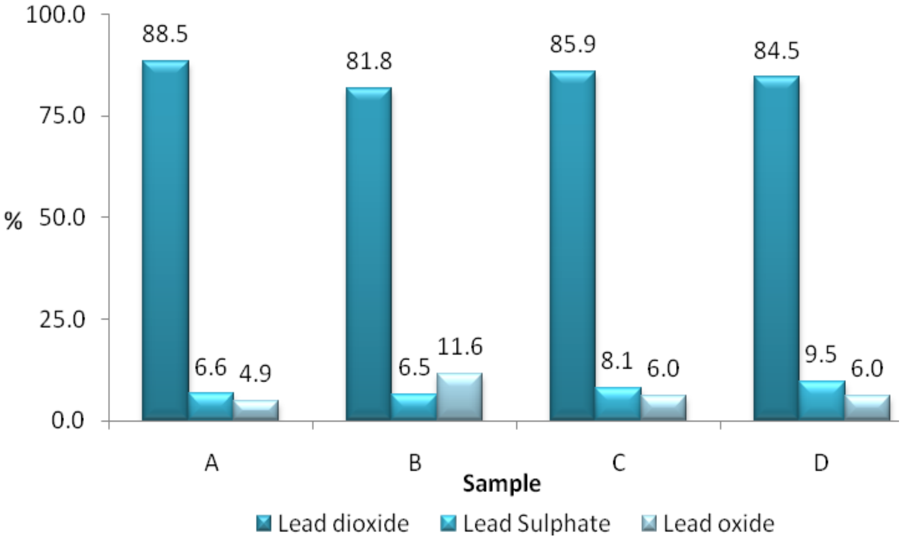


Figure 6. Chemical composition of formed positive plate

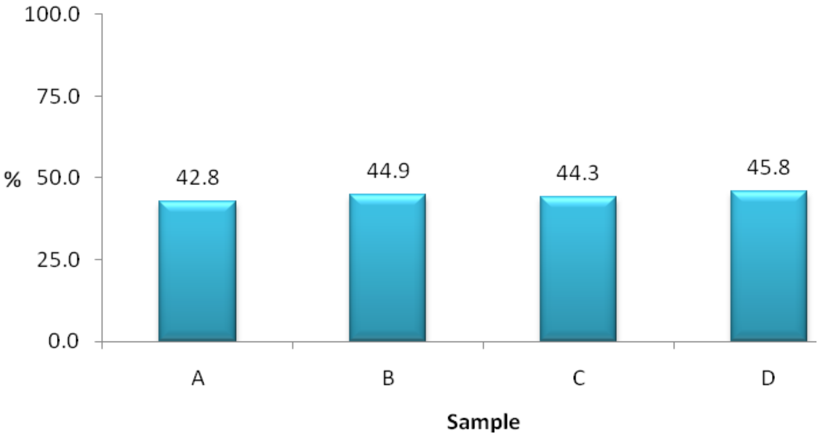


Figure 7. Porosity of formed positive plate

3.5 Electrical Performance

While it is necessary to evaluate positive plate at component level to understand the quality of formation, it is also important to evaluate performance at battery level in order to understand the overall effect of formation parameters. Formation parameters particularly temperature needs precise control during the formation of automotive battery. Apart from initial capacity, cold cranking, charge acceptance etc., also play important role in automotive battery quality. High temperature during formation (>77°C) has been shown to have negative impact effect on battery performance. The microstructure of negative active material in particular is affected by the temperature at which it is formed. The low temperature (5°C) formed material is finely divided and porous with very high surface area. The material formed at elevated temperature appears coarse, dendrite crystals of lead with low surface area. But the positive active material tends to form more rapidly and completely at elevated temperature. A compromise must be established to optimize among the active materials to get overall battery performance [13].

3.5.1 Capacity

The initial Capacity performance is given in Fig 8. The sample B delivered lesser capacity by 10-13 % than samples of A, C & D. Although higher current density and lower cycle time used in sample D, it has delivered equal to that of sample A. It indicates that positive and negative plates are converted adequately to deliver the required capacity. The capacity fall in sample B may be attributed to the lower electrolyte temperature [9] during formation compared to other samples.

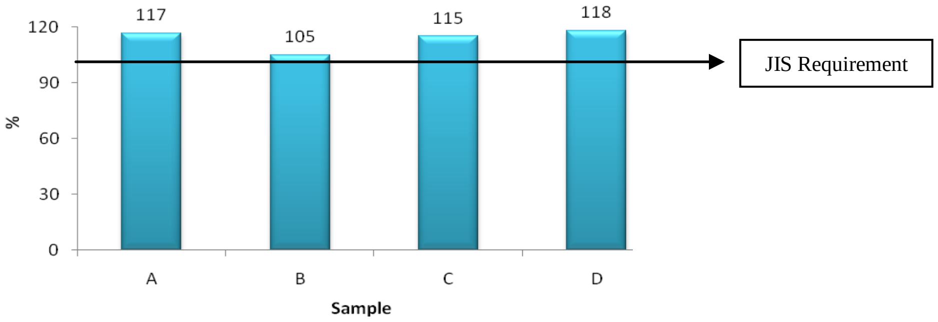


Figure 8. C20 Capacity performance

3.5.2. Cold Cranking

The cold cranking performance of the samples is given in Fig 9. In this sample B has given 10-24 % (time to 7.2V) more performance than other samples A, C and D. This is inline with the earlier findings of L. Prout et al [9] that lower electrolyte temperature during formation will result in better cold cranking performance.

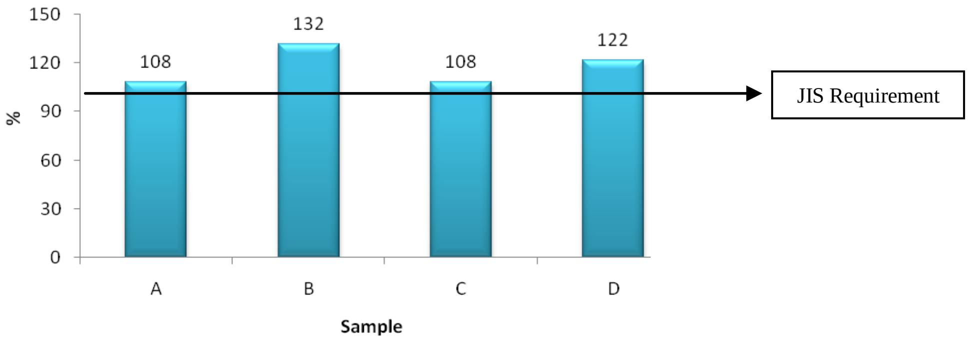


Figure 9. Cold Cranking Performance

3.5.3 Charge Acceptance

The charge acceptance behavior of the samples is given in Fig 10. Sample B has given 20 % more charge acceptance comparatively to the samples A, C and D. The charge acceptance is also similar to cold cranking, depend on the negative plate performance, as it is evident negative plate performs better when formed at lower temperature during formation.

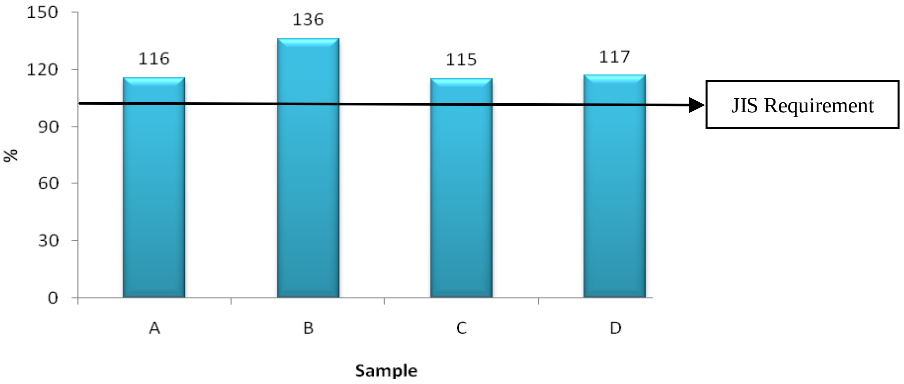


Figure 10. Charge Acceptance Performance

The battery electrical performance results shows clearly while choosing the new formation technique enough care is required in order to optimize the parameters to obtain desired results. While short term electrical performance gives indication about the suitability of the technique, in specific cases, endurance test is also recommended to conclude suitability of the technique.

4. CONCLUSION

The following are the salient observations from the present study

➢ The electrolyte temperature can be controlled efficiently by circulating the acid compared to the conventional formation methods.

- Higher current density formation to achieve low cycle time of up to 25 % was evident by acid circulation method.
- The Chemical analysis and SEM shows similar efficiency of conversion and uniformity as compared to the conventional formation
- The Electrical performance results such as capacity, cold cranking and charge acceptance further reveal the technical viability of this method
- While acid circulation gives advantage of reduced cycle time, one should be careful in maintaining optimal charge current density which would otherwise has a bearing effect on formation efficiency and initial capacity. Further, flow rate and inlet acid temperature play a vital role and adequate methods should be employed to control the above. Higher flow rate may physically disturb the paste material from the surface.
- The practical viability of adopting the new method as an industrial practice needs a thorough analysis, particularly from the view point of operational issues. The complexity of the equipment i.e., numerous pipes, conduits, valves, pumps etc. pose practical challenges. Hence overall energy consumption is a critical factor to decide upon.

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