Energy Storage Publishing

The International quarterly for manufacturers and users of electrochemical power www.bestmag.co.uk

bestmag

Batteries & Energy Storage Technology

No. 66
Autumn 2019

Resistance is futile...

Connectors— testing proves savings

Reprinted from Batteries and Energy Storage Technology magazine

Resistance is futile

(With a nod to the Borg from Star Trek) Dr Mike McDonagh summarises two years of laboratory testing that shows the importance of connectors, and their maintenance, for lead-acid battery formation and how they can lower resistance during battery formation to save your company from serious financial losses.

Since the end of 2017 *BESTmag*, in conjunction with UK Powertech and Digatron, have been examining the impact on the economics and product quality of battery production when using connectors that have been in service for just several months. The corroded condition of these connectors, which are found in virtually all lead-acid battery formation departments ***(Fig 1)***, is such that it produces a significantly higher resistance at the battery terminal and connector interface than that of new connectors.

This interface has been identified and the effect of this on the lead-acid battery formation process has been examined and partially quantified. In a series of articles and presentations at conferences, the tripartite team have reported on their ongoing studies of using standard formation connectors in modern formation departments.

Fig 1 (left): Lead-acid battery formation department

Original tests, going back to August 2017, identified that used connectors, even those with as little as four months on the clock, could result in high resistance connections between battery terminals and the connector leads used to carry the formation currents. This high resistance combined with normal working practices can lead to battery damage, higher energy costs and even department fires.

This discovery led to further work, in collaboration with major OEM lead-acid manufacturers, to identify the causes of the high resistance and to make some assessments of the impact of this on the integrity of the product and the financial and throughput implications for most lead-acid battery factories. Over almost two years the study has identified a unique corrosion layer to be the cause of the high resistance, it is formed as a result of process, environment, working practices and connector design on the inside of the connector lead terminals ***(Fig 2)***.

As part of these studies, the energy losses due to this resistance have been calculated and quantified for a multi-million battery production

Fig 2 (right): Typical level of connector corrosion in a battery formation department

facility. To test the findings, real formation programmes supplied by leading OEM manufacturers using new and old connectors have been run and analysed using Digatron formation test equipment at the test laboratory in Ashton-under-Lyne, UK.

This article summarises the work done so far and reports on the latest findings and their implications for costs, product quality and throughput, for a modern lead-acid battery formation department. Recommendations to overcome these problems by improved connector design, working practices and revised formation schedules are also made.

The original imperative for this study was the increase in damage to batteries during formation over the last five years. This was picked up by Mark Rigby of UK Powertech (a supplier of lead-acid battery formation connectors). His original observation was that formation currents had significantly increased in most of his customers' factories. The reason for this increase was simply to boost production output by shortening the formation time, which was, and still is, a bottleneck.

Because of innovations in battery cooling methods, which include electrolyte circulation equipment, battery temperatures during formation, which are the usual limitation for current input during the process, could be kept to the same low values, even with higher formation currents. Over several years of gradual improvement, manufacturers have been able to reduce formation times to half, or even less, than they were a decade ago. Whilst this sounds like good news it was Rigby who noted that although the processes of current input and battery cooling were greatly improved, the connector construction and design have remained unchanged for more than 20 years ***Fig 3***.

It was this observation that prompted the present far-reaching investigation which has been instrumental not only in identifying the problems but also in devising solutions. In fact, one company, part of a multinational group, has adopted the recommendations made in previous reports and has been able to show substantial cost savings in excess of €100,000 over four months.

This article gives the latest results of our own formation trials, which were obtained using green batteries supplied by one of the factories participating in this investigation. So far, we have had the cooperation of five factories from four countries who have provided valuable information and resources that have contributed to the successful completion of this phase of the testing.

This article also compares the predictions for energy and cost penalties from previous articles with the results from these formation trials. It will show they are at least partly measurable in a real formation situation, and furthermore, give a reasonably accurate prediction for the losses experienced in real formation departments. The testing and results are grouped in five sections:

- Initial voltage and resistance measurements for new and used connectors.
- Identification of energy losses and efficiency of charge acceptance for new and used connectors.
- Identification and characterisation of the high resistance corrosion layer.
- Measurement of the inefficiency in the formation

Fig 3: Standard lead alloy formation connector

process due to high resistance connections.

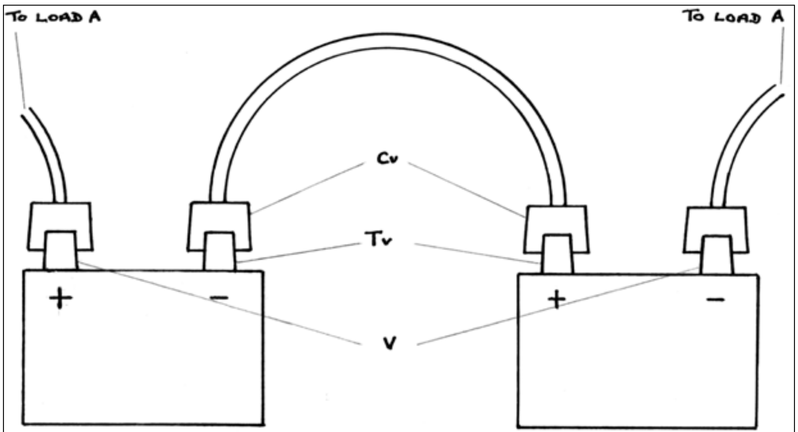
- Formation trials using real data and programmes from modern SLI manufacturing plants.

Initial identification of resistance losses for new and used connectors

The first work carried out in October 2017 took samples of connectors still in daily use in a battery manufacturer's formation department. They were tested on a special rig designed to provide identical conditions for the resistance tests ***Fig 4***. In this, the connectors were placed onto two SLI battery terminals connecting them in series. A current was passed through the connectors and the voltage drop was measured across the terminals and the connectors. The difference between these two measurements is the voltage due to the resistance between the battery terminal and the connector head, plus the resistance of the connector itself. Four connector conditions were measured: new connectors of old design, four-month-old used used connectors of old design, six-month-old used connectors of new design and new connectors of a new design. Three sets of voltage measurements were taken for each connector condition with up to 12 connectors in each category being used in the tests. The resistance of the connectors was calculated using a spreadsheet and then plotted onto graphs, ***Figs 5 and 6***.

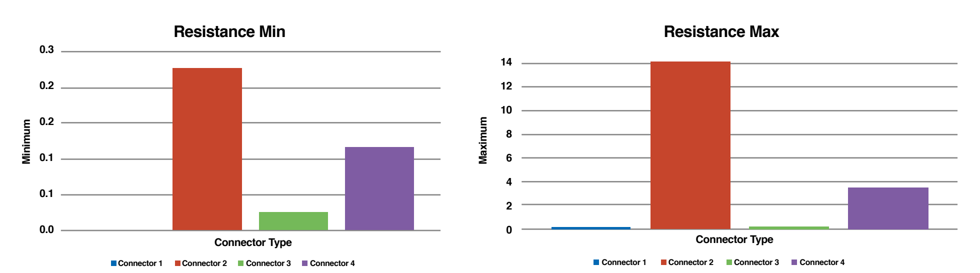
Immediately evident is the variation in the used connectors compared with the new ones. These connectors were placed onto the terminals under laboratory conditions and not in a working environment where operators have little time to complete the task (most likely performed in less than ideal ergonomic conditions). From the resistance values obtained it is possible to calculate the effective extra cost per one million batteries produced with an average capacity of 200 Ah.

Fig 4: Test rig to measure connector/battery terminal resistance



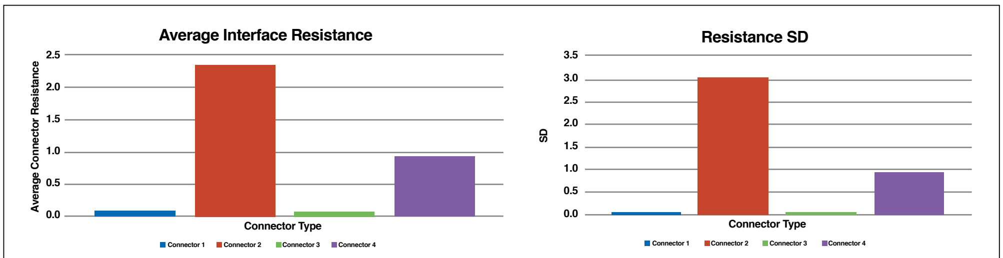
Tv =	voltage measurement from battery terminal to terminal under load A amps
Cv =	voltage measurement from one connector end to other connector end under load A amps
Tv-Cv =	the voltage between the terminals and the connector ends under load A amps
A =	current flowing in the circuit.
(Tv-Cv)/A =	Connection resistance between battery terminals and connector ends

Fig 5: Max and Min resistance results from test rig (mohms)



Connector 1 = new connector
Connector 2 = used 4- 6 month old connector
Connector 3 = new connector
Connector 4 = used 6 month old connector

Fig 6: Average connector/ terminal interface resistance and standard deviation (mohms)



Connector 1 = new connectors
Connector 2 = used 4- 6 month old connectors
Connector 3 = new connectors
Connector 4 = used 6 month old connectors

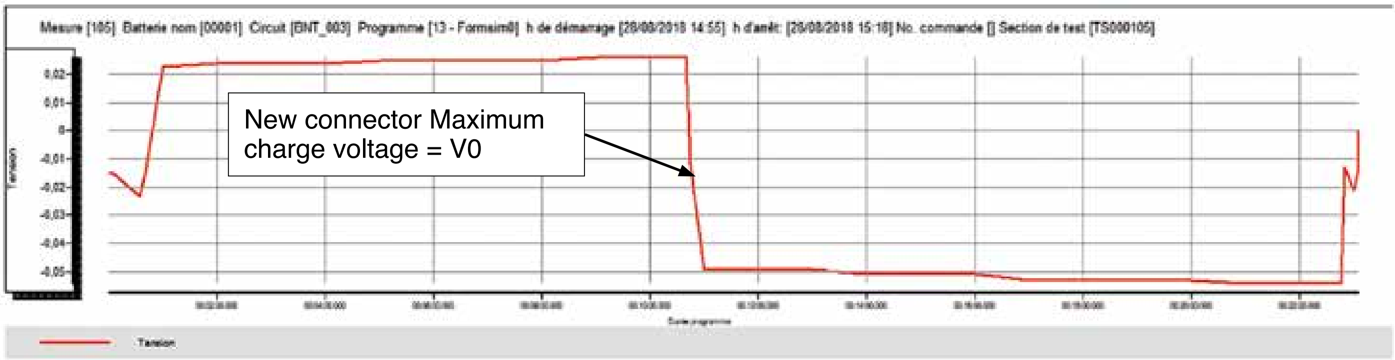


Fig 7: First connector trials using Digatron test equipment – new connector

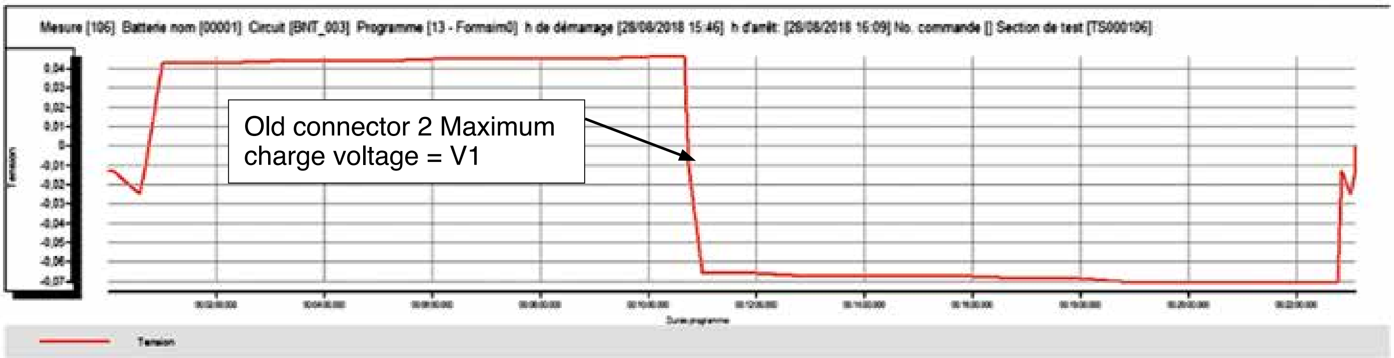


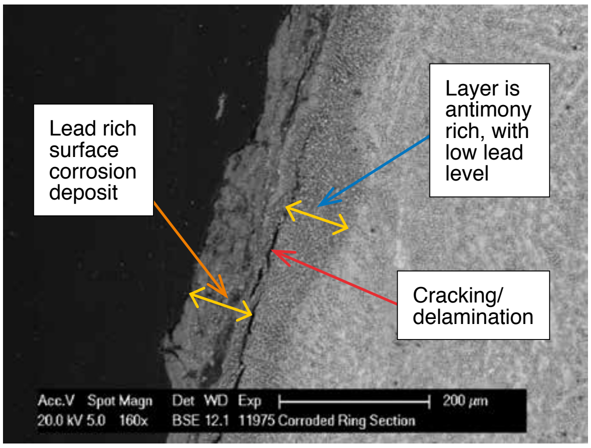
Fig 8: First connector trials using Digatron test equipment – used connector

The maximum losses could be as high as $1million based on a kWh price of US 18 cents. The average shows around $100,000 per million batteries. This is just energy loss. It does not take into consideration the battery damage and scrap losses, the rework from damaged lids/terminals and the possible damage to active material of the higher battery temperature due to the additional resistance heating from the used connectors.

Identification of energy losses and efficiency of charge acceptance for connectors

The next stage was to take real batteries and put them through a series of tests to reproduce the findings of the pillar/connector resistance tests. This was necessary to see if more energy was actually being consumed. To carry out these trials, Digatron supplied a battery formation and test unit containing four circuits, each with a 34V and 150 amp output. Trials were then started using selected 150 ah 12V leisure batteries. As with the terminal/connector resistance trials, new connectors were compared with used ones of the same type. The effect of this connector switch on the batteries' charging and discharging characteristics was measured using the Digatron equipment and compared in the graphical results ***Figs 7 and 8***. Unexpectedly, (from my point of view, at least) there was a distinct difference. This was despite my fears that any voltage differences would be swamped by differences in individual batteries' characteristics and the energy wastage going into heat and side reactions such as water loss and gassing. The results clearly showed a consistent and positive difference in energy output under constant voltage charging conditions.

Fig 9: Optical micrograph of corrosion layer on used connector lead alloy terminal head



Identification and characterisation of the high resistance corrosion

After these results we wanted to try to identify and

Element	Cone				Ring
	Reference	Corroded Surface	Crumbly Surface	Nodular Background	Inside Average
Oxygen		63.1	60.9	57.6	58.4
Sodium			0.5		0.8
Arsenic			0.3		0.2
Sulphur		19.2	16.9	21.3	19.9
Lead	73.5	16.4	12.3	19.1	16.2
Antimony	26.6	1.4	8.8	2.0	3.0
Iron			0.3		0.9
Nickel					0.5

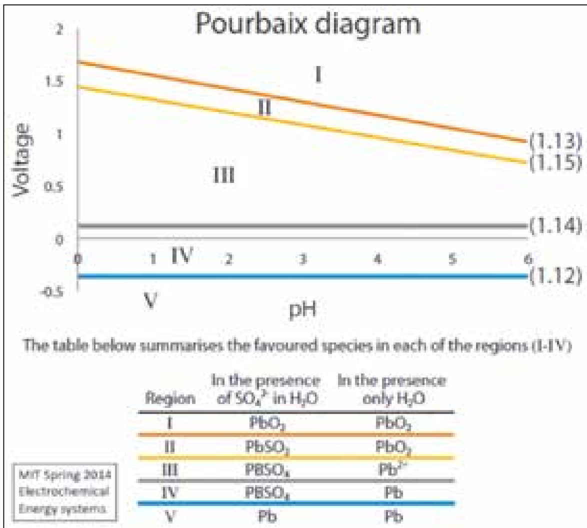
Table 1: EDX data from SEM showing relative proportions of elements contained in corrosion layer

characterise the reasons for the higher resistance of the used connectors. To do this we used scanning electron (SEM) and optical microscopy techniques, making use of the EDX facility on the SEM to identify and quantify the chemical species of any corrosion layer that might be present. Clearly identified was the inhomogeneous and fractious nature of the corrosion layer ***(Fig 9)*** using optical microscopy and the corrosion layer's chemical make-up of lead sulfate ***(Table 1)***, using EDX analysis. Also of note was the extensive pitting on the internal walls of the connector head, most likely the result of arcing during the formation process. Because the corrosion layer was predominantly lead sulfate on all connectors it is fairly conclusive that the layer is unlikely to be the result of the formation process. If it were it would be anticipated that a portion of the corroded connectors would contain lead dioxide and even leady layers within the corrosion products on the surface. The consistency and make-up of the layers points to a passivation reaction at low voltages likely to be caused by the presence of weak acid in the pH region of 1 to 5. The touching of the terminals to the connectors would set up conditions for a weak electrochemical cell of very low voltages, with $PbSO_4$ as the most thermodynamically stable compound. See modified Pourbaix diagram ***Fig 10***. The presence of an insulating compound (lead sulfate) and the fractious nature of the layer explains the high resistance of the connections made in the formation departments when using old connectors. It also explains the high variability of the results as the layer is bound to be inconsistent, especially if it is prone to breaking away from the surface of the connector.

Measurement of inefficiency in the formation process due to high resistance connections

The next set of tests were aimed at finding out the extent of the formation inefficiency that could be expected with these connectors. Because of the nature of formation, it was thought that simply overcharging batteries for extended periods as per standard formation schedules would not yield accurate results. The reasoning for this is that whilst charging with a fixed current will create a corresponding voltage in a battery, an additional resistance due to the connectors should push that voltage to a higher value according to ohms law. This is true, but there is a limit to how high a battery's voltage can go. This is because it is not an ohmic system as with an electrical resistance such as a wire, and parasitic chemical reactions that are triggered at different voltages will absorb

Fig 10: Modified Pourbaix diagram



Between pH 0 and 6 and potential levels of -0.2 to + 1.3 that lead is oxidised to Pb^{2+} and will form lead sulphate according to the reaction:

$$Pb + H_2SO_4 = Pb^{2+} + SO_4^{2-} + 2H^+$$

$$Pb^{2+} + SO_4^{2-} + 2H^+ + O^- = PbSO_4 + H_2O$$

The conditions at the interface between the connector head and the battery terminal post will determine the nature of the reactions on the surface of the lead post and connector as described above. The two parameters are pH (acid concentration) and the potential difference.

current. In these cases, more current results in more of the chemical products being produced e.g. more gassing, rather than a higher voltage. There are also the occasions when the total circuit voltage, and therefore the battery voltage, will be limited by the maximum output of the formation rectifiers. In this case, with constant current charging, the formation equipment would not be able to measure the effect of the higher resistance connections.

For these reasons, this set of tests charged batteries with new and used connectors at constant current with a voltage limit. This method provided a measure of the charge acceptance with the connectors adding to the total impedance. The time to reach the maximum voltage and the total Ah absorbed in a fixed period were measured. ***Figs 11 and 12*** show how the used connector caused a more rapid voltage rise and reduced the total Ah input in a given time, thereby reducing the efficiency of the formation process. This test showed two important points: firstly, that the inefficiency was measurable, and secondly, under constant current charging conditions, the inefficiency may not necessarily result in higher voltages and current absorbed in parasitic side reactions may not be measurable by formation equipment as additional energy use.

Formation trials using real data and programmes from modern SLI manufacturing plants

This observation set the scene for the last set of tests in which green batteries supplied by an international manufacturer were formed using the Digatron test equipment in the laboratory and the manufacturer's own formation programme. New and used connectors were compared to ascertain the effect the higher

Fig 11: Voltage and ampere hour limited formation simulation using old connectors

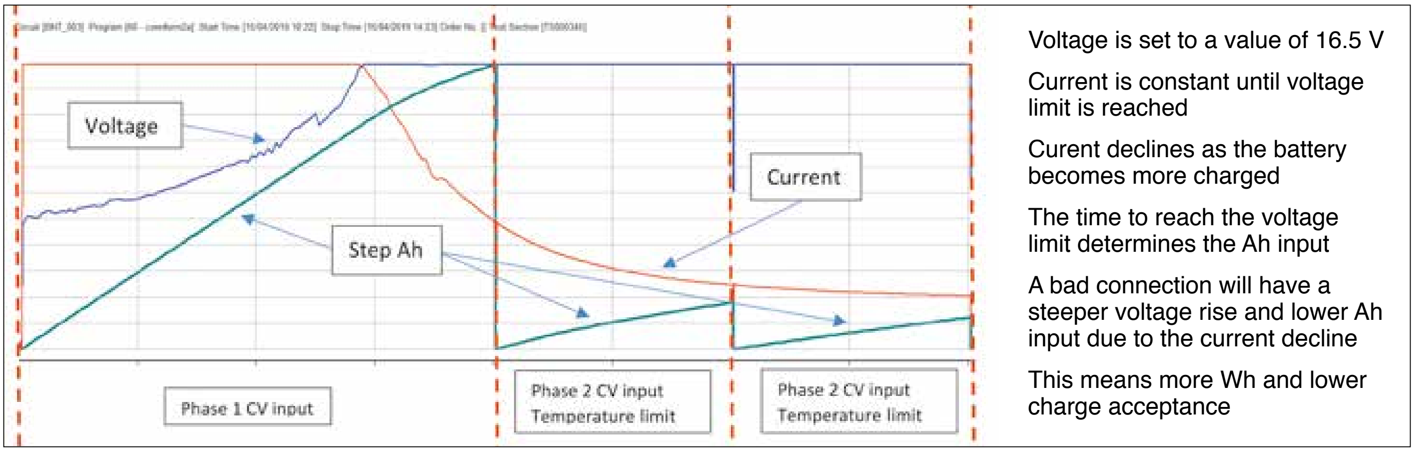
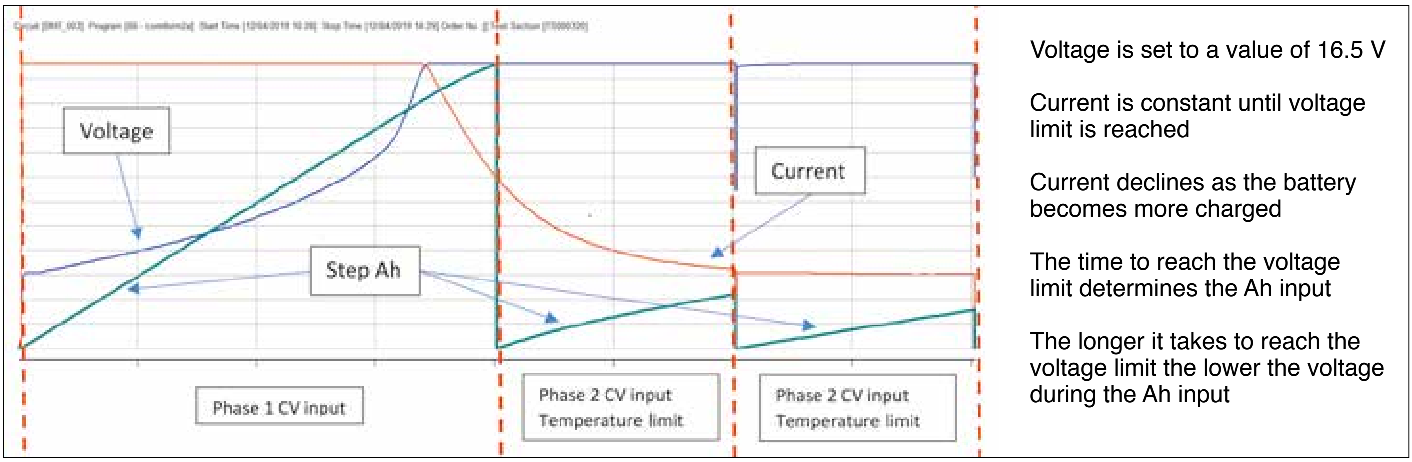


Fig 12: Voltage and ampere hour limited formation simulation using new connectors



resistance would have on the energy used, the maximum voltage reached and the temperature rise during the formation process.

The programme supplied by the manufacturer was temperature limited. This meant that when a threshold temperature was reached the current would be either stopped or reduced in order to allow the batteries to cool to a lower fixed point before resuming the full current input. Because this has an effect on the total time of the process, another consequence from this is the period of the programme could be extended beyond the allocated time in order to ensure that the total Ah input meets the scheduled level. In other words, the more it stops or slows down the current input, the longer it takes and the fewer formation cycles per week that can be achieved. This can have serious repercussions for a manufacturer's turnover if it is a regular occurrence.

Figs 13 and 14 show the results from the Digatron test unit for the green batteries formed using the supplied programme. ***Fig 13*** gives the results for formation using new connectors and ***Fig 14*** is for formation with used connectors. In both cases the programme was temperature limited. This means that when the battery temperature exceeded the set value, in this case 68°C, the current would be reduced or switched off completely until the cell temperature dropped to 65°C. It would then switch back to the full fixed current value of the programme.

From the Digatron graphs it can be seen that the programme was interrupted more often for the used connectors than for the new connectors. In total the extra time for the programme to complete for the used connectors was an additional 1.8 hours compared to the battery formed using the new connectors. The programme is designed to take 24 hours but in this case was prolonged by nearly 8%. This represents a loss of throughput close to 80,000 batteries per one million processed annually. In monetary terms it amounts to an income loss of around $1.6 million per annum for every one million batteries produced. For a five million batteries per annum facility, this would give a staggering $8 million per annum revenue loss.

These potential turnover losses are a direct consequence of the high resistance connections, which generate additional heat due to the I^2R effect. Because of the higher formation currents used in modern formation schedules, the resistance contribution to the heating effect would be exponential rather than linear. As formation schedules become shorter and currents increase it is likely that this problem will be even more critical in the

Fig 13: Digatron formation test results from temperature limited programme - voltage and accumulated watt hours, new connectors

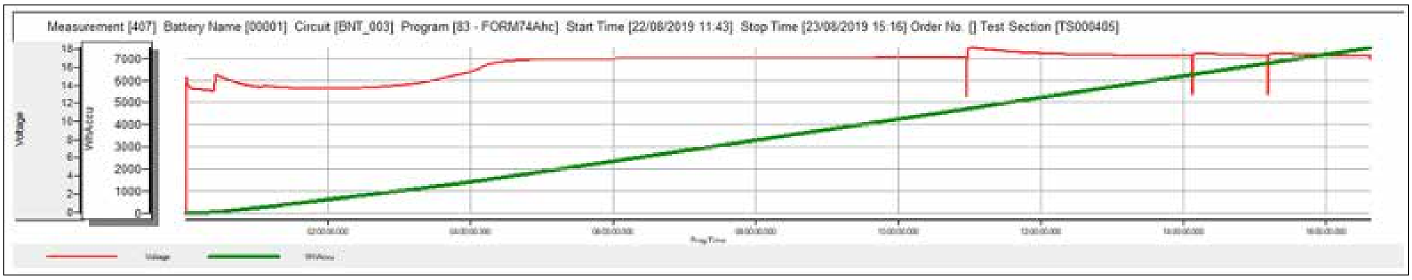


Fig 14:Digatron formation test results from temperature limited programme— voltage and accumulated watt hours, used connectors

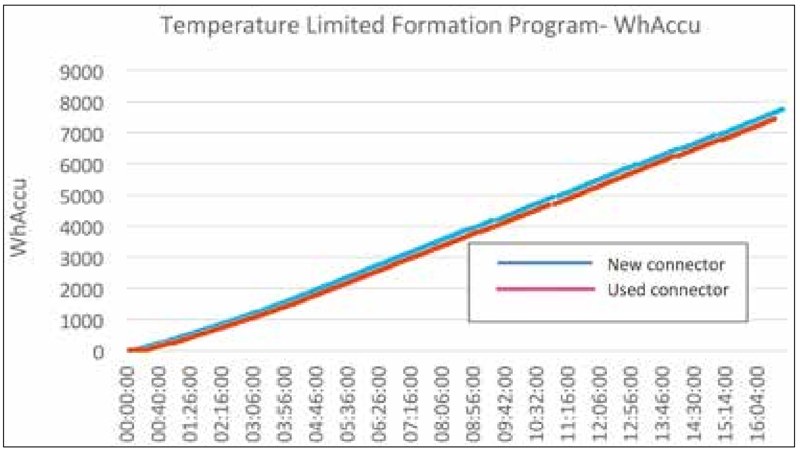


Fig 15: Comparison of accumulated watt hours from formation trials, new connectors vs. used connectors

future unless the problem of high resistance connections is tackled.

The turnover issue is clearly a major concern, but we also have to consider the initial premise of the tests, that the energy losses in formation are a result of the higher connection resistances. ***Fig 15*** shows the accumulated formation watt hours for the new and the used connectors. These clearly give a higher energy usage for the used connectors. Because this is a fixed current input with the same number of Ah input, the energy used is down to the voltage difference on charge between the two formation tests. The cause of the voltage difference is the higher resistance value of the interface between the battery terminals and the used connectors compared to that of the new connectors. In this case the total difference is around 5% which for a factory manufacturing five million batteries per year with an average capacity of 200 Ah would be:

200 x 17 x 5 x 5000000 x 0.05 = 850,000kWh = 153,000 USD per annum

This energy loss is measured in a test laboratory with sample connectors taken at random from a factory's formation department. It is not representative of the methods and practices that exist in a real production environment. It is likely the resistance at the terminal/connector interface will be substantially higher than that found in the laboratory.

Previous resistance trials have shown the average energy losses are likely to be around 7.5%, and in some cases, they exceeded 20%. In any event, energy losses alone do not represent the total picture. As seen above, the loss in revenue can be substantial depending on the formation parameters used to control the current input.

In addition to this, the higher resistance connections that are responsible for the extra rework and scrap burden have been estimated to be around 1.5% of the total manufacturing costs. For a battery factory manufacturing five million batteries per annum with an ex-works price of $20 per battery, this would amount to $1.5m per year.

At this point in our investigation into modern formation practices, it is fairly clear the condition of the connectors is responsible for major reductions in companies' profits. There are, however, other very significant aspects that contribute to this. There are three more parameters that are seen as contributing factors to the total formation losses. These are:

- the working practices, which include the methods of battery connection by the operators and the maintenance of the connectors, e.g. regular washing and correct storage
- the design of the connectors enabling easier fitting and prevention of acid ingress
- the formation programme

Whilst they may not provide easily quantifiable additional costs they can exacerbate and even contribute to the effects of the high resistance values measured.

With regard to the formation programme, the fixed voltage graphs clearly showed the extent of the inefficiency of high resistance connections. These losses may already be built into the charging programme, which, because they are derived practically, unwittingly allow for these inefficiencies. It may be possible therefore, that by using connectors with no corrosion layer to add a high resistance, using a programme that had a lower energy input would be possible. This would provide a measurable and predictable saving, simply by modifying the programme.

In the longer term more efficient formation programmes using newly developed low-energy, fast-charging techniques could be devised to give a more efficient and battery-friendly process. To achieve the condition where the terminal connections have minimal resistance, the working practices and connector design are vital components.

Fig 16 shows the new connector designs from UK Powertech, which are easier to fit due to the split lead alloy head, and also prevent acid ingress to the connector's internal surface. However, current connector designs in use by most companies would benefit from small but effective maintenance procedures such as regular washing and storage in dry conditions rather than leaving them in a plastic tub already badly contaminated with acid.

UK Powertech, Digatron and *BESTmag*, in collaboration with industry partners, have over the course of two years shown fairly conclusively that modern formation departments in lead-acid battery factories could well be losing 8% of their turnover and be incurring 3–7% higher energy costs, all resulting from the use of poor connections during the formation process.

We are now engaged in the next step— testing the effectiveness of the proposed solutions for connector design, working practices and formation programmes. The main areas for investigation are:

- the ergonomics for acid filling and manually fitting the connectors onto batteries
- the design of the connector to prevent acid ingress into the internal part of the connector head
- to facilitate an easier fit of the connector onto the terminal.

At this stage, the possibility of designing a more efficient formation programme to take advantage of the improvements being investigated is also underway. The full programme is given in ***Fig 17***. This is the work being done right now in the test laboratory to improve the efficiency of the formation process, reduce the operating costs, minimise scrap and improve battery quality. The findings to be published soon, exclusively in *BEST*.

Fig 16: New UK Powertech connectors

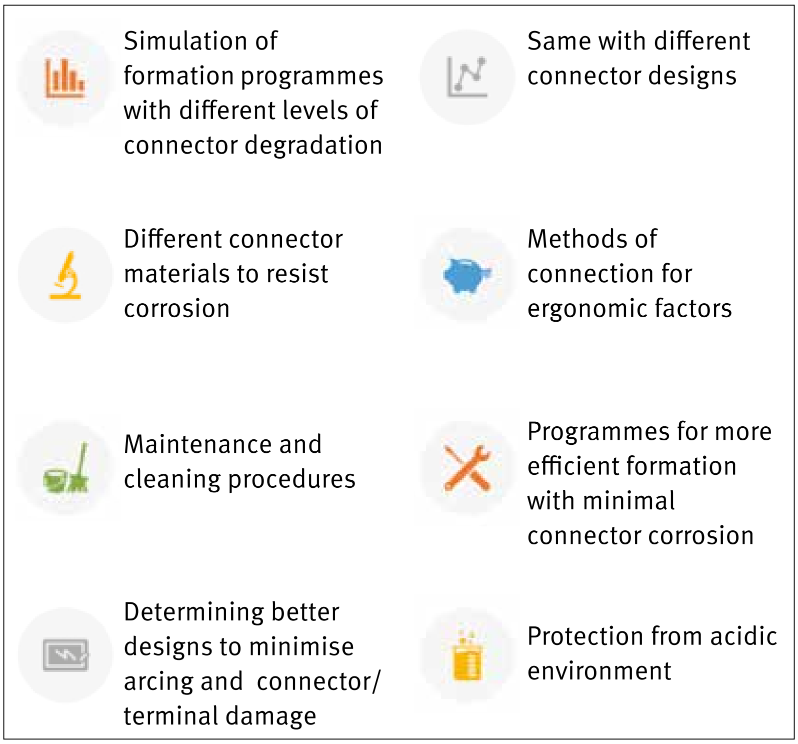


Fig 17: Current Development work for UK Powertech, Digatron and BESTmag