

THE TREATMENT OF SULPHATED STORAGE CELLS

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If a lead accumulator is neglected sufficiently, the final outcome is the formation of white lead sulphate over the surface of the plates, while the capacity of the cell drops towards or to zero. So far as I can find, very little has been published as to the best method of treating such cells and it therefore seemed desirable to study this problem somewhat in detail.

During the discharge of an accumulator there is formed on the grids a finely-divided lead sulphate. In so far as equilibrium is reached, the sulphuric acid solution is saturated with respect to lead sulphate. The slight temperature fluctuations cause the lead sulphate to recrystallize and to form a hard crust. With rising temperature, the solubility of lead sulphate in sulphuric acid increases, and the smallest crystals dissolve. When the temperature falls a little, crystallization takes place chiefly upon the solid lead sulphate and larger flakes are formed.

A cell may become sulphated in part or wholly by an overdischarge. This may be intentional, with the object of obtaining an excessive output of electrical energy for some special reason. It may happen through local action, leakage, or internal short-circuit. There may be impurities in the lead oxides used in making the cells, deleterious substances in the lead alloys used for the grids, or there is a possibility of impurities in the electrolyte. Impurities, such as salts of iron, will undergo alternate oxidation and reduction. They will diffuse from one electrode to the other and will attack the active material. Even a small amount of an iron salt is detrimental.¹

If too long a period elapses between discharge and charge, the conditions are exceptionally favorable for the caking of the lead sulphate. Excessive sulphating is certain to result

¹ Cf. Elbs: *Zeit. Elektrochemie*, 7, 261 (1900).

if the cells receive improper care when put out of commission. If the grids are only partially washed free from acid and are then allowed to dry, a uniform coating of white sulphate is sure to form.

The disastrous results of excessive sulphating are well known. Some of the most important ones are as follows: shedding of the active material, buckling, loss of capacity, increase of internal resistance, rise of temperature, etc. It is evident that the introduction of a non-conductor would tend to produce all of these results. Lead sulphate is an excellent non-conductor and hence is the cause of disaster to the cell. Since the formation of lead sulphate in the accumulator is accompanied by an increase of volume, this in itself becomes detrimental when sulphating is excessive.

Of course, the wise thing to do is to look after a storage battery so carefully that the cells never become badly sulphated. This can be done, but there are times when it is not done. People will always be careless and neglectful. When the white sulphate actually becomes visible, the feeling usually is that the cells are spoiled and that nothing much can be done with them.

A very few unsatisfactory methods of removing the sulphate have been suggested. One is to scrape off the white lead sulphate by means of a wire brush. This "carding" method removes much of the active material and therefore decreases the capacity of the cell. Such a method should be applied only as a last resort.

Prolonged charging at a low rate (one-fourth to one-half the normal charging rate) has been recommended by some. While this method gives a good reduction ultimately, the time involved is excessive and there is a very large waste of electrical energy. Charging at an abnormally high rate has also been recommended. At first it would seem as though this method and the preceding one were mutually exclusive. Some experiments soon showed that charging at a high rate is a combination of electrolytic carding with electrolytic reduction. The consumption of time and of electrical energy is

relatively low compared with the method of charging at a low rate. Against this advantage we must set the fact that the capacity of the cell is decreased owing to the removal of some of the active mass as sulphate, in consequence of the tumultuous evolution of gas.

Salomons¹ says: "Frequent and prolonged overcharging with currents about 30 percent below maximum, is the only way to reduce badly sulphated plates, which are frequently found when the cells are allowed to run too low or stand too long. When the positive plates are in a bad condition (generally due to the battery having been over-worked, *i. e.*, greatly exhausted, or owing to short circuits within the cell itself, which evidently produces a similar result, or to leakage), it is no easy matter to get them right again, since the conducting property of the paste has become very low. Under these circumstances, complex sulphates soon form and rapidly spread over the plates almost like a growth of mold. By patient and slow charging, this grey or white sulphate, from want of adherence to the healthy oxide forming below, soon falls off in the shape of scale or powder to the bottom of the pot; and care should be taken that no portion sticks between the plates.

"To return to the case for bad sulphating, a continual charging below maximum rate, half to start with, for a prolonged period will gradually reduce the unhealthy sulphate to the healthy form, and finally charge the plates by conversion of the PbSO_4 to PbO_2 . The task is tedious, but it must not be hurried, or the positives are certain to buckle. Most of the white sulphate will fall off in scales, but should any stick between the plates, it must be pushed down with a piece of wood or a flat strip of ebonite, the latter being the best. But on no account should a piece of metal or any other conducting substance be employed for this purpose. When white sulphate exists upon the positive plates, it shows that most of the oxide has been converted into PbSO_4 . These sulphates are very

¹ Management of Accumulators, 121, 143, 145, 147 (1906).

bad conductors. Consequently, when the white sulphate is observed, it may be concluded that a great resistance is offered to the current doing its work, and is in a manner equivalent to the plates having a much smaller active area. The maximum charging current is therefore too large; but the current may be increased as the white substance falls off or disappears. If the sulphating has become very bad, the scales often separate from the plate carrying with them blocks of paste which they overlie. This is very vexatious, for the capacity of the battery becomes much reduced by loss of active material, and great trouble is experienced in getting from between the plates these pieces, which, if not removed, short-circuit the cell.

"After bad sulphating the capacity of the cells must always be less, in consequence of the loss of some of the active material. When the fault is great, the best plan is to clean the battery.

"The cleaning of a battery consists in removing the sections from the cells (after a good charging), separating the sets of plates, and scraping the white deposit off the positives. There is no need to remove the plates from the lead strips, for, by bending them apart, plenty of room is allowed for manipulation. In cases where the plates cannot be parted, they must be reached as well as circumstances permit, and generally no difficulty occurs. The wire brush material sold under the name of 'carding' will serve to do the work. A piece of this is cut to six by four inches, and nailed to a block of wood half an inch thick, and having a handle, if found necessary, for reaching between the plates. The brush is now applied to the positives till they appear their proper color, and they are finally washed with the electrolyte and on no account with water, or sulphating will set in immediately. This done the cells are again made up, when the old solution may be used again, although it will generally be found more convenient to put in fresh electrolyte.

"If the positives are past recovery it is the cheapest to have a new set, which can be obtained from the makers at a very moderate cost in exchange for the old plates."

In Warwick's little book,¹ he discusses the effect of adding soda to the electrolyte. Some of his chemistry is queer, but the results are interesting.

"Mr. Barber-Starkey² found that adding a small quantity of carbonated soda to the acid electrolyte not only reduces the tendency of the elements to sulphate, but rapidly removes this salt when already formed. This action is probably due to the conversion of the sulphate, first into carbonated lead [?] and then into the peroxide, or it may be owing to the fact that sulphate of lead is sparingly soluble in a solution of sulphate of soda.

"As the results of some experiments made with a view of ascertaining the effect of adding sulphate of soda to storage battery solution, it is found that the addition of sodium sulphate to the ordinary acid electrolyte has a distinctly beneficial effect upon the working of the cell. It has been found that upon the addition of these soda salts a large proportion of the sodium sulphate is formed in close contact with the lead sulphate on the peroxide plate, and that this formation was favorable to the reduction of the latter substance, as a paste of equal parts of minium and lead sulphate is more readily reduced in solution of sodium sulphate than in dilute sulphuric acid.

"As an example of beneficial results to be derived from the use of an acid soda solution, the following may be worthy of mention. It is said that at the central News Office in Ludgate Hill, London, England, a number of large lighting cells had been idle and dry for about two years. The plates were found to be thickly incrustated with a hard white sulphate. With the ordinary electrolyte, and a charging current of from 10 to 15 amperes, no improvement was observed after two charges of eight hours per day; but after adding a half-pint of strong carbonate of soda solution to each cell, and with the same amount of current going in as before, the plates soon im-

¹ Warwick: "How to Make and Use the Storage Battery," 91, 93 (1896).

² Cf. Brit. Assn. Reports, 958 (1890).

proved, and in a few days all the elements presented a beautiful appearance.

"When removing sulphate by this method it is found the best way to take out the de-sulphating solution, after the plates have been brought to a healthy condition, and replace it by the ordinary dilute acid electrolyte, otherwise the negative plates are said to deteriorate."

As against this, Wade¹ found that addition of caustic soda to the acid electrolyte failed to give any very satisfactory results, the action varying without apparent reason.

In all these cases the caustic soda or the sodium carbonate was added to the acid electrolyte in relatively small amounts. Under these circumstances, the acid is nowhere near neutralized and we are dealing with a fairly strongly acid solution. When the cells are charged, there is a tendency to set free alkali at the cathode; but this is neutralized at once by the excess of acid and consequently there is a very little reduction of lead sulphate at the cathode. If the current density is very high, the amount of reduction will be increased; but it is easy to see that concordant results cannot be obtained under these conditions. The work to be described later will show how this method can be made to give concordant results.

After we had finished the experimental work, to be described in this paper, an article on "The Rejuvenation of Sulphated Lead Storage Cells" was published by Mr. J. O. Hamilton.² He used a solution of caustic soda and obtained excellent results. We confirm his conclusions, but our method is more easily controlled than his.

Borntraeger³ has suggested yet another method. Zinc plates were bound upon each side of the sulphated grids and the whole immersed in a 25 percent hydrochloric acid solution. A very satisfactory reduction is obtained in this way, but it would be very difficult to wash the chloride out completely and consequently the cell would soon go to pieces. This

¹ Secondary batteries.

² Railway Electrical Engineer, 2, June (1910).

³ Zeit. Elektrochemie, 5, 325 (1897).

method suffers under the further disadvantage that it is applicable only for the negative grids. With the positive plate we should get a layer of spongy lead superposed on the peroxide. Each plate would thus be equivalent to a short-circuited cell.

The reason for taking up the study of sulphated cells was that the laboratory fell heir to twelve badly sulphated cells which were utterly useless to anybody else. The cells were made by the National Storage Battery Company. They were Type U with five plates to a cell and a rated capacity of forty ampere hours. These cells had been purchased in November, 1906, and had been used for experimental purposes until February, 1908. The cells were then put out of commission. This was evidently done too hastily. The acid was not washed out of the pores of the plates. As a result of this and of the evaporation of the water, there was an apparently uniform coating of white sulphate over each cell, when the cells were turned over to us. Since all of the cells had received practically the same usage, treatment, etc., the material was unusually satisfactory for experimental purposes.

In order to save the large cells for the final test, it seemed desirable to prepare small experimental plates. Ordinary sheet lead was cut into strips 5 cm \times 10 cm. The smaller cells, made from two strips, were formed in sulphuric acid, sp. gr. 1.20, at the customary rate of 0.04 amp/cm² until the anode was oxidized to PbO₂. After a good coating of PbO₂ had been obtained, the cells were short-circuited and discharged to zero potential difference. This was repeated several times. Owing to the smoothness of the surface, all the lead sulphate fell to the bottom of the glass containers. Poor grids were also obtained when the charged plates were dried in the air instead of being discharged electrolytically. In order to eliminate the shedding, the lead strips were grooved by pressing a medium-meshed wire gauze against them. Little pockets were thus made and this type was placed in the usual acid and formed as before. When discharged to zero potential difference, no adherent coating of sulphate was obtained. It became evident that a porous mass is essential

to the formation of a good coating of sulphate, as this gives a larger crystallizing surface.

As a result of this experience, holes were bored at very close intervals in the 5 cm \times 10 cm strips of lead. A paste of 900 grams of red lead in 150 cc of sulphuric acid (sp. gr. 1.20) was placed in these perforations and pressed until it was very compact. In this way we obtained a grid which looked much like the commercial type. After the usual charge followed by a discharge to zero potential difference, this type became sulphated. After standing a few days, the whole grid became covered with sulphate. Another method employed for making a sulphated cell, was to make a paste of chemically precipitated lead sulphate. The grooved lead plates were painted with this paste and then dried. A coherent coating was obtained in this way.

The general methods employed in the following work may be classed under three main divisions: chemical reduction; electrolytic deposition and reduction; and solvent action.

We first tried the action of ferrous hydroxide on a sulphated plate. Different mixtures of ferrous sulphate and caustic soda were tried both hot and cold; but no reduction of the sulphate could be detected and consequently this method was abandoned as useless.

We next studied Borntraeger's zinc and hydrochloric acid method. Using a 25 percent hydrochloric acid, it was found that complete reduction took place. The limitations of the method have already been pointed out. With a view to modifying the method, a more careful study of it was made. It was found that a much more dilute acid could be used, a 10 percent hydrochloric acid giving splendid results. Zinc dust was applied to the grid in the form of a paste but has a tendency to work loose and consequently does not give so good results as sheet zinc.

Hoping to eliminate the hydrochloric acid and yet to get an efficient reduction, we precipitated zinc electrolytically upon the sulphated plate, using a zinc sulphate solution containing 100 g ZnSO_4 per liter. A current density of one ampere

per square decimeter gave very good deposits of zinc at first. After a short time it was noticed that no more zinc was deposited. The negative grid was then removed and placed in the ordinary storage battery acid. A fine partial reduction took place. Even when working with a concentrated solution of zinc sulphate not enough zinc could be precipitated to cause complete reduction of the lead sulphate. The cause of the trouble seems to be the sulphuric acid set free at the anode. Various methods were tried in order to eliminate this trouble. Zinc oxide and carbonate were both added in excess to the solution of zinc sulphate but without avail. Being insoluble, they settled to the bottom and the circulation is not sufficiently rapid to keep the solution between the plates in an approximately neutral solution. Since the positive and negative grids are very close together, the diffusion of the acid takes place very readily. With an excess of acid, hydrogen is set free instead of zinc.

When the current density was increased to three amperes per square decimeter, a deposit of zinc could be obtained on the sulphated grid in spite of the excess of acid; but a new difficulty arose. With the increased drop of potential through the solution, there came an increased tendency of the zinc to deposit on the best-conducting portion of the grids and to form trees. When this happened, the sulphate was torn off the grid and the active material was consequently wasted.

Under the best conditions this method only cures the sulphating of the spongy lead plate partially. At the anode there was a partial oxidation of the lead sulphate to lead peroxide owing to the low acid content of the initial zinc sulphate solution. When this method was tried on one of the large cells, the cell was brought back from practically zero capacity to about 75 percent of its rated capacity. While this is not a bad result, the method is expensive and inconvenient. Since we have worked out a much better method, we do not recommend this one.

A method very similar to the preceding one was also tried. Aluminum and caustic soda were substituted for zinc

and hydrochloric acid. This combination also reduces lead sulphate. When an aluminum sulphate solution was electrolyzed, practically the only action on the grids was a "carding" one, so no further tests along this line were made.

Under the second heading—that of electrolytic deposition of lead and subsequent electrolytic reduction of the sulphate in acid solution—there seemed to be great possibilities. If lead could be deposited in suitable form all round the particles of lead sulphate, it would then be a very simple matter to reduce the lead sulphate electrolytically. To test this, lead was deposited under varying conditions from plumbite, fluosilicate, acetate, and perchlorate solutions. The deposition was always accompanied by great shedding of the lead sulphate, due to the treeing of the deposited lead. This method was therefore ruled out as unsatisfactory.

With the third type—that of solvent action followed by re-deposition of the lead—we tried such solvents for lead sulphate as sodium acetate and sodium tartrate. Some of the lead sulphate was removed; but the re-deposition of the active material, thus removed, was far from satisfactory. Consequently no capacity tests on the large storage cells were made by this method.

During some experiments with ferrous hydroxide, in which an excess of sodium hydroxide was used, it was noticed that where the sodium hydroxide came in simultaneous contact with lead and lead sulphate, very beautiful crystals of lead were deposited. It seemed that a somewhat closer study of this phenomenon would be desirable. One of our sulphated lead grids was immersed in a solution containing 500 g NaOH per liter. The sulphate disappeared completely and splendid crystals of metallic lead were found deposited on the lead strip. On repeating the experiment, it was noticed that there was an intermediate formation of a greenish yellow salt. The most plausible explanation of this unexpected phenomenon was that it was due to impurities in the lead or in the solution which caused a reduction. To test this, a solution of sodium hydroxide was prepared from C. P. sodium peroxide and distilled

water. The lead sulphate was prepared from C. P. chemicals and the lead was tested carefully. In spite of all these precautions, the lead sulphate disappeared and crystals of lead were formed. The results of one series of experiments is given in Table I.

TABLE I

No.	g Na ₂ O ₂	Equivalent to g NaOH per liter	Time	Results	
				First	Final
1	8.4	65	46 hrs.	yellow	lead
2	9.48	70	46 hrs.	yellow	lead
3	10.15	75	46 hrs.	yellow	lead
4	10.8	80	46 hrs.	yellow	lead

Similar results were obtained when pure, electrolytic lead was covered with sulphate.

Having thus eliminated the possibility of any reducing agent in the solution or the lead, it was next thought that in some way a concentration cell had been formed and that the crystals of lead were due to the action of the hypothetical concentration cell. To test this assumption, a cylindrical, rotating, lead grid was covered with sulphate and placed in a caustic soda solution, No. 4 of Table I. After only twenty-seven minutes' rotation some reduction of the lead sulphate had taken place.

Since guessing seemed to be unprofitable, we then decided to ascertain the most effective concentration of sodium hydroxide. The results are given in Table II.

TABLE II

No.	g Na ₂ O ₂ in 300 cc H ₂ O	Equivalent to g NaOH per liter	Surface in cm ²	Results
1	23.40	80	40	Excess yellow salt, deposit too loose
2	21.94	75	40	Excess yellow salt, deposit too loose
3	20.48	70	40	Too loose a deposit
4	19.01	65	40	Fine reduction in three hours
5	14.63	50	40	Reduction but in too long a time

Thus we see that a concentration of 65 g NaOH per liter is the best. In Table III are some data which show that the presence of metallic lead is essential.

TABLE III

No.	Reaction	Results
1	NaOH on PbSO_4	No effect
2	Sodium plumbite on PbSO_4	No effect
3	NaOH on PbSO_4 in presence of lead	Complete reduction

The experiments described show that the apparent reduction of lead sulphate by sodium hydroxide is not due to impurities in the lead, the lead sulphate, or the caustic soda; and that the reaction does not occur when metallic lead is absent. Just how the lead acts is not yet clear.

In all the experiments in which crystals of lead were obtained, there was always the intermediate formation of a yellowish green substance. As yet, we have not obtained this substance in a pure enough state to warrant an analysis. A mixture of metallic lead with some of the yellowish green material was treated with different reagents. The results are given in Table IV.

TABLE IV

No.	Reagent	Result
1	H_2SO_4	No effect
2	NH_4Cl	Insoluble
3	H_2O_2 (in KOH)	No effect
4	$\text{Pb}(\text{CH}_3\text{CO}_2)_2$	Insoluble
5	HCl	Slightly soluble
6	HNO_3	Turns white
7	$\text{CH}_3\text{CO}_2\text{H}$	Completely soluble

Attempts were made to separate the lead from the yellowish green salt by floating the latter out. Chloroform was tried as the medium but tended to decompose the salt, and no clean separation was obtained. From Table IV we see that the intermediate salt (in presence of lead) does not behave

like any of the oxides of lead or like plumbic sulphate. The time at our disposal did not permit any further study of this interesting reaction, but the matter will be taken up later in this laboratory.

Since sodium hydroxide has such an effect on lead sulphate when the latter is in contact with metallic lead, attempts were accordingly made to apply this economically in the case of the sulphated storage cell. If a sodium sulphate solution is electrolyzed between two sulphated lead grids, the action of the current would tend to form caustic soda at the cathode. The cathode would then react with the caustic soda just as in the experiments previously described. In fact, the reduction of the lead sulphate should be extremely efficient, because the caustic soda would be formed just where it was needed, in the pores of the grid.

At the anode we should expect to get a more efficient oxidation of the lead sulphate to lead peroxide with a sodium sulphate solution than with a sulphuric acid solution. The potential of oxidizing agents is higher in a strongly acid solution than in a neutral or alkaline one and consequently it is easier to oxidize a substance to a higher stage of oxidation, other things being equal, in an alkaline or slightly acid solution than in a strongly acid one. It ought therefore to be possible to regenerate both plates of the battery simultaneously.

Varying concentrations of sodium sulphate were tried and it was found that the best results were obtained with a concentration of 45 grams per liter. The data are given in Table V.

TABLE V

Electrode surface = 40 cm²; current = 0.5 amp.; time = 8.5 hr.

g Na ₂ SO ₄ per liter	Results		g Na ₂ SO ₄ per liter	Results	
	Anode	Cathode		Anode	Cathode
30	shedding	poor	45	good	good
35	shedding	poor	50	shedding	shedding
40	less shedding	fair	80	shedding	shedding

Before applying these results in the final tests, some experiments were made with caustic soda and sodium carbonate solutions. The electrolysis of a sodium hydroxide solution should give us the maximum reduction at the cathode and maximum oxidation at the anode. The difficulty is that it is too efficient. Varying concentrations of sodium hydroxide were tried but the reduction is usually so rapid that grids were formed which began to shed after a little service. The manipulation or control of this solution is not easy unless one has had a great deal of practice. While a sodium hydroxide solution can be made to give good results, it is not so satisfactory as a sodium sulphate solution. Varying concentrations of sodium carbonate were also tested. The results are similar to those with the caustic solutions and for the same reasons.

The experiments with the home-made grids indicated that a concentration of about 45 g anhydrous sodium sulphate per liter should be the best; but the difference between our temporary grids and the commercial ones was so great that we did not feel at all certain that it was safe to reason from one to the other. Some actual runs were therefore made at various concentrations.

In order to obtain a comparison, one cell was charged and discharged a great many times at the normal rate with sulphuric acid as electrolyte. The data are given in Table VI.

TABLE VI
Five plates, normal capacity 40 ampere hours

Total input	903 amp. hours
Total output	519 amp. hours
Initial capacity	1 amp. minute
Normal capacity	40 amp. hours
Final capacity	27 amp. hours
Percentage capacity	67.5 percent

While it might be considered rather a feat to bring the cell from zero capacity nearly to 70 percent of its initial capacity, the run was not really satisfactory. The cell was in very poor

shape after this treatment, as the active material began to disintegrate and to shed.

Another cell of the same type was filled with sodium sulphate solution and charged at the normal rate until the reduction was complete. This took about 60 hours. Two lead dummies were placed in the container so that the end plates should be reduced rapidly. The data are given in Table VII.

TABLE VII
Five plates, normal capacity 40 ampere hours.

Anhydrous sodium sulphate	140 grams per liter
Initial capacity	1 amp. minute
Normal capacity	40 amp. hours
Final capacity	36 amp. hours
Percentage capacity	90 percent

A similar run was made with sodium carbonate as electrolyte instead of sodium sulphate. The reduction was about one-third the number of ampere hours required with the sodium sulphate solution but this apparent advantage is much more than counterbalanced by the deposit being too dense and by the excessive shedding. Only about 53 percent of the normal capacity could be obtained.

To test the effect of concentration of sodium sulphate, runs were made with a saturated solution and with a solution containing about 91 g hydrated sodium sulphate (equivalent to 40 g anhydrous salt) per liter. The data are given in Table VIII.

TABLE VIII
Five plates, normal capacity, 40 ampere hours

Sodium sulphate	Saturated solution
Initial capacity	1 ampere minute
Normal capacity	40 ampere hours
Final capacity	46 ampere hours
Percentage capacity	115 percent
Anhydrous sodium sulphate	40 grams per liter
Initial capacity	1 ampere minute
Normal capacity	40 ampere hours
Final capacity	50 ampere hours
Percentage capacity	125 percent

These cells have been giving these high percentage capacities right along since then, so there is no chance for error in regard to the facts. It is of course impossible to say whether these two cells were originally better than the other two cells of the same lot or whether there was some difference in the amount that they were used before they were allowed to spoil. All the plates in all the cells were covered with an apparently uniform shell of white sulphate, and the important thing is that they can be brought back into such good condition. It would not be safe to conclude from the two experiments tabulated in Table VIII that the dilute sodium sulphate worked any better than the concentrated solution. About 30 percent more ampere hours were necessary to produce complete reduction in the dilute solution than in the concentrated one and this difference is unquestionably a real one. So far as one can judge, the concentration of the solution is important only to the extent that the reduction takes place more rapidly in the concentrated solution than in the dilute one.

The tests so far had all been on cells which had become sulphated under rather unusual conditions. We have therefore tested two other wrecks on which we were able to lay our hands. The first was an old and badly buckled cell which was rescued literally from the scrap heap. The data are given in Table IX.

TABLE IX
Nine plates, normal capacity 60 ampere hours

Anhydrous sodium sulphate	120 grams per liter
Initial capacity	26 ampere hours
Normal capacity	60 ampere hours
Final capacity	48 ampere hours
Percentage capacity	80 percent

This condemned cell was restored so as to give 80 percent of its original capacity. Considering the condition it was in, this was as much as anybody could hope for.

Another cell was only partially sulphated over the surface but had been allowed to stand discharged for a long time. The data are given in Table X.

TABLE X

Two plates, normal capacity, 12 ampere hours

Anhydrous sodium sulphate	152 grams per liter
Initial capacity	3.75 ampere hours
Normal capacity	12 ampere hours
Final capacity	11.75 ampere hours
Percentage capacity	98 percent

Although this cell was apparently in poor shape, it was restored practically to its original state. These illustrations suffice to show the general applicability of the method.

When one starts with a battery in commission, the acid should be siphoned off and the solution of sodium sulphate run in. It is desirable, but not necessary, to place dummy plates outside the end plates. The cell can then be charged at the normal rate until the sulphate is entirely reduced. This can be determined by the eye; but, if that is inconvenient, a charge of sixty hours will probably be satisfactory. The sodium sulphate should then be siphoned off and the grids washed once with water. The amount of sodium sulphate remaining in the plates will have a beneficial rather than a deleterious effect. If the water is then drawn off and the normal battery acid run in, the battery should be as good as new, always supposing that the only damage is due to sulphating. In our tests the current efficiency was only about 80 percent, which is probably lower than it was when the cell was new, though we have no data on that point.

The cost of restoring a cell is low. For the small 40 ampere hour cells which we have studied, it has taken less than a kilowatt hour to bring them back to good condition. That means not over ten cents per cell for electrical energy. Sodium sulphate is cheap and can of course be used over and over again. While good results can be obtained with almost any concentration of sodium sulphate, the time necessary for reduction is increased when the solution is relatively dilute. On the other hand a saturated solution is objectionable owing to the possible crystallization. An arbitrary concentration of 200 grams $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ per liter is therefore recommended.

The process as outlined is very efficient and has the further advantage that it introduces no deleterious substances into the cell. Of course it is absolutely essential that the sodium sulphate shall be pure. The ordinary sodium sulphate always contains chloride. With chlorine in the cell the destruction of the plates is only a matter of time and not of very long time at that.

A representative of one of the large storage battery companies has stated that any sulphated cell which he has ever tested could be restored by charging for a long enough time at about half rate in the regular battery acid. No data have been published and consequently one does not know what the maximum degree of sulphating was or what the length of time was. Where the time involved is not excessive, this method has the advantage of eliminating the transfer of electrolyte.

If the time involved is excessive, as it is likely to be in the case of badly sulphated cells, the cost of time and of electrical energy will exceed the cost of handling. It would be a mistake to make any hard and fast rule as to which method to employ; but it seems probable that a prolonged over-charge at half rate in the regular battery acid will suffice for cells which are not badly sulphated. For extreme cases of sulphating the sodium sulphate method is unquestionably the only one which can be used. A special series of tests would be necessary to determine the relative merits of the two methods for intermediate cases.

The general results of this paper are as follows:

- (1) A badly sulphated cell can be restored by charging at the normal rate in a sodium sulphate solution.
- (2) It is desirable, but not necessary, to use lead dummies outside the end plates.
- (3) A concentration of about 200 g $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ per liter is recommended but the concentration can be varied within very wide limits.
- (4) It is essential to the life of the cell that the sodium

sulphate should meet the requirements as to purity which are laid down for battery acid.

(5) A very badly sulphated cell can be restored by about sixty hours' charge at normal rate.

(6) The cost of electrical energy to restore a 40 ampere hour cell should not exceed ten cents.

(7) Since sodium sulphate is not deleterious to the cell, it is not necessary that the sulphate solution should be washed completely out of the pores of the plates.

(8) It has been stated by others that a cell can be restored by charging a half of the normal rate for a long time in the regular battery acid. It seems probable that the time and electrical energy required would be excessive in the case of very badly sulphated cells.

Most of the experimental work recorded in this paper was done by Messrs. Daley, Graham, and Martin as senior research work. I am indebted to Mr. C. W. Bennett for some runs made after I left. The work was suggested by Professor Bancroft.

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