Effect of chlorine-containing species on lead/acid battery posts

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Abstract

Chloride in the electrolyte of lead/acid batteries has long been thought to cause early failure due to accelerated corrosion of the positive-plate group. This study investigates the effect of chloride species, added as either hydrochloric acid or sodium chloride, on positive posts of lead/acid cells under float conditions. The introduction of chloride from either source results in higher float currents and enhanced corrosive attack of the positive post above the electrolyte level. The presence of sodium chloride also promotes an additional and distinctive form of corrosion. Given these findings, a review of maximum chloride levels in industry standards for both battery acid and makeup water is indicated.

1. Introduction

1.1. Inconsistencies in standards

Throughout the industry, it is a widely held belief that the addition of chloride to the electrolyte can eventually degrade both the performance and the lifetime of lead/acid batteries. As a result, limits have been set for the chloride levels in both the starting sulfuric acid and the makeup water. Interestingly, there is little agreement over the maximum amount of chloride that can be tolerated. For example, the Australian Standards [1,2] fix the maximum permissible level of chloride at 30 ppm (referred to 1.840 sp. gr. acid) for acid and 20 ppm for makeup water. In the USA, a Federal Specification limits the allowable chloride in 1.835 sp. gr. acid to 10 ppm [3]. By contrast, the US National Electrical Manufacturers Association (NEMA) has an independent standard for makeup water for lead/acid industrial storage batteries, and this restricts the chloride to 25 ppm.

1.2. Chloride and other possible chlorine-containing species in batteries

During the charging of a lead/acid battery, the potential of the positive plate rises to values that are sufficiently high to oxidize all but the most stable of compounds. (Note, at typical float voltages, the positive-plate potential of a lead/acid battery lies close to 1.28 V versus an Hg/Hg_2SO_4 reference electrode.) Consid-

eration of electrochemical data [4] for the stability of chloride in acid media indicates that chloride will be oxidized to chlorine gas at a potential of around 0.74 V (versus Hg/Hg_2SO_4). Chloride ions can also undergo direct oxidation to both hypochlorite (ClO^-) and chlorate (ClO_3^-) at ~ 0.85 V (versus Hg/Hg_2SO_4). In addition, dissolved chlorine gas can be converted to ClO^-, ClO_3^- and/or perchlorate (ClO_4^-) ions at potentials that range between 1.34 and 1.63 V (versus Hg/Hg_2SO_4). Finally, perchlorate species can also be formed from ClO_3^-, but the reaction is not kinetically favoured at room temperature. During the charging of a lead/acid battery, therefore, it is possible for any foreign chloride ions to give rise to several, different, chlorine-containing species.

1.3. Chloride the aggressor

Many studies have demonstrated [5–16] that perchlorate can enhance the corrosion of lead in sulfuric acid solutions. Indeed, this property is exploited in the formation of Planté plates [16]. In this process, a small amount of perchloric acid is added to the sulfuric acid to accelerate the production of lead dioxide from the lead substrate and, thereby, to increase the charge capacity of the plate.

The aggressive attack of lead by perchlorate has been explained in terms of pitting corrosion [5,6,8,11,15,16]. In particular, it has been argued that perchlorate ions exert a destructive effect on the passivating layer of lead sulfate that readily develops on the lead surface

following reaction of the metal with the sulfuric acid. It has been advocated [5,14] that there is an optimum concentration of perchlorate that is conducive to pitting corrosion. Moreover, apart from the presence and quantity of perchlorate, the degree of pitting corrosion has been shown [5] to depend on several other factors, namely, surface treatment of the metal, bulk sulfuric acid concentration, and temperature.

It has come to the authors' attention that high levels of chloride contamination have been associated with a distinctive and acute form of corrosion in standby-power cells. Commonly, the initial presence of chloride has been related to the formation of discrete blisters (or nodules) on positive posts after several months of float duty. The phenomenon is usually confined to the vicinity of the electrolyte level (the so-called 'meniscus region'), but can be accompanied by a similar manifestation on the positive busbar and the adjoining plate lugs. In one particularly severe case, detachment of the plate group from the positive terminal post had occurred. Analogous behaviour has been displayed in cells undergoing service in a lighthouse in the Timor Sea, i.e., in a saline environment.

1.4. A neglected phenomenon

Despite the general concern over the possible debilitating effects of perchlorate-assisted corrosion on the well-being of lead/acid batteries, a survey of the published literature reveals that very little effort has been made to determine precisely the concentrations that are permissible for the precursor chloride species. Unfortunately, all of the reported studies of the preferential attack of perchlorate on either lead or lead alloys have been conducted on single, laboratory-scale electrodes, as opposed to practical battery plates. In addition, most of the investigations have utilized host sulfuric acid solutions of strength well below that used in batteries (viz., ~ 4.5 M), i.e., at concentrations more representative of those employed in the Planté process (viz., 0.5–1.0 M). Surprisingly, there have been no reports of experiments in which controlled levels of chloride have been added to actual lead/acid batteries.

Given both the present general lack of scientific information and the above-mentioned inconsistencies in national codes of industrial practice, a research programme has been implemented in the CSIRO laboratories to unravel the mechanisms responsible for chloride-related corrosion in lead/acid batteries. This work reported here examines the effect of chloride, introduced as either hydrochloric acid or sodium chloride, on the corrosion of pure-lead battery posts under float-charging conditions.

2. Experimental methods and materials

Corrosion tests were performed on battery terminal posts that were cast from lead (99.9% pure) by GNB Battery Technologies, Australia. The posts were cylindrical in cross section and measured approximately 50 mm (length) by 10 mm (diameter). Electrical connection to each post was made via a threaded titanium rod. The posts were suspended in glass cells that contained 400 ml of sulfuric acid solution (3.68 M, 1.215 sp. gr.). The position of each post was adjusted so that approximately half the length was submerged. The cells were maintained at 25 ± 0.5 °C by means of a temperature-controlled water bath. A multi-channel voltage source imposed a constant potential of 2.25 V across the two posts of each cell. The potentials of the positive electrodes were monitored (and are reported) against an Hg/Hg_2SO_4 (5 M H_2SO_4) reference electrode. The cell currents were measured by means of a small resistance that was placed in series with the power supply. The corrosion experiments were performed in sulfuric acid solutions that initially contained 0, 30, 150, 300, 450 or 600 ppm of chloride (added as either hydrochloric acid or sodium chloride). All chemicals were Analytical Reagent (AR) grade, or better. Double-distilled water was used throughout.

In order to study the effect of casting quality (i.e., number of defects, porosity, etc.) on corrosion behaviour, a series of posts was produced in the laboratory. For this, the factory castings ('factory' posts) served as the feedstock. Several factory posts were heated to 500 °C, under a nitrogen atmosphere, and were then poured into a mould that was held at 300 °C. After air-cooling for 2 min, the casting ('recast' post) was quenched in water.

Within each cell, the same type of post (factory or recast) was used for both the positive and the negative electrodes. At the conclusion of each experiment, the posts were removed from the electrolyte solution, washed carefully with acetone, and allowed to dry in air.

Electron probe microanalysis (EPMA) of the lead posts was conducted by means of a CAMECA (Paris, France) Camebax 'Microbeam' instrument that was operated at an accelerating voltage of 15 kV and a beam current of 38 nA. The elements analyzed, along with the respective analytical spectral lines, were: lead ($M\alpha$), sulfur ($K\alpha$), and oxygen ($K\alpha$). Raw intensity ratios were normalized by means of the 'PAP' matrix corrections [17]. A calibration analysis for each element was performed on a standard sample of anglesite ($PbSO_4$). Prior to analysis, both the standard and the unknown were coated simultaneously with a thin (~ 20 nm) film of carbon.

Analysis for sulfur (as sulfate in lead sulfate) in the corrosion products was also conducted with an LECO

(MI, USA) model CS-244 carbon and sulfur induction furnace. Sulfur was detected, as sulfur dioxide, with an IR detector.

2.1. Lead corrosion — effect of chloride, as HCl

The addition of known amounts of hydrochloric acid to the cell electrolyte allowed the effects of chloride to be examined without the introduction of foreign cations. Factory and recast posts (six cells of each type) were held at 2.25 V for 180 days in solutions that contained given amounts of chloride. As mentioned above, the base electrolyte was 3.68 M sulfuric acid; this concentration is typical of electrolyte in lead/acid batteries (fully-charged state) of the type designed for stationary (float) applications.

The appearance of the positive electrodes (factory posts) after corrosion treatment is shown in Fig. 1. The submerged parts of the post subjected to chloride-free solution are characterized by an even coverage of dark-brown material that is readily identified as lead dioxide. This coverage also extends above the electrolyte level, which suggests that there has been appreciable 'creep' or 'wicking' of electrolyte up the post.

The nature of the posts is changed appreciably by the addition of chloride to the electrolyte. At the lowest level of chloride (30 ppm), powdery white deposits
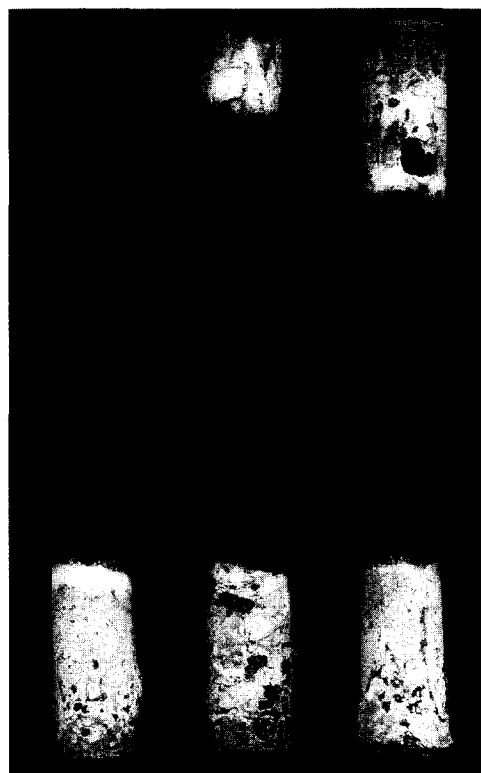
develop on the upper parts of the post, well above the level of the solution. On raising the chloride concentration to 150 ppm, the coverage by this white deposit increases and progresses down towards the solution. The extent of this behaviour is largely unaffected by further increases in chloride concentration. Analysis shows that the white material is composed mainly of lead sulfate. Recast posts behave in a similar fashion to original castings.

The cell currents were monitored during the experiments. Typical results (day 0 to day 75) are presented in Fig. 2. Only data for factory posts are shown, as the magnitude and variation of the float currents for both types of post (factory and recast) are similar. Clearly, cell currents increase with increasing concentration of added chloride.

The potential of each positive post was monitored against an Hg/Hg_2SO_4 reference electrode. For both the factory and recast posts, the potentials are in the range 1.220–1.260 V. The lowest values of potential correspond to the highest initial concentrations of chloride. This decrease in potential with increasing chloride level may be the result of one or both of the following factors: (i) modification of the oxygen and/or hydrogen overpotentials; (ii) additional electrochemical processes that involve chloride and/or chloride-derived species, e.g., the production of chlorine gas.

2.2. Lead corrosion — effect of chloride, as NaCl

Both factory and recast posts were electrolyzed for 40 days in sulfuric acid solutions that contained various levels of chloride ion added as sodium chloride. It is found that the presence of sodium chloride exerts a marked effect on the corrosion of both types of posts. Fig. 3 shows the recast posts at the completion of the corrosion test. As observed with the H_2SO_4/HCl ex-
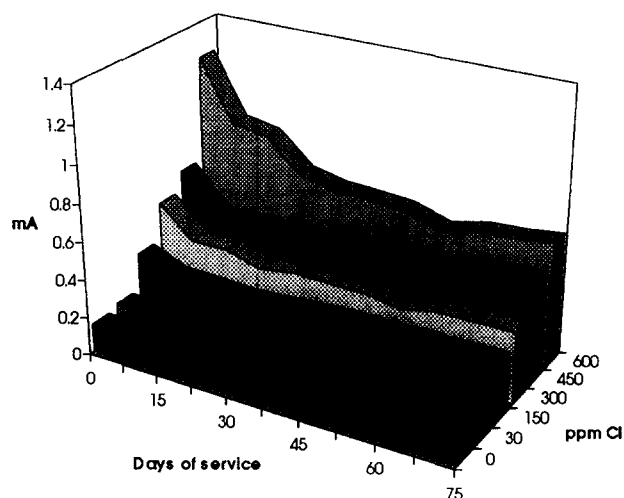

Fig. 1. Condition of factory posts electrolyzed as positive electrodes for 180 days at 2.25 V in 3.68 M H_2SO_4 containing Cl^- added as HCl (top, left to right: 0, 30, 150 ppm; bottom, left to right: 300, 450, 600 ppm).

Fig. 2. Float currents for factory posts electrolyzed at 2.25 V as positive electrodes in 3.68 M H_2SO_4 containing Cl^- added as HCl.
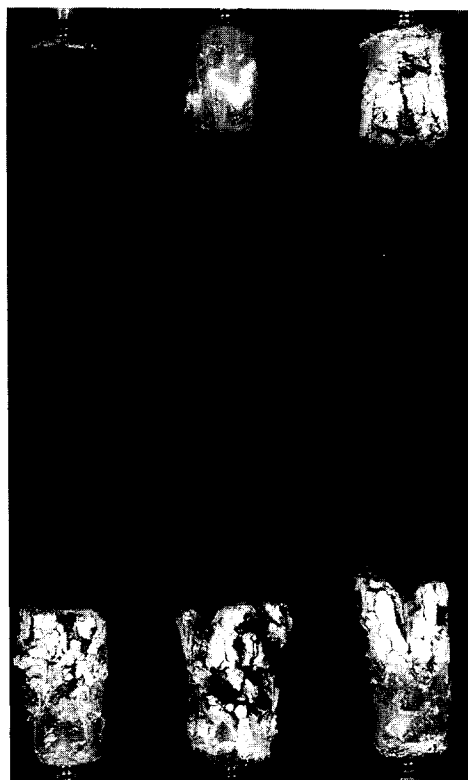
Fig. 3. Condition of recast posts electrolyzed as positive electrodes for 40 days at 2.25 V in 3.68 M H_2SO_4 containing Cl^- added as NaCl (top, left to right: 0, 30, 150 ppm; bottom, left to right: 300, 450 600 ppm).

periments, all posts exhibit: (i) increasing float currents with increasing initial concentration of chloride; (ii) appreciable levels of lead sulfate above the electrolyte level; (iii) a brown coloration below the electrolyte level due to the formation of lead dioxide. The results, however, differ from those obtained for the H_2SO_4/ HCl series. Both factory and recast posts display an additional and distinctive form of corrosion. This is manifested as fragile, whitish-brown blisters above the electrolyte level (Fig. 4). If disturbed, these blisters readily flake from the post. The blister corrosion is especially severe on the recast electrodes. It is likely, therefore, that the difference in the extent of the attack is related to variations in the casting quality of the posts.

Cross sections of the recast posts exposed to 150 and 450 ppm chloride were subjected to EPMA. Much of the corroded material is found to consist of $PbSO_4$. Regions with Pb:O ratios equivalent to PbO_2 are also present, but these are not as widespread as the $PbSO_4$. Phases with analyses corresponding to Pb and PbO are also detected (generally, adjacent to each other) but these are uncommon. Some sections of the blisters were removed from one side of the recast posts for chemical analysis. Atomic absorption spectroscopy was used to search for lead and sodium, and the LECO method was used for sulfur. Sodium was not detected
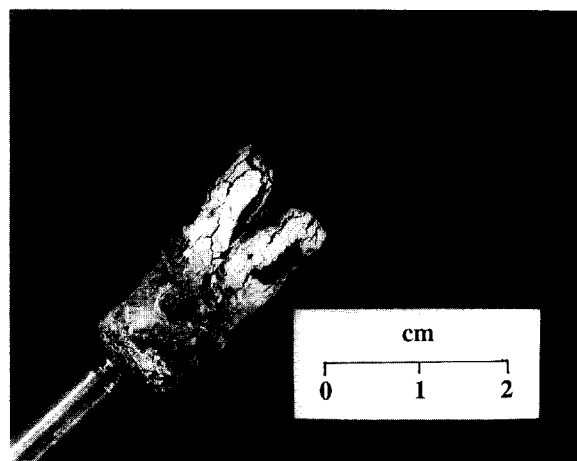

Fig. 4. Condition of recast post exposed to 600 ppm Cl^-, added as NaCl (same test procedure as Fig. 3).

in the corroded regions. In line with the results from EPMA, the abundances of lead and sulfur indicated that the composition is dominated by $PbSO_4$ (calculated on the basis that $PbSO_4$ contains 68.3 wt.% Pb, 10.6 wt.% S).

The positive-plate potentials were measured during the experiment. These are found to vary between 1.280 and 1.320 V, that is, some 60 mV higher than those recorded in the presence of hydrochloric acid. As blister formation does not occur at the lower potentials observed in the presence of HCl, it is concluded that both an elevated positive-plate potential and the presence of chlorine-containing species are required for the development of this destructive form of corrosive attack.

2.3. Effect of sodium ions

The influence of sodium ions themselves on the corrosion mechanism was evaluated. Three replicate cells, containing 150 ppm of sodium ions added as sodium sulfate, were operated for a period of 101 days. After this time, there were no signs of either blisters or lead sulfate on the positive posts in any of the cells. The surfaces of the posts appeared to be in an identical condition to those corroded in chloride-free sulfuric acid solution, namely, there was a uniform conversion to dark-brown PbO_2.

3. Discussion

The above studies have shown that the addition of chloride exerts a marked effect on the corrosion of pure-lead posts under conditions that simulate the typical float duty of lead/acid batteries. In general, it has been found that both the cell float current and the extent of corrosion increase with added chloride

concentration. This finding applies when chloride ions are introduced into the electrolyte as either hydrochloric acid or sodium chloride. In the presence of the latter compound, however, the nature of the attack is more complex: a distinctive type of 'blister' corrosion is observed above the electrolyte level. In addition, the positive-electrode potential, for each concentration of chloride, is slightly higher for the cells in which Na^+ is the counter-ion, rather than H^+.

Ahlberg and Berghult [15,16] have investigated the effect of cations, including Na^+, on the production of Planté plates. (As noted earlier, Planté formation involves the oxidation of lead in the presence of perchlorate, added as the acid.) These workers observed that substitution of perchloric acid with a metal (Li, Na or K) perchlorate salt influenced both the surface area and the electrical performance of the formed electrode. Specifically, they found that the electrode surface area decreased with increasing size of counter-ion. Thus, surface area was highest when perchloric acid was added, and lowest for the addition of perchlorate as the potassium salt. They also pointed out that as the amount of lead corrosion is not influenced by the cation, the lower surface area is not merely a result of less corrosion taking place. This conclusion is relevant to the present study because of the likely effect of change in electrode surface area on electrode potential.

The studies reported here indicate that the reduced surface area that is expected to develop in the presence of sodium ions [15,16] causes a shift of positive-post potential to higher values, relative to a sodium-free cell. This process occurs gradually, as the corrosion deposit forms. While there is no direct evidence of such a difference in surface area with the above electrodes, there appears to be no other obvious explanation of the results. Certainly, it is extremely hard to conceive of a direct chemical role for sodium in the electrochemical reactions taking place at the positive electrode. In concluding this discussion of the results, it should be emphasized that the data of Ahlberg and Berghult [15,16] were obtained in a system that was chemically relatively simple: the only chlorine-containing species present was perchlorate. By comparison, the above observations were made under conditions that should have given rise to a range of chlorine-containing species. The latter can undergo a variety of redox processes and, importantly, virtually no information is available on the effects of such species on the corrosive action that occurs within lead/acid batteries.

4. Conclusions

The intention of this study has been to provide more information on the factors that contribute to enhanced, and often catastrophic, corrosion of lead/acid battery posts in the presence of chlorine-containing species. Most importantly, it has been shown that the introduction of chloride, added as either hydrochloric acid or sodium chloride, can increase the rate of corrosion within lead/acid batteries. Moreover, the presence of sodium chloride can lead to the occurrence of a particularly aggressive type of attack that is called 'blister corrosion'. It has been found that the nucleation of the blisters is not related simply to the nominal concentration of chloride ions in the electrolyte solution. Rather, the occurrence of the phenomenon appears to depend on the surface structure and/or metallurgical properties of the post casting, as well as on the potential to which the post rises. Given this effect of sodium chloride, it is clear that special precautions must be taken in those battery applications where the risk of such chloride contamination is high, e.g., remote-area power supplies in coastal regions with high levels of airborne salt spray.

It has also been possible to clarify the role of perchlorate on the incidence of blister corrosion. A survey of the literature failed to reveal any case of blister corrosion in which only perchlorate had been added to the electrolyte. Therefore, it seems clear that one or more of the intermediate oxidation products, between chloride and perchlorate, is required for blister corrosion. Hence, it is recommended that the level of 'chloride' in lead/acid batteries must be kept to an absolute minimum. Even levels as low as 30 ppm can cause a significant increase in the rate of positive-post corrosion. In light of the results presented here, impurity limits specified for chloride ion both in battery-grade sulfuric acid and in makeup water should be reappraised. A set of guidelines, to be applied internationally, should be established.

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