Catalyst 201: Catalysts and Poisons from the Battery

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INTRODUCTION

Last year's paper offered a simplified explanation of what occurs inside a VRLA cell once a catalyst is introduced into it. A quick review of that paper will set the stage for what we found after 5 years of producing and selling catalyst products. The results of our long term tests showed that our original catalyst design could occasionally be poisoned by hydrogen sulfide. While many believed that this gas could not be produced by VRLA cells under normal conditions, we found that there is a cycle of production and absorption of hydrogen sulfide in VRLA cells and that a very low level equilibrium concentration can develop in the headspace of the cell. With this knowledge we developed a new design of catalyst product to survive the presence of this poison for at least the life of the VRLA cell it will be installed into.

A QUICK REVIEW

In last year's paper[1] we identified float current as an insightful measurement to use in assessing the health of a VRLA cell. The lower the float current the better. As we emphasized last year, we are not talking about lowering the float current by simply lowering the float voltage supplied to the battery. We are talking about lowering the float current while the charger/rectifier is set to the manufacturer's recommended float voltage. A lower float current leads to:

- Slower positive plate corrosion
- Less cell gassing (water loss) and therefore slower cell dryout
- Reduced cell heating
- Less risk of thermal runaway
- Increased cell life

We showed that a cell float current that is too high could be caused by a cell that is out of balance. By this we meant that the polarizations on the positive and negative plates were not at their optimum points. Polarization is an electrochemical way of looking at the charge on each individual plate inside a cell. We showed that a healthy VRLA cell would have the majority of the charge (polarization) placed on the positive plate while a minority of the charge would be on the negative plate. In an unhealthy, or out of balance, cell all of the charge is placed on the positive plate and none of the charge is placed on the negative plate. A high positive plate polarization leads to a high float current. Since the charge applied to a cell is distributed between the positive and negative plates, the key to keeping the positive plate polarization low is to make sure that the negative plate stays polarized. Keeping the negative polarized leads to a lower positive plate polarization, which in turn leads to a lower float current, which leads to a healthier cell and the benefits listed above.

Finally we showed that a relatively simple way to keep the float current low was to insert a precious metal catalyst into the headspace of a VRLA cell. VRLA cells were designed to have a very efficient transport of oxygen from the positive plate to the negative plate. This was to maximize the recombination of oxygen and hydrogen into water at the negative plate, which was intended to keep the water in the cell. When oxygen reaches the negative plate it depolarizes the plate a small amount. Unfortunately the oxygen transport is too efficient in high quality VRLA cells and leads to full depolarization of the negative plate. When a catalyst is inserted into the headspace, it takes in a small amount of the oxygen generated at the positive plate and combines it with the hydrogen formed at the negative plate to form water. Basically the catalyst prevents some of the oxygen produced from reaching the negative plate and depolarizing it. Since the negative plate remains polarized, the positive plate's polarization stays low (80 mV to 100 mV), which then leads to a lower float current.

ANOTHER MYSTERY

Five years ago, based on a solid understanding of what was causing the premature failure of many VRLA cells, Philadelphia Scientific launched its first commercial catalyst product. Over time and use we saw the return to health of many "failed" VRLA cells. The cells were not dead, their negative plates were just discharged and the addition of a catalyst helped to restore the electrochemical balance within the cell as evidenced by lower float current. But as with all new products there were still things still left to discover.

Throughout the development of our catalyst product, we have conducted lab tests and field trials. Over time, in some of these lab tests we saw the float current on some of our catalyst equipped cells begin to rise over time. Since we knew that float current is an excellent indicator of the state of balance within a cell, we became concerned. Eventually the float current of these cells rose to the level of the non-catalyst equipped cells that were on test with them. In our field tests we occasionally noticed that a test string's float current would rise to the same level that it was before we had installed the catalysts. After checking for a variety of potential problems, we decided to remove the catalysts and inspect them. To the naked eye the catalysts looked exactly as they had when installed into the cells. There were no signs of physical damage to the catalysts or the cells, yet we found that these catalysts would no longer recombine oxygen and hydrogen; they had stopped working. We could not find a discernable pattern as the catalyst failures were not numerous and were not consistent within a string of cells. But now our curiosity was piqued. Theoretically a precious metal catalyst will work forever, as it does not take part in the reaction. There is no reason for it to stop working unless it is physically blocked and prevented from contact with the gases it is to recombine or unless it becomes poisoned by its environment.

Our first step was to make sure that catalyst cartridge had not been blocked so that the gas could not access the catalyst material within the porous walls of the cartridge. Upon investigation, we found absolutely no evidence of any material coating the cartridge. This then led us to investigate the catalyst active material itself. During our investigation, we resorted to such devices as an electron microprobe to perform elemental analyses of the surface of our catalyst material. In every sample that we analyzed we always found elemental sulfur on the catalyst material that had stopped working. But how could sulfur contaminate the catalyst surface if the only things that the catalyst came into contact with were battery gasses? The answer was hydrogen sulfide. When hydrogen sulfide (H_2S) is exposed to a precious metal catalyst it is broken up into hydrogen gas and sulfur. The hydrogen gas is released and the sulfur is bonded on the surface of the catalyst itself. In this case, the catalyst actually takes part in the reaction and no longer is able to perform as a catalyst. Now that we had identified the culprit our next question was where did it come from? We had been told repeatedly that VRLA batteries do not normally produce H_2S and that it could not be coming from the cell. We had read of extreme cases where H_2S had been produced in thermal runaway scenarios[2], but our cells had certainly not seen any severe conditions like that. We began a series of experiments to determine if it was possible to produce H_2S in a VRLA cell. The summarized results that will be presented next were first reported in a paper at the 2001 Intelec in Edinburgh, Scotland.[3]

HYDROGEN SULFIDE IN VRLA CELLS

Our main goal was to prove that H_2S existed under everyday conditions in VRLA cells. What we ended up discovering was an H_2S cycle of production and absorption that was occurring inside the battery involving both the negative and positive plates. In the end, we concluded that H_2S was being produced by the negative plate in large concentrations. We also found that the positive plate was able to easily absorb even larger quantities of H_2S. We theorized that there must be an equilibrium that sets up in the headspace of the cell between the production and absorption of the H_2S so that the final concentration level of H_2S is very low. We put this theory to the test by sampling the gas in a number of VRLA cells and did find that H_2S existed in VRLA cells on float service, but only at levels below 1 ppm.

In the beginning of our investigation we tested a variety of common battery components, which led us to eventually isolate our search to a reaction on the negative plate between the lead and the sulfuric acid.. We designed and constructed a test rig to focus on just the negative plate by capturing the gasses produced by it. Figure 1 shows a drawing of this test rig.

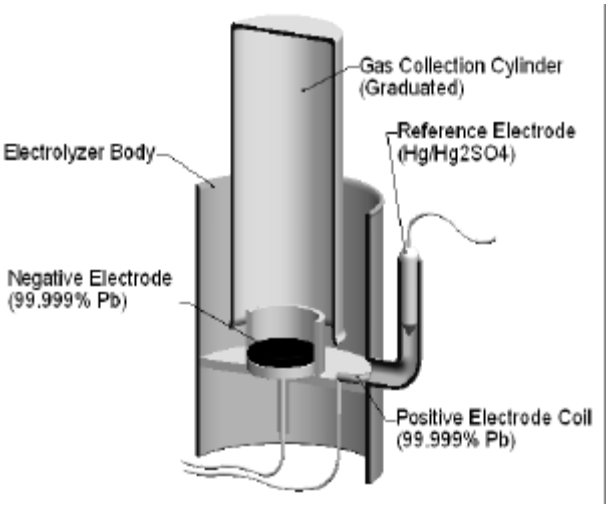

Figure 1

In the test rig we used extremely pure lead and sulfuric acid, much purer than is commonly used in VRLA cell production, to eliminate the possibility that contaminates could be the source of the H_2S. When a current was applied to the test rig it broke up the acid into its component oxygen and hydrogen gasses. A glass cylinder was used to collect the gas produced by the negative plate, which was later analyzed with our gas chromatograph (GC). Figure 2 shows the surprising results that we obtained when we applied different voltages to the test rig.

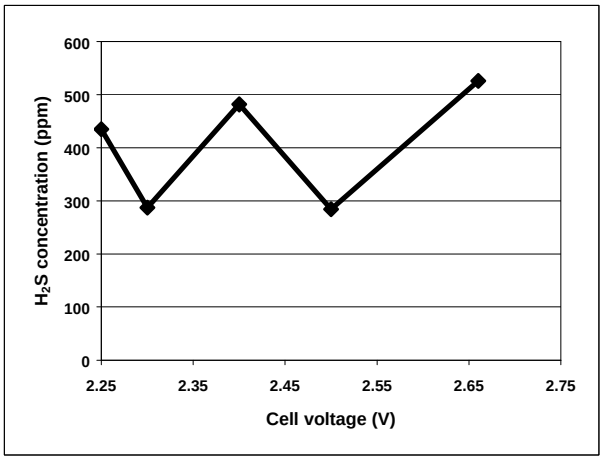

Figure 2

As can be seen in the graph, high concentrations of H_2S were produced regardless of what voltage was applied to the test rig. The test also confirmed that H_2S was produced at voltages that are normally used to float VRLA cells. We also found that there was no relationship between voltage and the concentration of H_2S produced.

The result that puzzled us the most was the high H_2S concentration of 400 ppm that we measured. Levels this high, which are hazardous to human health, would be immediately detected by anyone in a battery room as the human nose is extremely sensitive to this gas, but we had never heard of anyone smelling hydrogen sulfide in a stationary battery room. If negative plates in VRLA cells were producing H_2S as we just proved could happen and it was indeed poisoning our catalysts, what happened to the gas? Our attention then shifted to what could happen inside the cell to eliminate or absorb the H_2S.

After a literature search and some consultation with experts in the field, we focused on the lead oxides that make up the positive plate. We conducted two experiments to determine what was happening. In the first experiment we placed our test sample in a cylinder and ran a gas mixture of hydrogen with 100 ppm of H_2S into one end and through the sample. We analyzed the gasses coming out of the other end of the cylinder with our GC to determine how long it took before the H_2S made it through the bed of material. This we called the breakthrough time. Figure 3 is a schematic of this test.

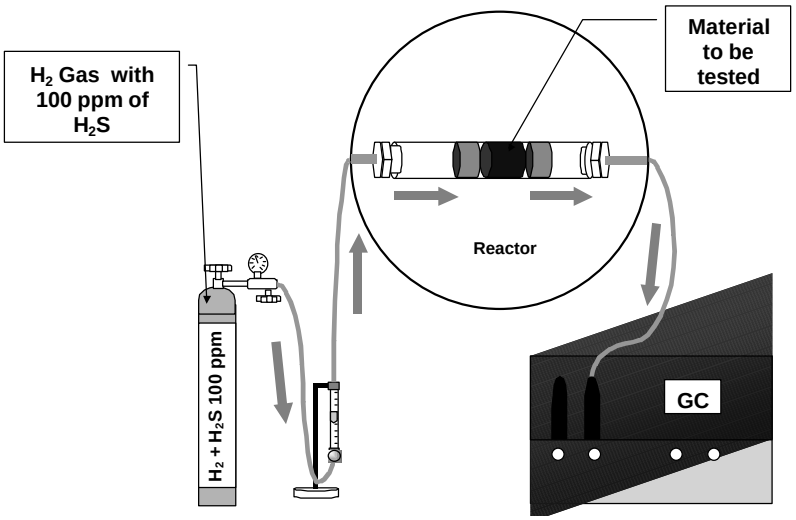

Figure 3

The test was run first with an empty chamber and then with a packed bed of PbO and finally with a packed bed of PbO_2. The results of this experiment are presented in Figure 4.

Test Material	Amount (Grams)	Breakthrough Time (Minutes)
Empty	0	0.01
PbO	2.194	120
PbO_2	1.978	360

Figure 4

As can be seen the GC instantly detected the H_2S when the test chamber was empty. We confirmed that both PbO and PbO_2 absorb H_2S since it took time to detect the H_2S as the gas was run through the sample. PbO_2 is by far the better absorber of H_2S as can be seen from the longer breakthrough time. Our next experiment was designed to prove that this could also happen in a real battery where there are large amounts of PbO_2 in the positive plate.

In our second test we ran the hydrogen with 100 ppm H_2S gas mixture through a 200 Ah VRLA cell that was on float at 2.27 Volts. The gas was fed into the back of the cell and came out of the front of the cell directly into our GC for analysis. Again we were measuring the concentration of H_2S in the gas that came out of the cell to determine when the battery stopped absorbing the H_2S. Figure 5 is a schematic of this experiment.

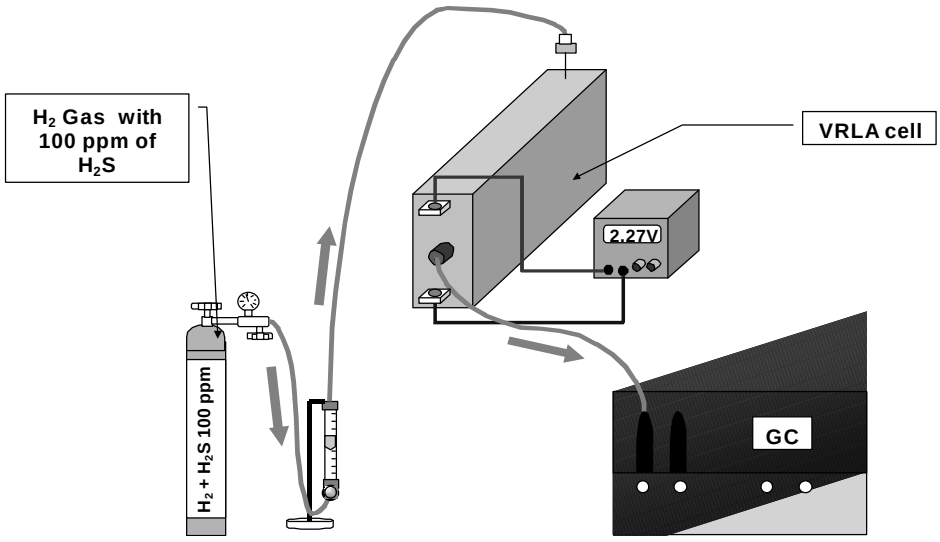

Figure 5

We fed the gas mixture into the cell at varying input rates and monitored the concentration of H_2S in the outflow gas over a period of 28 hours. Figure 6 displays the results of this experiment. The left axis is the H_2S concentration in the outflow gas, the right axis is the input gas flow rate and the bottom axis is the time of the test.

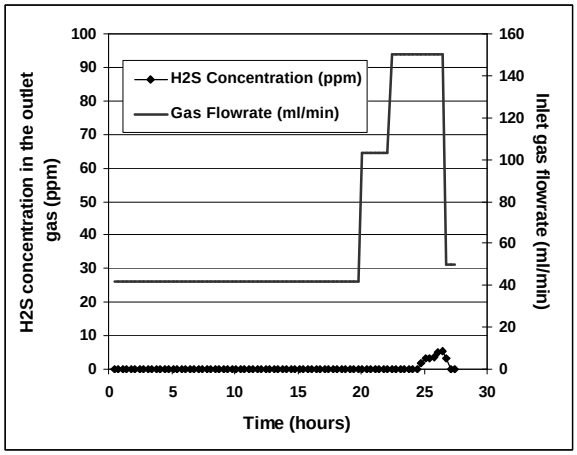

Figure 6

As can be seen from Figures 6, the vast majority of the H_2S was absorbed in the cell. 100 ppm of H_2S was put into the cell and the highest output concentration that we measured was only $1/10^{th}$ of that, or 10 ppm, and this level was measured only after we quadrupled the input flow rate. To give a since of scale to this experiment, we were only able to detect the 10 ppm when we pumped gas into the cell at a rate that is 1,000 times greater than the normal gassing rate for this cell on float.

The graph above shows that for the first 24 hours of the test no H_2S was detected in the outflow gas despite the fact that we had more than doubled the input flow rate to 103 ml per minute. It was not until we raised it to 150 ml/min that we started to detect the previously mentioned 10 ppm. It should also be noted that within 30 minutes of dropping the input rate back down to the initial input rate the measured H_2S concentration dropped back to zero. This experiment clearly indicated that H_2S was being absorbed in the battery and that large quantities of H_2S could be continually absorbed.

Based on both of these experiments, we now had an explanation of where the H_2S was going in the cell and we concluded that it must be the PbO_2 of the positive plate that was absorbing the H_2S and that it was being absorbed in huge quantities. The last step for us was to confirm that H_2S indeed existed in VRLA cells. So far we had shown how it

could be produced and how it could be absorbed, but had yet to measure it in a VRLA cell. We theorized that an equilibrium level must develop between the two processes, but did not know what level that was. To determine this level we used our GC to analyze the gas emissions from a variety of VRLA cells that we had on test in our lab.

On test in our lab we have a variety of VRLA cells produced by a cross section of battery manufacturers. The cells are on float service at 2.27 volts per cell and are at either 25°C of 32°C. The cells all range in age between brand-new and 7½ years old. From November 2000 until November 2002 we sampled gas on a weekly basis with our GC and since November 2002 we have continued to sample the gas but only on a monthly basis. The goal of this extensive GC sampling was to determine what concentration level of H_2S existed in VRLA cells. The results of our analysis indicated that H_2S was emitted from our test cells in a range from 0 ppm to just under 1 ppm, bet never more than 1 ppm. We attempted to determine if there was a pattern to the varied measurements that we collected but were unable to do so. We could detect no H_2S for weeks on a cell and then all of a sudden in that very same cell we would detect very low concentrations of the gas. To verify our results, we sent verification samples of the gasses to an outside lab that had a GC that was even more sensitive and precise than our GC. The results of the outside lab's testing absolutely confirmed our own GC's measurements and gave us the confidence to believe our own results.

The major findings from our sampling of VRLA cells were:

- H_2S was routinely detected in VRLA cells under normal float voltages and at routine operating temperatures.
- In 2 ½ years of testing, we never measured H_2S concentrations greater than 1 ppm. It is also important to note that the vast majority of measurements indicated concentrations much lower than 1 ppm.
- The levels of H_2S detected in the cells were inconsistent; the levels routinely varied between 0 ppm and 1 ppm without any discernable pattern.

A point to remember is that our proposed low equilibrium level is for float service only and that under non-normal conditions, such as those experienced in thermal runaway, the resultant H_2S amounts emitted by a cell could be much larger. We believe that the main reason for this is because in thermal runaway conditions the current drawn by the battery is much higher than normally experienced, which causes the cell to emit larger quantities of gas than when on float. We theorize that during this period of high gassing, the rate of emission of H_2S will most likely be faster than the rate of absorption of the PbO_2. In other words, we think that the gas will be flowing too fast to allow for full absorption of the H_2S on the PbO_2 and the end result is that large quantities of H_2S can escape the cell. We believe that this explanation most likely accounts for the blackened copper connectors that have been reported when such thermal runaway events have occurred. When copper is exposed to hydrogen sulfide, the resulting reaction produces copper sulfide, which is black in color.[4]

Putting all of the results of our testing together, we developed the following life cycle theory for H_2S in VRLA cells:

- H_2S can be produced in large amounts in VRLA cells in a reaction on the negative plate.
- H_2S can be absorbed in larger amounts in a VRLA cell by the PbO_2 of the positive plate.
- The equilibrium concentration level of H_2S that develops in the headspace of VRLA cells on float does not exceed 1 ppm.

The results of our work along with the confirmation of sulfur on catalyst material we had analyzed confirmed that H_2S was indeed the poison responsible for deactivating some of our catalysts. Based upon this we knew that we must design our future catalyst products to survive and operate in an environment that could contain H_2S.

DESIGNING A CATALYST TO SURVIVE POISONS

To improve the life of a catalyst in a VRLA cell we designed a new product so that all the gas it is exposed to enters at one end of a catalyst chamber and is forced through a filter bed before it can touch the catalytic active material. We also reduced the rate of reaction by choking back the gas flow to a controlled rate. The filter improves life by a factor of 9 and the reduction in reaction rate improves life by a factor of 5. Combining these two effects, the Microcat® catalyst has a theoretical life that is approximately 45 times longer than our original catalyst design.

The construction of the Microcat® catalyst is simply a cylinder with one end open. We put the catalytic material in the bottom and then add a layer of filter material on top. Finally we close the cylinder off with a disk of porous Teflon which forms a barrier to let gasses and water vapor pass through, but blocks any liquids like battery acid from getting inside. In operation, the gasses in the cell diffuse through the Teflon barrier and pass through the filter material before reaching the catalyst at the bottom of the cylinder. By the time the gas reaches the catalyst, the poisons in the gas have been filtered out. Figure 7 shows the different parts of the Microcat® catalyst.

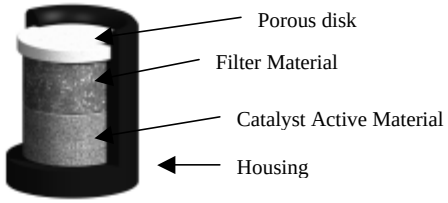

Figure 7

The Filter

There are two general kinds of poisons that filters can act on and eliminate. The poison filter that we have chosen is a dual acting filter that addresses both types. The first category of poison is termed "electron donor" in which the molecules of the poison are negatively charged. That means a positively charged filter is used to attract the poison molecules. Since H_2S is an electron donor we selected a positively charged filter material that can absorb 20 times as much H_2S as our catalyst material does for the same volume. But some of the poisons that can be produced in a battery are not electron donors and our other filter material takes care of them.

The other category of poison is called an electron receiver. The molecules are positively charged and the counteracting filter material must be negatively charged. There are some poisons sometimes found inside batteries that are electron receivers. These include Stibine and Arsine, which are produced by antimony and arsenic, respectively. Activated carbon is used to filter out the electron receiver poisons. It also does double duty in our design as the substrate for our other poison filter. Since the days of Thomas Edison, activated carbon has been used as a Stibine and Arsine filter in catalyst devices used for bulk gas recombination on flooded lead acid batteries.

Reduction in Reaction Rate

Reducing the rate of the reactions increases the life of the Microcat because the filter material is "used up" at a slower rate. There is a fixed amount of filter material inside the unit. As H_2S enters the catalyst chamber and gets used up, the H_2S "sticks" to the poison filter. As more poison molecules get trapped this way, the number of open sites gets reduced. So there is a fixed amount of poison that can be absorbed before the filter bed becomes inactive.

By carefully controlling the diameter of the opening, the thickness of our Teflon disk, and the pore density of the material, we can control the rate of diffusion through the disk. We have adjusted our design so that it will slow down the gas transmission rate to about 1/5 the rate of our first generation design. This means the same quantity of filter material will last five times as long as before.

It is important to note that the rate that the Microcat® catalyst can recombine Oxygen and Hydrogen is also reduced by limiting the gas flow. Our original catalyst was rated at 8 amps versus 1.5 amps for the Microcat. Since we are only recombining a small amount of gas to keep the cell in balance, this amount is still far more than most cells need.

SURVIVAL TESTING

To prove that our improved Microcat® catalyst design could survive H_2S in a VRLA cell, and to verify our theoretical numbers, we developed a series of accelerated tests so that we did not have to wait 20 years to prove that the design worked. Our goal was to design a catalyst that could last 20 years in a high quality VRLA cell that was used in normal float service. As we already stated, theoretically our Microcat® catalyst should last up to 45 times longer than our original design in the presence of H_2S. After a variety of accelerated tests we determined that our improved design is capable of lasting up to twice as long as a 20-year VRLA cell in the presence of low concentrations of H_2S.

The main test that we developed employed a shortened version of our Microcat® catalyst that had only $1/100^{th}$ of the H_2S filtering ability of the real design. In other words, this shortened unit would die 100 times faster than the full version of the design. Except for the fact that the unit was shortened all other aspects were the same as its full-grown brother. We put shortened Microcat® catalysts into two identical VRLA cells that were on float at 2.25 Volts and 32 °C. We monitored the cells for an increase in float current and gas emissions to determine when the test catalysts had

stopped working. The first shortened Microcat® catalyst stopped working after 407 days on test and the second stopped working after 273 days. Since these test units had $1/100^{th}$ of the H_2S absorption capacity of a full size Microcat® catalyst, the conversion to projected life is simply done by multiplying the number of survival days by 100. Unit one's survival time translated into 40,700 days (111 years) and unit two's survival time translated into 27,300 days (75 years).

After our accelerated testing we were left with a projected survival life that ran from 111 year to 75 years. Our theoretical calculations, based on the two design factors already described, told us that our Microcat® catalyst should last 45 times longer than our original design. We have seen our original design catalyst die in as short a time as one year and have also seen them never get poisoned; some units are now 5 years old. Based on this, we could say that the theoretical design life ranges from 45 years to forever.

Since our design goal for the Microcat® catalyst was to have it survive for the life of the VRLA cell, which is supposed to be 20 years, we were happy with our results. If we take the worst-case number that we came up with, it said that we should expect a Microcat® catalyst to survive for 45 years under normal float charge conditions. The one factor that we cannot predict is if there are other factors causing H_2S production in the cell. We limited our research to the most common cause, but we did also discover that there are other ways to produce H_2S in a VRLA cell by the introduction of other sulfur containing compounds. Our catalyst is just one component of many components that make up a VRLA cell and if it is to enjoy a long life the cell must be designed to minimize the production of H_2S. Fortunately most high quality VRLA manufactures are very concerned about the purity of their battery systems and select components that help to limit this.

CONCLUSION

What started out as an investigation into why some of our original version catalysts stopped working after a period of time led to the discovery of H_2S in VRLA cells and a new Microcat® catalyst product that contains a poison filter. After over two years of investigation and testing we came to the following major conclusions:

- Catalysts reduce float current in VRLA cells as long as they do not become poisoned.
- VRLA cells can and do produce H_2S, which poisons catalysts.
- H_2S is produced in large concentrations on the negative plate.
- H_2S is absorbed in larger concentration on the positive plate.
- An H_2S equilibrium level develops in the headspace of VRLA cells that does not exceed 1 ppm and most times is much less or even zero.
- The Microcat® catalyst has been designed to exist in a VRLA cell by reducing the rate that poisons can enter it and by incorporating a poison filter.
- Accelerated testing indicates that the Microcat® catalyst can survive the life of a VRLA cell under normal float conditions.

[1] Vanasse, H.A., Jones, D. *"Catalyst 101: The Basics of Using Catalysts in VRLA Cells,"* Conference Proceedings, Battcon 2002, Ft Lauderdale, FL, April 29-May 1, 2002.
[2] Robinson, R.S., Tarascon, J.M., and O'Sullivan, T. *"Hydrogen Sulfide and Sulfur Dioxide Evolution from Valve Regulated Lead Acid Battery"*, Intelec Proceedings, 1993.
[3] Vanasse, H.A., Vaccaro, F.J., Nikolov, V.R. *"Hydrogen Sulfide in VRLA Cells,"* Intelec Proceedings, Edinburgh, Scotland, October, 2001.
[4] Robinson, R.S., Tarascon, J.M., and O'Sullivan, T. *"Hydrogen Sulfide and Sulfur Dioxide Evolution from Valve Regulated Lead Acid Battery"*, Intelec Proceedings, 1993.