THE MAGIC OF WATER TREATMENT

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THE MAGIC OF WATER TREATMENT

I arrived on the scene at Leckie Smokeless on November 27, 1978. My knowledge of water treatment and acid mine drainage at the time was merely that I had heard of it. However, during the next few weeks I was introduced to a device up on the mountain that treated acid water. This device would soon cause me to make up some new four letter words. It was an automatic (float-activated) sodium hydroxide dispenser. I could not get the thing to work right. The water in the test tube was always purple or red and the guy from DNR kept telling me it ought to be green. This was my initiation to water treatment and for those who are curious, it wasn't long be-Fore I took a sledge hammer to that device and replaced it with a valve for drip treatment.

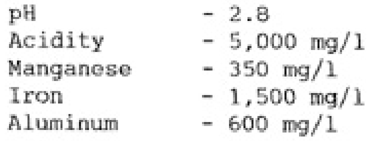
Three or four years passed by rather quietly and then BOOM! All of a sudden, Buck Lilly was born. Buck Lilly was the name given to our refuse site in honor of the gentleman who previously surface mined the area. We had been dumping our refuse in an unreclaimed pit and

I never suspected there could possibly be any water problems. The floor of the pit dipped back to the wall, the spoil material in front was a calcareous shale, and I really hadn't had a bad problem anywhere on the property. But Murphy said "this guy is just right, let's get him". So, Buck Lilly began to discharge acid water from several seeps at the toe of the refuse area. I began a fast and furious treatment program with the enthusiastic help of Ben Faulkner, our previous DNR inspector who had found the problem. We hired Ben to solve the problem he found. No matter how hard we tried, nothing worked. I blew tankers of lime in the pond, pumped in tankers of sodium hydroxide, and even tried flocculants. But nothing worked. We could get the pH up but we couldn't precipitate the iron. It was obvious to Ben what the problem was. It was the discharge pipe. It wasn't discharging water from off the surface of the pond. So he waded out into the water up to his shoulders and beat the top of the pipe off with an ax. To make a long story short, the pond was equipped with a perforated riser and the acid had eaten out the bottom causing the pipe to act like a vacuum cleaner sucking iron sludge from the bottom of the pond and discharging it into the stream. Needless to say, cleanout costs at the pond had been minimal so far. I immediately learned that from then on, all ponds would discharge water only from the surface whether by T-skimmers, sluiceways, or some other surface skimming method. Once the true problem was discovered, the perforated riser was completely torn out and replaced by two 24" PVC T-skimmers. It was as though we had won the lottery, BINGO! The water was perfect, or so I thought.

Since the problem was solved, we set up two 3000-gallon sodium hydroxide tanks on the hill above the pond and ran a hose down to the entrance channel. Control of NaOH flow was by a manual valve. All went well until the valve broke and both tanks (or 6000 gallons) of sodium hydroxide went into the pond. You guessed it, I had both tanks plumbed together -to last longer. Fortunately, all of it went in the pond. Unfortunately, 20% sodium hydroxide has a specific gravity of approximately 1.2, meaning that most of the stuff was laying on the bottom of the pond. Well, as Murphy would have it, this all occurred on a weekend. When I checked the pond Monday morning, I was discharging bad water and who rolls up on the embankment? Naturally, my inspector. Well, we knew that there was plenty of NaOH in the pond but it was just in the wrong place. So we got some primers off the strip job and began to have a ball trying to mix the stuff up. As might be expected, this didn't work, but by then the NaOH truck had shown up and refilled my tanks. That was great because we immediately started treatment again. But there was still one problem. The pond was still bad and the discharge was awful. To treat the whole pond from the entrance channel would probably take several days, so we got the hydroseeder and tried spraying lime on the pond. We even threw gallon jugs full of sodium hydroxide out in the pond. Does any of this sound familiar yet'? We finally got the pond back in shape and made a pact that we would never go through this again.

Fortunately, another employee, Gene Keaveny (Dr. Gene) came up with a brilliant idea. Gene purchased three $6.99 lawn sprinklers (the type you see on the golf course) and hooked them up to the sodium hydroxide tank. He dispersed them across the pond by floats made from tubes, styrofoam, milk jugs, etc. When Gene turned on the valve, we were totally amazed. The tanks were high enough that they produced sufficient head to cause each sprinkler to cover a 50 foot diameter area. Since the NaOH had a specific gravity of 1.2, it treated from the surface down. From then on, if we had a mishap with our regular treatment system, we could be back within effluent limitations in an hour and a half. You need to remember that this pond is 400 feet long, 150 feet wide, 10 to 12 feet deep, and has flow rates up to 600 gallons per minute of water with these characteristics:

pH - 2.8
Acidity - 5,000 mg/l
Manganese - 350 mg/l
Iron - 1,500mg/1
Aluminum - 600 mg/l


pH - 2.8
Acidity - 5,000 mg/l
Manganese - 350 mg/l
Iron - 1,500 mg/l
Aluminum - 600 mg/l

At that particular time, 20% sodium hydroxide cost between $.35 and $.40/gallon and my water treatment costs were continually escalating. In addition to reagent cost, my pond would fill up with a gross looking sludge and I'd have to spend $15,000.00 to lease a mud-cat dredge to clean the pond. I figured there had to be something else out there to help me with this problem. That's when Roger Hall introduced me to surfactants. I got in contact with several people who sold surfactants (soap) and they told me that tiny bugs were my problem and I could clean them up with their soap. Now don't that beat all. After being educated about Thiobacillus bacteria and after many leaching tests had been performed on my refuse, I decided to try the surfactant offered by Andesco Technologies. Jim Greskovich runs Andesco and is a super guy to work with. During the next few months, Jim spent his time instructing me in the technical aspects of acid mine drainage. All his tests proved that the payback would be in the form of reduced sodium hydroxide consumption as we continued surfactant treatment. My cost records have proven that point to this day, but there was always something that bothered me about the way we initially applied the Antec 128. Jim would come to Leckie every two months and we would spray the entire dump. This was fine except, based on the leachate tests, this didn't make the most sense. All the leachate tests proved conclusively that treatment of refuse with surfactant as it came out of the prep plant obtained the most optimum results. When Antec 128 was applied every two months, the refuse produced a range of good to bad water depending on the length of time since treatment. By treating the refuse at the plant as it came out on the belt, water quality improved considerably, there are a few catches to this procedure, but I don't want to take up time in this paper to explain them call me.

During my soap phase, the state introduced me to my soon to be mentor in acid mine drainage: Dr. Frank Caruccio and his wife Dr. Gwen Geidel. These two people probably helped me more than all the others put together. The state of West Virginia was kind enough to include Leckie in it's research concerning AMD, and Dr. Frank and Dr. Gwen visited me quarterly. We began the project by trying to define the groundwater system within the refuse dump. The doctors would send me a list of things to do and we would do them.

By the way, that's how Gene got his title. He was doctored by the doctors. I learned much during my association with Frank and Gwen and I will always be ever grateful. Upon completion of their project, I was still looking for a cheaper way to treat the water. It didn't look as though I could now economically remedy my problem but only search for cheaper ways to treat. Along came some guys who wanted to "zap" my pond.

Two gentlemen, who heard through a friend of a friend that I was always looking for a new way to treat water, approached me with the idea of using electricity to treat the water. This was an appealing idea so we met. They informed me that the technology was not new, but previous tests had utilized the wrong type of_____________. Sorry, I can't tell you. I signed one of those confidentiality statements. After much planning, we agreed on the best course of action and assembled our own set up by using spare parts and cables from the deep mines. The only thing that we had to purchase was the________________. We hooked the device up and from the air it must have appeared like a giant spider had spun a web across the pond. With everything set, we threw the switch. Zap - Boom - Kapowie! After burning up and blowing several transformers and resistors, we figured out the load on the system and adjusted accordingly. We hit the switch and the pond began to bubble like it was right out of a monster movie. The system was absolutely safe unless you got between an anode and cathode. This happened to a few unsuspecting creatures (bugs, frogs, etc.) and it was not a pretty sight. For some reason, within a day or two of assembling this puzzle it became imperative to clean the sludge from the pond. Before I was able to get to Buck Lilly, the crane had been moblized and, not knowing what all the cables were doing in the pond, hooked on and swung the whole system over the hill. You could have retired trying to figure out how to untangle all the knots and snarls. But we perservered and were able to salvage bits and pieces. Since the remainder of the system was not very large, I used it in conjunction with sodium hydroxide. Before I leave this system, I want to say that I believe it has potential and I wish those two guys the best of luck in their endeavor.

It was now 1987 and I attended the Surface Mine Drainage Task Force Symposium held in Morgantown. At this particular meeting, Dr. Caruccio gave a talk concerning the possibility of pumping treated water back through acid-producing refuse or spoil. This idea hit me like a bolt of lightening! In a sense it would be like treating with surfactants only in the opposite direction. Surfactants depend on an acid environment to kill the Thiobacillus bacteria, whereas alkaline water would raise the pH of the system putting the little suckers to sleep or into a dormant state. I went home from this symposium ready to pump, pump, and pump. Unfortunately, I didn't have a pump. Well I put this idea on the back burner for a while and continued status quo. By this time there were rumors that sodium hydroxide was going to take several price increases. What an understatement! Along with these rumors, the boss wanted me to find a different chemical to treat the water in the preparation plant. Leckie produces a high grade, mid-volatile coal which goes to Europe for steel making. The buyers of our coal were complaining that the sodium and potassium content of the coal had to come down. The potassium acted as a catalyst in the coking cycle and the sodium was leaving a residue on the walls of the furnace. Because we used sodium hydroxide in the plant, excess sodium was making its way to Europe in our coal's moisture content. So I set out once again to look for an alternative.

While looking for a replacement, I ran across a material called solid caustic. No, this is not flakes or powder but a 75 lb. pony keg full of solid NaOH. The caustic is actually poured into these drums while in a molten state. The fact that I wasn't paying to transport water (as is the case with 20% sodium hydroxide) really appealed to me. The next step was deciding where and how to use it. The where part was easy. I was using briquettes at several locations on the property and I was fed up with the handling problems. Although the briquettes came in plastic lined bags, they were still prone to moisture and would disintegrate unless stored inside some type of structure. Also, they were extremely prone to rat-holing which required continuous attention. I bought ten drums of the solid caustic and went to work. The drums were metal and had sealed lids so I could set them out in the weather or wherever I wanted. Based on my consumption of briquettes to drums, I reduced my treatment costs at each site by 30 - 50%, and material handling was considerably easier. At the time, I was paying $7.50 a bag for briquettes and $40.00 a drum for the caustic. In case you are wondering, Jim Greskovich with Andesco is the distributor for these drums and has developed a very simple but effective system for their use. In my earlier days of experimentation, I used a sophisticated technique in treating with drums. I'd break a limb off a tree, stick one end in the water I wanted to treat and the other in the drum. I'd then punch a couple of small holes in the drum and regulate flow volume by how far I stuck the limb in the water. Slightly rotating the drum once a day eliminated rat holing. Isn't it amazing how college prepares you for these scientific challenges? I definitely recommend that any of you using briquettes call Jim Greskovich immediately.

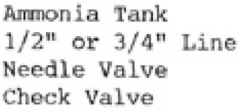
Well, back to the search. I recalled that several people had previously mentioned trying anhydrous ammonia but I had shyed away because of the potential environmental problems I'd heard about. However, my options were running out and with the price increases in sodium hydroxide, I had to play or pay.

The age of ammonia dawned for me in 1987. 1 took several trips to look at other installations and read all the literature I could find concerning any and all possible environmental concerns. From what I read, this chemical was like any other. If you abused it, you would have problems, if proper controls were administered, there should be no problems. I contacted several ammonia companies asking for quotes and about the possibility of getting tanks. The company that impressed me the most was National Ammonia Company of Philadelphia, Pa. These people were quick to respond to my questions and ready to assist me technically. They knew very little about AMD but they knew a lot about ammonia. Within a couple of days of contacting them, National Ammonia sent down their salesman, Jim Hajek. Jim's a super guy. He helped during all stages of the operation by giving safety talks and sharing valuable information concerning the ammonia itself. Did you know there are two types of ammonia on the market? Refrigeration grade is pure, while commercial or industrial grade may or may not be pure. I could have saved a few pennies by going commercial but I wanted to know what I was treating with and refrigeration grade is guaranteed. The first tank I hooked up was at a small pond close to the preparation plant with low flows. This pond generally costs me about $9,000.00 a year to treat with sodium hydroxide so I felt this could be a good place to get my feet wet. I injected $5.00 worth of ammonia in the pond that day and it stayed treated for a week. At that point I learned how extremely concentrated and potent anhydrous ammonia was.

From this initial pond, I went to Buck Lilly and installed three 1,000-gallon tanks in parallel and hooked the pond up like I had seen at other sites. Every NH_3- treated pond I had seen elsewhere had floating injectors on the pond operated by a pH controller at the discharge pipe. When the pH reached the low set point, a solenoid valve opened and released ammonia until the upper set point was obtained. I soon learned that this type of injection method could cause potential problems. Since I'm in the engineering department, I really don't do anything (Ha Ha) so I had plenty of time to evaluate how the ammonia reacted. I would sit for (it seemed) hours and watch how the ammonia would disperse through the ponds. I have not seen any other chemical do this before. It was as though the ammonia was searching for something to react with. While watching the injectors operate, it occurred to me that since ammonia was continually being dispersed from a single source when the valve was open, the water must vary in pH from the discharge point back to the injector. obviously the water is quickly treated immediately around the injector, so continued treatment must mean that an aqua solution of ammonia is building up and spreading away from the source. To make it plain and simple, the pH probe at the discharge shut off the valve in the middle of the pond when the upper set point pH was reached. However, a large amount of water between the injector and the discharge point was overtreated. This super highly-ammonia-treated water would reach the discharge pipe and exit the pond. What complicates this phenomenon is the fact that ammonia is lighter than water and will rise towards the surface. If you have only one pond and are treating it injector style, you will only be treating the surface and are prone to dramatic quality variation based on weather events. on the other hand, if you have several ponds in series the problems are not as severe.

I still believe using an injector system is not efficient nor prudent in most cases. In noting all these problems, I decided that ammonia should not be any different than sodium hydroxide. To maximize the efficiency of any chemical for treatment it should be used continuously and only to the extent necessary. Keeping that in mind, we set out to install an injector that would operate continuously in the entrance channel of our ponds. Initially all our attempts were futile due to a very simple problem that I kept overlooking. The problem was so bad that I was ready to give up until I saw what was happening to sodium hydroxide prices. In June of 1987, 1 was paying $.27 per gallon for 20% sodium hydroxide and by December 1988 the price was hovering around $.50 to .55 gallon. For those who don't feel like that's too bad, if your total treatment cost last year was $100,000. it essentially doubled to $2000,000 this year. Big, big bucks -- huh? With this in mind, we diligently worked on an injector which would continuously and consistently release NH_3. The continuous part was easy but the consistent part is what caused us problems. Let me explain! With a manual ammonia system, you will normally have the following components:

Ammonia Tank
1/2" or 3/4" Line
Needle Valve
Check Valve

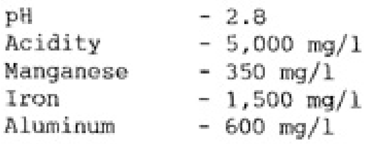

Ammonia Tank
1/2" or 3/4" Line
Needle Valve
Check Valve

When all of these components are hooked up and in place, the needle valve is used to adjust the flow of ammonia. The tricky part is that anhydrous ammonia is in a liquid form but begins to vaporize at a -280F. As you open the needle valve to begin treatment, you obviously provide a means for the pressure in the tank to be relieved due to vapor generation for water treatment. The more you open the valve, the more you will begin to see the pressure in the tank drop over time depending on the ambient temperature. In the summer months, this pressure drop is usually negligible. But in the winter, this drop can be devastating. The drop in pressure means that the ambient temperature is not high enough to generate adequate ammonia vapor to meet your demand. Therefore, you will see fluctuations in your water quality when manually operating with a needle valve having a set orifice size. There are three ways to remedy this problem, one of which does not require electricity and two which require at least 220 vac.

Method 1 is really a physical way to minimize the problem. Depending on your water quality this may or may not work. If it is extremely bad and your consumption is abnormally high, you will have to use method 2, or 3, or both. The theory behind Method 1 is quite simple and is related to surface area. The greater the contact area of anhydrous ammonia with the inside of the tank, the greater the vapor generation. Initially at Buck Lilly, I had three 1,000-gallon tanks. I would operate a tank until it was used up and then switch to the next tank. I found that because of my vapor demand, the pressure in an individual tank would drop quickly and force me to another tank prematurely to benefit from the untapped pressure in the full tank. To remedy this problem I hooked all three tanks up in parallel and operated them simultaneously. This took advantage of the inside surface area of all three tanks and offered a more consistent treatment. This did not eliminate the problem but did increase the time period between pressure drops. Another obvious solution is to get a larger tank. Method I is mandatory if power is not available and the raw water quality demands a high yield generation of ammonia vapor.

Method 2 offers the ability for compensation of pressure swings by the use of a proportional valve. As expected, this system requires power and the following:

- all the components from method 1
- proportional valve
- pH controller
- pH probe



pH - 2.8
Acidity - 5,000 mg/l
Manganese - 350 mg/l
Iron - 1,500 mg/l
Aluminum - 600 mg/l

A proportional valve responds to fluctuations in pH similar to a metering pump in a preparation plant. If the pH in your entrance channel drops below your set point, then a signal from the control opens the valve up proportionately to reattain the set point. This is entirely different from a solenoid valve so don't even try to compare them. The pH swing in the entrance channel may vary due to weather events or fluctuation of the ammonia tank pressure indicating the use of a proportional valve. Depending upon the quantity and quality of water, method 2 alone may not be enough.

Method 3 involves the installation of an ammonia vaporizer on the tank. The vaporizer is simply a heating element, such as those in a water beater, which is contained in a submarine-like tube. The tube is connected to the ammonia tank to a liquid valve and to a vapor valve. As the liquid passes over the element, vapor is generated which flows back in the tank building up pressure. The pressure is controlled by a pressure switch with a high and low setting dependent upon your need. With the vaporizer installed, a constant pressure may be maintained enabling the water treater to minimize fluctuations in treated water quality.

Obviously the optimum system would be a combination of methods 2 and 3. A proportional valve supported by a vaporizer will furnish an almost perfect pH control within ± .2 of one pH unit. However, many of our ponds don't have power available and most of us don't have any money, so method 1 will work fine. Leckie currently utilizes method 1, method 3, and methods 2 and 3.

After implementing the NH_3 project we acquired a pump for the Buck Lilly pump back project. Several sediment type ditches were dug down into the refuse dump. The treated water from the pond was then pumped and allowed to leach through the refuse and eventually end up back at what I affectionately call Buck Lilly No. 1 and 2 seeps. How do I know the water was coming back to my seeps? After previously looking at dye and potassium bromide as tracers, there was no doubt what would be the best: Ammonia' The water I was pumping through the dump was treated with ammonia and was easily detected back at my seeps. I pumped from December of '87 through May of '88. The iron and acidity readings consistently dropped during this period. What does baffle me is that the manganese and aluminum seem to be unaffected. Does anybody have any theories? Well, in May I had to quit pumping to the dump because the famous drought of 1988 was beginning. What water I had was treated and pumped to the preparation plant to be used as make up water. This lasted until September. Throughout this period, the iron and acidity contents of the seeps rose back up at about the same rate as they fell. When pumping resumed, I observed the same type of drop in metals as had previously occurred between January through May. Attached with this paper is a graph depicting the results. I plan to continue this project and find out just how low iron and acidity levels will drop.

If you are contemplating using anhydrous ammonia at your site for water treatment, do the following:

First:	Analyze your receiving streams for existing total nitrogen, ammonia, nitrites, nitrates, alkalinity, acidity, pH, and sulphates. You may be located in an area where the existing NH_3 level is too high already and more ammonia could damage the stream environment. This happens in some areas and is sometimes associated with raw sewage, farm drainage, hatchery effluent, etc.
Second:	If you found the stream quality low or absent of ammonia, then proceed by performing a Benthic study of your receiving stream. Study above and below the confluence of the discharge and the stream. Contention is that ammonia treatment can cause problems associated with the micro- and macro-communities so it is obviously wise to document your pre-ammonia water quality. Also, there exists a fear that acidity will be created downstream as ammonium is nitrified, but so far this has only been demonstrated in the lab and not in the field.
Third:	Find someone who is using ammonia and see if your application of ammonia is consistent with what they have learned concerning its implementation.
Fourth:	Request in writing to the state to modify your NPDES permit to include ammonia as a chemical to treat water at your site. Be sure to include your background data to justify your request. If approved, you will be sent DMMR's

which require you to sample the stream for total ammonia converted to un-ionized ammonia, nitrites, nitrates, alkalinity, acidity, and pH. Un-ionized ammonia has been proven to be harmful -to aquatic life and, based on limits established by the water resources board, must be kept less than .02 ppm in trout streams and .05 ppm in all other streams. Un-ionized ammonia is calculated by using total ammonia, temperature, and pH. These parameters are combined into an empirical formula (I love empirical formulas) to yield un-ionized ammonia. If the receiving stream pH is low and the water temperature is low, you've got it made. What's low and what's cold? Study the formula and figure it out yourself.

Formula

$$\text{Un-ionized ammonia} = 1.2\,\frac{\text{Total ammonia-N}}{1 + 10\,(pK_A - pH)}$$

$$\text{Where:}\quad pK_A = 0.0902 + \left(\frac{2730}{273.2 + T}\right)$$

$$T = {}^{\circ}\ \text{centigrade}$$

Fifth: With your NPDES permit modification approved, contact an ammonia company, preferably National Ammonia, and inquire about tank availability and chemical costs. Knowing that you will use x gallons of 20% sodium hydroxide or y tons of hydrated lime, you can take one of Jeff Skousen's Greenlands articles and figure out your ammonia consumption. Depending on what the amount of NH 3 turns out to be, you can determine what size tank is needed. obviously ammonia is like many other chemicals. The larger delivery you can take, the lower the price of the ammonia. So do your payback analysis on tank costs vs. product cost and consumption. National Ammonia has a technical representative named John Adair who can tell you where to get all your hardware -to operate the system.

Sixth: Once you know tank sizes and their locations, comply with SARA Title 3 or "Community Right To Know" by notifying:

1. Your local fire department with information regarding the amount and location of ammonia to be used. This will enable them to react to an emergency properly with ammonia.
2. Your local emergency planning commission - in West Virginia this is often your County Commissioner
3. Your state emergency planning commission

Seventh: Establish your monitoring parameters. I would advise you to establish several downstream sampling points in addition to your permit and monitor for at least:

pH
Alkalinity
Acidity
Total Ammonia
Nitrates
Nitrities
Dissolved Oxygen

Take these downstream results and constantly compare them with upstream samples.

Finally: Use of ammonia is not for everyone. Only responsible persons who will safely administer and constantly monitor it should be allowed to treat with ammonia.

Question: Is it worth all the fuss to use ammonia?

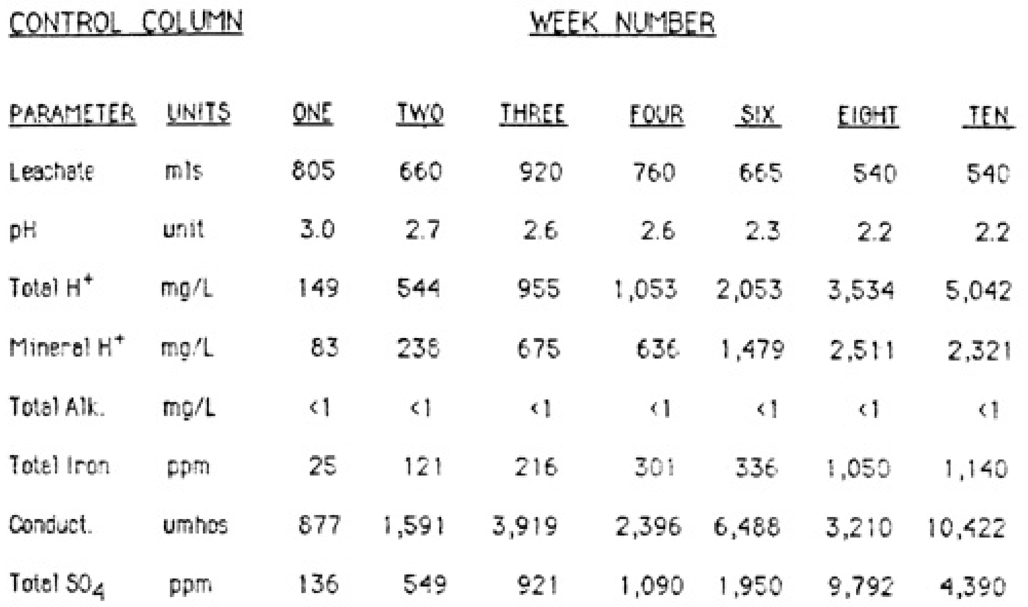
Answer: Yes. Even with the extra monitoring, Benthic studies, and all else that has been discussed, switching to ammonia from sodium hydroxide reduced my treatment costs by 70 to 80%.

There are many other areas concerning water treatment and AMD amelioration Leckie has been involved with, but I know you are either tired of reading my jibberish or bored, so I will save the rest for the next segment of "The Magic of Water Treatment". Stay Tuned!

APPENDIX

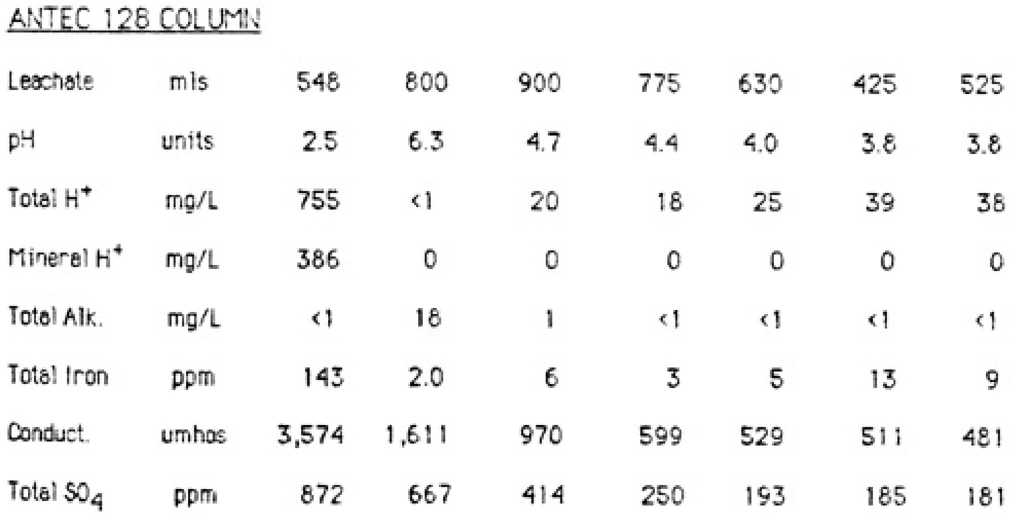
The following charts, graphs, and other information are included to supplement the written text and clarify certain information.

Pages	Description
12-20	Leach analysis of refuse and coal seams at Leckie.
21-24	Water quality analysis for seeps 1 and 2 in 1985 and 1989.
25	Water quality analysis before and after electricity treatment.
26-27	Safety sheet for anhydrous ammonia.
28-33	Articles concerning medical response to over-exposure to ammonia.
34	Iron and acidity values of Seep 1 during pump back project.
35-37	Cost analysis between NaOH and NH_3.



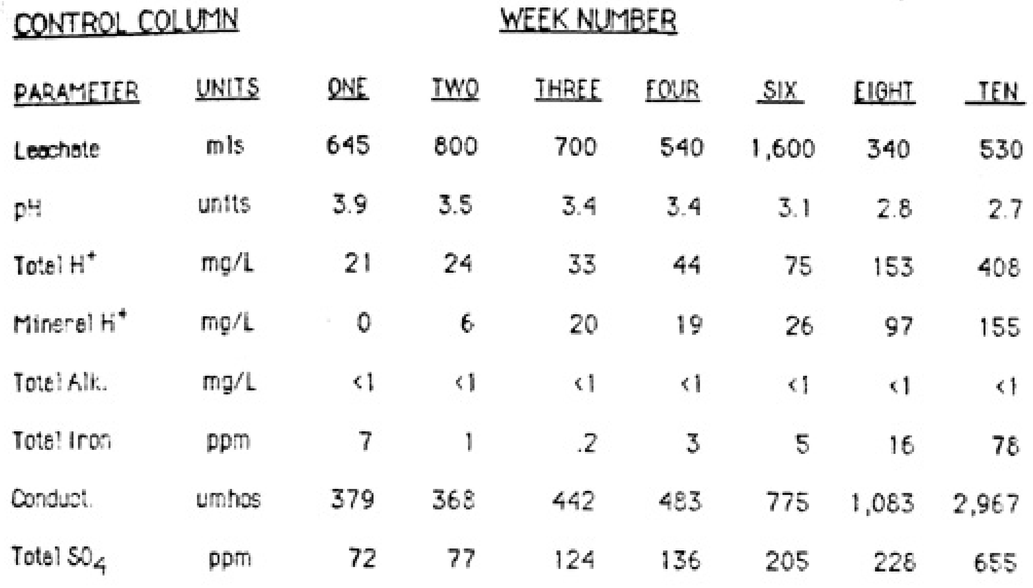
CONTROL COLUMN WEEK NUMBER

PARAMETER	UNITS	ONE	TWO	THREE	FOUR	SIX	EIGHT	TEN
Leachate	mls	805	660	920	760	665	540	540
pH	unit	3.0	2.7	2.6	2.6	2.3	2.2	2.2
Total H^+	mg/L	149	544	955	1,053	2,053	3,534	5,042
Mineral H^+	mg/L	83	236	675	636	1,479	2,511	2,321
Total Alk.	mg/L	<1	<1	<1	<1	<1	<1	<1
Total Iron	ppm	25	121	216	301	336	1,050	1,140
Conduct.	umhos	877	1,591	3,919	2,396	6,488	3,210	10,422
Total SO_4	ppm	136	549	921	1,090	1,950	9,792	4,390



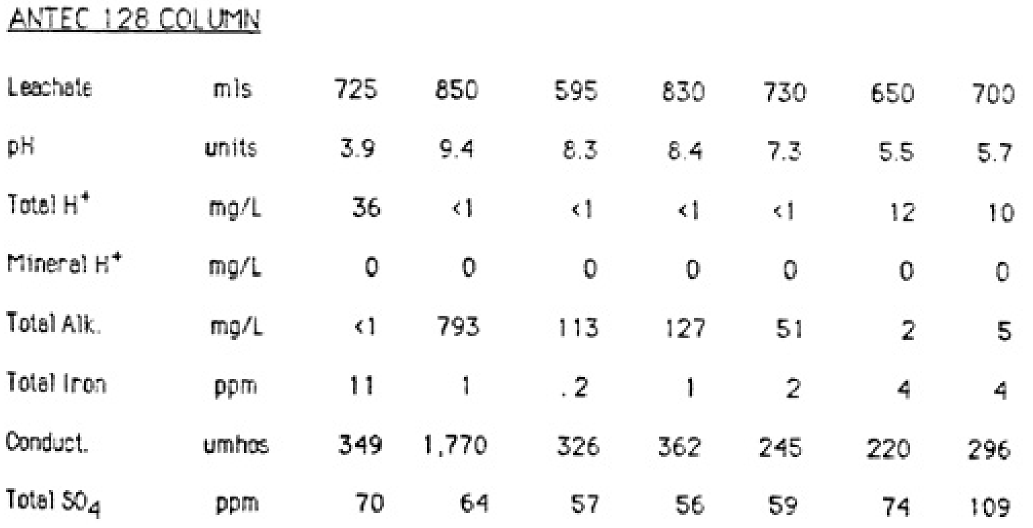
ANTEC 128 COLUMN

Leachate	mls	548	800	900	775	630	425	525
pH	units	2.5	6.3	4.7	4.4	4.0	3.8	3.8
Total H$^+$	mg/L	755	<1	20	18	25	39	38
Mineral H$^+$	mg/L	386	0	0	0	0	0	0
Total Alk.	mg/L	<1	18	1	<1	<1	<1	<1
Total Iron	ppm	143	2.0	6	3	5	13	9
Conduct.	umhos	3,574	1,611	970	599	529	511	481
Total SO$_4$	ppm	872	667	414	250	193	185	181



CONTROL COLUMN

PARAMETER	UNITS	WEEK NUMBER ONE	TWO	THREE	FOUR	SIX	EIGHT	TEN
Leachate	mls	645	800	700	540	1,600	340	530
pH	units	3.9	3.5	3.4	3.4	3.1	2.8	2.7
Total H$^+$	mg/L	21	24	33	44	75	153	408
Mineral H$^+$	mg/L	0	6	20	19	26	97	155
Total Alk.	mg/L	<1	<1	<1	<1	<1	<1	<1
Total Iron	ppm	7	1	.2	3	5	16	78
Conduct.	umhos	379	368	442	483	775	1,083	2,967
Total SO$_4$	ppm	72	77	124	136	205	228	655



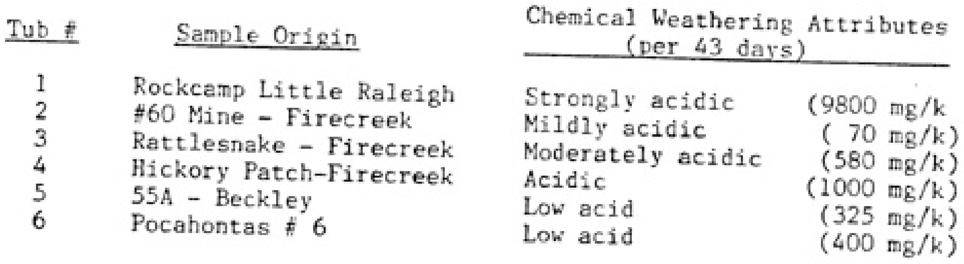
ANTEC 128 COLUMN

Leachate	mls	725	850	595	830	730	650	700
pH	units	3.9	9.4	8.3	8.4	7.3	5.5	5.7
Total H$^+$	mg/L	36	<1	<1	<1	<1	12	10
Mineral H$^+$	mg/L	0	0	0	0	0	0	0
Total Alk.	mg/L	<1	793	113	127	51	2	5
Total Iron	ppm	11	1	.2	1	2	4	4
Conduct.	umhos	349	1,770	326	362	245	220	296
Total SO$_4$	ppm	70	64	57	56	59	74	109

SIMULATED WEATHERING TESTS OF SELECTED REFUSE SAMPLES

As discussed in the report of March 21, 1985, five samples of refuse from the preparation plant were subjected to simulated weathering tests. The results of those tests indicated the refuse from the Rockcamp Little Raleigh was strongly acidic, although at that time the tests had been run for only 14 days. On March 24, 1985 a sixth sample, refuse collected from the Pocahontas #

6, was added to the series. The simulated weathering tests were extended to 93 days, with the exception of the Pocahontas # 6 which was run for 43 days. The cumulative acid plots versus time are presented in Figures I through 6. The results of the simulated weathering tests clearly identify the Rockcamp Little Raleigh refuse sample as the major problem refuse (producing 23 g of acidity per kg of sample at a 93 day period). Based on the comparison of all samples, we would rank them as follows (to accomodate sample W 6, all acid production potentials are listed per 43 day period):



Tub #	Sample Origin	Chemical Weathering Attributes (per 43 days)	
1	Rockcamp Little Raleigh	Strongly acidic	(9800 mg/k
2	#60 Mine - Firecreek	Mildly acidic	(70 mg/k)
3	Rattlesnake - Firecreek	Moderately acidic	(580 mg/k)
4	Hickory Patch-Firecreek	Acidic	(1000 mg/k)
5	55A - Beckley	Low acid	(325 mg/k)
6	Pocahontas # 6	Low acid	(400 mg/k)

Although large size samples were used in the study, 5 to 9 kg, it is emphasized that the inherent heterogeneity of the refuse material precludes a rigorous interpetation of these data. What can be conclusively stated is that all refuse samples have the capability of producing acidic leachates, though to varying degrees. If the samples used in the tests are in fact representative of the field and mine settings, then, obviously, the Little Raleigh is the major problem acid produ?cer and should be selectively handled. However, the distribution of acid production potentials of the Firecreek samples (from 70 mg/k to 1000 mg/k) further emphasizes the variability to be expected and the required moderation in the interpretation of the results.

In general, though, the refuse material may be characterized by these results. Should more detailed and precise data be required, it is recommended that triplicate samples of each refuse source be collected and analyzed to determine the expected variation in acid production between and within samples. In our opinion, however, these additional studies are not warranted by the nature of the problem.

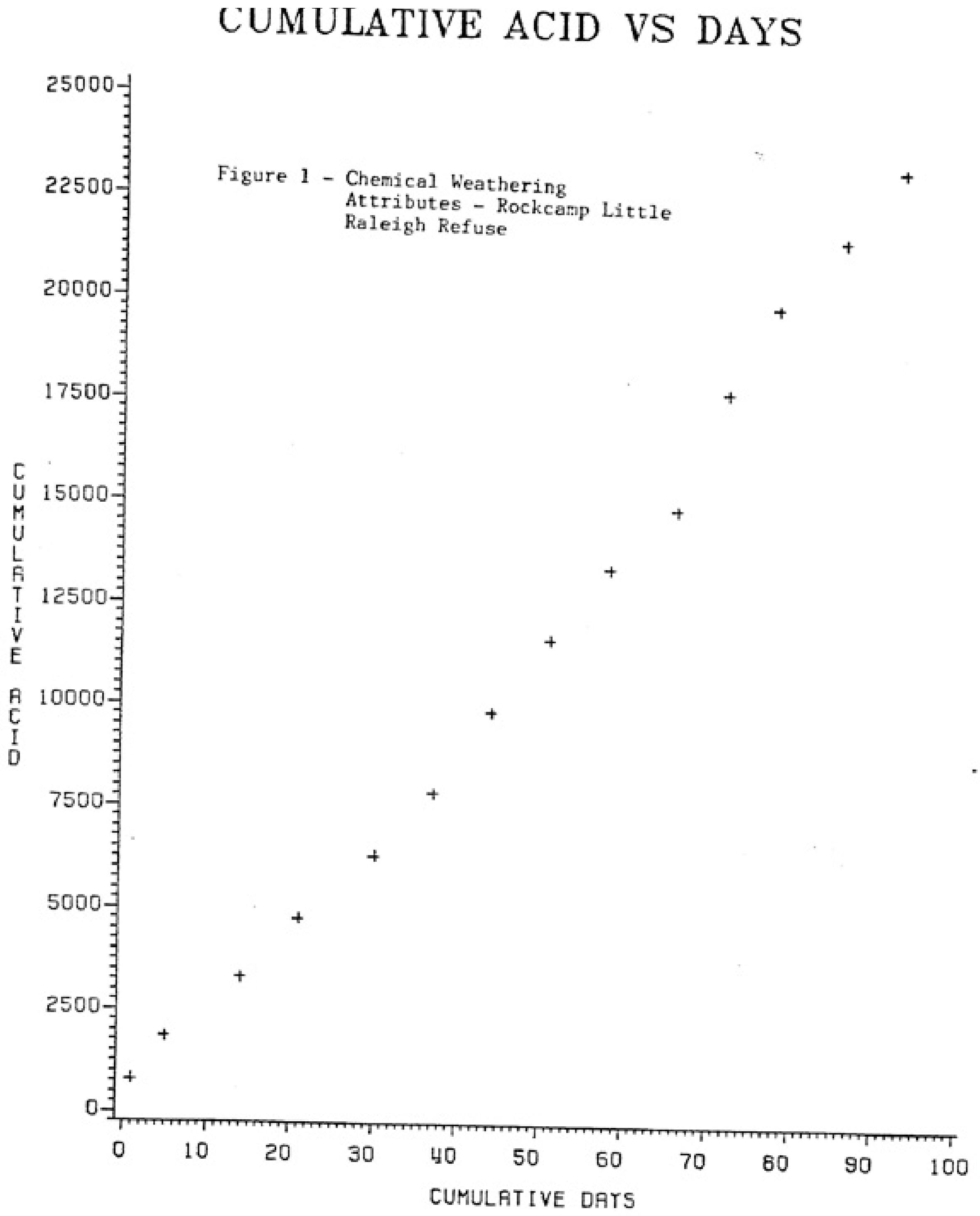


Figure 1 - Chemical Weathering Attributes - Rockcamp Little Raleigh Refuse

LECKIE SMOKELESS TUB 1

15

CUMULATIVE ACID VS DAYS

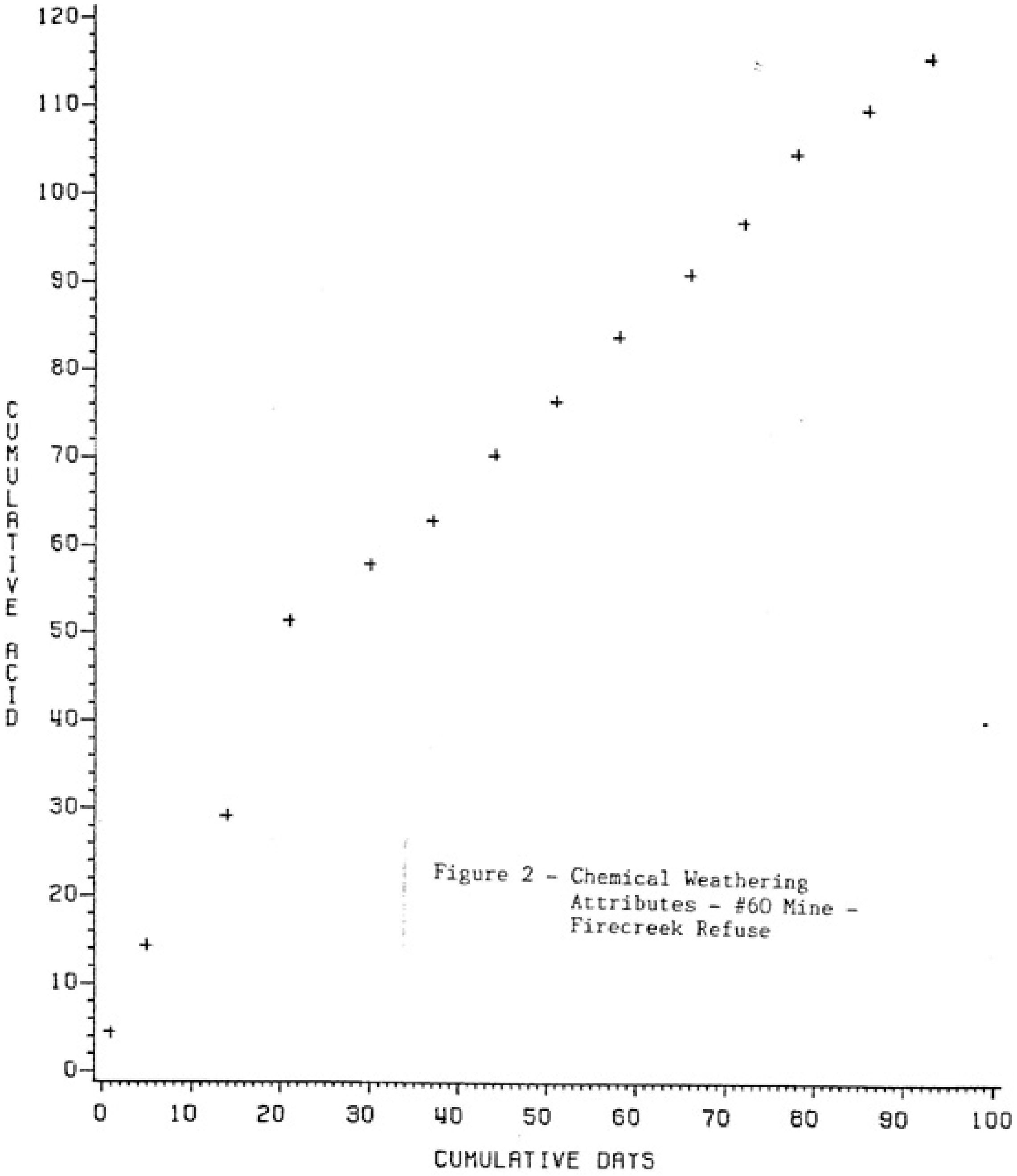


Figure 2 - Chemical Weathering Attributes - #60 Mine - Firecreek Refuse

LECKIE SMOKELESS TUB 2

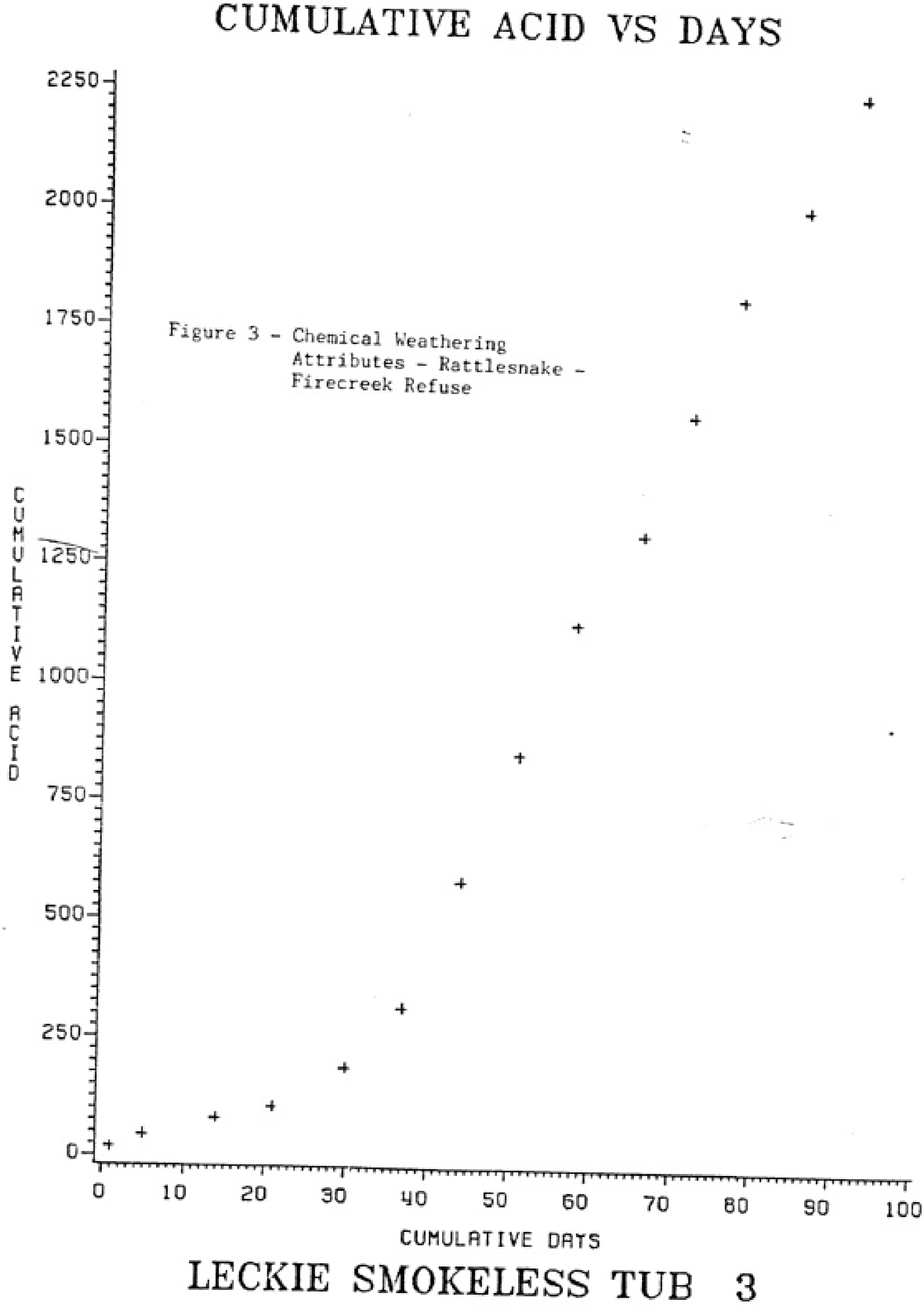


Figure 3 - Chemical Weathering Attributes - Rattlesnake - Firecreek Refuse

CUMULATIVE ACID VS DAYS

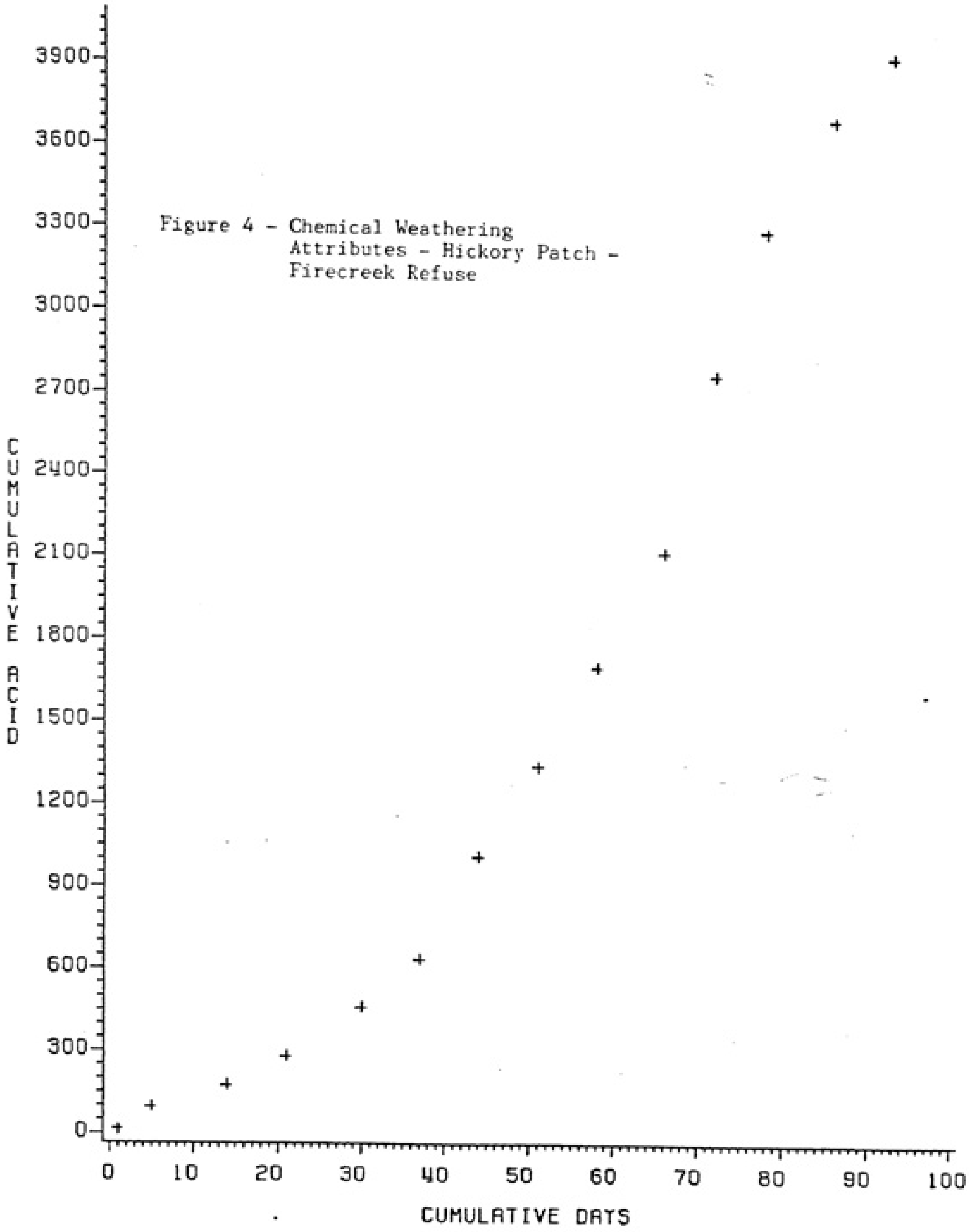


Figure 4 - Chemical Weathering Attributes - Hickory Patch - Firecreek Refuse

LECKIE SMOKELESS TUB 4

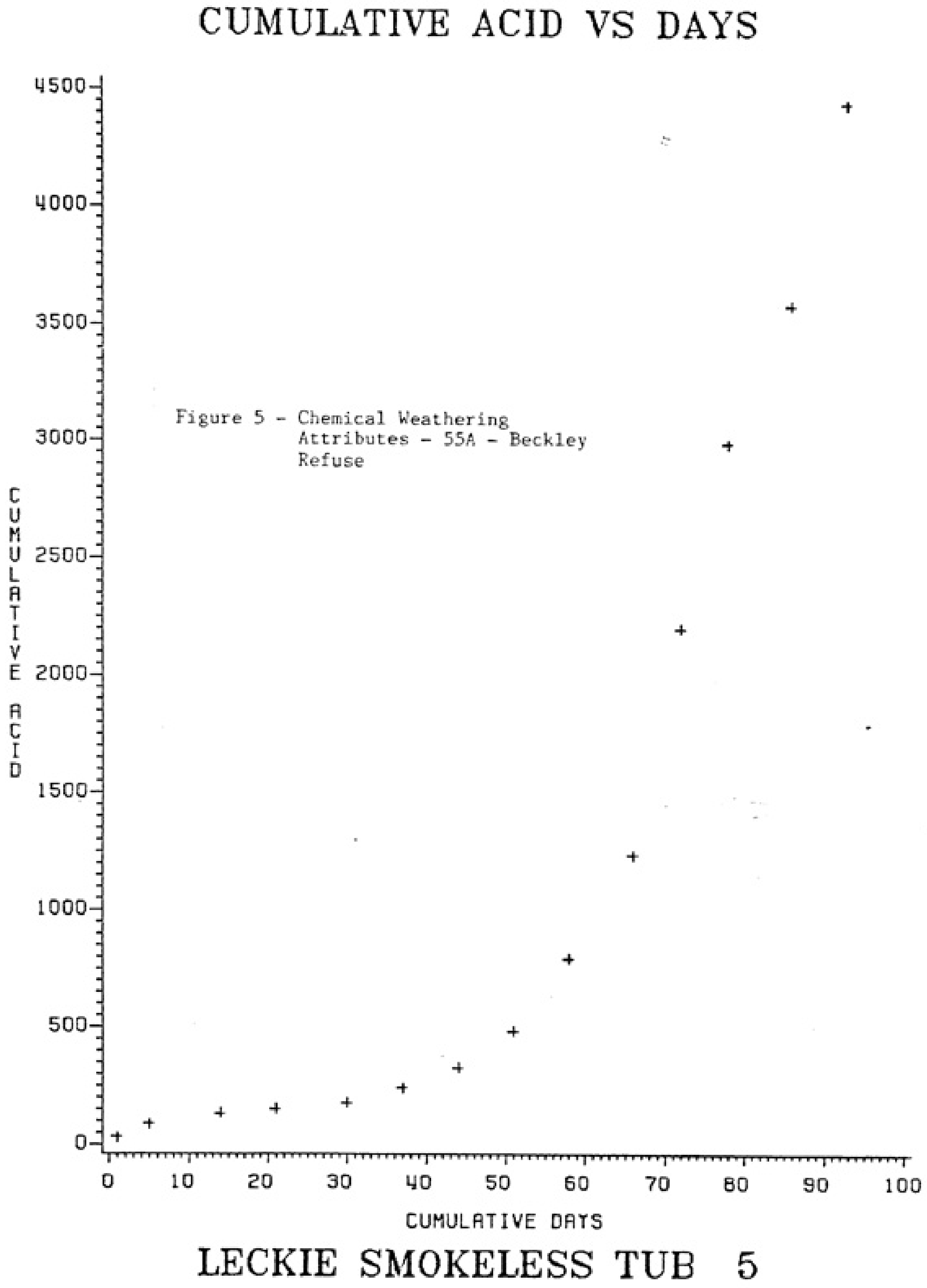


Figure 5 - Chemical Weathering Attributes - 55A - Beckley Refuse

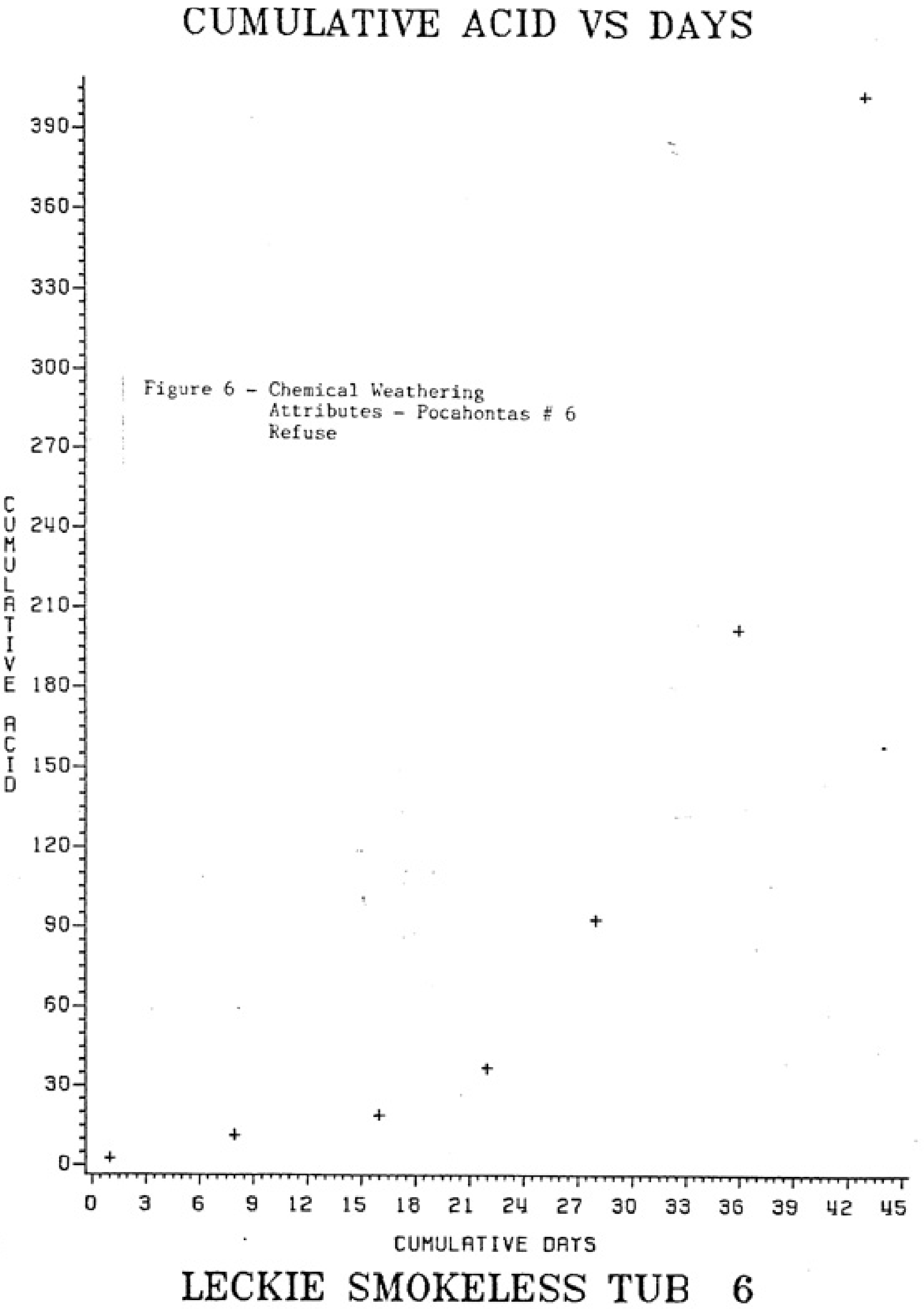
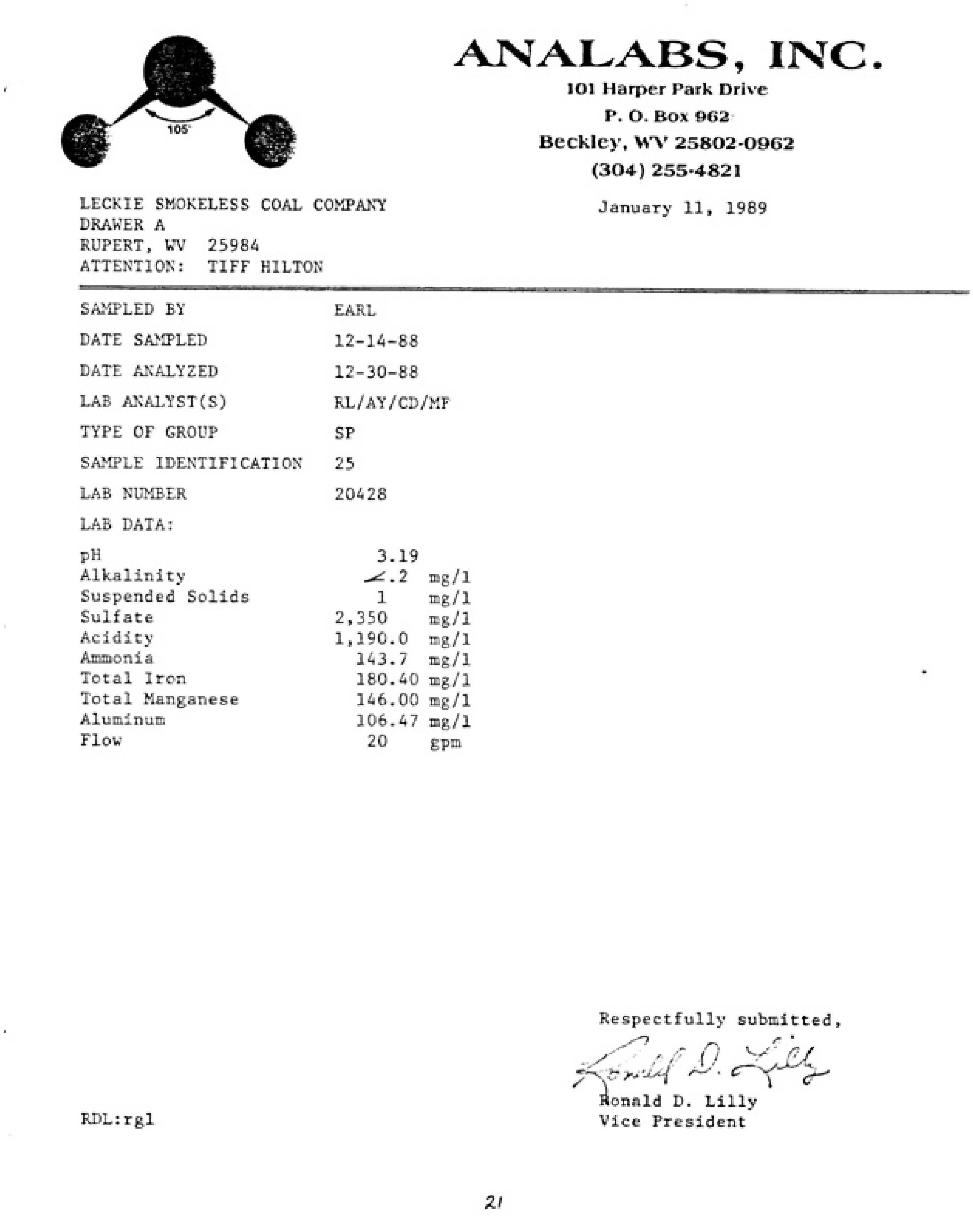


Figure 6 - Chemical Weathering Attributes - Pocahontas # 6 Refuse



ANALABS, INC.
101 Harper Park Drive
P. O. Box 962
Beckley, WV 25802-0962
(304) 255-4821

January 11, 1989

LECKIE SMOKELESS COAL COMPANY
DRAWER A
RUPERT, WV 25984
ATTENTION: TIFF HILTON

SAMPLED BY	EARL
DATE SAMPLED	12-14-88
DATE ANALYZED	12-30-88
LAB ANALYST(S)	RL/AY/CD/MF
TYPE OF GROUP	SP
SAMPLE IDENTIFICATION	25
LAB NUMBER	20428

LAB DATA:

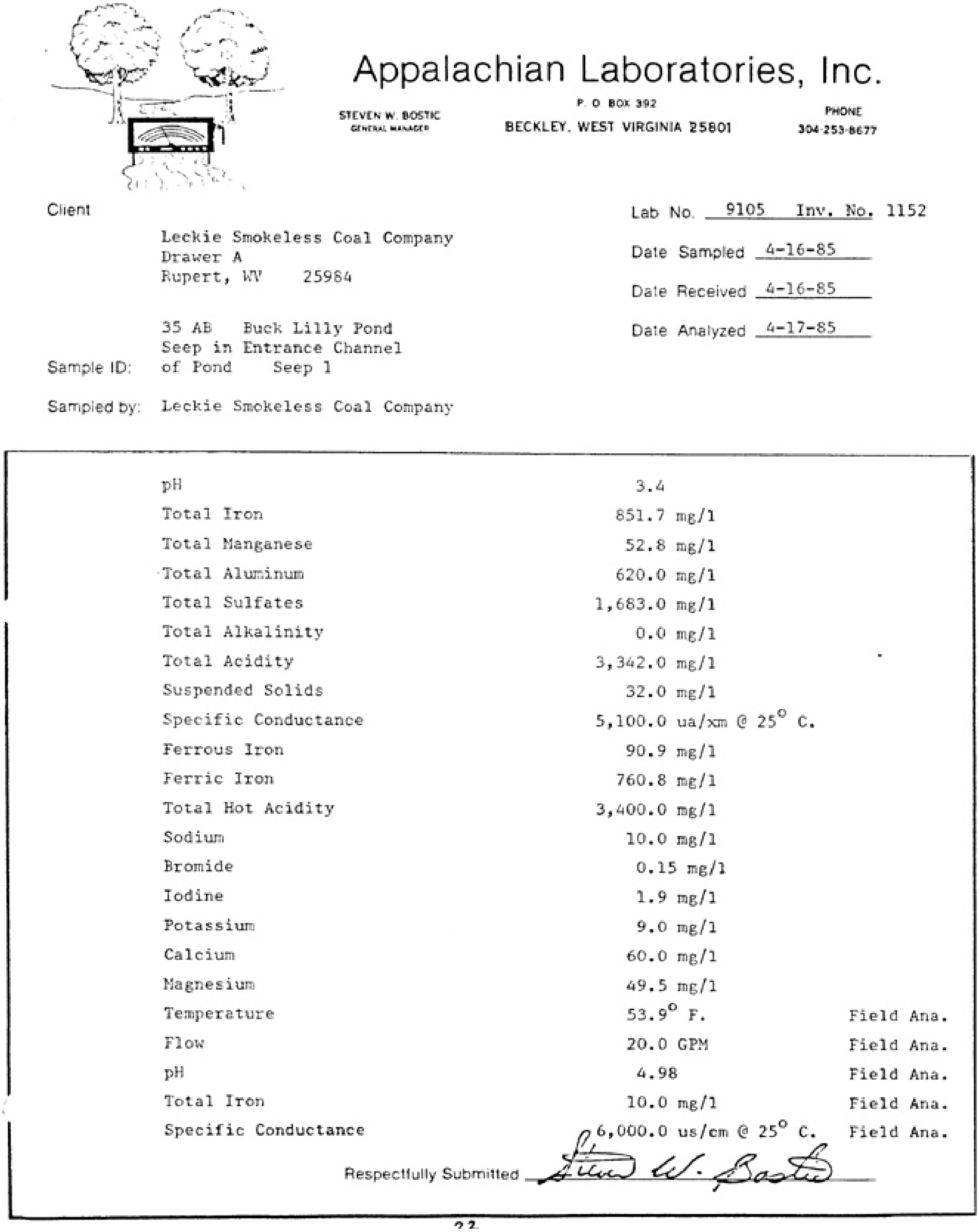
pH	3.19	
Alkalinity	<.2	mg/l
Suspended Solids	1	mg/l
Sulfate	2,350	mg/l
Acidity	1,190.0	mg/l
Ammonia	143.7	mg/l
Total Iron	180.40	mg/l
Total Manganese	146.00	mg/l
Aluminum	106.47	mg/l
Flow	20	gpm

Respectfully submitted,

Ronald D. Lilly

Ronald D. Lilly
Vice President

RDL:rgl



Appalachian Laboratories, Inc.

STEVEN W. BOSTIC
GENERAL MANAGER

P. O. BOX 392
BECKLEY, WEST VIRGINIA 25801

PHONE
304-253-8677

Client
Leckie Smokeless Coal Company
Drawer A
Rupert, WV 25984

Lab No. 9105 Inv. No. 1152

Date Sampled 4-16-85

Date Received 4-16-85

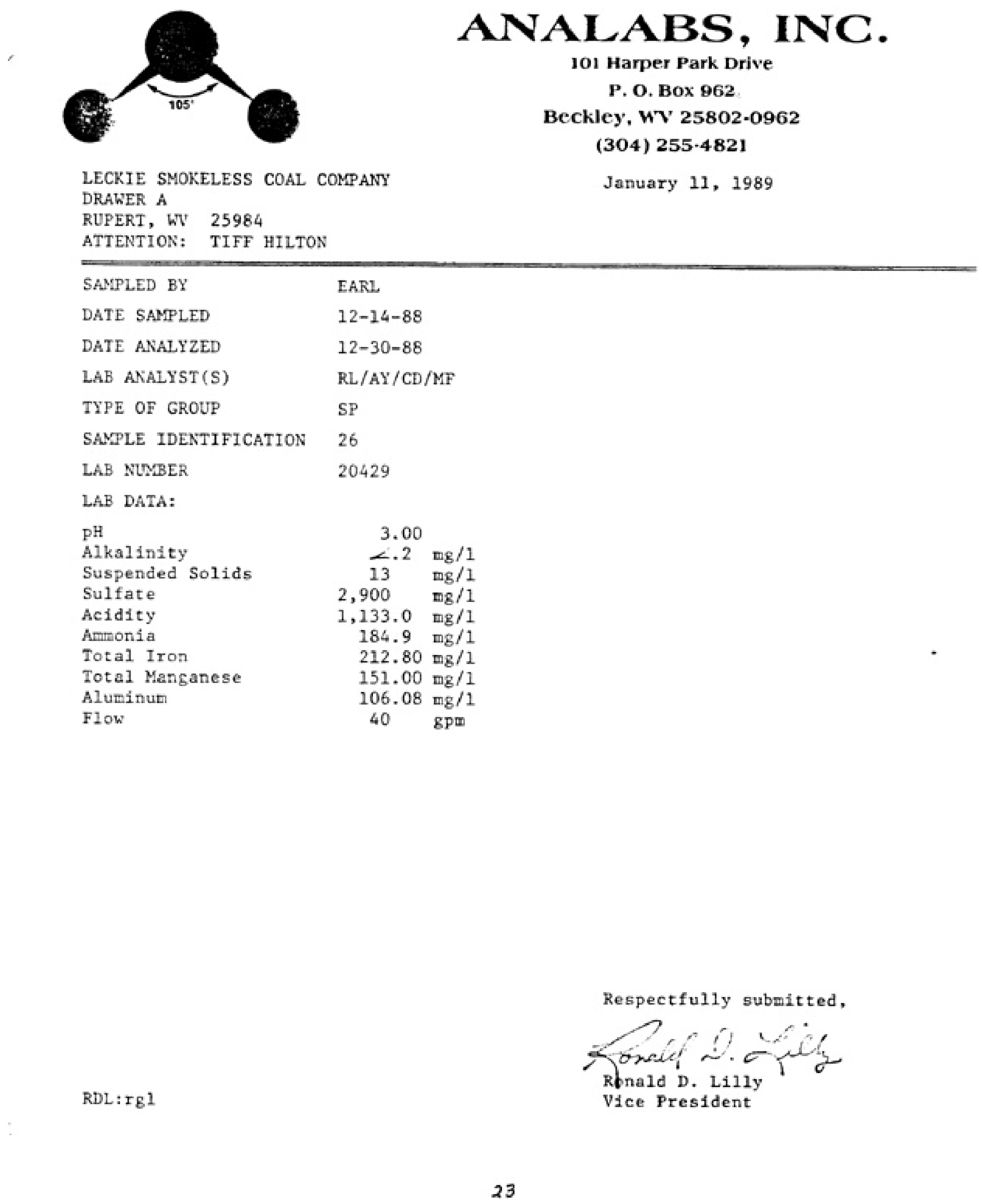
Date Analyzed 4-17-85

Sample ID: 35 AB Buck Lilly Pond
Seep in Entrance Channel
of Pond Seep 1

Sampled by: Leckie Smokeless Coal Company

pH	3.4	
Total Iron	851.7 mg/l	
Total Manganese	52.8 mg/l	
Total Aluminum	620.0 mg/l	
Total Sulfates	1,683.0 mg/l	
Total Alkalinity	0.0 mg/l	
Total Acidity	3,342.0 mg/l	
Suspended Solids	32.0 mg/l	
Specific Conductance	5,100.0 ua/xm @ 25° C.	
Ferrous Iron	90.9 mg/l	
Ferric Iron	760.8 mg/l	
Total Hot Acidity	3,400.0 mg/l	
Sodium	10.0 mg/l	
Bromide	0.15 mg/l	
Iodine	1.9 mg/l	
Potassium	9.0 mg/l	
Calcium	60.0 mg/l	
Magnesium	49.5 mg/l	
Temperature	53.9° F.	Field Ana.
Flow	20.0 GPM	Field Ana.
pH	4.98	Field Ana.
Total Iron	10.0 mg/l	Field Ana.
Specific Conductance	6,000.0 us/cm @ 25° C.	Field Ana.

Respectfully Submitted Steven W. Bostic



ANALABS, INC.
101 Harper Park Drive
P. O. Box 962
Beckley, WV 25802-0962
(304) 255-4821

January 11, 1989

LECKIE SMOKELESS COAL COMPANY
DRAWER A
RUPERT, WV 25984
ATTENTION: TIFF HILTON

SAMPLED BY	EARL
DATE SAMPLED	12-14-88
DATE ANALYZED	12-30-88
LAB ANALYST(S)	RL/AY/CD/MF
TYPE OF GROUP	SP
SAMPLE IDENTIFICATION	26
LAB NUMBER	20429

LAB DATA:

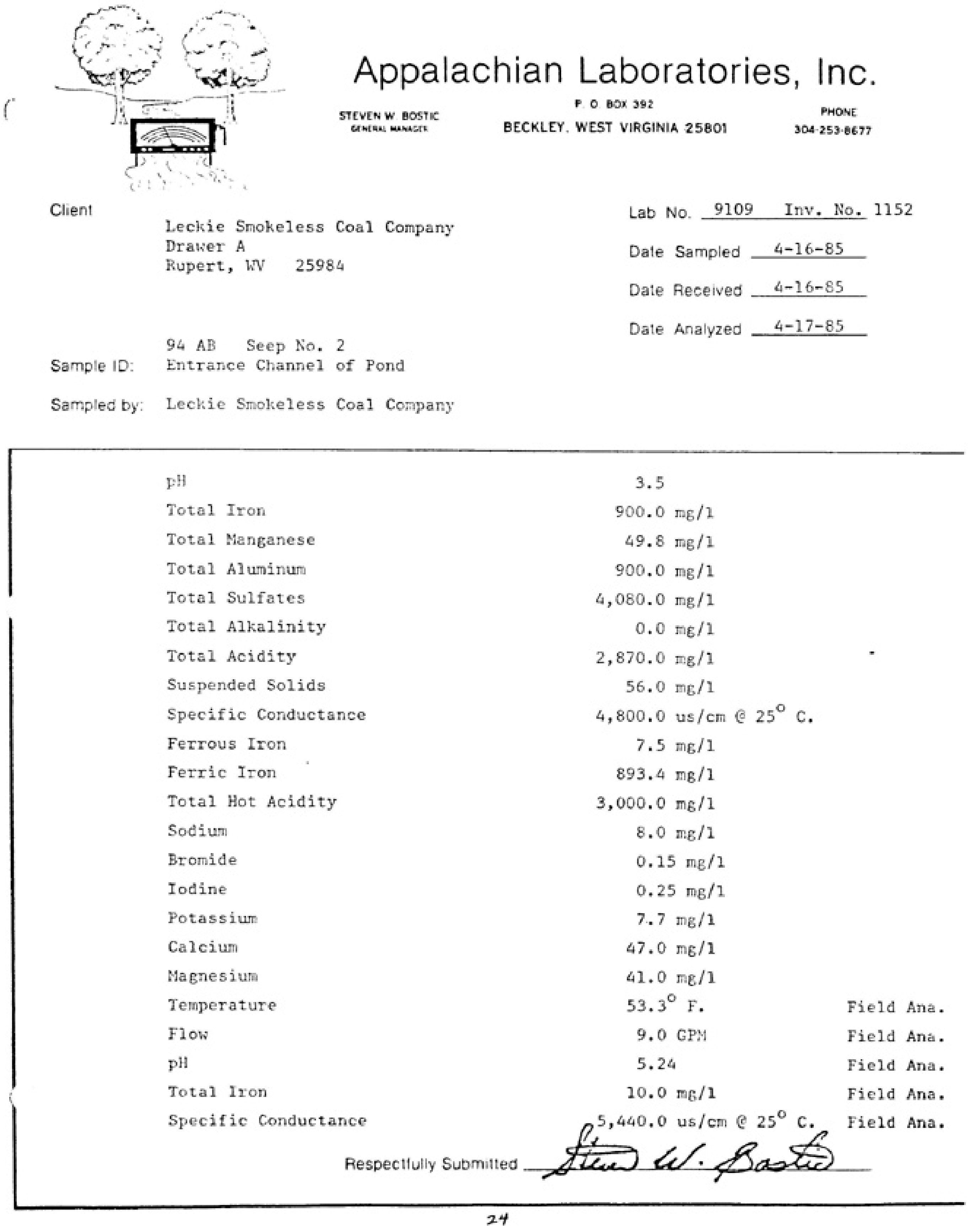
pH	3.00	
Alkalinity	<.2	mg/l
Suspended Solids	13	mg/l
Sulfate	2,900	mg/l
Acidity	1,133.0	mg/l
Ammonia	184.9	mg/l
Total Iron	212.80	mg/l
Total Manganese	151.00	mg/l
Aluminum	106.08	mg/l
Flow	40	gpm

Respectfully submitted,

Ronald D. Lilly

Ronald D. Lilly
Vice President

RDL:rgl



Appalachian Laboratories, Inc.

STEVEN W. BOSTIC
GENERAL MANAGER

P. O. BOX 392
BECKLEY, WEST VIRGINIA 25801

PHONE
304-253-8677

Client
Leckie Smokeless Coal Company
Drawer A
Rupert, WV 25984

Lab No. 9109 Inv. No. 1152

Date Sampled 4-16-85

Date Received 4-16-85

Date Analyzed 4-17-85

Sample ID: 94 AB Seep No. 2
Entrance Channel of Pond

Sampled by: Leckie Smokeless Coal Company

pH	3.5	
Total Iron	900.0 mg/1	
Total Manganese	49.8 mg/1	
Total Aluminum	900.0 mg/1	
Total Sulfates	4,080.0 mg/1	
Total Alkalinity	0.0 mg/1	
Total Acidity	2,870.0 mg/1	
Suspended Solids	56.0 mg/1	
Specific Conductance	4,800.0 us/cm @ 25° C.	
Ferrous Iron	7.5 mg/1	
Ferric Iron	893.4 mg/1	
Total Hot Acidity	3,000.0 mg/1	
Sodium	8.0 mg/1	
Bromide	0.15 mg/1	
Iodine	0.25 mg/1	
Potassium	7.7 mg/1	
Calcium	47.0 mg/1	
Magnesium	41.0 mg/1	
Temperature	53.3° F.	Field Ana.
Flow	9.0 GPM	Field Ana.
pH	5.24	Field Ana.
Total Iron	10.0 mg/1	Field Ana.
Specific Conductance	5,440.0 us/cm @ 25° C.	Field Ana.

Respectfully Submitted Steve W. Bostic

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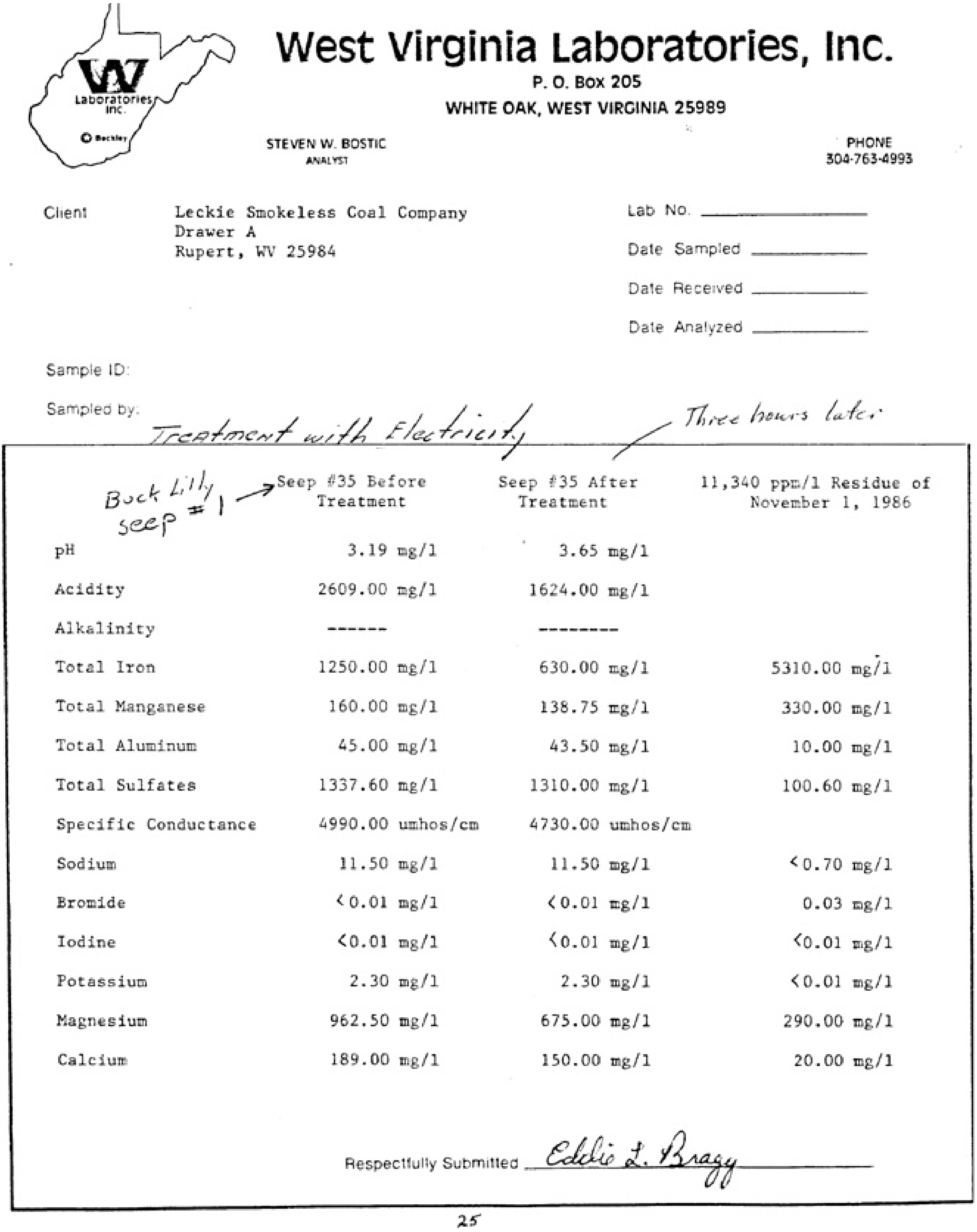

West Virginia Laboratories, Inc.
P. O. Box 205
WHITE OAK, WEST VIRGINIA 25989

STEVEN W. BOSTIC
ANALYST

PHONE
304-763-4993

Client
Leckie Smokeless Coal Company
Drawer A
Rupert, WV 25984

Lab No. ____________

Date Sampled ____________

Date Received ____________

Date Analyzed ____________

Sample ID:

Sampled by:

Treatment with Electricity — Three hours later

Buck Lily seep #1 →

	Seep #35 Before Treatment	Seep #35 After Treatment	11,340 ppm/1 Residue of November 1, 1986
pH	3.19 mg/1	3.65 mg/1	
Acidity	2609.00 mg/1	1624.00 mg/1	
Alkalinity	------	--------	
Total Iron	1250.00 mg/1	630.00 mg/1	5310.00 mg/1
Total Manganese	160.00 mg/1	138.75 mg/1	330.00 mg/1
Total Aluminum	45.00 mg/1	43.50 mg/1	10.00 mg/1
Total Sulfates	1337.60 mg/1	1310.00 mg/1	100.60 mg/1
Specific Conductance	4990.00 umhos/cm	4730.00 umhos/cm	
Sodium	11.50 mg/1	11.50 mg/1	<0.70 mg/1
Bromide	<0.01 mg/1	<0.01 mg/1	0.03 mg/1
Iodine	<0.01 mg/1	<0.01 mg/1	<0.01 mg/1
Potassium	2.30 mg/1	2.30 mg/1	<0.01 mg/1
Magnesium	962.50 mg/1	675.00 mg/1	290.00 mg/1
Calcium	189.00 mg/1	150.00 mg/1	20.00 mg/1

Respectfully Submitted Eddie L. Bragg

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MATERIAL SAFETY DATA SHEET

ANHYDROUS AMMONIA

DISTRIBUTORS:
NATIONAL AMMONIA COMPANY
BOWER AMMONIA & CHEMICAL COMPANY
NORTHEASTERN AMMONIA COMPANY, INC.
AL WELLS, INC.
TACONY & VANKIRK STS., PHILADELPHIA, PA 19135

CORPORATE EMERGENCY TELEPHONE NUMBER: 215-535-7530 CHEMTREC (CMA) 800-424-9300

DESCRIPTION

CHEMICAL NAME: Ammonia, anhydrous
CAS REGISTRY NO.: 7664-41-7
SYNONYMS: Ammonia, liquefied
CHEMICAL FAMILY: Ammonia
FORMULA: NH_3
MOL. WT.: 17.03
COMPOSITION: 99+% ammonia

STATEMENT OF HEALTH HAZARD

HAZARD DESCRIPTION: Irritant and corrosive to skin, eye, respiratory tract and mucous membranes. May cause severe burns, eye and lung injuries. Skin and respiratory related diseases aggravated by exposure.
Not recognized by OSHA as a carcinogen.
Not listed in the National Toxicology Program annual report.
Not listed as a carcinogen by the International Agency for Research on Cancer.

EXPOSURE LIMITS: Vapor - 50 ppm, 35 mg/m³ PEL (OSHA)
25 ppm, 18 mg/m³ TLV (ACGIH)

EMERGENCY TREATMENT

EFFECTS OF OVEREXPOSURE: Eye: lachrymation, edema, blindness. Moist skin: irritation, corrosive burns, blister formation. Contact of liquid with skin freezes the tissue, then produces a caustic burn. Inhalation: heavy: acute exposure may result in severe irritation of the respiratory tract, glottal edema, bronchospasm, pulmonary edema, respiratory arrest. Chronic effects: bronchitis. Extreme exposure (5000 ppm) can cause immediate death from spasm, inflammation or edema of larynx.

EMERGENCY AID: Eye: Flush with copious amount of water for 15 min. Eyelids should be held open and away from eyeball to ensure thorough rinsing. SPEED AND THOROUGHNESS IN RINSING THE EYE IS MOST IMPORTANT IN PREVENTING LATENT PERMANENT INJURIES. Inhalation: move to fresh air. Administer oxygen or artificial respiration if necessary. Skin: flush affected area with copious amount of water for 15 min. Remove contaminated clothing while flushing. Do not rub affected area. Do not apply ointments to skin burns. IF SYMPTOMS PERSIST OR EXPOSURE IS SEVERE, SEEK PROMPT MEDICAL HELP.

NOTE TO PHYSICIAN: Eye injury may appear as delayed phenomenon. Pulmonary edema may follow chemical bronchitis. Supportive treatment with necessary ventilatory actions, including oxygen, may warrant consideration.

PHYSICAL DATA

BOILING PT.: -33°C (-28°F)
FREEZING PT.: -78°C (-108°F)
VAPOR PRESSURE: @ 25.7°C: 10 atm
VAPOR DENSITY (Air=1): 0.6
SPECIFIC GRAVITY: 0.618
SOLUBILITY IN WATER: 0°C: 89.9g/100cc; 100°C: 7.4g/100cc
PERCENT VOLATILE: 100%
EVAPORATION RATE (Water=1): faster than water if in liquid form
APPEARANCE AND ODOR: Colorless gas, pungent odor.

FIRE AND EXPLOSION HAZARD DATA

FLASH POINT: None
AUTOIGNITION TEMP.: 651°C (1204°F) catalyzed by iron; 850°C (1562°F) uncatalyzed
FLAMMABLE RANGE IN AIR: 16% to 25% by Volume
EXTINGUISHING MEDIA: Water spray or fog

SPECIAL FIRE-FIGHTING PROCEDURES: Must wear protective clothing and respiratory protection. See PROTECTIVE EQUIPMENT. Stop source if possible. Cool fire-exposed containers with water spray. Stay upwind and use water spray to knock down vapor and dilute. Let fire burn.

UNUSUAL FIRE AND EXPLOSION HAZARDS: Not generally a fire hazard. If relief valves are inoperative, heat-exposed storage containers may become explosion hazards. Contact of ammonia with chemicals such as mercury, chlorine, iodine, bromine, silver oxide, or hypochlorites can form explosive compounds. Special hazard with chlorine to form chloramine gas, also a primary skin irritant and sensitizer. Combustion may form toxic nitrogen oxides.

Revision: June, 1987

MATERIAL SAFETY DATA SHEET

ANHYDROUS AMMONIA (Continued)

CHEMICAL REACTIVITY

STABILITY: Stable at room temperature. Exothermic reaction with acids.

CONDITIONS TO AVOID: Avoid mixing with chlorine bleach, sulfuric or other strong mineral acids; contact with galvanized steel, copper, brass, bronze, gold, mercury, silver, strong oxidizers, hypochlorites and halogens. See EXPLOSION HAZARDS.

HAZARDOUS DECOMPOSITION PRODUCTS: Hydrogen and nitrogen gases above 450°C.

SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN: Wear respiratory protection and protective clothing; see PROTECTIVE EQUIPMENT. Shut off source if possible. Stay upwind from spills or leaks. Contain spill by diking and use water spray to absorb ammonia gas and dilute. Caution: Adding water to large spills may increase volatilization of ammonia, thus may increase possibility for exposure.

WASTE DISPOSAL: Listed as hazardous substance under CWA (40 CFR 116.4, 40 CFR 117.3 Reportable Quantity, 100#/45.4kg). Classed as a hazardous waste under RCRA (40 CFR 261.32 Corrosive, No. D002). Comply with all regulations. Spill will evaporate. Contaminated water may be used on agricultural land as fertilizer. Keep spill from entering streams or lakes.

SPECIAL PROTECTION AND PROCEDURES

RESPIRATORY PROTECTION: MSHA/NIOSH approved air-purifying type with full facepiece for work purposes, self-contained breathing apparatus for entry and escape in emergencies. Refer to 29 CFR 1910.134 and ANSI: Z88.2-1969 for requirements and selection.

VENTILATION: Engineering control to 50 ppm or less. Respiratory protection for higher vapor concentration. Refer to 29 CFR 1910.134 and ANSI: Z9.2-1960 for requirements and selection.

PROTECTIVE EQUIPMENT: Gas-tight chemical goggles, respiratory protection, impervious outer clothing, gloves, overshoes as needed. Cotton work clothes recommended. Refer to 29 CFR 1910.132 to 1910.136 for requirements.

SPECIAL PRECAUTIONS

HANDLING AND STORING: Store in cool, well-ventilated area with containers tightly closed. OSHA 29 CFR 1910.111 prescribes handling and storage requirements for anhydrous ammonia as a hazardous material.

WORKPLACE: PROTECTIVE EQUIPMENT as discussed above should be near, but outside of ammonia area. Eyewash and safety shower in immediate vicinity. See 29 CFR 1910.141 for workplace requirements.

DISPOSAL: Anhydrous ammonia is listed under RCRA and FWPCA. See WASTE DISPOSAL. Suitably diluted, ammonia may be disposed of on agricultural land as a fertilizer.

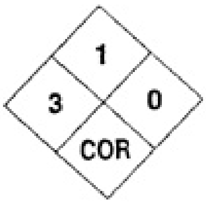
PERSONAL: Check availability of emergency equipment. Follow proper procedures. Wear needed protective equipment. Do not wear contact lenses without gas-tight chemical goggles.

LABELING AND SHIPPING

HAZARD CLASS: Nonflammable gas
PROPER SHIPPING NAME: Anhydrous Ammonia—Nonflammable Gas UN 1005 (RQ)
PLACARD: Nonflammable Gas

Label: Nonflammable Gas UN 1005
IDENTIFICATION NO.: UN 1005

National Fire Protection Assoc. Hazard Rating:



Hazardous Materials Identification System Label:

ANHYDROUS AMMONIA	
HEALTH	3
FLAMMABILITY	1
REACTIVITY	0
PERSONAL PROTECTION	H

OTHER REGULATORY REQUIREMENTS

Under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 any accidental environmental release of this chemical equal to or over the reportable quantity of 100 lbs. must be reported promptly to the National Response Center, Washington, D.C. (1-800-424-8802). Any consumer product containing 5% or more ammonia requires a POISON label under FHSA (16 CFR 1500.129(1)).

Ammonia Emergencies:

Medical Response

by James E. Lessenger, M.D.

The use of anhydrous ammonia is so commonplace among retailers that its transport, storage, and application are often viewed—and dangerously so—as routine, even hazard-free operations. More and more retail employees are coming in contact with some phase of ammonia handling, thus increasing potential risks. Promoting a safety ethic at your business may help avoid needless injuries and fatalities caused by ammonia mishaps. Understanding ammonia properties (*see box*) and their effect on the body will also help you respond to an emergency if it does occur.

Potential For Injury

An anhydrous emergency can occur at any step during the manufacture, storage, transportation, transfer, or use of the chemical. The greatest volume of release occurs during transportation accidents, especially rail car accidents where the rupture of a tank can form millions of cubic feet of ammonia vapor clouds.

Knowing NH_3 Properties

At room temperature, ammonia is a pungent colorless gas, but when pressurized or refrigerated in nurse or storage tanks, it is a colorless liquid. When released from its container, ammonia forms an expanding white cloud which is usually lighter than air and easily follows air currents.

With an expansion ratio of 850 to 1, a given volume of liquid ammonia will expand 850 times to encompass a potentially extensive area. Because liquid ammonia boils at minus 28 degrees, the expanding gas has the potential to freeze both equipment and flesh.

Ammonia is, under most conditions, a stable compound, but under conditions of high temperature and contact with certain metals or fuels, it can be explosive and may burn. Its inflammability limits are 16 to 25 percent by volume in air and its ignition temperature is 1,200 degrees.

Most anhydrous ammonia is manufactured by a process in which natural gas, air, and steam are reacted in the presence of a catalyst and pressure to produce ammonia. In this process, water is excluded, thus the term "anhydrous."

Anhydrous ammonia is easily absorbed by water—at a ratio of 1,176 to 1 at 32 degrees. That is, one volume of water can absorb 1,176 volumes of ammonia, a factor that aids firefighters in controlling ammonia clouds. But, it also contributes to human toxicity, since ammonia will keep spreading across contacted skin until the chemical is diluted by skin moisture. ☐

On the other hand, transfer procedures in fields or at distribution sites are the greatest source of accidents, due primarily to the large number of transfers and the carelessness of workers involved. However, ruptured pipes, explosions of overpressurized storage tanks, and fires can also lead to a release.

In industry, there are two basic means of exposure: spray and gas. A spray of an ammonia stream from a ruptured tank or line can be expected to cause primarily eye and skin damage, while a gas cloud will cause varying degrees of lung injury and, depending on the concentration, eye and skin damage as well.

Impact on the Body

Anhydrous ammonia is an alkali. Compared to acids, which tend to burn and seal-off a wound, alkalis cause liquefaction of tissue. In other words, alkalis turn tissue into a sticky "goo" and mix with this tissue, causing further damage. As a result, anhydrous ammonia burns keep spreading until the chemical is diluted.

In addition to liquefaction, supercooled anhydrous spray causes a freeze-dry effect like frostbite when it hits skin. The spray is also capable of freezing clothing to skin so that, if the clothing is incorrectly removed, whole sections of skin can be torn off. Other circumstances of injury in anhydrous emergencies include: blast effects from exploding tanks, burns from high temperature explosions, and chemical injection injuries.

As already mentioned, anhydrous primarily affects three areas of the body: the lungs, eyes, and skin. In the lungs, anhydrous causes destruction of delicate respiratory tissue, resulting in pulmonary and respiratory distress. The effect on the eyes depends on whether a spray or gas is involved, but everything from mild irritation to eye destruction can occur. Again, skin damage depends upon the length and concentration of exposure, and can range from mild irritation, to a darkened freeze-dry burn, to tissue destruction.

Immediate Response Steps

The specific response to an anhydrous ammonia emergency will depend upon the situation, of course, but there are some common steps to follow. In most instances, it will be possible to perform these steps in rapid succession or simultaneously. The four steps are: evacuation, cardiopulmonary resuscitation, decontamination (flushing), and alert.

■ *Evacuation.* The victimized worker must be removed from the source of the problem. This may simply mean pointing a nozzle away or turning off the valve to a ruptured line. However, it could mean being caught up in an expanding cloud of gas. Workers exposed to such a cloud should drop to the ground, put on respirators, and move upwind and upgrade if possible. A moist handkerchief over the nose and mouth can also be helpful. Fellow workers should not try to enter an ammonia cloud without protective equipment or they will risk becoming additions to the casuality list, thus compounding the problem. The source should be immediately shut off, if this can be done quickly and easily.

■ *Cardiopulmonary Resuscitation.* If the worker has stopped breathing, mouth-to-mouth resuscitation should be attempted as soon as safely possible. If there is no pulse, closed chest massage should be started. Prepare your workers for such an emergency by arranging CPR instruction from the local Red Cross.

■ *Flushing/Decontamination.* As quickly as possible, and simultaneously with first aid or CPR, decontaminate the victim. Starting with the eyes, the whole body or exposed area must be flushed with generous amounts of water; this includes the hair, ears, underchin, and armpits. Any water source is acceptable, such as showers, hoses, or irrigation canals. Contaminated clothing should be removed — but only after careful flushing and warming, to prevent the already-mentioned problem of skin sticking to the clothing.

A special point on skin burns, regardless of severity: creams, ointments or jellies should not be used for the first 24 hours because they "lock in" the ammonia in liquefied skin and extend the injury.

■ *Alert.* Call for help. Notify firefighters and ambulance personnel immediately and warn them about the type of hazard to which they are responding (*see accompanying story*). At the same time, tell them the safest approach route so response can be both rapid and free of mishap. In some situations the accident site may be so far from emergency teams that it would be quicker to bring the victim to the hospital. If that's the case, remember to decontaminate the victim before accompanying him in a closed vehicle.

Pre-planning for each of the four emergency response steps can help avoid life-threatening indecision if an ammonia mishap occurs. Also, it is a good policy to have any exposed worker examined by a physician, regardless of the degree of injury. Certainly any worker with extensive skin damage, eye injury or breathing problems needs to be seen in a hospital emergency department as rapidly as possible.

The Aftermath

While engineers determine what caused the accident, safety people need to critically evaluate the emergency response. A meeting with ambulance personnel, workers, victims, nurses, and physicians can be valuable in identifying the heroes of the day who should be thanked or awarded. It can also be valuable in identifying breakdowns in emergency response procedures in need of improvement.

Aggressive rehabilitation of an injured worker is good policy; and it is probably best to return him or her to work as soon as possible, even if on limited duty.

Preparing For the Worst

Training and prior planning are the keys to a successful emergency response, just as aggressive safety policies are the keys to prevention.

It is important to train employees on what to do if exposed to anhydrous ammonia, especially the need for quick and aggressive decontamination. It is equally important to plan escape routes and practice response procedures so that responding medical personnel can quickly and safely care for possible victims. ■

Emergency Team Actions

Paramedics or ambulance crews responding to ammonia emergencies will continue and complete rescue procedures already begun by workers at the accident site. Before loading the victim in the ambulance, they will pay careful attention to thorough decontamination of the victim.

Clothing saturated with ammonia, for example, can release a cloud of gas within the closed confines of the ambulance and disable the crew. Therefore, following extensive flushing with water, exposed clothing will be removed, with careful attention to avoid removing skin with it.

In mass casuality situations, a triage scheme, based on wartime disasters, can be used to select those patients needing immediate care. In severe injuries, airways need to be established, intravenous lines started, and pulmonary problems aggressively treated.

Tetanus shots must be given if indicated and eye care begun at once. Specialized treatment units, like burn units and intensive care wards, may be utilized.

In less severely injured patients, X-rays, special laboratory tests, and careful examinations can be helpful in determining whether or not hospitalization or further treatment is necessary.

Many areas of the United States and Canada now have an Emergency Medicine Service system that organizes emergency response. Plant medical and safety people need to be aware of this system and should make prior arrangements for proper integration of responses. ☐

13. EXPOSURE AND EMERGENCY ACTIONS

13.1 General

13.1.1 Call a physician immediately for any person who has been burned or overcome by ammonia.

13.1.2 The patient should be removed to an area free from fumes, preferably a warm room. He should be placed in a reclining position with head and shoulders elevated and kept warm by the use of blankets or other cover, if necessary.

PRIOR TO MEDICAL AID BY THE PHYSICIAN, FIRST AID MEASURES SHOULD BE TAKEN. THOSE PRESENTED HEREIN ARE BASED UPON WHAT IS BELIEVED TO BE COMMON PRACTICE IN INDUSTRY. THEIR ADOPTION IN ANY SPECIFIC CASE SHOULD, OF COURSE, BE SUBJECT TO PRIOR ENDORSEMENT BY A COMPETENT MEDICAL ADVISOR.

13.2 First Aid Suggestions

13.2.1 Eyes. If contacted by ammonia, the eyes must be flooded immediately with copious quantities of clean water. Speed is essential. In isolated areas, water in a squeeze bottle which can be carried in the pocket is helpful for emergency irrigation purposes. Eye fountains should be used, but if they are not available, water may be poured over the eyes. In any case, the eyelids must be held open and irrigation must continue for at least 15 minutes. The patient must receive prompt attention from a physician, preferably an ophthalmologist. Persons subject to ammonia exposure should not wear contact lenses.

13.2.2 **Skin.** If liquid ammonia contacts the skin, the area affected should be immediately flooded with water. If no safety shower is available, immerse in any available water. Water will have the effect of thawing out clothing which may be frozen to the skin. Such clothing should be removed and flooding with water continued for at least 15 minutes. Do not apply salves or ointments or cover burns with dressings; however, the injured area should be protected with a clean cloth prior to medical care. Do not attempt to neutralize the ammonia.

13.2.3 **Nose and Throat.** If ammonia has entered the nose or throat and the patient can swallow, have him drink large quantities of water. NEVER GIVE ANYTHING BY MOUTH TO AN UNCONSCIOUS PERSON.

13.2.4 Inhalation

13.2.4.1 Any conscious person who has inhaled ammonia causing irritation should be assisted to an uncontaminated area and inhale fresh air.

13.2.4.2 A person overcome by ammonia should immediately be carried to an uncontaminated area. If breathing has ceased, artificial respiration must be started immediately, preferably by trained personnel. If breathing is weak or has been restored by artificial respiration, oxygen may be administered.

13.3 Physiological Effects

13.3.1 Persons having chronic respiratory disease or persons who have shown evidence of undue sensitivity to ammonia should not be employed where they will be exposed to ammonia.

13.3.2 Ammonia is not a cumulative metabolic poison; ammonium ions are actually important constituents of living systems. However, ammonia in the ambient atmosphere has an intense irritating effect on the mucous membranes of the eyes, nose, throat, and lungs. High levels of ammonia can produce corrosive effects on tissues and can cause laryngeal and bronchial spasm and edema so as to obstruct breathing. The pungent odor of ammonia affords a protective warning, and conscious persons will avoid breathing significantly contaminated air. Unconscious persons, however, are not similarly protected.

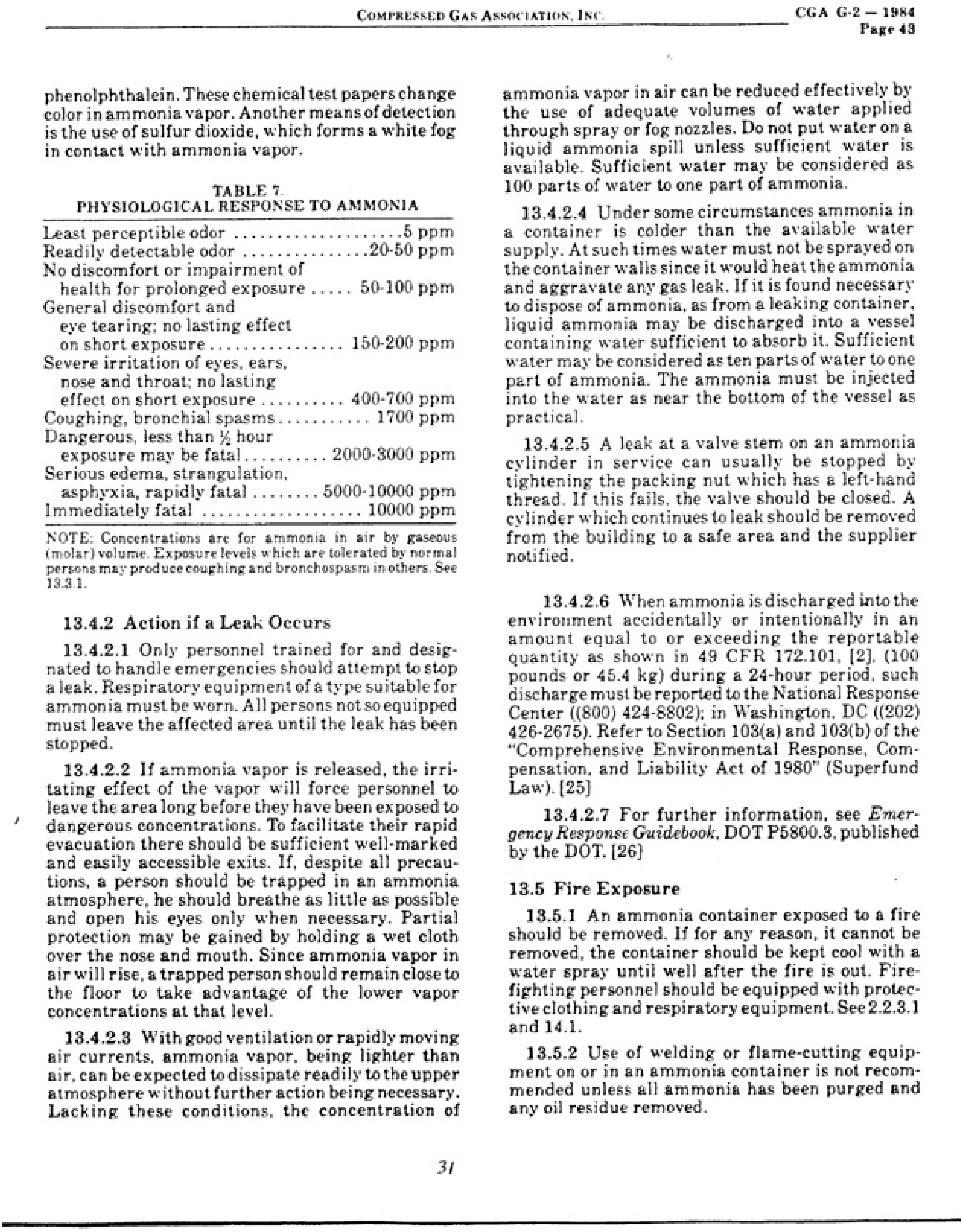
13.3.3 Table 7 indicates human physiological response to various concentrations of ammonia in air.

13.3.4 In accordance with DOL regulations as set forth in 29 CFR 1910.1000, [7], an employee's exposure to ammonia must be limited to a concentration not to exceed 50 ppm of ammonia in air by volume based upon an 8-hour time weighted average. Concentrations in the range of 20-50 ppm are readily detectable and it is therefore unlikely that any individual would become overexposed unknowingly.

13.3.5 Since liquid ammonia vaporizes readily and has a great affinity for water, it may cause severe injury to the skin by freezing the tissue and subjecting it to caustic action. A chemical burn, which may be severe, will result.

13.4 Controlling Leaks

13.4.1 **Leak Detection.** A leak in an ammonia system can be detected by odor. The location of a leak may be determined by using moist red litmus paper or moist filter paper impregnated with



phenolphthalein. These chemical test papers change color in ammonia vapor. Another means of detection is the use of sulfur dioxide, which forms a white fog in contact with ammonia vapor.

TABLE 7.
PHYSIOLOGICAL RESPONSE TO AMMONIA

Least perceptible odor	5 ppm
Readily detectable odor	20-50 ppm
No discomfort or impairment of health for prolonged exposure	50-100 ppm
General discomfort and eye tearing; no lasting effect on short exposure	150-200 ppm
Severe irritation of eyes, ears, nose and throat; no lasting effect on short exposure	400-700 ppm
Coughing, bronchial spasms	1700 ppm
Dangerous, less than ½ hour exposure may be fatal	2000-3000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5000-10000 ppm
Immediately fatal	10000 ppm

NOTE: Concentrations are for ammonia in air by gaseous (molar) volume. Exposure levels which are tolerated by normal persons may produce coughing and bronchospasm in others. See 13.3.1.

13.4.2 Action if a Leak Occurs

13.4.2.1 Only personnel trained for and designated to handle emergencies should attempt to stop a leak. Respiratory equipment of a type suitable for ammonia must be worn. All persons not so equipped must leave the affected area until the leak has been stopped.

13.4.2.2 If ammonia vapor is released, the irritating effect of the vapor will force personnel to leave the area long before they have been exposed to dangerous concentrations. To facilitate their rapid evacuation there should be sufficient well-marked and easily accessible exits. If, despite all precautions, a person should be trapped in an ammonia atmosphere, he should breathe as little as possible and open his eyes only when necessary. Partial protection may be gained by holding a wet cloth over the nose and mouth. Since ammonia vapor in air will rise, a trapped person should remain close to the floor to take advantage of the lower vapor concentrations at that level.

13.4.2.3 With good ventilation or rapidly moving air currents, ammonia vapor, being lighter than air, can be expected to dissipate readily to the upper atmosphere without further action being necessary. Lacking these conditions, the concentration of ammonia vapor in air can be reduced effectively by the use of adequate volumes of water applied through spray or fog nozzles. Do not put water on a liquid ammonia spill unless sufficient water is available. Sufficient water may be considered as 100 parts of water to one part of ammonia.

13.4.2.4 Under some circumstances ammonia in a container is colder than the available water supply. At such times water must not be sprayed on the container walls since it would heat the ammonia and aggravate any gas leak. If it is found necessary to dispose of ammonia, as from a leaking container, liquid ammonia may be discharged into a vessel containing water sufficient to absorb it. Sufficient water may be considered as ten parts of water to one part of ammonia. The ammonia must be injected into the water as near the bottom of the vessel as practical.

13.4.2.5 A leak at a valve stem on an ammonia cylinder in service can usually be stopped by tightening the packing nut which has a left-hand thread. If this fails, the valve should be closed. A cylinder which continues to leak should be removed from the building to a safe area and the supplier notified.

13.4.2.6 When ammonia is discharged into the environment accidentally or intentionally in an amount equal to or exceeding the reportable quantity as shown in 49 CFR 172.101, [2], (100 pounds or 45.4 kg) during a 24-hour period, such discharge must be reported to the National Response Center ((800) 424-8802); in Washington, DC ((202) 426-2675). Refer to Section 103(a) and 103(b) of the "Comprehensive Environmental Response, Compensation, and Liability Act of 1980" (Superfund Law). [25]

13.4.2.7 For further information, see *Emergency Response Guidebook*, DOT P5800.3, published by the DOT. [26]

13.5 Fire Exposure

13.5.1 An ammonia container exposed to a fire should be removed. If for any reason, it cannot be removed, the container should be kept cool with a water spray until well after the fire is out. Fire-fighting personnel should be equipped with protective clothing and respiratory equipment. See 2.2.3.1 and 14.1.

13.5.2 Use of welding or flame-cutting equipment on or in an ammonia container is not recommended unless all ammonia has been purged and any oil residue removed.

14. SAFETY AND SECURITY

14.1 Safety Equipment

14.1.1 OSHA Requirements. Personal protective equipment including respiratory equipment and protective clothing must be provided, used and maintained in accordance with the applicable provisions of 29 CFR 1910, Subpart I, "Occupational Safety and Health Standards." [7]

14.1.2 Normal Conditions. A person subject to ammonia exposure under normal operating conditions must be provided with and must wear approved ventilated chemical splash goggles and rubber or plastic gauntlet type gloves. A full face shield may be worn over the goggles, but not as a substitute for the goggles.

14.1.3 Emergency Conditions. Protective clothing and safety equipment must be provided and made readily available at an ammonia installation for emergency use or rescue purposes in accordance with federal, state, provincial or local requirements. Such clothing and equipment may include one or more of the following depending upon the size and nature of the installation.

14.1.3.1 Gas Mask. The gas mask must be of a type with a full facepiece and green ammonia canister or red universal canister. Under extreme exertion conditions, such a mask generally provides respiratory protection for about 5 minutes in concentrations around 3% or 15 minutes in a concentration of 1%. Because a gas mask is an air-purifying device, it is essential that its use be restricted to an atmosphere which contains sufficient oxygen to support life (at least 19.5% by volume). A canister must not be opened until ready for use and must be discarded after use. A canister is stamped by the manufacturer with an expiration date indicating its approved life span. It must not be used after this date. A canister must be stored where it is easily accessible and where there is no danger of ammonia contaminating it. Spare canisters should be kept readily available.

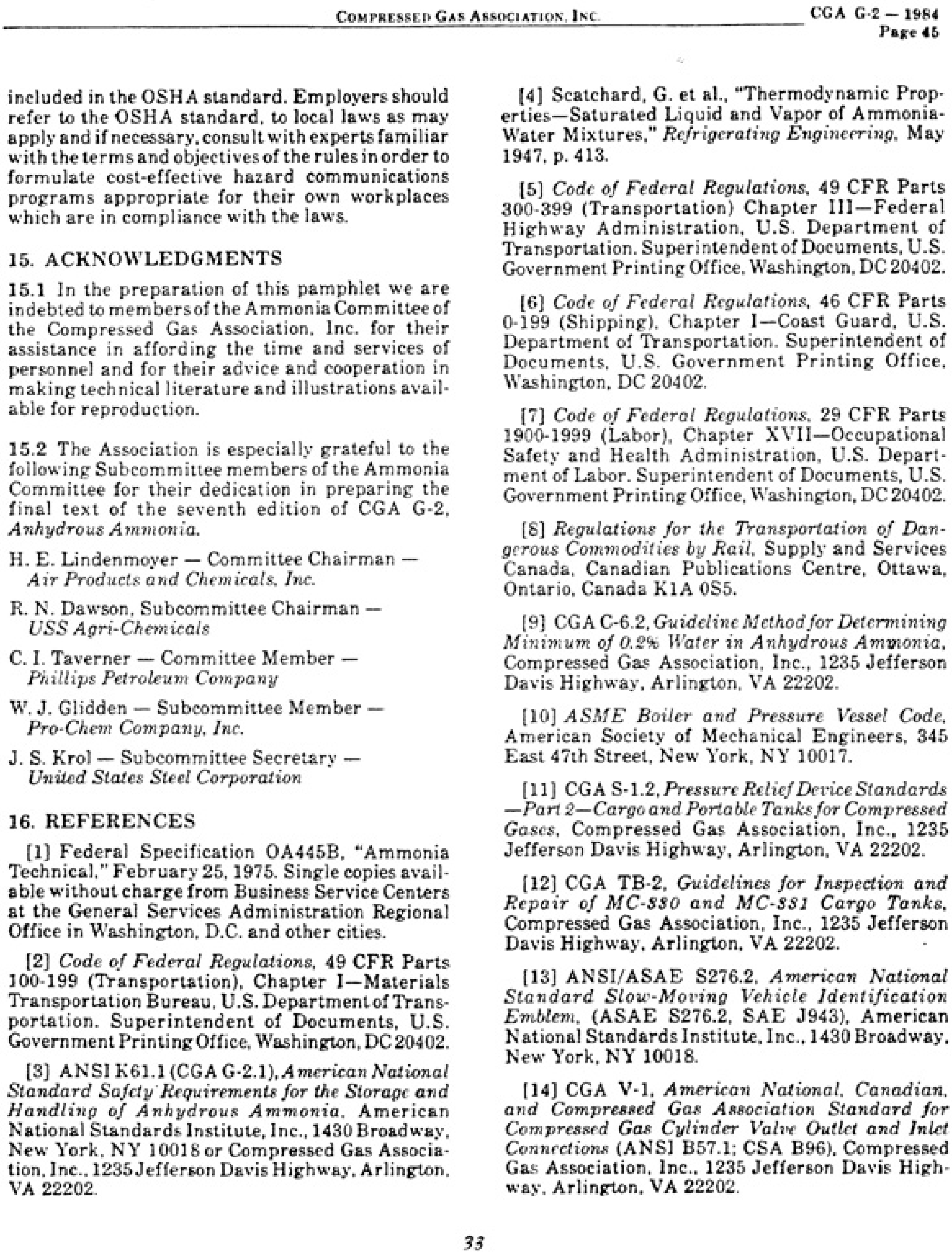
14.1.3.2 Self-Contained Breathing Apparatus. For protection in atmospheres containing more than 3% ammonia, self-contained air breathing apparatus of the positive pressure type must be used. Such equipment should be used when the concentration is unknown or the operator must work in the atmosphere for an extended period of time determined by the quantity of air available, the degree of exertion by the user, and other factors. Persons utilizing self-contained breathing apparatus or a gas mask must be trained in the proper use of the equipment and such equipment must be maintained in accordance with the manufacturer's recommendations.

14.1.3.3 Protective Clothing. Personnel engaged in emergency or rescue operations and subject to high ammonia concentrations should be provided with and wear protective gloves, boots, slicker or pants and jacket impervious to ammonia. Garments worn beneath the rubber or plastic outer clothing should be made of cotton. A hard hat should also be worn if required by local conditions or practice.

14.1.3.4 Safety Shower. Since it is important to immediately flood with water the parts of the body contacted by ammonia, easily accessible showers must be provided, preferably of the treadle type. These showers must be capable of supplying large quantities of water. Bubbler type fountains for irrigation of the eyes must be available.

14.2 Security. To minimize the potential for trespassing or tampering, locations which include ammonia storage and container loading or unloading facilities should be protected when not attended. Protection may be provided by perimeter fencing or other enclosure. If guard service is available, it should include surveillance of the ammonia installation. Guard personnel should be properly trained in handling emergencies involving ammonia. In lieu of an enclosure, suitable locking devices may be provided to prevent unauthorized valve or equipment operation. Adequate lighting should be provided to illuminate storage areas and container loading or unloading facilities during all operating periods. Lighting during other than operating periods may be desirable for security purposes.

14.3 OSHA Hazard Communication Standard. The Occupational Safety and Health Administration (OSHA) has promulgated a hazard communication standard, 29 CFR 1910.1200. [7] The standard is intended to ensure that the hazards of listed chemicals, including ammonia, are identified and that this information and information on protective measures is passed on to manufacturers, distributors and their employees. The information is to be provided by means of hazard communications programs including hazard warning labels, material safety data sheets, employee training and access to written records. Some provisions of the standard become effective November 25, 1985 with full implementation of the standard by May 25, 1986. Several states and municipalities have also adopted "right-to-know" laws that require employers to inform employees about toxic or hazardous chemicals in the workplace. The provisions of these laws vary considerably and many involve aspects not



included in the OSHA standard. Employers should refer to the OSHA standard, to local laws as may apply and if necessary, consult with experts familiar with the terms and objectives of the rules in order to formulate cost-effective hazard communications programs appropriate for their own workplaces which are in compliance with the laws.

15. ACKNOWLEDGMENTS

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H. E. Lindenmoyer — Committee Chairman —
Air Products and Chemicals, Inc.

R. N. Dawson, Subcommittee Chairman —
USS Agri-Chemicals

C. I. Taverner — Committee Member —
Phillips Petroleum Company

W. J. Glidden — Subcommittee Member —
Pro-Chem Company, Inc.

J. S. Krol — Subcommittee Secretary —
United States Steel Corporation

16. REFERENCES

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[2] *Code of Federal Regulations*, 49 CFR Parts 100-199 (Transportation), Chapter I—Materials Transportation Bureau, U.S. Department of Transportation. Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

[3] ANSI K61.1 (CGA G-2.1), *American National Standard Safety Requirements for the Storage and Handling of Anhydrous Ammonia*, American National Standards Institute, Inc., 1430 Broadway, New York, NY 10018 or Compressed Gas Association, Inc., 1235 Jefferson Davis Highway, Arlington, VA 22202.

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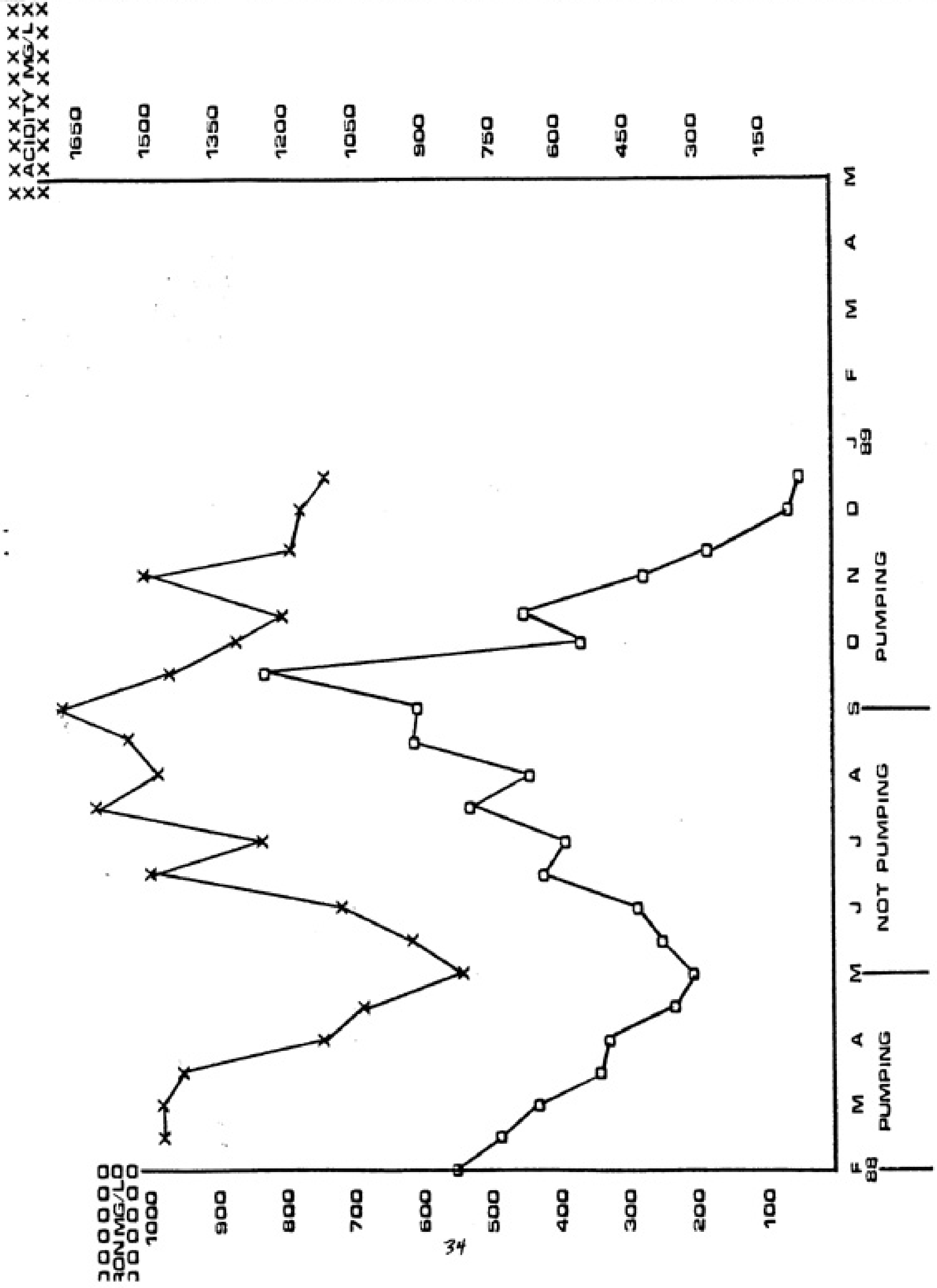
[12] CGA TB-2, *Guidelines for Inspection and Repair of MC-330 and MC-331 Cargo Tanks*, Compressed Gas Association, Inc., 1235 Jefferson Davis Highway, Arlington, VA 22202.

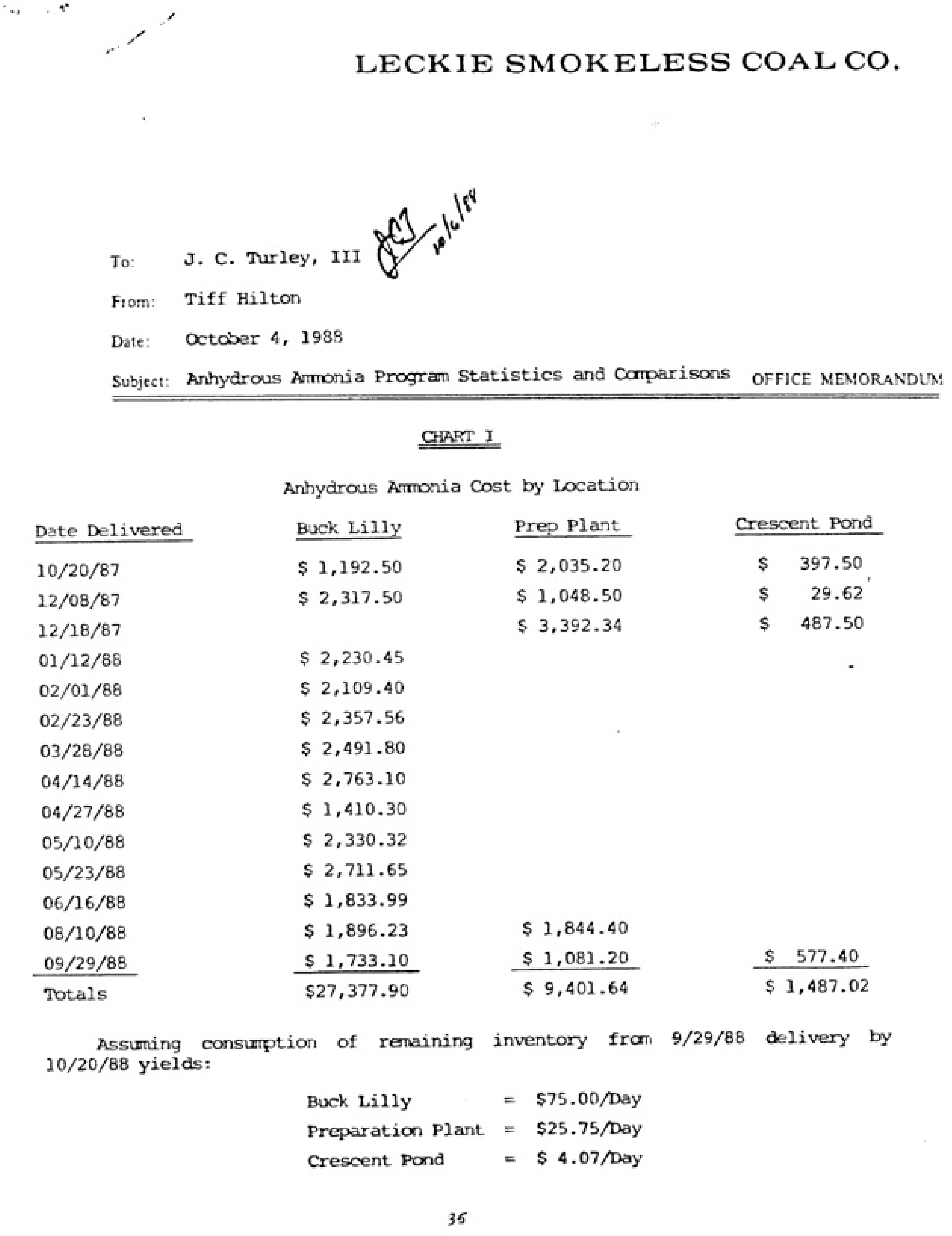
[13] ANSI/ASAE S276.2, *American National Standard Slow-Moving Vehicle Identification Emblem*, (ASAE S276.2, SAE J943), American National Standards Institute, Inc., 1430 Broadway, New York, NY 10018.

[14] CGA V-1, *American National, Canadian, and Compressed Gas Association Standard for Compressed Gas Cylinder Valve Outlet and Inlet Connections* (ANSI B57.1; CSA B96), Compressed Gas Association, Inc., 1235 Jefferson Davis Highway, Arlington, VA 22202.

BY ______ DATE ______ SUBJECT **B. LILLY PUMP PROJECT** SHEET NO. ______ OF ______

CHKD. BY ______ DATE ______ JOB NO. ______





LECKIE SMOKELESS COAL CO.

To: J. C. Turley, III 10/6/88

From: Tiff Hilton

Date: October 4, 1988

Subject: Anhydrous Ammonia Program Statistics and Comparisons

OFFICE MEMORANDUM

CHART I

Anhydrous Ammonia Cost by Location

Date Delivered	Buck Lilly	Prep Plant	Crescent Pond
10/20/87	$ 1,192.50	$ 2,035.20	$ 397.50
12/08/87	$ 2,317.50	$ 1,048.50	$ 29.62
12/18/87		$ 3,392.34	$ 487.50
01/12/88	$ 2,230.45		
02/01/88	$ 2,109.40		
02/23/88	$ 2,357.56		
03/28/88	$ 2,491.80		
04/14/88	$ 2,763.10		
04/27/88	$ 1,410.30		
05/10/88	$ 2,330.32		
05/23/88	$ 2,711.65		
06/16/88	$ 1,833.99		
08/10/88	$ 1,896.23	$ 1,844.40	
09/29/88	$ 1,733.10	$ 1,081.20	$ 577.40
Totals	$27,377.90	$ 9,401.64	$ 1,487.02

Assuming consumption of remaining inventory from 9/29/88 delivery by 10/20/88 yields:

Buck Lilly = $75.00/Day
Preparation Plant = $25.75/Day
Crescent Pond = $ 4.07/Day

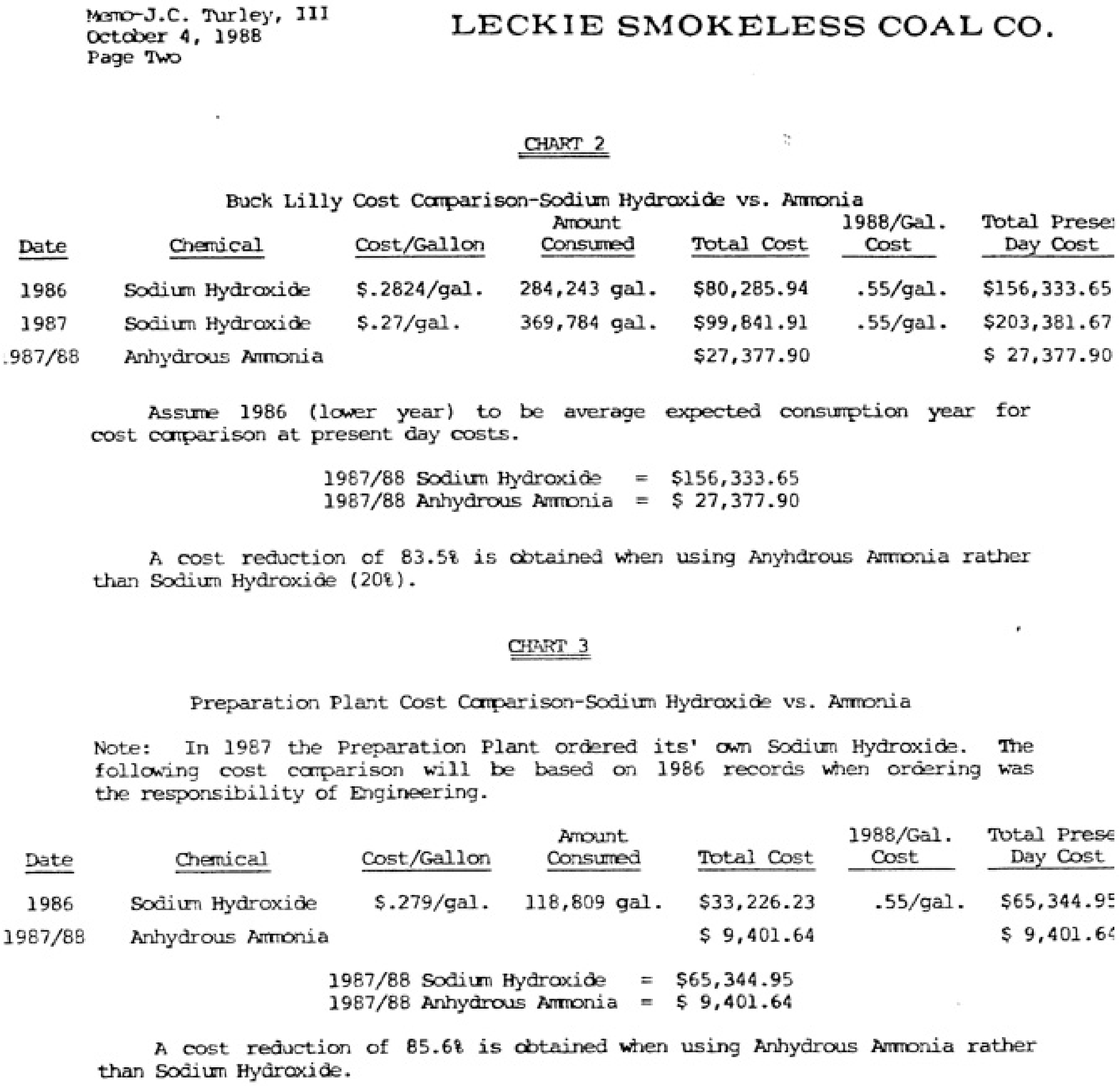


CHART 2

Buck Lilly Cost Comparison-Sodium Hydroxide vs. Ammonia

Date	Chemical	Cost/Gallon	Amount Consumed	Total Cost	1988/Gal. Cost	Total Prese Day Cost
1986	Sodium Hydroxide	$.2824/gal.	284,243 gal.	$80,285.94	.55/gal.	$156,333.65
1987	Sodium Hydroxide	$.27/gal.	369,784 gal.	$99,841.91	.55/gal.	$203,381.67
987/88	Anhydrous Ammonia			$27,377.90		$ 27,377.90

Assume 1986 (lower year) to be average expected consumption year for cost comparison at present day costs.

1987/88 Sodium Hydroxide = $156,333.65
1987/88 Anhydrous Ammonia = $ 27,377.90

A cost reduction of 83.5% is obtained when using Anyhdrous Ammonia rather than Sodium Hydroxide (20%).

CHART 3

Preparation Plant Cost Comparison-Sodium Hydroxide vs. Ammonia

Note: In 1987 the Preparation Plant ordered its' own Sodium Hydroxide. The following cost comparison will be based on 1986 records when ordering was the responsibility of Engineering.

Date	Chemical	Cost/Gallon	Amount Consumed	Total Cost	1988/Gal. Cost	Total Prese Day Cost
1986	Sodium Hydroxide	$.279/gal.	118,809 gal.	$33,226.23	.55/gal.	$65,344.9
1987/88	Anhydrous Ammonia			$ 9,401.64		$ 9,401.6

1987/88 Sodium Hydroxide = $65,344.95
1987/88 Anhydrous Ammonia = $ 9,401.64

A cost reduction of 85.6% is obtained when using Anhydrous Ammonia rather than Sodium Hydroxide.

CHART 4

Crescent Pond Cost Comparison-Sodium Hydroxide vs. Ammonia

Date	Chemical	Cost/Gallon	Amount Consumed	Total Cost	1988/Gal. Cost	Total Prese Day Cost
1986	Sodium Hydroxide	$.28/gal.	18,000 gal.	$ 5,142.18	$.55/gal.	$ 10,078.2
1987	Sodium Hydroxide	$.27/gal.	31,266 gal.	$ 8,442.05	$.55/gal.	$ 17,196.7
1987/88	Anhydrous Ammonia			$ 1,487.02		$ 1,487.0

Because of recent degradation of raw water quality assume 1987 to be the average consumption year for a cost comparison at present day costs.

1987/88 Sodium Hydroxide = $17,196.76
1987/88 Anhydrous Ammonia = $ 1,487.02

A cost reduction of 91.3% is obtained when using Anhydrous Ammonia rather than Sodium Hydroxide.

CHART 5

Present Day Cost/Year Comparison-Sodium Hydroxide vs. Ammonia

Chemical	Buck Lilly	Prep Plant	Crescent Pond	Total
Sodium Hydroxide	$156,333.65	$65,344.95	$17,196.76	$238,875.36
Anhydrous Ammonia	$ 27,377.90	$ 9,401.64	$ 1,487.02	$ 38,266.56

Having used Anhydrous Ammonia over the previous twelve months saved Leckie Smokeless Coal Co.:

$200,608.80

CHART 6

Final Daily Cost Comparison

Chemical	Buck Lilly	Prep Plant	Crescent Pond	Total Daily
Sodium Hydroxide	$428.31/Day	$179.02/Day	$47.11/Day	$654.44/Day
Anhydrous Ammonia	$ 75.00/Day	$ 25.75/Day	$ 4.07/Day	$104.82/Day

Sodium Hydroxide = $654.44/Day
Anhydrous Ammonia = $104.82/Day