Actodemil®, a Proven Non-Thermal Technology for Safe, Rapid Deployment and Environmental Protection for Disposition for Disposition of M6 Propellants and CBI Stored at Camp Minden, Louisiana

Response to Questions from EPA Dialogue Committee

March 6, 2015

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Response to Questions, March 6, 2015

ARCTECH appreciates the Citizen's Committee efforts to pursue non-thermal alternatives. This is an effort that stalled approximately eight years ago when the Congress and the Army stopped funding non-thermal solutions in favor of open burn and other thermal methods. The Committee has brought renewed hope for those who have strived for decades to advocate change.

Since 1984, ARCTECH's founder has dedicated his career to environmentally safe methods to recycle toxic weapons including M6. During the time when there was a Federal commitment to alternatives, ARCTECH produced profound results. We understand that some Committee members apparently do not trust the various reports showing the recycle-to-fertilizer option, and/or have questions about the process.

Therefore, we are finalizing an alternative to fertilizer that will meet all state and federal criteria. Understandably, this proven alternative will take a few more days to finalize, as does the various details. For example, ARCTECH's Teaming Partner OHI, which has 20+ years experience handling weapons, has revised the site plan to fit into the 25-acre area that available. Thankfully, the National Guard has extended the request for information to March 18th, enabling ARCTECH's local and national team to submit a proposal to the Guard that meets all objectives. To accommodate the concern about trucks, ARCTECH is also going to pursue the use of the rail system.

ARCTECH appreciates the effort, questions and inputs from the Committee. While ARCTECH stands by the results provided, the fact is the core process neutralizes the weapons and enables alternatives to fertilizer.

While ARCTECH is open to making revisions, it is important to Note: there have been several references to situations that ARCTECH did not participate including in Oregon and in Region 4.

Being familiar with the various thermal and non-thermal methods, ARCTECH's process is perhaps the only non-thermal solution that will meet the goals of getting the job done safely, on a timely basis and within budget constraints.

We respectfully request the Dialogue Committee give serious consideration to ARCTECH-OHI's non-thermal proposal especially given the effort to meet the Committee's inputs. This will enable a full proposal on the 18th.

The following are responses to questions received from;
1) Col. Stuckey
2) Karen Price,Louisiana Department of Environmental Quality
3) Mickey Walsh
4) Jenny Reynolds.

Attachments:

1. **White Paper, Dr. Solim Kwak, Senior Science Advisor, Defense Ammunitions Center, US Army Joint Munitions Command—an Evaluation of Options for Propellant Disposal**
2. **25 Acre Site Concept**
3. **Independent Lab Reports on Actodemil® Product from Single Base Propellant**
4. The UTS list of 135 Organics and 8 Toxic Metals Showing Actodemil product meets the limits
5. An independent lab report for ActoHAX™ derived from lignite—Shows free of any toxic organics and metals.
6. **Humic Acid Tech Bulletin.**

#1). Questions From: Ronnie D NFG NG LAARNG (US) Stuckey

To: dbicz@arctech.com
Cc: Douglas Sarno
Cc: Various Others

a. The EPA Region 4 provided the following comment "several years ago Anniston tried to convert small quantities of propellant to fertilizer but that was abandoned after a worker was killed from the process." I have also heard that Toole attempted to use this same process but did not have any success. Can you provide any comments regarding the above statements?

Dr. Walia reports that ARCTECH has never had any safety problems with Actodemil®. He never heard of the situation. In the late 90's he had heard of some accident resulting from pug mill grinding of repellants at Anniston Ballistic Missile Depot. Meanwhile, ARCTECH has calls into Region 4 to get the facts including the name of the organization. We have also conducted an extensive web search- to no avail. Can you provide any intel?

b. Can you provide references to confirm the info provided in your presentation?

Dr. Solim Kwak is the Senior Science Advisor, Demil Technology, Defense Ammunitions Center, US Army Joint Munitions Command. Dr. Kwak was the Army's Contract Officer for technical oversight for all the Actodemil® projects performed for the US Army.

Please note Attachment #1: "Development of US-ROK Joint Munitions, Demilitarization Facility Concept and Demilitarization of Propellants" a comprehensive report describing Actodemil® projects and alternative solutions for disposal of propellants. He can be reached at McAlester Army Ammo Plant 918 420 8618.

c. Maybe I missed it in your presentation, but how much fertilizer will be created from 16 million lbs of M6 propellant? What do you plan to do with this fertilizer? How will it be packaged and stored pending final use?

Process produces ≈ 800 gallons of liquid fertilizer (assuming land application approach) per ton of material processed. If all 16M pounds was converted into fertilizer ≈ 6.4M gallons. ARCTECH's sales team is in discussions with several potential users of the fertilizer, which is proven to enhance crop growth.

However, in deference to the Committee's concerns, ARCTECH will propose one or two alternatives exits beyond fertilizer, which would reduce the amount of fertilizer to a fraction. Details are being finalized in time for the proposal due on the 18th.

d. You mentioned that you will need 50 acres to set up your equipment. I am assuming that this must be cleared land and your planning for equipment set up needs to assume that we only have 25 acres cleared and immediately available. So additional time needs to be added to clear additional land.

In the desire to provide as complete a response to the Dialogue Committee, a preliminary estimate was made. Based on updated analysis, only 25 acres are needed. DDDESB Guidance 6055.09-M, *DoD Ammunition and Explosives Safety Standards*, provides guidance on quantity distance arcs required for explosive operations. M6 and Clean Burning Igniter are considered Hazard Division (HD) Class 1.3 material (i.e., Mass fire, minor blast, or fragmentation hazard). Volume three of the DDESB 5055.09M lists the Inhabited Building Distance (IBD) and Public Traffic Route Distance (PTRD) at 110 feet for 4,000 pounds of HD1.3 class material. However, following further DDESB guidance, DDESB Technical Paper 16, minimal separation distance for teams working on-site is 200

feet. Therefore, 200 feet will be the default stand-off distance for operations (i.e., handling, transport, staging, and processing) maintained at all times. A 200 foot radius = 125,600 ft^2 or 2.883 acres (≈3 acres per line). Please see Attachment #2 a draft layout of processing areas is shown in the attached Figure within Area E. Neutralization tanks and chemical storage areas can also be included within Area E outside of the individual safety arcs of the stations (for example in the middle area of area E).

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Note, if material is assumed to possess a detonation hazard, it must be assessed as HD 1.1 class material, which has a QD calculated at 590 feet based upon the net explosive weight TNT equivalent of M6 (.73 TNT equiv factor).

e. And again maybe I missed it but please explain what equipment will be used for this process, is it readily available and if it requires 50 acres, explain the logistics associated with setting up a site this large in just 30 days.

Equipment to be utilized is modified commercial equipment (e.g., tanks, mixers, pumps). The commercial equipment is readily available within the commercial marketplace. Modifications will take an estimated at 6-8 weeks to complete. However, equipment for multiple lines can be modified at once by utilizing multiple fabrication / machine shops. Equipment procurement and modification for Line 1 can begin at the same time planning and permitting is occurring to minimize delays.

ARCTECH will team will a local construction company to perform the required site setup (e.g., land cleaning, minimal access road construction, staging area, electrical connections). The lines will utilize commercially available products such as portable spill containment systems to setup the staging and processing area lanes.

f. Will any of the waste water need to be processed thru the Camp Minden Waste Water Treatment plant....and if so how much (gal per day)?

This is not needed, but ARCTECH will consider. This is under review. If this option is used, it would add only a small fraction to the daily capacity. ARCTECH may contact you with some questions before the 18th.

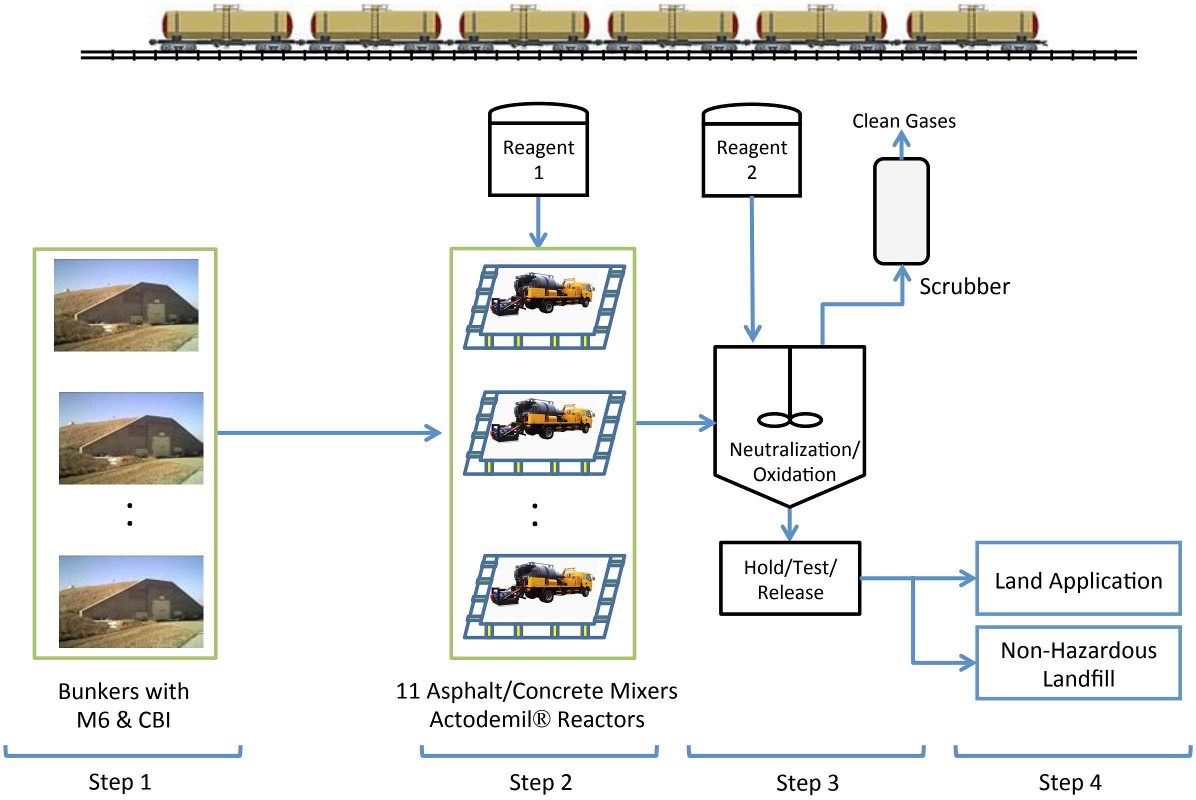
2). Questions from Karen\Geesey\Price (DEQ)" Karen.Price2@LA.GOV

Subject: Follow-up questions for Arctech regarding M6/CBI disposal at Camp Minden
Date: Thu, March 05, 2015 4:59 pm
To: "'dbicz@arctech.com'" <dbicz@arctech.com>
Cc: Doug Sarno <doug@forumfg.com>

Thank you for your presentation to the Camp Minden Technical Committee. I have a few follow-up questions if you could address:

1. Would you provide a process flow diagram or schematic of the process and of the pollution control system?

Rapid Deployment Approach of Actodemil® for Safe Disposition of M6 Camp Minden Propellants for 80,000 lbs per Day



2. Can you identified successful demil projects your company completed in the United States and what type and amount of material was processed? **In addition to comments further down regarding M6:**

- **Hawthorne Army Depot—50 lb to 1000 lb of single, double and triple base**
- **McAlester Army Ammunition Plant—a total of 20 tons of single, double and triple base in 2000 pound batch**
- **Radford Army Ammunition Plant—a total of seven (7) manufactured plant wastes feasibility tests in 2-5 pound batches.**
- **Iowa Ammunition Plant—feasibility proven for depleted uranium containing double base.**
- **NAVY EOD Tech Div-US NAVY Actodemil® feasibility tests for high explosives from anti tank and anit personnel mines.**
- **US Army Chemical Demil facility at Johnston Island in Pacific—designed, built, operated Humasorb® technology for treatment of twenty (20) toxic metals.**
- **US Army Chemical Demil Program—Actodemil® selected in a competition for non-thermal demil of chemical weapons as an alternative to incineration.**

Actodemil® feasibility proven for environmentally safe disposal of explosives, chemical agents and all the components of chemical shells.

- **US Army Non-Stockpile Chemical Weapons Program—proven feasibility of Actodemil®/Humasorb® for retrofitting explosive detonation mobile units.**
- **US Army Demil Program—Proven feasibility of Actodemil® for environmentally safe, non-thermal destruction of Ammonia Perchlorate for the missile demilitarization.**

In addition there were many successful projects in the commercial sector as well as foreign demil.

3. Can indicate identify the waste streams and how much waste material will be generated from this process?
Based on the Committees input, two alternatives to fertilizer are being considered. Both involve safe disposal. One or both will be presented once all the final calculations and negotiations are integrated.

4. Can you identify all off-gases produced from this process, the amounts of each, and what air pollution controls are used for each?
During second step for neutralization/oxidation, NOx gases are generated. They are scrubbed in the ActoHAX™ reagent to a compliance level approved by LaDEQ.

5. Can you identify recycled or byproduct material and how much is generated? Please refer to C above. Please identify an end user to any material? **Confidential business discussions have been underway, including getting shipping quotes to use the Mississippi. But, in deference to the Committee's suggestions, ARCTECH with local input is rapidly assessing the other options**. Do you have any documentation of interest from end user? **ARCTECH had several prospects for fertilizer but given the time needed to pursue alternatives suggested by various Committee members, we ask the Committee provide a conditional approval to allow for consideration at the next stage.**

6. Please identify an studies or sampling regarding dioxins? **Actodemil® technology is low temperature process, below the boiling point of water and no dioxins are expected to be formed.**

The temperature of the combustion gases (i.e., flue gases) is perhaps the single most important factor in forming dioxin-like compounds. Temperatures between 200 and 450 °C are most conducive to the formation of CDDs/CDFs, with maximum formation occurring at around 350 °C. If the temperature falls outside this range, the amount of CDDs/CDFs formed is minimized."
Source: http://www.epa.gov/ncea/pdfs/dioxin/2k-update/pdfs/Dioxin_Chapter_2.pdf

7. You identified the potential to provide 11 train systems toward this process at Camp Minden. Can you indicate the train systems that are currently available to be deployed and the location of each train available? For any train that must manufactured, please indicate the timeframe necessary to acquire materials and fabricate the train for operation.

See response above. Equipment to be utilized is modified commercial equipment (e.g., tanks, mixers, pumps). The commercial equipment is readily available within the commercial marketplace. Modifications will take an estimated at 6-8 weeks to complete. However, equipment for multiple lines can be modified at once by utilizing multiple fabrication / machine shops. Equipment procurement and modification for Line 1 can begin at the same time planning and permitting is occurring to minimize delays.

In deference to concerns expressed by Committee members about truck traffic, ARCTECH anticipates using Camp Minden rail line. This will eliminate the need for truck traffic in the Minden area

8. Can you provide any and all analytical data, including but not limited to air emissions, effluent testing, solid or hazardous waste testing. Please identify if any of the data relates to propellant, and specifically M6.
   In step 2 of Actodemil® process, NOX is released. It is then scrubbed with Actodemil® reagent. Actodemil® being a batch process, it lends to hold, test and release. All the effluents are completely tested for explosives and toxic chemicals per the U.S. Code of Federal regulation limits for toxic chemicals in wastes and recycled waste products for land applications. Please note Attachment #3-an independent Lab Report of Actodemil® of Single Base Propellant same components as in M6.

Thank you.
Karen Price
Louisiana Department of Environmental Quality
Inspection Division/Waste
Senior Environmental Scientist
225-219-3612
Karen.Price2@la.gov

3) Questions From: "Mickey Walsh" <mickey.walsh@comcast.net

Subject: FW: QUESTIONS FOR ARCH TECH—from several Committee Members
Date: Thu, March 05, 2015 6:19 pm
To: <dbicz@arctech.com>
Cc: "'Douglas Sarno'" <doug@forumfg.com>

these are the chemical questions
(1) nitro group reduction process with humic acid on 1 million pounds of nitrocresols.

(2) amide formation process between carboxylate salts and anilines under basic conditions--no such process
(3) the use of lignite as a source of humic acid.(heavy metals/mercury in product?) (MSDS available?)

(4)We want to understand the chemistry for these concerns. Please develop a chemical flow chart.

Answers to Chemical Questions:

A brief intro to the Actodemil® process is as follows to answer the questions about the underpinning chemistry:

Actodemil® is a two step process. First step is hydrolysis with highly alkalized organic water soluble humic/fulvic humate salt (ActoHAX™). It is made to 6 N KOH or NaOH and proprietary additives. KOH is used if the end product is for land applications. NaOH is used if the end product will be disposed. If end use is as fertilizer then KOH is preffered as it provides potash in the end product useful as macronutrient for growing plants. ActoHAX™ is preheated to 80 °C, below the boiling point of water in a vessel. Propellants and explosives (explosive chemicals) without grinding and size reduction are gradually added to the preheated ActoHAX™. During this process the contents of vessel are kept gently mixed. After the addition of predetermined amount of explosives are added. Digestion is considered complete based on the pH and alkalinity measurement of the resultant liquid. In number of runs in 2,000 lbs batches, for single base, will approximately requires 6 hour so hours will be required. It is inherently safe as the explosives are being reacted under water -ased reagent. At the end of this step, the energetic properties of the explosive chemical are eliminated. The resultant solution is then transferred to another vessel reactor fitted with a mixer for Step 2 neutralization/oxidation. During this step Phosphoric acid is added to lower the pH to near neutral or what is desired based on the end use purpose of the product. The vessel reactor in this step is closed at the top and any NOx gas is swept from the headspace and is directed to a vessel containing ActoHAX™ reagent wet scrubber to capture the NOx gas. The spent scrubber reagent is mixed with end use product so that no liquid waste is generated.

Another important attribute of the Actodemil® chemistry is that ActoHAX™ reagent can be used to wet the M6 propellants as they are retrieved from the bunkers. It will absorb nitrogen oxide even if the stabilizer, the Diphenylamine is depleted. Diphenylamine is incorporated in M6 to absorb nitrogen oxide which results during the decay of nitrogen chemicals. Thus this attribute offers an simple approach to desensitize the propellants during retrieval as well as transfer to the Actodemil® Step 1 treatment.

The resultant liquid can be used for

a. Land application at 5-10 gallons/acre for pastures, crops and other land applications.

b. Or alternatively the resultant liquid is treated in a proprietary system to remove the water. Only by product from this process are salts. These can be disposed in local land fill as non hazardous or hazardous depending up on the local regulations. There is no wastewater effluent result from this approach.

In number of Actodemil® projects for the US Army, the resultant product was analyzed at an independent lab and results showed it met the criteria of the US Government Federal Code of Federal Regulations Title 40 generally referred to as Universal Treatment Standards (UTS). This standard sets the allowed limits of 134 toxic organic and 8 toxic metals of concern in wastes and/or recycled waste products for land application. These limits are based on extensive toxicological research data on these chemicals of concern. This UTS criteria is also included in the US EPA 1997 Munitions Rules and adopted by LA DEQ. This Rule sets the rules for disposing munitions. A copy of the independent lab analysis for a Single Base propellant is given in Attachment 3. The UTS list is included in the Attachment 4.

Question (1) nitro group reduction process with humic acid on 1 million pounds of nitrocresols.

Answer: The above referenced lab report of the product from the scaled up Actodemil® of single base propellants shows no nitrocresols because of the well proven but unique chemistry applied in the Actodemi process. The nitrocresols are transformed to polyphenolics same as polyphenolic groups in the humic acid.

Polyphenolic are oligomers, polymers with a few repeating units. In Actodemil® chemistry, creosols reacted with aldehyde humic complex under alkaline/heat conditions to form polyphenol. Aldehydes are constituents in oil and glucose used as foods and even in perfumes.

Please note References below.
References:

- CRESOL NOVOLAC (polyphenol polymers): SYNTHESIS, PROPERTIES, AND PROCESSABILITY
http://scholar.lib.vt.edu/theses/available/etd-04262001-142525/unrestricted/SLGETD.pdf
- Phenol-aldehyde chemicals polymers (polyphenyl)
file:///C:/Users/User/Downloads/CH%2013%20Phenolic%20Resin.pdf

Our above explanation of pathway that no nitrocresols are in the product is further confirmed by the nitrogen mass balance calculations based on the nitrogen content of the components in single base propellant and actual lab analysis of nitrogen components in the product for nitrates and nitrite.

Energetic components of the single base propellant are as follow: Nitrocellulose=85%, DNT=9%, and Diphenylamine 2%.

Final product was analyzed for nitrite and nitrate anions by HPLC (high performance liquid chromatography) using PRP-X110S Anion Exchange Column and Waters431 Conductivity Detector. The concentration of nitrite and nitrate was 77,142.98 mg/L and 48,435.41 mg/L, respectively.

Input total nitrogen in 2,000 lbs of propellant was 251.55 lbs (223.55 lbs from NC and 27.67 lbs from DNT and 0.33 lbs from Diphenylamine). Meanwhile, total nitrogen in 800 gallon of final product was 22.77 lbs (156.75 lbs from nitrite and 73.02 lbs from nitrate).

Thus, 91.34% of input nitrogen from single base propellant was converted to nitrite and nitrate forms in the final product. The remaining nitrogen was released as NOx in these tests.

The above stated mass balance confirms that the nitrogen components in the propellant are transformed to useful nitrate and nitrite if used for land application. If nitrocresols were remained un-transformed then one cannot explains such high amount of nitrite and nitrates in the liquid as well as emitted as NOx gas. This is further confirmed by the attached independent lab analysis that not only the five toxic forms of isomers of nitrocresols are absent but also the other nitrogen containing organic chemicals are absent. Most of the nitrogen taken up by plants in the soil is in the form of NO_3^-. However, nitrite (NO_2^-) is unstable form of nitrogen and is easily converted in soil by Nitrobacteria bacteria to Nitrate.

Question (2) amide formation process between carboxylate salts and anilines under basic conditions--no such process

Answer: We agree

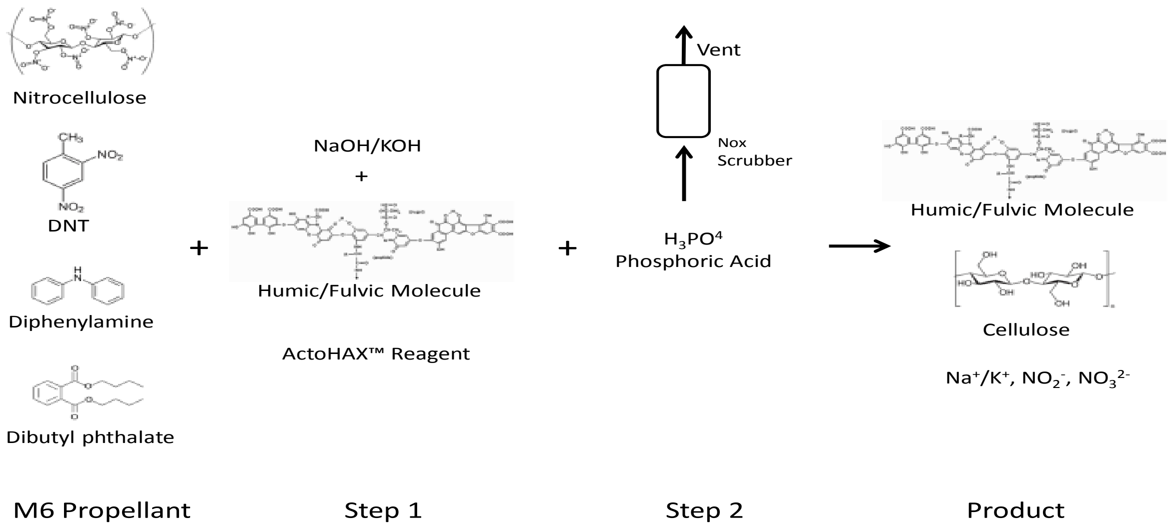
Question (3) the use of lignite as a source of humic acid.(heavy metals/mercury in product?) (MSDS available?)

Answer: We use humic rich lignite. We use our proprietary process to convert it into organic humic/fulvic liquid product. This is then formulated into ActoHAX™ or A-HAX™. It is free of any toxic metals including mercury etc. An independent lab report is included in Attachment 5 for both toxic organics and metals. It shows ActoHAX™ made from several batches are free of any toxic organics and metals.

Question (4) We want to understand the chemistry for these concerns. Please develop a chemical flow chart.

Answer: Please note below:

Actodemil® Chemical Flow Chart



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4) Questions From: Jenny Reynolds [mailto:jennylaspirit@yahoo.com]
Sent: Thursday, March 05, 2015 3:12 PM
To: Mickey Walsh
Subject: QUESTIONS FOR ARCH TECH

To send before 5pm today. Send to the vendor POC. Then send to Doug and copy all members of the DC, as Col. Stucky did yesterday.

ArchTech (Actodemil)

1. Please quantify and identify the estimated amount of any waste. **To reiterate, to accommodate the Committee's issues, ARCTECH is going to adapt one or two proven alternatives in place of fertilizer. This will take several business days to complete.**

2. Please quantify the estimated amount of end product/fertilizer to be produced. **Please refer to above.**

3. What is the estimated length of time for processing the M6 into the final end product? **Once all 11 lines are operational, the production capacity will be 80,000 pounds per day. At this capacity, the process will take approximately 240 work days to complete.**

4. What are the detection limits for testing for total organic compounds? **In compliance to the US Federal Code of Regulations for Universal Treatment Standards.** Are you able to test for specific organic compounds? **Yes. All the regulated 135 organic compounds.** Is it possible for organic chemicals to reform in your process? **Actodemil's unique chemistry results in irreversible transformation.**

5. What is the plan for the end product? **As noted previously, we are altering the original plan to accommodate inputs from the Committee.**

6. Would storage be required for the end product? If so, what type, conditions, and packaging? How long would it need to be stored? **This will be addressed in the near future. Time is required to accommodate the Committee.**

7. Who would own the end product upon completion of the process? **If the land application (i.e., fertilizer) approach was going to be utilized, the end product would belong to the proposed user. However, we are offering an alternative approach of not producing an end product and conceding to some in the Committee who are not in favor of using it as fertilizer.**

8. Are there infrastructure requirements? If so, please list. **Sites will have to constructed for the processing lines. Temporary construction methods such as gravel roads and portable spill containment systems can be utilized to minimize setup time and to make site breakdown easier. Storage tanks will also be required to store chemicals and end product until either used in the process or shipped off-site as fertilizer. One option is to utilize existing railroad infrastructure within Camp Minden. ARCTECH would need support from the installation in setting up such an arrangement so as not to conflict with mission requirements of Camp Minden.**

9. Is ArchTech planning on partnering with a prime or are they willing to be the prime? **Current teaming includes OHI, an experienced explosives handling company. Pending is agreement with local contractor for site setup and construction support. ARCTECH has been approached by several companies including two large firms, but no teaming arrangements have yet been established. ARCTECH is open to partners who can add value, contingent on staying within budget parameters.**

10. Is the equipment used in the Actodemil process already permitted for use in the approved DDESB process? **Site specific equipment and processes would need to be approved, if DDESB approval is required. It's unclear if DDESB approval is required under a State contract, it is under an Army / DoD contract. If DDESB approval is required, an Explosives Safety Submission (ESS) is usually completed as well. OHI has experience developing and working under an ESS. Current example includes Fort Story, VA. Site specific ESS approvals take on average 2-3 months to obtain. If DDESB approvals are required, has the National Guard engaged DDESB to request an accelerated review and approval process. As a contractor, ARCTECH cannot make such a request of DDESB.**

11. Will ArchTech consider an NDA with members of the Technical Workgroup to discuss the data which clarifies the questions about the chemical destruction of the DNTs and other organics of concern?
ARCTECH has been fully forthcoming and provided all the details of the process.

12. Is there noise associated with this process? If so, please define in estimated decibels.
Noise would be limited to processing areas and are not expected to be at levels above typical construction sites. Workers operating mixers and equipment will wear approved hearing protection. Noise is not expected to be an issue of concern for other installation personnel and any neighbors outside of Camp Minden as the operations will have a built in buffer area due to explosives safety quantity distance concerns outlined above.

13. What is the published peer-reviewed scientific proof that humic acid can serve as a reducing agent for the nitro groups on nitroaromatic compounds? **See attachment #6 : Humic Acid Tech Bulletin. It provides detailed info of Humic acid science as well as references.**

14. It was indicated that the humic acid used in the Actodemil would be able to sequester the over 1 million pounds of nitrocresols that are known to be created from basic hydrolysis of DNT. How has this been proven? **This is not the Actodemil chemistry**. **Please refer to the chemical answers above.**

15. Is the laboratory you use for testing of water and emissions accredited by the state and EPA? **Yes, ARCTECH has used and will continue to use accredited labs**

Attachments:

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MY DEAR AND
MOST HIGHLY RESPECTING
DR. D WALIA. SWK

DEVELOPMENT OF US-ROK JOINT MUNITIONS DEMILITARIZATION FACILITY CONCEPT

AND

DEMILITARIZATION OF PROPELLANTS

10 MAY 2007

SOLIM S. W. KWAK

SENIOR SCIENCE ADVISOR
DEFENSE AMMUNITION CENTER
US ARMY JOINT MUNITIONS COMMAND

DEVELOPMENT OF US-ROK JOINT MUNITIONS DEMILITARIZATION FACILITY CONCEPT

AND

DEMILITARIZATION OF PROPELLANTS

10 MAY 2007

SOLIM S. W. KWAK

SENIOR SCIENCE ADVISOR
DEFENSE AMMUNITION CENTER
US ARMY JOINT MUNITIONS COMMAND

DISCLAIMER

This report recounts and discusses the author's recollections and understanding concerning the events, issues, facts and studies pertaining to the US-ROK joint munitions demilitarization facility concept development, the negotiation and establishment of the 2003 US-ROK Joint Demilitarization Facility Memorandum of Agreement (2003 MOA), and the technical assessments and circumstances leading to making a decision for demilitarizing recovered propellant, by a humic acid enhanced base hydrolysis, to liquid fertilizer in Korea.

The author is solely responsible for the overall contents of the report, the selection of topics reviewed, the specific technical discussions presented, the analyses and evaluations performed, and the conclusions and recommendations derived from analyses.

It must be understood that the contents of this report do not reflect the official positions or policies of USFK, ROK MND, JMC, DAC, nor any other US and ROK government entities.

SOLIM S. W. KWAK
10 May 2007

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FIGURES AND TABLES

EXECUTIVE SUMMARY

1. Concept Development and Agreement

The United States (US) has pre-positioned and continues to store a large quantity of conventional munitions in the Republic of Korea (ROK). These aging or obsolete munitions require removal or demilitarization to free up the limited and valuable storage facilities in Korea for more advanced ammunition. The US and the ROK agreed to develop a concept for constructing a US-ROK joint munitions demilitarization facility to demilitarize the US-titled excess ammunition as well as the ROK-titled ammunition in Korea. Based on this demilitarization concept and principle, a Memorandum of Agreement (MOA) for Construction, Operation, and Maintenance of a Joint Munitions Demilitarization Facility (DEFAC) was negotiated and signed, in 2003, by the US Forces in Korea (USFK) and the Republic of Korea Ministry of National Defense (ROK MND), each representing their government.

The 2003 agreement specifies that the ROK will provide the land and utilities, as well as design, construct, operate, and maintain the facility. The US will provide the standard demilitarization systems such as the APE 1401 Autoclave System, APE 2048 Flashing Furnace, APE 1236 Deactvation Furnace and the newly developed waste treatment technologies for treating explosives wastes or explosives contaminated wastes that will be generated at the Joint Munitions DEFAC in the Republic of Korea. The explosives waste treatment technologies selected are the Molten Salt Oxidation (MSO) System, the Supercritical Water Oxidation (SCWO) System, and the Propellant Conversion to Fertilizer (PCF) System.

2. US-ROK Joint Munitions MOA Status

It is noted here that, today (as of April 2007), both the US and the ROK agreed, and the ROK is ready, to proceed with the demilitarization facility construction under a newly established MLSA IAs (Mutual Logistics Support Agreement Implementation Arrangements between USFK and ROK MND) while the basic 2003 MOA is being renegotiated and revised for approval and concurrence by the US Department of Defense and the US State Department.

3. Technical Consultation Meeting at DAC

In May 2004, the US Army Defense Ammunition Center (DAC) hosted a US-ROK Demilitarization Technical Consultation Joint Working Group meeting. The purpose of the meeting was to review and discuss the construction Technical Data Package (TDP) for the joint DEFAC to be built in Korea. The 4-day TDP meeting was principally attended by the engineering staffs from the Ammunition Equipment Directorate of Tooele Army Depot (AED/TEAD), the ROK Agency for Defense Development (ROK ADD), USFK, the US Army Pacific Command (USARPAC), the Joint Munitions Command Program Manager for Korea Demil (JMC PM for Korea Demil), the ROK Ministry of national Defense Program Manager for Demilitarization (ROK MND Demil PM) and DAC.

During a courtesy visit with Mr. James Q. Wheeler (DAC Director), COL Chang Ho-Kyung (the ROK delegation lead) inquired about the possibility of producing a dry fertilizer from the propellants demilitarized at the ROK Joint Munitions DEFAC. Subsequently, Mr. Wheeler requested his Senior Science Advisor, Dr. Kwak, to prepare this report assessing the processes available to convert propellant to fertilizer. The published demilitarization processes to convert propellant into fertilizer were reviewed and analyzed.

4. Propellant Conversion Studies

A series of significant propellant conversion studies were conducted by TPL, Inc., New Mexico. The objective of the studies was to develop a process for producing a dry fertilizer from propellants. Unaltered whole propellant grains and powdered propellants were applied to the test soils. These two TPL studies showed that Sorghum grown in soil that received the whole propellant grains gave better results than the soil receiving the propellants that were ground to a powder form. Phytotoxicity to plants due to the presence of the burn rate modifier and the stabilizer was noted. To further improve the performance and to remove the phytotoxicity, the TPL developed a conversion process in which propellants were hydrolyzed in a hot solution of sodium hydroxide. The hydrolysate was neutralized with ammonium phosphates and then semi-dried. Peat moss and other chemical ingredients were admixed to the semi-dried product. The product was further air dried by spreading the product on a concrete pad and then was pelletized. The final product was successfully test marketed as "Peaceful Green Formulation Fertilizer" emphasizing that the fertilizer was produced from demilitarization of the military propellants to a peaceful civilian product. Another propellant conversion study was also conducted by ARCTECH, Inc., Virginia. The ARCTECH approach was a direct and modified alkaline hydrolysis of propellants to a liquid fertilizer. Propellants were hydrolyzed with a solution of potassium hydroxide and humic acid. The resultant hydrolysate was neutralized with phosphoric acid. The conversion process produced a dark liquid fertilizer with humic acid. This liquid fertilizer was shown to improve the growth of corn, alfalfa and other crops.

These studies have shown that the gun propellants (single, double, and triple base) can be safely demilitarized to fertilizer using the alkaline hydrolysis process. The reagent chemicals for alkaline hydrolysis are costly primarily due to high-cost hydroxide chemical needed to demilitarize complex organic molecules in the propellant compositions. The conversion costs are currently estimated to be $1 to $1.5 per pound of propellant. However, these costs are expected to decrease with an increase in the volume of propellants being processed, as well as through sale of the fertilizer in the established agricultural markets for liquid fertilizers in the future.

5. Demilitarization Criterions

Demilitarization of explosives and propellants must meet two fundamental and critical demilitarization requirements.

First, the explosives and propellants must be processed in a manner such that all of the military and energetic characteristics are completely destroyed and removed (i.e., fully demilitarized). Second, the end-products from the demilitarization operation must not exhibit hazardous characteristics, which includes ignitability, corrosivity, reactivity and leachability. For propellants, these requirements necessitate the complete oxidation of the propellant compositions by combustion or the conversion of the propellants using a chemical reaction such as alkaline hydrolysis to an inert material.

6. Farming and Fertilizer Use in Korea

Fertilizer and their use are rapidly changing all over the world, including in Korea, due to the recognition of adverse environmental impacts caused by use of traditional chemical fertilizers and the need to create environmentally sustainable agricultural practices, while increasing crop quality and yields. A review of agricultural practices in Korea indicates that a number of new strategies are being implemented which includes limiting the use of excessive chemicals and improving the productivity with organic inputs. Both solid and liquid organic fertilizers are utilized, but with increasing demand for liquid organic fertilizers which can be applied cost effectively as both foliar spray and in-soil applications.

7. Recommendations

For the US-ROK Joint Demilitarization Program at Hwang-Gan Facility in Korea, it is recommended that JMC and DAC continue to support the alkaline hydrolysis (specifically the humic acid enhanced alkaline hydrolysis process) for demilitarizing the recovered propellants. The liquid fertilizer produced from demilitarization of propellants should be further customized by adding micronutrients and other chemicals to meet and accommodate the needs of local farmers and ranchers. However, any of the reformulation efforts for producing the customized liquid fertilizer formulations and the subsequent distribution of the reformulated liquid fertilizers in the ROK is the responsibility of the established ROK fertilizer manufacturers, not the US Government.

Author's Note

It is recommended that, to fully understand and appreciate the basic concept developed for establishing a US-ROK Joint Munitions Demilitarization Facility in Korea, and the events and technical circumstances leading to a decision for a chemical conversion of recovered propellants to liquid fertilizer in Korea, the reviewers of this summary to read the entire report.

ACKNOWLEDGMENT

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Solim S. W. Kwak
10 May 2007

INTRODUCTION

In May 2004, the United States Army Defense Ammunition Center (DAC) hosted a Joint Technical Consultation Meeting (TCM) to review and discuss the Construction Technical Data Package (TDP) for the United States-Republic of Korea (US-ROK) Joint Munitions Demilitarization Facility (DEFAC) that will be established in the ROK. The meeting was attended principally by the engineering staffs from the Ammunition Equipment Directorate (AED), Tooele Army Depot (TEAD); the Republic of Korea Ministry of National Defense (ROK MND); the ROK Agency for Defense Development (ROK ADD); the US Army Pacific Command (USARPAC), the Joint Munitions Command (JMC) Project Manager for Pacific Demilitarization Program; the Product Manager for Demilitarization (PM for Demil) and the DAC.

During the 2004 May TDP meeting at DAC, COL Chang Ho-Kyung, ROK MND delegation lead, visited Mr. James Q. Wheeler, the DAC Director. At this courtesy visit, COL Chang discussed two technical issues related to the Joint US-ROK Demilitarization program: the revised timelines for the construction of the ROK Joint Munitions DEFAC and the propellant conversion system that was being developed and validated at DAC for the ROK DEFAC. COL Chang stated his preference for a dry fertilizer over the liquid fertilizer that would be produced from demilitarization of propellants at the Joint Munitions DEFAC. His inquiry was based on the assumption that farmers in Korea are familiar with and prefer a dry fertilizer. Subsequently, Mr. Wheeler requested, Dr. Solim SW Kwak, his Senior Science Advisor, conduct a technology assessment and prepare a report. The report was to contain background information to support a decision for demilitarizing propellants by conversion to liquid fertilizer in Korea, and on the Joint US-ROK Demilitarization Facility (DEFAC) Program concept development. In particular, for the propellant conversion to a liquid fertilizer, his interest was on the technical feasibility, advantages and/or disadvantages of producing a dry fertilizer, and marketability of liquid fertilizer in Korea. In essence, Mr. Wheeler was asking for justifications for the Joint DEFAC Program and the propellant conversion to liquid fertilizer in Korea. It is worthy to note that, in 1998, at the inception of the US-ROK Joint Munitions Demilitarization Program, an initial demilitarization technology integration assessment was conducted by Dr. Kwak (DAC) and Mr. Terry Hackett (JMC). At that time, various demilitarization and disposal options for explosives and propellants were identified and each option was evaluated.

This inquiry for a dry fertilizer stemmed from a luncheon conversation between MG Kwan-Soon Choi, the Director General, Logistics Management Bureau, ROK MND and Dr. Kwak in Seoul in 2002. At that luncheon, MG Choi explained to Dr. Kwak and others that most Korean farmers own small plots and are familiar with using dry fertilizer. MG Choi then asked about the possibility of either directly converting propellants to a dry fertilizer or indirectly converting the liquid fertilizer produced from the demilitarization of propellants at the ROK Join Munitions DEFAC to a dry fertilizer. Dr. Kwak explained to MG Choi that the direct conversion of propellants to a dry fertilizer might be difficult for a variety of reasons, but that it is theoretically possible to convert the liquid fertilizer to a dry fertilizer. Dr. Kwak further explained to MG Choi that it would require time and considerable resources to research and develop a conversion technique for converting the liquid fertilizer to a dry fertilizer. It should be noted that this 2002 discussion in Seoul was not a formal request from MG Choi and Dr. Kwak's response was not a commitment on behalf of the US on this subject. No formal communications existed between the US and the ROK governments on this issue.

This report has two parts. The first part reviews the development of the Joint US-ROK Demilitarization Program concept. The intent of this first section is to familiarize readers with how the joint munitions demilitarization program concept was conceived and developed. This section contains (1) Executive Summary, (2) Introduction, (3) Joint Munitions DEFAC (DEFAC) Program Concept Development (historical background), and (4) The status of the US-ROK Joint Munitions DEFAC. The second part of this report contains technical discussions associated with the production of fertilizers from propellants. It contains (1) Evaluation of options for propellant disposal, (2) Farming and liquid fertilizer in Korea, (3) Fertilizer from propellant studies, (4) Dry fertilizer from propellant, (5) Liquid fertilizer from propellant, (6) Summary of concluding analyses, (7) Recommendations, and (8) References. A summary of this report, titled Executive Summary, is included at the head of this report before the acknowledgment. The purpose of the executive summary was to condense the report for the readers that are with busy schedules and limited times.

DEFAC PROGRAM CONCEPT DEVELOPMENT

Since the late 1950s, under the Mutual Logistics Support Agreement (MLSA), the United States has pre-positioned, and continues to store, a large quantity of conventional munitions in the ROK. A recent survey shows that there are over 150,000 short tons of munitions in the JMC demilitarization candidate stockpiles in the ROK. Today, these aging or obsolete munitions require disposal or demilitarization to free up the valuable storage space for the more advanced high technology munitions. Execution of the maintenance or demilitarization of the US ammunition in the ROK is governed under the Single Ammunition Logistics System-Korea (SALS-K) Agreement. Under this agreement, the excess or aging US titled ammunition are to be retrograded to the US or destroyed in the ROK when no longer wanted. The cost of retrograding these conventional munitions to the US would be significant. In addition, the SALS-K agreement stipulates that in the event of retrograde for other than to demilitarize, the US may have to compensate the ROK for the past storage, land use, and security that the ROK provided. This cost could be substantial.

For the US and the ROK, the mutually beneficial disposition principle for these aging munitions is to jointly demilitarize them in the ROK rather than to retrograde them to the US and demilitarize. It is believed that this joint demilitarization effort would benefit both the US and the ROK. The US will demilitarize its aging assets locally with a considerable cost savings and the ROK will acquire a modern demilitarization facility, technologies and capability that will enable the ROK to demilitarize the aging ROK munitions. Notwithstanding the obvious benefits, the ROK MND (through MG Lee, BG Jong, MG Kim, and MG Choi over the years) has expressed their concerns for the potential environmental contaminations and impacts arising from demilitarizing the large US and ROK ammunition inventories at the Joint Munitions DEFAC in Korea. To address these ROK environmental concern, the JMC/DAC team (Mr. Terry Hackett of JMC and Dr. Solim Kwak of DAC) proposed a strategy of establishing a modern, comprehensive, non-polluting, closed-loop, and integrated demilitarization facility in Korea. When established and become fully functional, the new facility will demilitarize munitions safely and effectively using the highest explosive safety and environmental standards. All explosive-containing waste streams resulting from the demilitarization operations at the Hwang-Gan DEFAC will be treated, so that theoretically no pollutants will be released into the ROK environment.

Based on this munitions disposition principle, an agreement was negotiated and the Memorandum of Agreement (MOA) for Construction, Operation and Maintenance of a Joint Munitions DEFAC in Korea was formally signed, in 1999, by the USFK and ROK MND representing their government. This original 1999 MOA was renegotiated to enhance and improve the language and contents of the agreement. A revised MOA was signed in 2003. The revised MOA, in its Preamble and Purpose Chapter, states that a joint munitions DEFAC is to be established in Hwang-Gan, Korea to demilitarize the obsolete, unserviceable, and unwanted US titled munitions stored in the ROK, as well as the ROK titled munitions in a manner other than the open burning and open detonation (OB/OD) method. The 2003 MOA defines that the ROK MND will provide the land and utilities, as well as design, construct, operate, and maintain the new Joint Munitions DEFAC, and that the US will provide the Ammunition Peculiar Equipment (APE) demilitarization systems and the explosives wastes and explosives-contaminated waste streams treatment technologies.

It must be noted here that, today (as of April 2007), both the US and the ROK agreed, and the ROK is ready, to proceed with the facility construction under a newly established MILSA IAs (Mutual Logistics Support Agreement Implementation Arrangements) while the basic 2003 MOA is being renegotiated and revised for approval/concurrence by the US Department of Defense and the US State Department.

HWANG-GUN DEMILITARIZATION FACILITY

1. DEFAC Site and Surrounding Communities

A number of candidate sites including Jechon, Kumho, Yunchon and Hwang-gun in Korea were considered for the new Joint Munitions DEFAC site. In 1998, the ROK MND/ROKA, assisted by a team of ammunition and safety engineers from the USA, selected Hwang-Gun in the Chungcheon Buk-do Province near the Ammunition Depot 8 (AD-8) as its new DEFAC site. The Hwang-Gun DEFAC site has limited access, surrounded by steep and heavily forested hills, and is relatively isolated from major metropolitan areas. The Hwang-Gan site is surrounded by 17 small farming communities of villages and small towns. The main crops farmed in the surrounding areas of the DEFAC are rice and ginseng.

2. Integrated Demilitarization System for DEFAC

From the very inception of the US-ROK Joint Munitions Demilitarization Program, both the US and the ROK focused on transition and application of modern demilitarization and treatment technologies based on an established and proven demilitarization policy in the US: the "Resource Recovery and Recycle (R3)" concept. In the US, under this concept, munitions items designated for disposal were considered as valuable assets rather than liabilities, and the energetics and the components of munitions are recovered and recycled when cost effective. Many alternative demilitarization technologies were developed to maximize this concept and to reduce the traditional munitions demilitarization by OB/OD method. For instance, an explosives melt-out technology, Autoclave, was developed by the US Army to recover and reuse explosives from bombs and projectiles. Other examples are the development of a flashing furnace system in which the empty projectile and bomb bodies (recovered from melt-out or washout operations) were thermally treated, by burning off any esidual explosives, allowing the clean scrap metal to be recycled, and the development of a cost effective process for converting white phosphorus to commercial grade phosphoric acid.

When fully established, the demilitarization operations at the Joint Munitions DEFAC will include the carefully selected energetic materials reclamation systems and waste treatment technologies. The two core and most fundamental demilitarization systems being provided by JMC for the Joint Munitions DEFAC in Korea are the Ammunition Peculiar Equipment (APE) 1401 Autoclave Melt-out system and the APE 2048 Flashing Furnace. These two core demilitarization systems are the standard and fully proven US demilitarization systems being managed by the Demil/APE Management Division, Logistics Integrated Directorate, JMC. Each APE system is equipped with a pollution abatement system. The waste stream treatment technologies for treating explosive wastes or contaminated wastes are being provided by DAC. These production scale prototype technologies were collaboratively conceived, developed, engineered, constructed and test validated by DAC partnering with the commercial demilitarization industry (such as GA, MSE and ARCTECH) and the National Defense Research Laboratories (such as Livermore, Sandia and Los Alamos). The three explosive wastes and explosives-contaminated waste treatment technologies selected for the US-ROK Joint Munitions DEFAC are the Molten Salt Oxidation (MSO) System for treating, by destroying the explosive, contaminated solids; the Supercritical Water Oxidation (SCWO) system for treating, by oxidizing pollutants at a supercritical condition, pink water; and the Demilitarization of reclaimed propellants, by a Humic acid enhanced hydrolysis, for converting propellants to a liquid fertilizer (PCF).

The US provided integrated demilitarization system, when operated in accordance with established explosive operation standards and standard operating procedures will not pollute or harm the environment at the facility from any contaminations resulting from operating the DEFAC. Each demilitarization system and explosive wastes treatment system has a comprehensive, sophisticated, automated monitoring and a data logging system that monitors and records the concentration of toxic contaminants in its effluents.

3. AMMUNITION PECULIAR EQUIPMENT (APE)

The Joint Munitions Command (JMC), that manages the Pacific Demilitarization Program, selected three major APE demilitarization systems as core technologies for the Joint munitions DEFAC in Korea. They were the APE 1401 Autoclave Melt-out system, APE 2048 Flashing Furnace and APE 1236 Deactivation Furnace.

APE 1401 - The APE 1401 Autoclave system was selected to remove and recover TNT and Comp B explosives from projectiles and bombs. The major subsystems include the steam heated melt-out kettles in which explosives are melted out of the projectile bodies, the molten explosives collection system consisting of a transfer manifold and a melt collection kettle, and a Belt Flaker System on which the molten explosives are chilled and solidified into thin flakes.

APE 2048 - The empty casings from the autoclave melt-out process are often contaminated with small amounts of residual explosives. These minute residual explosives on the metal casings are thermally oxidized and destroyed in the APE 2048 Flashing Furnace. The pollution abatement system for the APE 2048 Flashing Furnace consists of an afterburner, a cyclone and a baghouse.

APE 1236 - The small caliber ammunition and other munitions components will be destroyed by incineration in the APE 1236 Deactivation Furnace System. The system consists of a rotary kiln retort, a feed conveyer, an afterburner, high and low temperature gas coolers, a particulate removing cyclone, a baghouse, and an induction fan. The US will also provide the front end disassembly equipment such as the APE 1001 Pull Apart Machine, APE 1042M3 Debanding Machine and APE 1106M2 Deprimer Machine.

These three technologies have proven to be the most reliable demilitarization equipment at a number of military demilitarization facilities in the US.

In 2003, the APE 1236 Deactivation Furnace was removed from the list of equipment provided by the US. Both sides agreed that the ROK MND would procure and install an APE 1236 equivalent furnace system with a wet scrubber for the Hwang-Gun Joint Munitions DEFAC operation.

4. Explosives Contaminated Waste Streams

From the inception of this Joint Demilitarization Program and on several occasions during the US-ROK Demilitarization

Joint Technical Consultation meetings held in Seoul, Korea, the ROK MND representatives repeatedly expressed concerns for the potentially harmful impacts on their environments from a large production scale demilitarization operation in Korea. This deep concern stems from the fact that lately the Korean public has become keenly aware of its polluted environment brought on by rapid industrialization and the public is especially sensitive to polluted streams and rivers. The idea of discharging untreated pink water into their streams and rivers is not an acceptable option in Korea today.

The US suggested that there would be adequate pollution control systems as an integral part of each APE system. Both the US and the ROK agreed that the proposed new ROK Joint Munitions DEFAC would be a modern, comprehensive, closed-loop, non-polluting, and fully integrated demilitarization facility. This new US-ROK joint demilitarization facility is to be capable of not only efficiently demilitarizing various munitions but also will be able to effectively treat all explosives contaminated waste streams (i.e., gas, liquid, and solid wastes), and propellants that would be generated from the demilitarization operations at the new facility. For example, the ROK Joint Munitions DEFAC will have a treatment system for the pink water from the autoclave explosives melt-out operations. The autoclave explosive melt-out operations will produce both explosives particles and pink water. Pink water contains dissolved explosives and it will be treated before discharging into the ROK environment.

5. Explosives Contaminated Waste Treatment Technology

In the US, beginning in the 1980's, under an Office of the Secretary of Defense Demilitarization Research and Development (R&D) Program that was managed by the DAC, a number of significantly advanced and new explosives contaminated waste treatment technology R&D efforts were jointly conducted among the military service laboratories, national laboratories, industry, academia, and DAC. For example, Supercritical Water Oxidation (SCWO) technology for treating explosively contaminated liquids was independently researched at the Sandia National Laboratory, General Atomics and Aerojet under DAC guidance. Molten Salt Oxidation (MSO) technology for treating explosively contaminated solids was collaboratively developed by the Lawrence Livermore National Laboratory and the Naval Surface Warfare Center (NSWC), Indian Head. The propellant conversion technology for demilitarizing reclaimed propellants was researched independently by ARCTECH and TPL. A propellant conversion system was collaboratively designed, engineered, constructed, and tested by ARCTECH and DAC. The biodegradation technology for treating the energetic materials and contaminated wastes was developed by the U.S. Air Force at Tyndall AFB under DAC guidance. The sunlight catalyticphotolysis technology for treating explosive contaminated wastes was jointly researched by Oklahoma State University (OSU) and DAC.

6. Analysis of Joint Munitions DEFAC Waste Streams

a. Propellants - When constructed and fully operational, the ROK Joint Munitions DEFAC will demilitarize approximately 45 tons of 105 mm projectiles per shift-per day and subsequently will produce approximately 3 tons of double base propellants per single shift working day.

b. Pink Water - The sources of "pink water" are the steam condensates from the autoclave melt-out kettle and the scrubber liquid from the explosive fume scrubber. In addition, the water from the floor and equipment wash-down operations will contain substantial amounts of dissolved explosives as well as explosives particles. When projectiles and bombs with Comp B are melted-out, its pink water will contain dissolved TNT and RDX. Normally, at room temperature, the concentration of the dissolved explosives in "pink water" is less than 10,000 ppm. At the ROK DEFAC, the autoclave meltout system will generate approximately 7,000 gallons of waste water per day containing dissolved and suspended explosives.

c. Solid Wastes - Explosives waste and explosives contaminated charcoal, explosives sludge, solid explosives particles, and enriched pink water are also generated each day at the Joint Munitions DEFAC. Some explosives chips and crumbs are produced from flaking and boxing operations. The explosives-contaminated activated charcoal and flocculent will be collected from the charcoal columns and settling tanks of the conventional pink water treatment system. Explosives contaminated resins will be collected from the deionized water and the water treatment system for the SCWO system. The sludge contaminated with explosives and propellants will be collected from the sump, the wet scrubber and the settling tanks. The explosive contaminated oil-water emulsion mixture will be produced from the oxidant supply compressor system. Some small amounts of solid explosive particles will be collected from the threads and the inside surfaces of projectiles and bombs during the final visual inspection after the items are de-kettled. The US-ROK Joint Munitions DEFAC will produce approximately 7.2 pounds of solid wastes each hour.

7. Demilitarization/disposal of Explosives Wastes at DEFAC

a. Propellants - The reclaimed propellants will be demilitarized by an advanced humic acid enhanced alkaline hydrolysis conversion process to a liquid fertilizer. Eight hundred gallons of a concentrated liquid fertilizer will be produced from each ton of propellants processed. The conversion process will not produce hazardous wastes.

b. Pink Water - Pink water will be processed through a combined treatment system consisting of a conventional water treatment system and a SCWO system. The conventional waste treatment system at Joint Munitions DEFAC contains settling tanks, filtration systems, and carbon absorption columns. This baseline technology is effective for removing the suspended solid explosives from waste streams and for reducing the concentration of dissolved explosives in the processed water. The residual explosives in the treated water will be completely destroyed by processing through the SCWO system.

The clean water is recycled to the boiler as feed water to generate working steam.

c. Contaminated Solids - The explosive contaminated solid wastes will be prepared and destroyed in the MSO system.

d. Operation Data - Use of these three advanced waste treatment technologies as an integrated system at the Joint Munitions DEFAC marks their first production-scale integration. Because this is the first time the three explosives waste treatment technologies are being integrated with the standard APE systems, empirical operational data will be collected during operation of the Joint Munitions DEFAC. Such data will be invaluable to the US in furthering the development and application of these technologies in demilitarization. Collaboratively, the scientists and engineers from JMC, DAC, TEAD, and ROK ADD will collect and analyze the empirical data from the Joint Munitions DEFAC operation for the destruction efficiencies, feed rates, operational parameters, and interfaceability with other standard demilitarization systems.

8. Overall Design Consideration

The proposed Hwang-Gun DEFAC demilitarization system will be a non-polluting and closed loop, integrated demil system. The following proactive approaches will be incorporated in designing the Joint Munitions DEFAC to minimize or eliminate the release of any contaminants into the environment.

The overall integrated demilitarization system design would: (1) include provisions for control of emissions, (2) incorporate spill or release contaminants, thereby preventing any potential discharge, (3) institutionalize rigorous operator O&M procedures trainings, (4) establish safe and appropriate management for any accidental spills and discharge, and (5) establish, if possible, a baseline site contamination by conducting the initial environmental survey at DEFAC site. Furthermore, the Standard Explosive Safety Protocols mandate that, (6) when incidents occur where explosives are being handled, the explosives operations would be suspended until the explosives spills are cleaned up, repair to the faulty equipment is made, the incidents are independently investigated, the explosives safety SOP is approved by the impounded Explosives Safety Investigating Panel. Explosives operations would be restarted only when the independent safety review board is satisfied.

9. Integrated Mass Flows

A simplified integrated demilitarization mass flow schematic chart is provided at the end of this section (refer the mass flow chart, Figure 1, with reading). The munitions to be demilitarized are delivered to the Disassembly Operations room and disassembled. This disassembly operation includes depalletizing, debanding of the rotating band, removal of propellants, and removal of fuze to get the munitions ready for the autoclave explosive meltout operation. The prepared munitions are loaded into the Autoclave Meltout Kettles. Steam at 15 psi is turned on to heat munitions outside skin. The heat thus transferred into the munitions causes the explosives to melt and flow out of the munitions into a molten TNT collection system.

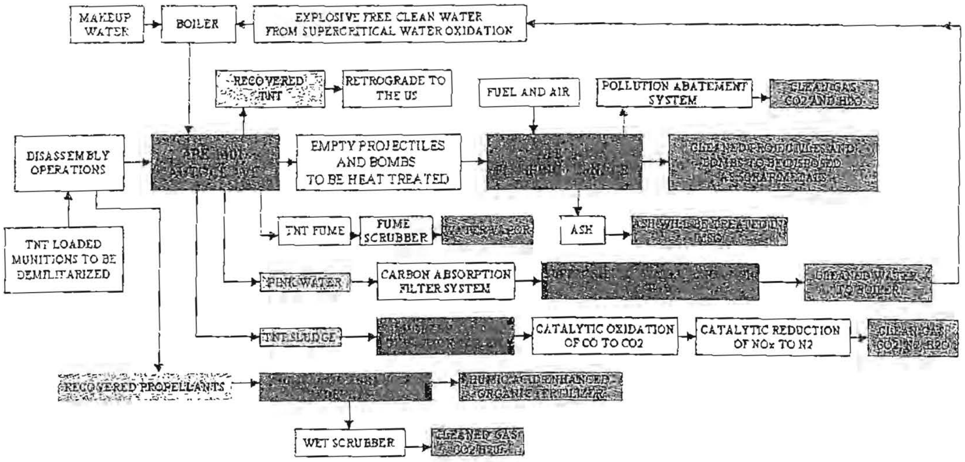
The Autoclave meltout operation produces three waste streams and one byproduct. (1) One of the three waste streams is the TNT fumes, which will be collected and treated through a TNT fumes scrubber. This scrubber absorbs the TNT fumes such that clean effluent without the presence of any TNT fumes is released into the air. (2) The second waste stream is pink water (TNT dissolved in steam condensate), which is processed through a series of activated charcoal filters in which the dissolve TNT is removed from the effluent stream. The TNT breakthrough concentration point is 2ppm. The effluent from the carbon filters is further processed in the Supercritical Oxidation (SCWO) System, which is operated at 3600 psi and 900 degrees C in which all TNT and TNT fragments are completely oxidized. The resulting clean water is recycled to the steam boiler to generate more steam for the APE 1401 autoclave system. (3) The third waste stream is the TNT sludge and explosives contaminated wastes, which will be processed in a Molten Salt Oxidation (MSO) System. The TNT sludge and explosives wastes will be oxidized in the molten sodium carbonate/potassium carbonate bath in the MSO reactor that is operated at 890 degrees C. The oxidation gases are processed first through in a catalytic oxidation system where carbon monoxide (CO) is oxidized to carbon dioxide (CO2), and then processed through a second catalytic system in which nitrogen oxides is reduced to nitrogen gas. The cleaned gas consisting of nitrogen gas and carbon dioxide and water is then released into the atmosphere.

The munitions items that were processed through the Autoclave meltout may still have some small amount of residual TNT in its cavity or on its threads. To be safely disposed in accordance with applicable safety requirements, these items must be thermally treated in a flashing furnace. The munitions items are loaded on a car bottom platform and pushed into the APE 2048 Flashing Furnace chamber where the items are cooked at 1600 degrees F for over 30 minutes to oxidize the residual TNT completely. The combustion gas is processed through an afterburner to complete the oxidation process. The effluent gas from the afterburner will go through an additional standard pollution abatement system consisting of a particulate removal cyclone and a baghouse. The thermally-treated munitions items now can be disposed safely as clean certified scrap metals.

The reclaimed TNT is tested for moisture content at the Joint Munitions DEFAC Operation Support Laboratory. Dry TNT product will be packaged to be shipped to the USA to be reused.

The reclaimed propellants will be demilitarized using a USA patented Humic acid enhanced hydrolysis process. The hydrolysis process will convert the propellant grains to a humic acid rich organic liquid fertilizer concentrate. The product will be removed from the Joint Munitions DEFAC site regularly every two days to a Korean fertilizer company to be reformulated for final disposition. The gas from the hydrolysis process consisting of ammonia gas and NOx will be scrubbed out through an alkaline/acid wet scrubber system. Ammonia gas will be scrubbed with phosphoric acid and NOx gas is scrubbed with a KOH solution. The neutralization end products from the scrubbing actions will be mixed in with the fertilizer products. This is possible because potassium nitrate and ammonium phosphate are the commercially available fertilizers. The clean gas from the scrubber is carbon dioxide and water. Analytical operations support at this laboratory will be jointly managed by Dr. Park and Dr. Kwak.

SIMPLIFIED INTEGRATED DEMIL TECHNOLOGY AT DEFAC (US PROVIDED)



NON-POLLUTING AND CLOSED LOOP
DEMIL TECHNOLOGY INTEGRATION FOR
US-ROK JOINT MUNITIONS DEMIL FACILITY
DR. SOLIM SW KWAK
SENIOR SCIENCE ADVISOR
US ARMY DEFENSE AMMUNITION CENTER
27 FEBRUARY 2006

EVALUATION OF OPTIONS FOR PROPELLANT DISPOSAL

The 2003 MOA states that all products, byproducts, and residues from the demilitarization operations at the ROK Joint Munitions DEFAC are the responsibility of the US. The intent of the Joint Program is to locally dispose all demilitarization byproducts in an environmentally acceptable manner. Effective disposal of propellants poses a unique challenge. Some of these propellants are unstable and dangerous due to the depletion of necessary quantities of stabilizers in the propellants. Innovative and effective demilitarization techniques will be required for the proper disposition of these propellants. Nine potential disposal and demilitarization options for the reclaimed propellants at the ROK Joint Munitions DEFAC were evaluated. Each option is described in the following paragraphs.

1. Retrograde/Long-term Storage of Recovered Propellants

The reclaimed propellants generated at the ROK Joint Munitions DEFAC can be retrograded and demilitarized in the US. Retrograding the 6,250 tons of loose reclaimed propellant grains to the US will be a challenging undertaking. It could be unsafe and would be expensive. The recovered propellant would require a periodic testing for the remaining effective stabilizer level to ensure the continued safe handling and storage. Long-term storage of the reclaimed propellants in Korea is another option if such storage space is available. Long-term storage of the reclaimed propellants would require a large storage facility in Korea. Any new magazine construction

Requirement for ammunition would be considered a serious issue in Korea, and in particular, construction of new magazines for reclaimed propellant would be difficult. It would be contrary to the primary purpose of the Joint US-ROK Demilitarization Program to free up existing storage spaces in the ROK.

2. Land Burial and Dumping of Propellants

In the past, particularly at the conclusion of WW II, some obsolete and excess ammunition was disposed of by landfill or sea dump in the oceans. This practice is no longer allowed in the US or in the ROK.

3. Thermal Disposal of Propellants

Propellants can be destroyed by open burning. Open burning used to be an established and widely accepted demilitarization method in the US. The destruction of propellants by open burning method is relatively simple, safe and cheap. Because open burning of propellants is simple, safe, and economical, starting in the 1950s and until recently, tens of millions of pounds of excess and obsolete propellants were disposed by this method at a number of military as well as commercial demilitarization facilities in the US. An external ignition source causes the ignition of propellants, and once ignited, propellants burn self-sustained but uncontrolled until they expire. Historically, open burning operations were conducted either in pits or in an open land surface area. Recently, burn trays have been developed to better control the burning process as well as contain any leftover residues. Increasing environmental concerns and restrictions have limited the practice of open burning, and at many military installations, production scale open burning operations have been limited except for emergency purposes. Currently in the US, the open burning of propellants is permitted at several of the demilitarization facilities including the McAlester Army Ammunition Plant (MCAAP). Similarly, in Korea, under the existing SALS-K agreement, the ROK Army is allowed to open burn small batch quantities of propellants generated from maintenance or demilitarization operations. Open burning of propellants as a production scale demilitarization operation is prohibited in Korea.

Explosives, propellants and contaminated wastes can be destroyed by incineration in a furnace. An incineration furnace uses large amounts of heat and excess air to oxidize the hazardous energetic materials. Dry propellant grains can be incinerated in a furnace. Since dry propellant grain burns fast and hot, the overall throughput would be severely limited. An advanced safer feed system for introducing dry propellant to a furnace would need to be developed. Slurried propellant can also be incinerated in a furnace. However, the burning of propellant slurry in a furnace would be expensive. The feed rate would be slow due to the large amount of water (up to 80%), which must be evaporated. Some propellants contain heavy metal compounds such as lead carbonate as a burn rate modifier. Incineration of propellant containing metal burn rate modifiers would pose a challenge as well because the stack emissions would contain metals, which would have to be scrubbed and properly disposed. Burning the propellants with heavy metal burn rate modifiers in a furnace is not advisable. In the ROK, the incineration of propellants would be classified as destruction of hazardous waste and consequently the operation would be strictly regulated. Obtaining an operation permit for a propellant incinerator would be time consuming and would be a rigorous process. In addition, the ROK public opposition to incineration can be significant. Thus, fundamentally, incineration of propellants is not practical.

4. Alkaline Hydrolysis of Propellants

The chemistry and process mechanics of alkaline hydrolysis of propellants is well established, although the full characterization of products in hydrolysate is difficult and is not fully understood at this time. Propellants are hydrolyzed in a warm concentrated caustic solution. The hydrolyzed material is a dark caustic liquid. The caustic product is then neutralized with an acid to produce a hydrolysate, a pH neutral fertilizer material. It is known that toxic compounds such as cyanides and formates are detected in the hydrolysate from the alkaline hydrolysis of propellants. The hydrolysis of propellants produces nitrous oxide as a gas byproduct. Buelow reported that the hydrolysate from propellant contained formate, oxylate, cyanate, propionate, urea, nitrate, nitrite and carbonates in concentrations ranging from 860 to 6,900ppm when a triple propellant (M31A1E1) was reacted with sodium hydroxide at 93 degrees C. and most of the nitrogen was converted to nitrous oxide (N_2O) and given off as emission gas. Post treatment for the final disposal of the products of the hydrolysis is not easy. In practice, the hydrolysate from the alkaline hydrolysis of propellants is neutralized with acid and the resulting neutralized product is destroyed by secondary disposal techniques such as SCWO or a biodegradation process. Often the secondary treatment technology is much more complex and expensive than the hydrolysis itself.

5. Reformulation to New Propellants

It is possible to reformulate old propellants into new propellants. The reformulation process would be a multi-step process. First, the old propellant must be characterized. Second, the old propellant would have to be size reduced by grinding. Then new chemical ingredients and solvent are mixed with the ground propellant to produce a homogenous mixture. Rolls of propellant carpet would be produced from which the new propellant grain can be extruded. From an explosives safety viewpoint, the grinding of propellant, wet or dry, is an extremely hazardous operation. A reformulation operation at the ROK Joint Munitions DEFAC would require a heavy capital investment by the US and the market for the reformulated propellants in Korea is uncertain. Further, the new propellant will require an extensive re-qualification test and would require rewriting of the military specification for using the reclaimed propellants.

6. Flashless Powder

Reformulating reclaimed propellants into gunpowder for hunting guns is possible. A process being developed is to grind the propellants, reformulate, and load it into cartridges for use in sport hunting. This reuse option requires the propellant to be dry ground, which can be a dangerous operation. In the US, the direction of this propellant recycling effort has evolved from sportsman gunpowder to a more specific special operations end use. Propellant reuse for Flashless (smoke-less) powder R&D effort has shown that the powder exhibits unique characteristics not founded in conventional commercial small arms. This technology is currently under going small-scale experiments and the process has been validated for scale up in the US. In Korea, gun ownership is strictly regulated, hunting sports are limited and the market for gunpowder is uncertain and doubtful. Further, the sportsman gunpowder remanufacturing process would require a large US investment at the ROK joint munitions DEFAC and ultimately the US government liability issues in Korea must be seriously considered.

7. Gel Blasting Explosives

Gel blasting explosives are produced for the mining and quarry industry. The gel blasting explosives market in the US is well established. Propellants can be reformulated into gel explosives. The technique for converting propellants to gel explosives is mature, and is an attractive propellant recycling method. Reformulation would be required because the chemical compositions of the military propellants are different from the commercial gel explosives. Typically, the commercial gel explosives contain ammonium nitrate, perchlorates, nitrocellulose, nitroglycerin, sulfates and other chemical ingredients. Due to the expanding economy and booming construction, there should be a very active quarry industry in Korea. TPL Inc., a gel explosives manufacturer in the US, indicated that it can not meet the demands of the commercial gel explosives market.

The concern is whether the quarry industry in Korea can absorb the six (6) tons of gel explosives produced each day. In Korea, gel explosives from propellants must compete with and penetrate the existing commercial gel explosives market. This could be difficult. The gel explosives must compete with common blasting explosives such as ammonium nitrate (AN). Typically, AN is sold at approximately $0.50 per pound, which fluctuates depending upon the price of petroleum and natural gas. Gel explosives would be an alternative option for propellants only if they are priced below that of AN. Also, gel explosives can be produced from propellants containing lead or perchlorates. There is a concern for the long-term adverse impacts on humans and the environment due to lead and perchlorate residues remaining from incomplete detonation of gel explosives made from the propellants containing these compounds.

8. Dry Fertilizer from Propellants

a. Whole Grain and Powdered Propellants as Fertilizer

Nitrogen is one of the essential constituents of fertilizers. The main constituent of propellants are nitrogen-containing organic chemical compounds such as nitroglycerin, nitrocellulose, and nitroguanidine. Propellants can be beneficial to plants if the nitrogen from the nitrogen-containing chemical functional groups on propellants can be converted to chemical forms that can be absorbed by plants. Stoller and others conducted feasibility studies of using propellants as a fertilizer. In the study, Stoller and others successfully demonstrated the effectiveness of propellants as fertilizer, measured by assessing the ability of nitrocellulose based propellants to release nitrogen into the soil and utilized by the plants in terms of plant growth height and plant mass increase as well as leaf color and vigor of the plant. The results showed that the height of a representative sorghum receiving single base propellant increased by 26.47% compared to a representative plant of the untreated control lot. Plant growth was also measured in the plant mass increases. The results showed that the sorghum grown on the lot treated with 105 lbs propellant/acre weighed 68% more than the sorghum grown on the untreated lot. For single base propellant, the whole grain propellant gave better growth results than the ground powder propellant. It was found that the nitrogen release rates were better for the pure dry nitrocellulose (NC) then the NC propellants. This test result suggests that it may be necessary to chemically convert nitrocellulose molecules to achieve a controlled rate of nitrogen release. The test results also indicated that the untreated propellant stabilizers such as diphenylamine and ethyl centralite were found to be toxic to plants.

Today, it is doubtful that this method of directly applying untreated propellants to the soils would be acceptable to the explosives safety and the security communities at large. The larger concern is liability. For example, if a farmer in Korea is given or has purchased bags of dry propellant as fertilizer and stored them at his home and there was a fire or detonation resulting in injury or property damage, the farmer will probably hold the US or ROK government responsible for the damages.

b. Peaceful Green Formulation from Liquid Product

Nitrocellulose-based propellants were converted to solid fertilizers by first denitrating propellant by alkaline hydrolysis with potassium hydroxide to a liquid product, then combining the liquid fertilizer product with peat moss, ammonium phosphates and other nutrient chemicals to produce a moist fertilizer. The resulting moist mixture was cured by air-drying to yield a dry fertilizer, the Peaceful Green Formulation fertilizer. Chemical analysis showed that the 11-16-11 Peaceful Green formulation contained 14.56% nitrogen, 26.12% potash, 32.66% phosphate, 15.08% peat moss, and 10.36% urea, 0.02% orthoboric acid, 0.196% copper sulfate, 0.8% iron, 0.154% manganese sulfate, 0.0005% sodium molybdenum tetroxide and 0.05% zinc sulfate. The micronutrients were considered essential for bacteria as well as for plants. Peaceful Green fertilizer from single base propellant was tested by the Department of Agronomy and Horticulture at the New Mexico State University. The test results have shown that the chemical treatment of propellants by a KOH alkaline hydrolysis greatly improves the performance of nitrocellulose and single base propellant. The experimenters concluded that this improved fertilizing ability is due to release of nitrogen from the nitrocellulose during the alkaline hydrolysis chemical reactions. They also determined that dinitrotoluene and diphenylamine in single and double base propellants clearly showed phytotoxicity caused by the presence of these stabilizers. The Peaceful Green Formulation Fertilizer was test marketed in New Mexico and California.

c. Conclusions from Stoller Studies

The results from the second study showed that the whole grain, un-reacted NC, and unreacted double based propellants were not as effective as the hydrolyzed propellant fertilizer. It is somewhat contrary to the results from the first study where it was shown that the whole grain propellants did exhibit good fertilizing characteristics. It is fundamental to understand that the nitrogen in the propellants is not free nitrogen. The functional group of nitro and nitro esters are covalently bonded onto the long chain hydrocarbon molecules, and there is no known mechanism by which the plants can utilize the nitrogen of propellant directly as nutrients. It requires a chemical process to break down the molecular structure first, to free up the nitrogen that is useful to plants. The nitrocellulose based propellants can be converted for use as fertilizer by hydrolysis. The alkaline hydrolysis with potassium hydroxide was found to convert all of the nitrogen from nitrocellulose into a form available for plant nutrition. The results suggest that it will be necessary to ensure that the hydrolysis product of dinitrotoluene is not toxic or hazardous. Nitroguanidine, as found in triple base propellants, does not make a good fertilizer and cannot be reformulated. The Stoller report concluded that there exists a specialized market in amateur vegetable and flower gardening for a Peaceful Green Fertilizer formulation.

9. Liquid Fertilizer from Propellants

a. Conversion Process - The humic acid enhanced alkaline hydrolysis is a chemical conversion process, which causes the permanent and irreversible demilitarization and destruction of propellants. The process converts propellants to a liquid fertilizer by breaking down the propellant into nitrates, nitrites and dissolvable hydrocarbons. The product is a concentrated fertilizer that is rich in dissolved organic matter and nutrients. The nutrients are chelated onto humic acid and slowly released to plants. This conversion process has been demonstrated for demilitarizing single, double, and triple base propellants. The process converts 2,000 pounds of propellants to approximately 800 gallons of liquid fertilizer. Approximately 8,000 gallons of liquid fertilizer were produced during the validation tests by processing 10 tons of single, double and triple base propellants of different compositions and different grain sizes. Tests showed that the product complies with the regulatory limits of reactivity, toxic chemical leaching procedure (TCLP), and universal treatment standard (UTS) parameters, which are required for land application of any fertilizer product.

b. University Studies - Three universities conducted plant growth tests with the humic acid liquid fertilizer from propellants. The greenhouse and nutrient uptake tests were conducted at the University of Nevada. The turf grass studies were conducted at the Virginia Tech State University, and the humic acid fertilizer study was conducted at the University of Minnesota. These university studies showed that the humic acid liquid fertilizer produced from the recycling of propellants is safe and helps increase plant yields and quality. The end product has been characterized as effective in enhancing crop growth, demonstrating its economic value. Separately, ARCTECH reported that the humic acid liquid fertilizer product was distributed to various farmers and ranchers around McAlester, Oklahoma, and was applied to a variety of grasses, corn, soybean and other crops. This land application showed that the application enhanced the growth of crops and the product did not exhibit phytotoxicity.

FARMING AND LIQUID FERTILIZER IN KOREA

It would be helpful to review the farming practices and fertilizer uses in Korea in making a rational assessment. Over the last three decades, Korea has experienced dramatic changes in farming practices as a result of Government supported programs for development and dissemination of improved agricultural technology. The goal of the program was to achieve self-sufficiency in staple foods and to increase farm incomes. Until the 1920s, Korean farmers made little use of chemical fertilizer. Farming mainly depended on natural soil fertilizer and organic manure, with only 21,000 metric tons of chemical fertilizer consumed in 1925. However, at this time, rice yields from paddy fields were less than 1.2 metric tons per hectare. By 1937, 57,000 metric tons of chemical fertilizers were being applied and average national rice yields had increased to two metric tons per hectare.

In the early 1960s, Korea still suffered from a food deficit. With encouragement from government programs, farmers began widespread use of agricultural chemicals for fertilizers, pest management and weed control. In addition, high yielding rice varieties bred by crossing Japonica and Indica types were disseminated throughout Korea, and as a result, average rice yields soared to 4.5 metric tons per hectare. By the mid-1970s, self sufficiency in rice crop was achieved and Korea recorded a surplus in rice production. In the 1980s chemical fertilizer consumption reached almost 700,000 metric tons per year.

However, this dramatic success in agricultural productivity in Korea has resulted in deterioration of the soils through excessive use of chemicals. The Rural Development Administration has carried out a large-scale soil-testing program. The results showed a steady decline of organic matter in the soils since 1936 while the phosphorus content has increased. Excessive use of chemical fertilizers has given rise to salt accumulation. The other adverse impacts being noted are the contamination of aquifer and water sources with nitrates resulting from leaching from residual chemicals in the soils. Today soil management for sustainable agriculture, while maintaining high crop yields, has become a priority in Korea. A number of strategies are being implemented including limiting the use of excessive chemicals and improving productivity with organic fertilizer.

A major shift has taken place from traditional farming to growing high cash value crops. A large infrastructure of plastic greenhouses now exists, particularly in the vicinity of metropolitan areas, to meet the year-round need for produce. In these operations, both solid and liquid organic fertilizers are utilized but with increasing demand for liquid organic fertilizers, which can be applied cost effectively as both foliar spray and soil applications.

FERTILIZER FROM PROPELLANT STUDIES

A literature search for the production of fertilizers from propellants was conducted. Seven published articles, two reports on dry fertilizer and five reports on liquid fertilizer, were selected for analysis. These reports were considered pertinent to the propellant conversion to fertilizers program and merited thorough review and analysis.

DRY FERTILIZER FROM PROPELLANT

1. Stoller, Kidd, McCaslin Study

In 1993, Stoller, Kidd, and McCaslin (Ref 6) published the results of their study titled "Reuse of Nitrocellulose (NC) Based Gun Propellants for Agricultural Applications" at the Nitrocellulose Fines Separation and Treatment Workshop sponsored by Purdue University. The study was conducted under the Phase I Small Business Innovative Research (SBIR) Program managed by the Naval Surface Warfare Center (NSWC), Crane, IN. The investigation was based on the premise that propellants can be beneficial to plants if the nitrogen of the nitrogen containing chemical functional groups on propellants can be converted to a form of chemical that can be utilized by plants.

Two Greenhouse/multi-pot fertilizer application experiments were conducted on sorghum. The first experiment used whole grain and ground single base propellant. The second experiment included single base propellant, pure NC, extracted nitroguanidine (NQ), and other byproducts. The effectiveness of propellant as fertilizer was determined by measuring the ability of propellant to release nitrogen into the soil and by assessing the ability of plants to utilize the released nitrogen. The test results were measured in terms of plant growth height and plant mass increase as well as leaf color and vigor of the plant.

The results from the first study showed that sorghum grown on the lot treated with 105 lb/acre of whole grain single base propellant was 21.5 inches tall while the height of sorghum on the untreated control lot was only 17 inches. This result represents a 26.47% growth increase. However, the height of sorghum grown on the lot treated with 105 lb/acre of powdered propellant was noted to be 19.7 inches tall. This result somewhat contradicts the idea that the powdered fertilizer would provide the nutrients to plants more efficiently than the solid whole grains. For comparison, the sorghum grew 73.53% taller on the lot with urea than the sorghum on the untreated lot. The results also showed that the sorghum grown on the lot treated with 105 lbs/acre of whole grain single base propellant yielded a weight 68% greater than the sorghum grown on the untreated lot. Again, this result was compared with the weight of sorghum grown on the lot with urea weighing 420.59% more than the weight of sorghum gown on the untreated lot.

The conclusions from the first study were that whole grain propellant gave better results than ground powdered propellant, and that the nitrogen release rates were different for single base propellant, pure NC, extracted NQ, and the extracted water. The test clearly confirmed the phytotoxicity effects of stabilizers, ethylcentralite and diphenylamine. It would probably require tailoring the nitrocellulose molecule by chemically converting it to increase the rate of nitrogen release and to increase performance.

2. Kroh and Schilling Study

In 1997, Kroh and Schilling (Ref 7) published their final report titled "Commercial Uses for Reformulated Navy Gun propellants". The study was conducted from December 1993 through June 1996 under the Phase II Small Business Innovative Research (SBIR) Program managed by the Naval Surface Warfare Center (NSWC), Crane, IN. Kroh and Schilling stated that the previous experiments in the Phase I study showed that raw propellants, in whole grain form or in powder form, when added to soil, are highly resistant to degradation by soil and rumen microbes. Consequently, they proposed and conducted a base hydrolysis in the phase II study. Because nitrocellulose is an ester of nitric acid and cellulose (a polyhydroxy compound), base hydrolysis was proposed for removing the nitrate group from the cellulose backbone. Three test materials; pure NC, single base propellant, and double base propellant, were chosen for reaction with hot aqueous KOH. The process produced a dark liquid fertilizer. A dry fertilizer was produced from this liquid fertilizer.

Conversion of nitrocellulose-based propellants to dry fertilizers was accomplished in three step processes. They were (a) denitration of propellant with KOH to liquid product, (b) combination of liquid denitrated product with other materials such as peat moss to make a dry fertilizer with the desired nutrients, and (c) curing into the final product to a solid fertilizer. The propellants were denitrated by reacting with KOH solution in a 150 gallon jacketed stainless steel reactor. Two hundred seventy (270) pounds of propellant were reacted with 70 pounds of KOH dissolved in 20 gallons of water. The reaction temperature was maintained at 96 degrees C. The hydrolysis reaction was exothermic and the hydrolysis product was a black liquid. The resulting hydrolysate was neutralized with mono- and di-ammonium phosphates. Dry fertilizer, Peaceful Green Formulation, was produced by adding peat moss and nutrient chemicals to the partially air-dried hydrolysate product. Specifically, a Peaceful Green Formulation was produced by adding to the hydrolysate 303 pounds of peat moss, 614 pounds of mono- and di-ammonium phosphates, 168 pounds of urea, 12.2 pounds of iron, 3.68 pounds of zinc sulfate heptahydrate, 3.29 pounds of copper sulfate pentahydrate, 2.57 pounds of manganese sulfate hydrate, 1.91 pounds of boric acid, and 9.9 grams of sodium molybdenum tetroxide dehydrate. When mixing was complete, the moist solid fertilizer was spread on the floor to dry and cure. During the air-drying and curing, the peat moss bacteria converted nitrite to nitrate.

An independent analysis of the composition of Peaceful Green Formulation was conducted. The analysis showed that the 11-16-11 Peaceful Green Formulation contained 14.56% organic matter from propellant, 26.12% potassium hydroxide, 16.33%

monammonium phosphate, 16.33% diammonium phosphate, 15.08% peat moss, and 9.54% urea. The amounts of micronutrients found in the formulation were 0.02% orthoboric acid, 0.196% copper sulfate, 0.8% iron, 0.154% manganese sulfate, 0.0005% sodium molybdenum tetroxide and 0.05% zinc sulfate. These trace minerals are essential for bacteria as well as for plants. It is known that in addition to the primary nutrients of NPK, plants require small amounts of certain trace elements.

A series of field tests with a converted solid fertilizer from propellants were conducted by the Department of Agronomy and Horticulture at the New Mexico State University. Experiments were conducted with four groups: The first group received no fertilizer. The second group received urea fertilizer at a 200 pounds N/acre ratio. The third group received the dried fertilizer from propellant at a ratio of 200 pounds N/acre. The fourth group received the dried fertilizer from propellant at a ratio of 400 pounds N/acre. Each group had four plots. After fertilizer application, sorghum seeds were planted. The plants were harvested 38 days later, dried, and weighed. The weights of the dried sorghum grown on the test plots receiving no fertilizer were 2.0 pounds, 2.1 pounds, 1.9 pounds, and 2.0 pounds for plot 1, plot 2, plot 3 and plot 4, respectively. The dried sorghums receiving urea fertilizer at a 200 lbs N/acre ratio weighed 1.8, 1.8, 2.3 and 2.3 pounds from plots 1, 2, 3, and 4 respectively. The weight of dried sorghums receiving the dry fertilizer from propellant at a 200 pounds N/acre ratio were 1.8, 1.8, 1.6, and 2.3 pounds from plot 1, 2, 3, and 4 respectively. The weight of dried sorghum from plots receiving the dry fertilizer from propellant at a ratio of 400 pounds for each plot were 1.0, 1.9, 1.2, and 2.1 pounds for plots 1, 2, 3, and 4 respectively. The test results are summarized in Table 1.

Table 1. Summary of Sorghum Growth

Application	Plot 1	Plot 2	Plot 3	Plot 4
No Fertilizer	2.0	2.1	1.9	2.0
Urea, 200 lbs N/acre	1.8	1.8	2.3	2.3
Prop Fertilizer, 200 lbs N/acre	1.8	1.8	1.6	2.3
Prop Fertilizer, 400 lbs N/acre	1.0	1.9	1.2	2.1

Analysis of the test results revealed no significant difference among the treatments. Since the subplots with no fertilizer performed as well as subplots receiving fertilizer, it can be concluded that the test soil was not deficient in nitrogen to begin with or a wrong soil was chosen for this experiment. The report concluded that the un-treated whole grain nitrocellulose and double base propellant have virtually no fertilizing ability. This conclusion contradicts the conclusion from the phase I study. The results from the Phase II study indicated that the chemical treatment of propellants using potassium hydroxide hydrolysis has somewhat improved the performance of nitrocellulose and single base propellant as fertilizer. The phytotoxicity caused by the presence of dinitrotoluene and dipheylaime in propellants was noted during the study.

The phase II study showed that nitrocellulose base propellants can be reformulated by hydrolysis for use as fertilizer. Alkaline hydrolysis with potassium hydroxide was found to convert all of the nitrogen in nitrocellulose into a form available for plant nutrition. The tests indicated that for propellants containing dinitrotoluene, it would be necessary to ensure that the hydrolysis product is not toxic or hazardous. And Nitroguanidine in triple base propellants would not make a good fertilizer.

The Peaceful Green Formulation Fertilizer was test marketed in New Mexico and California. The report concluded that a speciality market for a reformulated dry fertilizer product from propellants such as Peaceful Green Formulation fertilizer exists for amateur vegetable and flower gardening.

LIQUID FERTILIZER FROM PROPELLANT

The basic chemistry for a humic acid catalyzed base hydrolysis of propellants was invented by ARCTECH. A conversion process system engineering for scale-up, design, construct, and validation test has been performed by ARCTECH and DAC jointly. The efficacy of the liquid fertilizer has been studied by three US universities: The nutrient uptake tests were conducted at the University of Nevada, the phytotoxicity studies were conducted at the Virginia PolyTech State University, and the turf grass (Bentgrass and Ryegrass) growth tests were conducted at the University of Minnesota.

1. Chemistry of Humic Acid Hydrolysis for Propellants

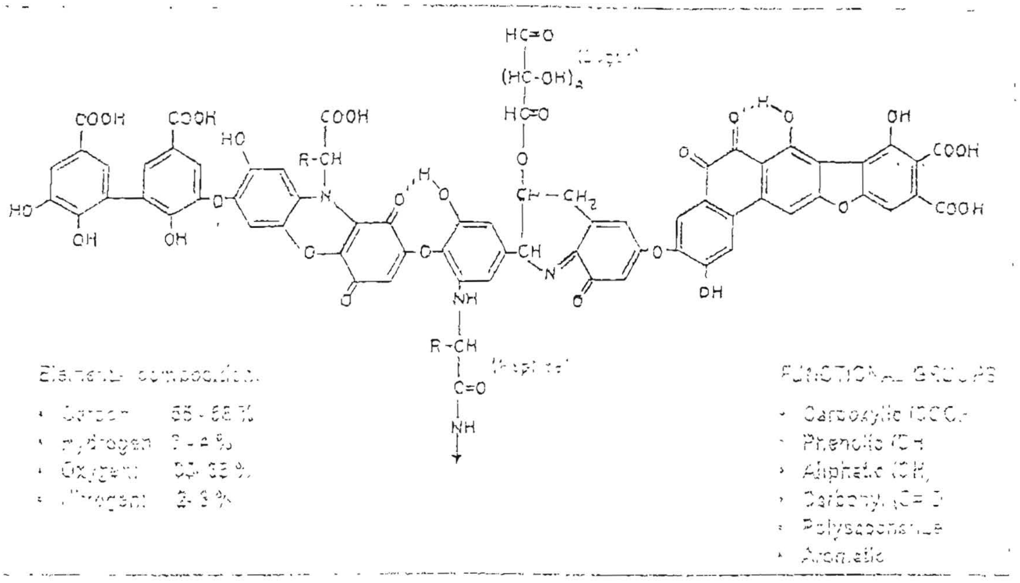
A straight alkaline hydrolysis (base hydrolysis) will break down the larger nitrogen containing organic compounds such as nitrocellulose (NC), nitroquanidine NQ), and nitroglycerin (NG) in propellants to smaller organic compounds such as formate (HCOOX), oxalate (XOOCCOOX), propionates (CH3CH2COOX), urea (NH2CONH2), and cyanate (XNCO). Additional steps are required to complete the destruction of these toxic byproducts, such as by supercritical water oxidation or biotreatment.

It was discovered that a humic acid enhanced alkaline hydrolysis of propellants has a distinct improvement over the straight alkaline hydrolysis. It was found that when propellants were hydrolyzed in the presence of humic acid, the smaller fragment organic compounds were not produced and the result was complete mineralization.

Humic acid (approx C72H60O30N4.30H2O) is a complex organic macromolecule comprised of many aromatic structures linked by alkyl, ether, and similar bridges. The aromatic groups carry substituents such as carboxylate (RCOOX), phenolate (C6H5OX), enolic groups (RHC=CHOH) and alkyl-hydroxyl RCH2-ROH) side chains. It was found that under the alkaline reaction condition of the humic acid hydrolysis for propellants, the smaller carboxylate molecules are produced as a first step. These carboxylate groups react with phenolic and other hydroxyl groups in humic acid and are incorporated into the humic acid molecule as esters. Cyanate and urea are mineralized and adsorbed in the humic acid. If DNT is present, a simple straight alkaline hydrolysis will not completely destroy it. In the presence of humic acid, amines are incorporated as amides by reacting with the carboxylate groups in the humic acid. Thus, humic acid enriched hydrolysis will not produce any toxic byproducts. The hypothetical structure of humic acid is shown in Figure 2.

Figure 2

Proposed Hypothetical Structure of Humic Acid



2. Humic Acid Enhanced Base Hydrolysis Study

Propellants are demilitarized by a humic acid enhanced alkaline hydrolysis. The final product from the humic acid enhanced hydrolysis conversion process is a concentrated liquid fertilizer product that can be safely land-applied as a viable fertilizer material for agricultural applications. No wastes were generated from the conversion process. Gas emissions were captured and recovered through a four tower wet scrubber system. The chemistry of the Humic Acid Enhanced Alkaline Conversion of Propellants to Liquid Fertilizer was invented by Dr. Walia and his group at ARCTECH. The chemistry and process was U.S. patented (Ref 8). In 1997-2004, the Propellant Conversion process was further engineered and developed into a prototype process system and scale-up tested at Hawthorne Army Depot (HWAD) in Nevada and at the McAlester Ammunition Plant (MCAAP) in Oklahoma in collaboration with DAC (Ref 9, 10 and 11).

The process has been demonstrated for the US Army for destruction of single, double, and triple base propellants comprising nitrate esters of various chemical compositions and sizes. The process converts 2,000 pounds of propellants to 800 gallons of liquid fertilizer that is NPK balanced, rich in organic matter and humic acid. Approximately 8,000 gallons of liquid fertilizer material were produced from the validation tests conducted at DAC in McAlester, OK in 2001-2002 by processing 10 tons of single, double and triple base propellants. The test was conducted using the transportable prototype conversion unit with a capacity to process one ton per shift. These tests were conducted at DAC to establish and validate that the process equipment setup was appropriate for the effective processing of propellant to fertilizer. In addition, tests were conducted to establish that operations could be conducted on a continuous basis i.e., several batches continuously to simulate a full-scale facility. The results from the validation tests showed that the process is effective in completely and irreversibly demilitarizing propellants producing a liquid fertilizer material that can be safely applied on the ground. Residual concentration of energetic compounds in all of the tests was insignificant and the destruction efficiencies of these compounds were 99.5%-99.9%, and that the technology is suitable for many single, double, and triple base propellants of different compositions and different grain sizes. The validation tests showed that the conversion process is safe because all reaction activities were conducted at atmospheric pressures and at 190 degrees F, which is well below the boiling point of water and the auto-ignition temperature of the propellants.

One observation that was made during the validation test at DAC with triple base propellant (containing more than 7% ethylcentralite) was that some of the ethylcentralite did not completely hydrolyze. The partially hydrolyzed ethylcentralite that was floating on the top of the hydrolysate in the reaction tank was scooped out and removed. Theoretically, ethlycentralite will break down by hydrolysis. If the hydrolysis reaction had continued for an additional 4-6 hours, then all of the ethylcentralite would have been completely reacted.

The fertilizer product from several test runs has been carefully tested and found to be in compliance with the Toxic Characteristic Leaching Procedure (TCLP), reactivity, and Universal Treatment Standards (UTS) parameters that are required for land application of a recycled fertilizer and/or soil amendment. These parameters are required to be met under the US EPA Munitions Rule, which permits the recycling of propellants to produce a fertilizer so long as the requirements of TCLP, reactivity and UTS are met.

The TCLP is an analytical parameter that evaluates the potential for toxic chemicals to be leached out from liquids that are applied to soils in the environment. The UTS parameters includes a comprehensive list of various toxic metals, volatile and semi-volatile organic compounds that are considered toxic to human health and the environment and specifies a "not-to-exceed" limit for each of those compounds. The reactivity tests measure the amount of HCN gas that can be produced from cyanide ions that may be present in the product.

The liquid fertilizer product was test marketed to various farmers and ranchers around McAlester, Oklahoma. The product was applied to a variety of grasses, corn, soybean and other crops. The product did not exhibit phytotoxicity, and in fact the application of the product enhanced the growth of crops. The application tests showed that the humic acid enhanced liquid fertilizer is not designed to replace commercial fertilizer but rather to enhance its use.

3. Greenhouse Study at the University of Nevada

Greenhouse tests were conducted at the University of Nevada at Las Vegas (Ref 12) on corn and alfalfa with liquid fertilizers derived from single, double, triple base propellants and with a product which was a mixture of each of the three products. A series of inhibitory tests were first conducted to examine for signs of product toxicity by exposing the liquid products from propellants to fifteen dominant bacterial isolates found in desert subsoil in Nevada. Optical density readings of fifteen dominant desert subsoil isolates and E-coli were conducted using a DU65 Spectrophotometer at 600 nanometer. The bacterial concentrations in the subsoil were determined. Bacterial lawns were prepared by inoculating R2A agar plates with 100 microliter (uL) of appropriate concentrations of each enriched isolate. Sterile concentration disks were inoculated with 5 uL of a single liquid product and laid on an inoculated plate in triplicate. This was done for each test concentration of each product for each isolate. Sixteen negative controls were prepared with blank disks. Plates were incubated at room temperature until a lawn formed, and then the plates were examined for zones of inhibition.

The results of these tests indicated that no zones of inhibition were found with any of the product dilutions or the pure liquid product. In fact, in some plates it appeared that the test product enhanced the growth of isolates. It was concluded that the test products have no inhibitory or toxic effects on the desert subsurface soil isolates used in the experiment.

In tests using corn and alfalfa, the seedlings were first grown under a 16-hour photoperiod. When seedlings reached 2 inches in height, they were used for testing. The control sample for the tests was watered with Hoaglands solution, which is a normal conventional fertilizer. The test samples were watered with the Hoaglands solution and the three different application rates of the different liquid fertilizers from propellants. The pH varied between 6 and 6.5. The nutrient solution was renewed every 2 to 3 days to prevent significant nutrient depletion. Measurement of growth rate, biomass production, photosynthesis, stomatal conductance, and chlorophyll concentrations were made to determine the effects of the test products on growth and development of crop plants. Above and below ground biomasses were sampled at sequential harvests. The sampling interval was monthly for the alfalfa study and biweekly for the corn study. Above ground productivity was estimated by adding the increase of the biomass of the leaves, structural tissues and any reproductive tissues during the sampling intervals. Estimates of chlorophyll concentrations in the treated plants were used as a crude indication of nitrogen status. All experiments were conducted three times. Results from similar experiments were normalized and pooled. Standard error rarely exceeded 5% of the mean. Nutrient analysis was confined to NPK as these nutrients are growth limiting for these species.

The results from the tests with corn showed that no phytotoxicity was evident in the plants with which liquid fertilizer product was applied. The product enhanced growth characteristics in plants. The growth characteristics were significantly better with liquid fertilizer products containing organic humus as compared to the control sample irrigated with water or Hoaglands solution. The biomass of the plants increased approximately 4 fold with most of the growth allocated to the shoot, resulting in taller plants and irrigation with the liquid product caused a significant increase in blade length. The results also showed no destructive effects of the products on chlorophyll concentration, no deleterious effects of the products on photosynthesis or conductance were found, and the results of the nutrient analysis at the final harvest indicated that the test products applied nitrogen and potassium to the leaves equivalent to that found in leaves of the control plants.

The results from the tests with alfalfa showed that no phytotoxicity was evident in the plants fertilized with any of the products applied and that dilution of at least 1:25 is required to enhance growth characteristics. The test results showed that during the first and second harvests conducted one month and two months after seed emergence, the biomass accumulation in the plants irrigated with the test products was higher than the control and the chlorophyll concentration in the plants irrigated with the product was higher than that of the control. Uptake of nitrogen, phosphorus, and potassium in the plants watered with the test products were all within the acceptable range.

4. Dosage Response Study at the University of Minnesota

Plant dosage response studies were conducted by the US Department of Agriculture, Agricultural Service, Soil and Water Management Research Unit at the University of Minnesota (Ref 13). The studies were conducted on turf grass (bentgrass and ryegrass) using newly developed laboratory screening techniques for examining growth enhancement of plants. A pouch method adapted from Nelson and Craft (Ref 14) was designed for this study. Three samples, consisting of a mixed liquid fertilizer sample, a treated mixed liquid fertilizer sample which was vigorously mixed to remove any residual volatile organics, and a plain humic acid solution, were tested. The control samples were commercially available fertilizers such as ammonium nitrate, calcium orthophosphate, and potassium nitrate at a NPK ratio of 4:1:4. Growth pouches were 16X18 cm in size. Fifteen ryegrass seeds were placed in the filter paper pocket in each pouch, containing solutions of the test liquid fertilizer samples and control fertilizers. After a seven-day germination period in an incubator at 20 degrees C, the seedlings were thinned to 10 plants for each pouch. Growth chambers were set at 20 degrees C, 16 hours in light and 8 hours in dark. The liquid fertilizer solutions were added to the pouches as required during the growth period. Plants were allowed to grow for three additional weeks before being harvested. At harvest, all plants were removed from the pouch, and shoots and roots were separated and placed into vials. Plant tissues were dried at 65 degrees C, and weighed to measure the tissue mass.

The results of the dose response screening studies showed that at higher concentrations of humic acid, the plant growth parameters (root and shoot weight) were below that of the control. The best results were obtained with the application of the liquid fertilizer samples at a concentration of 50 to 100 ppm of humic acid. The most prominent plant growth parameter impacted by the application of the liquid fertilizer sample was the shoot weight, which was 20 to 300% more than that of the control. Root weights were in general either comparable to or below that of the controls. These studies confirm that the product has to be diluted before any increased effects on plant growth parameters are observed.

5. Turf Growth Study at the Virginia Polytech University

The effect of humic acid liquid fertilizer on turf grasses was tested by the College of Soil and Environmental Sciences at the Virginia Technology University (Ref 15). Two types of turf grass, Poa Pratensis L. (Kentucky Blue grass) and Festuca Arundinacea Schreb (tall fescue) were used for the tests. These grasses were first grown in the field, and then transported to containers, six inches in diameter, filled with a sand loam soil. The control container received 0.675 g of a soluble 20-20-20 commercial fertilizer. The test liquid fertilizer products were applied to each grass species at 3 different application rates, 2.5 gal per acre, 5 gal per acre, and 10 gal per acre. Chlorophyll content and photosynthetic capacity for each of the grass species were determined with a Dual Wavelength Chlorophyll Flurometer. The average of three measurements for each container was subjected to a statistical analysis. Foliage was collected and roots were washed and weighed after drying them in an oven at 60 degrees C for 24 hours.

The results of the plant tests with turf grasses showed that the liquid fertilizer from propellants performed better than the control fertilizer and for both Kentucky Blue Grass and tall fescue, the photosynthetic capacity and the chlorophyll content for all liquid fertilizer tested were either comparable or better than the control fertilizer. For example, with Kentucky bluegrass the photosynthetic capacity with the mixed liquid fertilizer product was 25 % higher than with the control alone, while the chlorophyll content showed an increase of about 16% over the control. The results for tall fescue were an increase of 17% in photosynthetic capacity and 22% in chlorophyll content over the control. The root weights of the samples applied with the liquid fertilizer product were higher than the control. The shoot weights were comparable to the control, and in only some cases higher than the control. The benefits of using the liquid fertilizer from propellants containing humic acid are progressively better over a period of time. There was no phytotoxicity for any of the four products tested.

SUMMARY OF CONCLUDING ANALYSES

In the previous section, nine propellant disposal and demilitarization options were reviewed. The first seven disposal options for propellants were determined not suitable or appropriate for implementation at the ROK Joint Munitions DEFAC. This conclusion is based on the following analysis: (1) Retrograding and long term storage would be excessively costly. (2-3) Land burial, dumping, and thermal destruction by OB/OD are no longer allowed in Korea. (4) Alkaline hydrolysis would require a costly secondary treatment. (5) Reformulation to new propellant would not be safe due to grinding operation. (6-7) Flashless powder and gel blasting explosives would be limited to selected propellants and uncertain gel explosives markets in Korea. The quarry industry in Korea would not be able to absorb the six tons of gel explosives produced each day. These options are summarized in Table 2.

Table 2: Propellant demilitarization methods in ROK

Methods	Suitabilit	Reasons
Retrograde and storage	No	Safety issues; space for storage
Land burial and dumping	No	Not acceptable anywhere in the world
Open burning	No	Prohibited in ROK
Incineration	No	Public opposition
Reformulation to new propellants	No	High cost; uncertain market for new propellants in ROK
Reformulation to flashless powder	No	Liability issues; uncertain market in ROK
Reformulation to blasting gel	No	Higher cost than competing products; uncertain market in ROK
Conversion to fertilizer	Yes	Recommended in the report

The remaining two options, the dry and liquid fertilizers, will be further examined here by considering the critical requirements for explosives and technical complexity for each option.

Three fundamental and critical requirements must be met when producing an acceptable fertilizer from propellants. First, the propellants must be processed in a manner such that all of the military and energetic characteristics of the propellants are destroyed and removed (i.e., fully demilitarized). Second, the resultant product must not exhibit properties of hazardous chemicals, which include ignitability, corrosivity, reactivity and leachability, and should meet the regulatory requirements for application on agricultural lands.

Third, the resultant fertilizer should be effective and capable of being successfully tested and marketed to the agricultural community.

Demilitarization system can be complex or simple. A complex demilitarization system could contain many dependent chemical and mechanical unit operations that are interfaced and interlocked. A complex treatment system requires sophisticated, expensive automation. It would require highly skilled technicians for maintenance and operation. Both the alkaline hydrolysis and the humic acid enhanced alkaline hydrolysis for propellants that will be re-examined are relatively simple processes. Propellants are hydrolyzed simply and safely in a heated tank at atmospheric pressure.

In addressing the issue of producing a solid dry fertilizer from propellants as was requested by COL Chang, ROK MND, I have researched appropriate publications and discussed the issue with recognized experts in the propellant demilitarization community. We have identified only seven published reports and projects that came close to addressing propellant conversion to fertilizer. The first two studies were conducted by Stollar and his group at TPL, Inc. under the SBIR Program sponsored by the NSWC/Crane Division. These two studies produced dry solid fertilizers. The third, fourth and fifth were the humic acid enhanced hyrolysis of propellant conversion studies conducted at HWAD and at MCAAP Plant by Walia and his group from ARCTECH. These three projects were performed to validate the conversion technology and demonstrate the scale up capability. The last three studies were conducted at universities to determine the effectiveness of the liquid fertilizer. It is interesting and significant to note that all eight projects were supported by the Explosives Demilitarization Program managed by DAC. Other than the eight publications listed here, I am not aware of any technical discussions on the topic of propellant conversion to fertilizer that were presented at the Global Demilitarization Symposium or at the Demilitarization Users Group Meetings in the past 8 years. This fact corroborates the lack of other technology or approach for producing a fertilizer from propellants.

Stoller and his group at TPL Inc. investigated the conversion of propellants to produce a solid fertilizer for agricultural use. Highlights from the studies that are relevant to the production of solid fertilizer are reviewed. The first study determined that unprocessed propellants were effective for use as a fertilizer. Double and triple base propellants were found to be toxic to plants because of the presence of stabilizers and burn rate deterrent chemicals in the propellants. The Stoller group established that the nitrogen in the propellants is in a form that cannot be easily absorbed by plants, and therefore has to be chemically converted to make the nitrogen available for plant uptake. The first study concluded that in order to use propellants as a fertilizer, chemical conversion treatment of the propellants would be required. In the second study, chemical treatment of hydrolysis was performed by adding liquid potassium hydroxide to propellants, which then produced a liquid product.

Subsequently, the liquid product from the hydrolysis of propellants was dried to remove some of the water and then supplemented with peat moss and a variety of macro and micronutrients to produce a solid product. The study indicated that the solid fertilizer from chemical processing of the propellants had to be of a certain particle size and carefully formulated to avoid harming the plants. Very small pellets of solid fertilizer made from the alkaline hydrolysis of propellants were found to be harmful to plants because the application of the pellets resulted in a rapid release of concentrated nutrients into the soils, thus burning the plant's roots and shoots. The solid fertilizers, Peaceful Green Formulation, from the conversion of propellants were test marketed in New Mexico and California.

The report suggests that there is no known chemistry to directly convert the dry propellant to dry fertilizer. However, as these studies have proven, it is possible to chemically convert propellants to a liquid fertilizer and then produce a dry fertilizer by evaporating water from each batch of liquid product. Peaceful Green Fertilizer (the 11-16-11 formulation) is a complete fertilizer, containing nitrogen, phosphorus, potassium, and the six micronutrients in amount appropriate for general vegetable and flower gardening. The Peaceful Green Fertilizer process will produce over fifty-five (55) tons of dry fertilizer from converting one ton of propellant. The quantity of the finished product is enormous because of the addition of the large amount of peat to the liquid fertilizer to produce a dry fertilizer. The processing for a Peaceful Green Formulation Fertilizer would be expensive and thus the product would have to be marketed at a much higher price than the commercially available fertilizer.

The humic acid enhanced conversion of propellants to liquid fertilizer is a process that completely and irreversibly destroys the energetic nature of the propellants. The conversion operations are fully automated and a maximum of two personnel are adequate for processing each batch of propellants. The process produces an organic rich humic acid fertilizer, a characteristic that makes it very appealing to farmers. It is important to note that the liquid fertilizer product has met all regulatory requirements for land application. The efficacy of the liquid fertilizer has been subjected to independent studies. During the scale up engineering tests at Hawthorne Army Depot in 1998-1999, three universities conducted plant growth tests with the liquid product from processing single, double, and triple base propellants.

The greenhouse and nutrient uptake tests were conducted at the University of Nevada. The turf grass studies were conducted at the Virginia Polytech University. The humic acid fertilizer study was conducted at the University of Minnesota. These university studies have shown that the liquid fertilizer produced from recycling of propellants using the ARCTECH technology is safe and helps increase plant yield and quality. A series of technology validation tests were conducted in 2001-2002. Ten tons of single, double and triple base propellants were processed yielding approximately 8,000 gallons of concentrated liquid fertilizer. The liquid fertilizer product was sold to various farmers and ranchers around McAlester, Oklahoma that were growing a variety of grasses, corn, soybean and other crops. This application test showed that the liquid product did not exhibit phytotoxicity and that the product has enhanced the growth of crops. The liquid fertilizers yielded by the ARCTECH method contain approximately 30% organic materials, 25% NPK and humic acid, and 45% water. One limitation is that the humic acid enhanced fertilizer, when concentrated to dryness, will be too strong and harmful to plants when applied directly as dry fertilizer. The summary of the discussions is given in Table 3.

Table 3: Technologies for conversion of propellants to fertilizer

Process Technologies	Description	Results	Note
Direct application (Solid fertilizer)	Direct use of propellants as solid fertilizer	Whole grain solid propellant applied to sorghum enhanced growth by 25% in height and 68% in weight	Whole grain propellants preformed better than powder propellants
Base hydrolysis followed by compounding (Solid fertilizer)	Hydrolyze propellants with KOH; resulting solution mixed with peat moss and other ingredients and then dried to form solid fertilizer	Tested in New Mexico and California as dry fertilizer and showed improvement in fertilizing activities. Plant growth enhancement (in %) was not reported	The product showed phytotoxicity
Humic acid enhanced base hydrolysis (Liquid fertilizer)	Hydrolyze propellants with KOH and humic acid; resulting solution is used as liquid fertilizer	Tested in Nevada, Oklahoma, Minnesota, and Virginia showed plant growth enhancement 20% to 400% depending on types of crops	The product showed no phytotoxicity

Analysis shows that the humic acid enhanced base hydrolysis produced better fertilizer than base hydrolysis alone. The liquid fertilizer product enhances plant growth without any effect of phytotoxicity.

RECOMMENDATIONS

It is recommended that USFK, JMC and DAC continue to support the US-ROK Joint Munitions DEFAC project where the aging and obsolete US titled as well as ROK titled munitions would be demilitarized safely, effectively and in an environmentally sound manner in a modern, integrated demilitarization facility.

It is also recommended that USFK, JMC and DAC continue to support the propellant demilitarization by hydrolysis process, especially the humic acid enhanced base (alkaline) hydrolysis process for demilitarizing obsolete single, double, and triple base propellants to a liquid fertilizer. It is also recommended that in Korea, the liquid fertilizer produced from the demilitarization of propellants should be further customized (reformulated) by adding micronutrients and other chemicals to meet and accommodate the needs of local farmers and ranchers. However, any of the reformulation efforts for producing the customized liquid fertilizer formulations and the subsequent distribution of the reformulated liquid fertilizers in the ROK are the responsibility of the established ROK fertilizer manufacturers, not the US Government.

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APPENDICES

A. JOINT US-ROK MUNITIONS DEMILITARIZATION FACILITY MOA

B. SLSA-K

C. MLSA -IAs

D. OVERVIEW OF DEMILITARIZATION AND EXPLOSIVES WASTE TREATEMENT TECHNOLOGY

E. UNIVERSITY OF NEVADA STUDY

F. UNIVERSITY OF MINNESOTA STUDY

G. UNIVERSITY OF VIRGINIA TECHNOLOGICAL STUDY

NOTES

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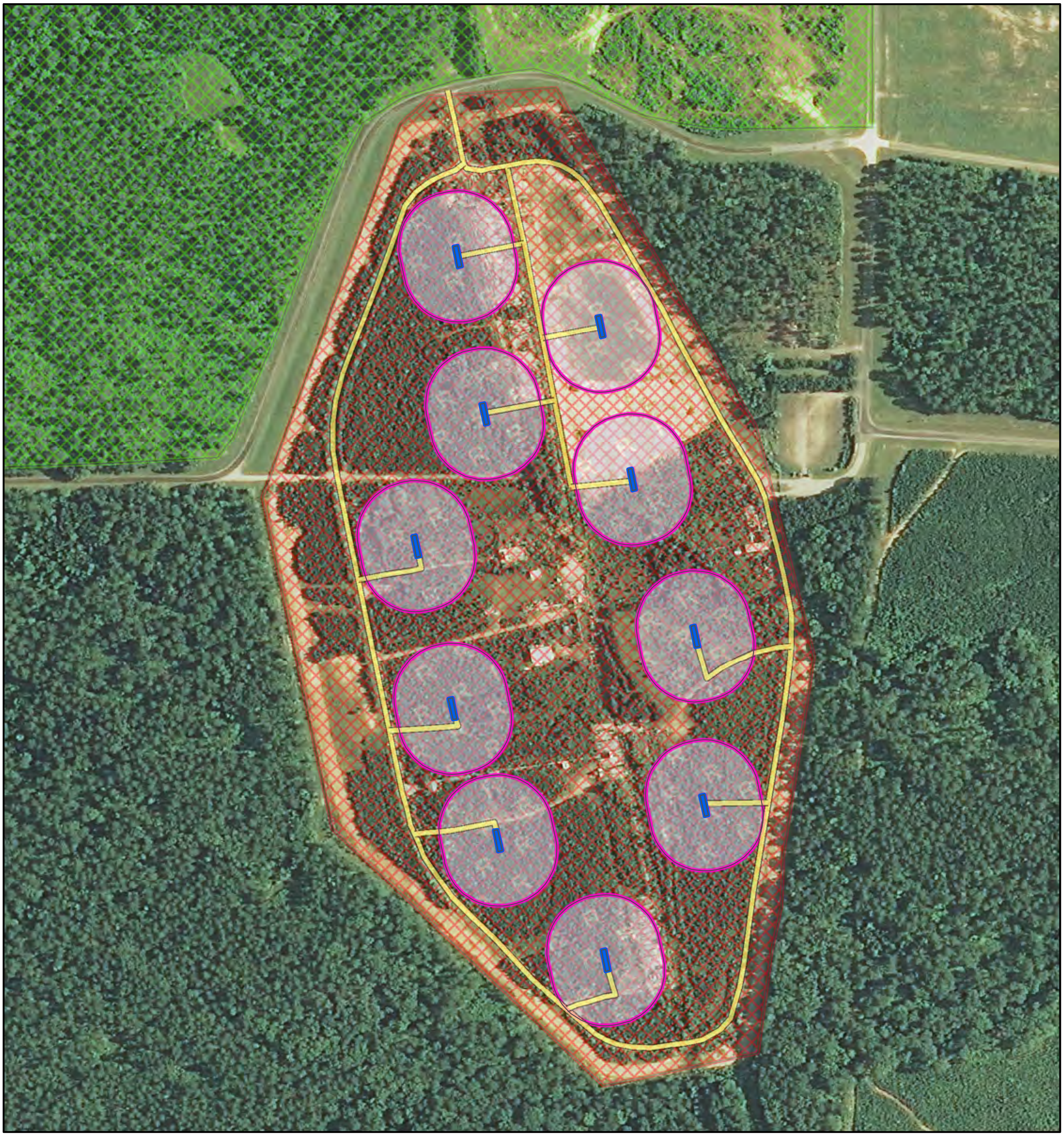

Draft - Locations TBD

CAMP MINDEN

Webster County, Lousiana

Area E: Detail

0 500 1,000
Feet

LEGEND

Base features

- ▨ Storage Igloos
- ▨ Areas "E" and "I"
- ▨ Other Base Features

Project features

- ■ Spill Containment Stations
- ▢ 200' Separation Distance
- ═ Station Access Roads (Existing & Proposed)

N

CLIENT:	Arctech	CLIENT ID:	SB-1
PROJECT ID:	Actodemil	DATE SAMPLED:	10/27/01
PROJECT #:	9605	NEL SAMPLE ID:	R0110114-01
TEST:	**Volatile Organic Compounds by EPA 8260B, December 1996**		
METHOD:	EPA 8260B	EXTRACTED:	10/31/01
MATRIX:	Aqueous	ANALYZED:	10/31/01
DILUTION:	0.043	ANALYST:	PDE - Reno Division

PARAMETER	**Result mg/kg**	**Reporting Limit**	**PARAMETER**	**Result mg/kg**	**Reporting Limit**
Acetone	ND	1.08 mg/kg	1,3-Dichloropropane	ND	0.21 mg/kg
Benzene	0.4	0.21 mg/kg	2,2-Dichloropropane	ND	0.21 mg/kg
Bromobenzene	ND	0.21 mg/kg	1,1-Dichloropropene	ND	0.21 mg/kg
Bromochloromethane	ND	0.21 mg/kg	cis-1,3-Dichloropropene	ND	0.21 mg/kg
Bromodichloromethane	ND	0.21 mg/kg	trans-1,3-Dichloropropene	ND	0.21 mg/kg
Bromoform	ND	0.21 mg/kg	Ethylbenzene	ND	0.21 mg/kg
Bromomethane	ND	0.21 mg/kg	Hexachlorobutadiene	ND	0.21 mg/kg
2-Butanone	ND	1.08 mg/kg	2-Hexanone	ND	1.08 mg/kg
n-Butylbenzene	ND	0.21 mg/kg	Iodomethane	ND	0.21 mg/kg
sec-Butylbenzene	ND	0.21 mg/kg	Isopropylbenzene	ND	0.21 mg/kg
tert-Butylbenzene	ND	0.21 mg/kg	p-Isopropyltoluene	ND	0.21 mg/kg
Carbon disulfide	ND	0.21 mg/kg	Methylene chloride (Dichloromethane)	ND	0.21 mg/kg
Carbon tetrachloride	ND	0.21 mg/kg	4-Methyl-2-pentanone	ND	1.08 mg/kg
Chlorobenzene	ND	0.21 mg/kg	MTBE	ND	0.21 mg/kg
Chloroethane	ND	0.21 mg/kg	Naphthalene	ND	0.21 mg/kg
Chloroform	ND	0.21 mg/kg	n-Propylbenzene	ND	0.21 mg/kg
Chloromethane	ND	0.21 mg/kg	Styrene	ND	0.21 mg/kg
2-Chlorotoluene	ND	0.21 mg/kg	1,1,1,2-Tetrachloroethane	ND	0.21 mg/kg
4-Chlorotoluene	ND	0.21 mg/kg	1,1,2,2-Tetrachloroethane	ND	0.21 mg/kg
Dibromochloromethane	ND	0.21 mg/kg	Tetrachloroethene (PCE)	ND	0.21 mg/kg
1,2-Dibromo-3-chloropropane (DBCP)	ND	0.21 mg/kg	Toluene	8.9	0.21 mg/kg
1,2-Dibromoethane (EDB)	ND	0.21 mg/kg	1,2,3-Trichlorobenzene	ND	0.21 mg/kg
Dibromomethane	ND	0.21 mg/kg	1,2,4-Trichlorobenzene	ND	0.21 mg/kg
1,2-Dichlorobenzene (o-DCB)	ND	0.21 mg/kg	1,1,1-Trichloroethane (1,1,1-TCA)	ND	0.21 mg/kg
1,3-Dichlorobenzene (m-DCB)	ND	0.21 mg/kg	1,1,2-Trichloroethane (1,1,2-TCA)	ND	0.21 mg/kg
1,4-Dichlorobenzene (p-DCB)	ND	0.21 mg/kg	Trichloroethene (TCE)	ND	0.21 mg/kg
Dichlorodifluoromethane (Freon 12)	ND	0.21 mg/kg	Trichlorofluoromethane (Freon 11)	ND	0.21 mg/kg
1,1-Dichloroethane (1,1-DCA)	ND	0.21 mg/kg	1,2,3-Trichloropropane	ND	0.21 mg/kg
1,2-Dichloroethane (1,2-DCA)	ND	0.21 mg/kg	1,2,4-Trimethylbenzene	ND	0.21 mg/kg
1,1-Dichloroethene (1,1-DCE)	ND	0.21 mg/kg	1,3,5-Trimethylbenzene	ND	0.21 mg/kg
cis-1,2-Dichloroethene	ND	0.21 mg/kg	Vinyl chloride	ND	0.21 mg/kg
trans-1,2-Dichloroethene	ND	0.21 mg/kg	o-Xylene	ND	0.21 mg/kg
1,2-Dichloropropane	ND	0.21 mg/kg	m,p-Xylene	ND	0.21 mg/kg

QUALITY CONTROL DATA:

Surrogate	**% Recovery**	**Acceptable Range**
4-Bromofluorobenzene	109	86 - 115 %
Dibromofluoromethane	106	86 - 118 %
Toluene-d8	92	88 - 110 %

ND - Not Detected

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CLIENT:	Arctech	CLIENT ID:	SB-1
PROJECT ID:	Actodemil	DATE SAMPLED:	10/27/01
PROJECT #:	9605	NEL SAMPLE ID:	R0110114-01
TEST:	**Semi-Volatile Organic Compounds by EPA 8270C, December 1996**		
METHOD:	EPA 8270	EXTRACTED:	10/31/01
MATRIX:	Aqueous	ANALYZED:	11/2/01
DILUTION:	0.2	ANALYST:	PDE - Reno Division

PARAMETER	Result mg/kg	Reporting Limit	PARAMETER	Result mg/kg	Reporting Limit
Acenaphthene	ND	2. mg/kg	2,4-Dimethylphenol	ND	2. mg/kg
Acenaphthylene	ND	2. mg/kg	Dimethylphthalate	ND	2. mg/kg
Aniline	ND	2. mg/kg	4,6-Dinitro-2-methyl phenol	ND	10. mg/kg
Anthracene	ND	2. mg/kg	2,4-Dinitrotoluene (DNT)	ND	2. mg/kg
Azobenzene	ND	2. mg/kg	2,6-Dinitrotoluene (DNT)	ND	2. mg/kg
Benzo (a) anthracene	ND	2. mg/kg	2,4-Dinitrophenol	ND	10. mg/kg
Benzo (b&k) fluoranthene	ND	2. mg/kg	Di-n-octyl phthalate	ND	2. mg/kg
Benzoic Acid	ND	10. mg/kg	Fluoranthene	ND	2. mg/kg
Benzo (g,h,i) perylene	ND	2. mg/kg	Fluorene	ND	2. mg/kg
Benzo (a) pyrene	ND	2. mg/kg	Hexachlorobenzene	ND	2. mg/kg
Benzyl alcohol	ND	4. mg/kg	Hexachlorobutadiene	ND	2. mg/kg
bis (2-Chloroethyl) ether	ND	2. mg/kg	Hexachlorocyclopentadiene	ND	2. mg/kg
bis (2-Chloroethoxy) methane	ND	2. mg/kg	Hexachloroethane	ND	2. mg/kg
bis (2-chloroisopropyl) ether	ND	2. mg/kg	Indeno (1,2,3-c,d) pyrene	ND	2. mg/kg
bis (2-Ethylhexyl)phthalate	ND	2. mg/kg	Isophorone	ND	2. mg/kg
Butylbenzylphthalate	ND	2. mg/kg	2-Methylnaphthalene	ND	2. mg/kg
4-Bromophenyl phenyl ether	ND	2. mg/kg	2-Methylphenol	ND	2. mg/kg
4-Chloroanaline	ND	4. mg/kg	4-Methylphenol	ND	2. mg/kg
Carbazole	ND	2. mg/kg	Naphthalene	ND	2. mg/kg
4-Chloro-3-methyl phenol	ND	4. mg/kg	2-Nitroaniline	ND	10. mg/kg
2-Chloronaphthalene	ND	2. mg/kg	3-Nitroaniline	ND	10. mg/kg
2-Chlorophenol	ND	2. mg/kg	4-Nitroaniline	ND	4. mg/kg
4-Chlorophenyl phenyl ether	ND	2. mg/kg	Nitrobenzene	ND	2. mg/kg
Chrysene	ND	2. mg/kg	2-Nitrophenol	ND	2. mg/kg
Dibenzo (a,h) anthracene	ND	2. mg/kg	4-Nitrophenol	ND	10. mg/kg
Dibenzofuran	ND	2. mg/kg	N-Nitrosodi-n-propylamine	ND	2. mg/kg
Di-n-butyl phthalate	ND	2. mg/kg	N-Nitroso-Dimethylamine	ND	2. mg/kg
1,2-Dichlorobenzene (o-DCB)	ND	2. mg/kg	N-Nitrosodiphenylamine	ND	2. mg/kg
1,3-Dichlorobenzene (m-DCB)	ND	2. mg/kg	Pentachlorophenol	ND	10. mg/kg
1,4-Dichlorobenzene (p-DCB)	ND	2. mg/kg	Phenol	ND	2. mg/kg
2,4-Dichlorophenol	ND	2. mg/kg	Phenanthrene	ND	2. mg/kg
3,3'-Dichlorobenzidine	ND	4. mg/kg	Pyrene	ND	2. mg/kg
Diethylphthalate	ND	2. mg/kg	1,2,4-Trichlorobenzene	ND	2. mg/kg

QUALITY CONTROL DATA:

Surrogate	% Recovery	Acceptable Range
2,4,6-Tribromophenol	23	0 - 161 %
2-Fluorobiphenyl	27	16 - 127 %
2-Fluorophenol	33	0 - 88 %
Nitrobenzene-d5	31	9 - 132 %
p-Terphenyl-d14	51	16 - 163 %
Phenol-d5	31	0 - 63 %

ND - Not Detected

This report shall not be reproduced except in full, without the written approval of the laboratory.

CLIENT:	Arctech	CLIENT ID:	SB-1
PROJECT ID:	Actodemil	DATE SAMPLED:	10/27/01
PROJECT #:	9605	NEL SAMPLE ID:	R0110114-01
TEST:	**Semi-Volatile Organic Compounds by EPA 8270C, December 1996**		
METHOD:	EPA 8270	EXTRACTED:	10/31/01
MATRIX:	Aqueous	ANALYZED:	11/2/01
DILUTION:	0.2	ANALYST:	PDE - Reno Division

PARAMETER	Result mg/kg	Reporting Limit	PARAMETER	Result mg/kg	Reporting Limit
Pyridine	ND	2. mg/kg			
2,4,5-Trichlorophenol	ND	2. mg/kg			
2,4,6-Trichlorophenol	ND	2. mg/kg			

QUALITY CONTROL DATA:

Surrogate	% Recovery	Acceptable Range
2,4,6-Tribromophenol	23	0 - 161 %
2-Fluorobiphenyl	27	16 - 127 %
2-Fluorophenol	33	0 - 88 %
Nitrobenzene-d5	31	9 - 132 %
p-Terphenyl-d14	51	16 - 163 %
Phenol-d5	31	0 - 63 %

ND - Not Detected

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CLIENT:	Arctech	CLIENT ID:	**Method Blank**
PROJECT ID:	Actodemil	DATE SAMPLED:	NA
PROJECT #:	9605	NEL SAMPLE ID:	103101-8260B-BLK
TEST:	**Volatile Organic Compounds by EPA 8260B, December 1996**		
METHOD:	EPA 8260B	ANALYST:	PDE - Reno Division
MATRIX:	Aqueous	EXTRACTED:	10/31/01
		ANALYZED:	10/31/01

PARAMETER	**Result µg/L**	**Reporting Limit**	**PARAMETER**	**Result µg/L**	**Reporting Limit**
Acetone	ND	25 µg/L	cis-1,2-Dichloroethene	ND	5 µg/L
Benzene	ND	5 µg/L	trans-1,2-Dichloroethene	ND	5 µg/L
Bromobenzene	ND	5 µg/L	1,2-Dichloropropane	ND	5 µg/L
Bromochloromethane	ND	5 µg/L	1,3-Dichloropropane	ND	5 µg/L
Bromodichloromethane	ND	5 µg/L	2,2-Dichloropropane	ND	5 µg/L
Bromoform	ND	5 µg/L	1,1-Dichloropropene	ND	5 µg/L
Bromomethane	ND	5 µg/L	cis-1,3-Dichloropropene	ND	5 µg/L
2-Butanone	ND	25 µg/L	trans-1,3-Dichloropropene	ND	5 µg/L
n-Butylbenzene	ND	5 µg/L	Ethylbenzene	ND	5 µg/L
sec-Butylbenzene	ND	5 µg/L	Hexachlorobutadiene	ND	5 µg/L
tert-Butylbenzene	ND	5 µg/L	2-Hexanone	ND	25 µg/L
Carbon disulfide	ND	5 µg/L	Iodomethane	ND	5 µg/L
Carbon tetrachloride	ND	5 µg/L	Isopropylbenzene	ND	5 µg/L
Chlorobenzene	ND	5 µg/L	p-Isopropyltoluene	ND	5 µg/L
Chloroethane	ND	5 µg/L	Methylene chloride (Dichloromethane)	ND	5 µg/L
Chloroform	ND	5 µg/L	4-Methyl-2-pentanone	ND	25 µg/L
Chloromethane	ND	5 µg/L	MTBE	ND	5 µg/L
2-Chlorotoluene	ND	5 µg/L	Naphthalene	ND	5 µg/L
4-Chlorotoluene	ND	5 µg/L	n-Propylbenzene	ND	5 µg/L
Dibromochloromethane	ND	5 µg/L	Styrene	ND	5 µg/L
1,2-Dibromo-3-chloropropane (DBCP)	ND	5 µg/L	1,1,1,2-Tetrachloroethane	ND	5 µg/L
1,2-Dibromoethane (EDB)	ND	5 µg/L	1,1,2,2-Tetrachloroethane	ND	5 µg/L
Dibromomethane	ND	5 µg/L	Tetrachloroethene (PCE)	ND	5 µg/L
1,2-Dichlorobenzene (o-DCB)	ND	5 µg/L	Toluene	ND	5 µg/L
1,3-Dichlorobenzene (m-DCB)	ND	5 µg/L	1,2,3-Trichlorobenzene	ND	5 µg/L
1,4-Dichlorobenzene (p-DCB)	ND	5 µg/L	1,2,4-Trichlorobenzene	ND	5 µg/L
Dichlorodifluoromethane (Freon 12)	ND	5 µg/L	1,1,1-Trichloroethane (1,1,1-TCA)	ND	5 µg/L
1,1-Dichloroethane (1,1-DCA)	ND	5 µg/L	1,1,2-Trichloroethane (1,1,2-TCA)	ND	5 µg/L
1,2-Dichloroethane (1,2-DCA)	ND	5 µg/L	Trichloroethene (TCE)	ND	5 µg/L
1,1-Dichloroethene (1,1-DCE)	ND	5 µg/L	Trichlorofluoromethane (Freon 11)	ND	5 µg/L

QUALITY CONTROL DATA:

Surrogate	**% Recovery**	**Acceptable Range**
4-Bromofluorobenzene	105	86 - 115
Dibromofluoromethane	108	86 - 118
Toluene-d8	94	88 - 110

ND - Not Detected

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CLIENT:	Arctech	CLIENT ID:	**Method Blank**
PROJECT ID:	Actodemil	DATE SAMPLED:	NA
PROJECT #:	9605	NEL SAMPLE ID:	103101-8270-BLK

TEST: **Semi-Volatile Organic Compounds by EPA 8270C, December 1996**

METHOD:	EPA 8270	ANALYST:	PDE - Reno Division
MATRIX:	Aqueous	EXTRACTED:	10/31/01
		ANALYZED:	11/2/01

PARAMETER	Result µg/L	Reporting Limit	PARAMETER	Result µg/L	Reporting Limit
Acenaphthene	ND	10 µg/L	2,4-Dichlorophenol	ND	10 µg/L
Acenaphthylene	ND	10 µg/L	3,3'-Dichlorobenzidine	ND	20 µg/L
Aniline	ND	10 µg/L	Diethylphthalate	ND	10 µg/L
Anthracene	ND	10 µg/L	2,4-Dimethylphenol	ND	10 µg/L
Azobenzene	ND	10 µg/L	Dimethylphthalate	ND	10 µg/L
Benzo (a) anthracene	ND	10 µg/L	4,6-Dinitro-2-methyl phenol	ND	50 µg/L
Benzo (b&k) fluoranthene	ND	10 µg/L	2,4-Dinitrotoluene (DNT)	ND	10 µg/L
Benzoic Acid	ND	50 µg/L	2,6-Dinitrotoluene (DNT)	ND	10 µg/L
Benzo (g,h,i) perylene	ND	10 µg/L	2,4-Dinitrophenol	ND	50 µg/L
Benzo (a) pyrene	ND	10 µg/L	Di-n-octyl phthalate	ND	10 µg/L
Benzyl alcohol	ND	20 µg/L	Fluoranthene	ND	10 µg/L
bis (2-Chloroethyl) ether	ND	10 µg/L	Fluorene	ND	10 µg/L
bis (2-Chloroethoxy) methane	ND	10 µg/L	Hexachlorobenzene	ND	10 µg/L
bis (2-chloroisopropyl) ether	ND	10 µg/L	Hexachlorobutadiene	ND	10 µg/L
bis (2-Ethylhexyl)phthalate	ND	10 µg/L	Hexachlorocyclopentadiene	ND	10 µg/L
Butylbenzylphthalate	ND	10 µg/L	Hexachloroethane	ND	10 µg/L
4-Bromophenyl phenyl ether	ND	10 µg/L	Indeno (1,2,3-c,d) pyrene	ND	10 µg/L
4-Chloroanaline	ND	20 µg/L	Isophorone	ND	10 µg/L
Carbazole	ND	10 µg/L	2-Methylnaphthalene	ND	10 µg/L
4-Chloro-3-methyl phenol	ND	20 µg/L	2-Methylphenol	ND	10 µg/L
2-Chloronaphthalene	ND	10 µg/L	4-Methylphenol	ND	10 µg/L
2-Chlorophenol	ND	10 µg/L	Naphthalene	ND	10 µg/L
4-Chlorophenyl phenyl ether	ND	10 µg/L	2-Nitroaniline	ND	50 µg/L
Chrysene	ND	10 µg/L	3-Nitroaniline	ND	50 µg/L
Dibenzo (a,h) anthracene	ND	10 µg/L	4-Nitroaniline	ND	20 µg/L
Dibenzofuran	ND	10 µg/L	Nitrobenzene	ND	10 µg/L
Di-n-butyl phthalate	ND	10 µg/L	2-Nitrophenol	ND	10 µg/L
1,2-Dichlorobenzene (o-DCB)	ND	10 µg/L	4-Nitrophenol	ND	50 µg/L
1,3-Dichlorobenzene (m-DCB)	ND	10 µg/L	N-Nitrosodi-n-propylamine	ND	10 µg/L
1,4-Dichlorobenzene (p-DCB)	ND	10 µg/L	N-Nitroso-Dimethylamine	ND	10 µg/L

QUALITY CONTROL DATA:

Surrogate	% Recovery	Acceptable Range
2,4,6-Tribromophenol	36	0 - 161
2-Fluorobiphenyl	32	16 - 127
2-Fluorophenol	22	0 - 88
Nitrobenzene-d5	36	9 - 132
p-Terphenyl-d14	49	16 - 163
Phenol-d5	14	0 - 63

ND - Not Detected

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CLIENT:	Arctech	CLIENT ID:	**SB-1**
PROJECT ID:	Actodemil	DATE SAMPLED:	10/27/01
PROJECT #:	9605	NEL SAMPLE ID:	R0110114-01
TEST:	**Inorganic Non-Metals**		
MATRIX:	Aqueous	ANALYST:	TBA - Division

PARAMETER	RESULT	REPORTING LIMIT	D. F.	METHOD	UNITS	ANALYZED
Cyanide, Reactive	ND	0.1	5	SW846 Chapter Seven	mg/L	11/4/01

D.F. - Dilution Factor

ND - Not Detected

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NEL LABORATORIES

CLIENT:	Arctech	CLIENT ID:	**Method Blank**
PROJECT ID:	Actodemil	DATE SAMPLED:	NA
PROJECT #:	9605	NEL SAMPLE ID:	011104CNR-BLK
TEST:	**Non-Metals**		

PARAMETER	RESULT	REPORTING LIMIT	D. F.	METHOD	UNITS	ANALYZED
Cyanide, Reactive	ND	0.02	1	W846 Chapter Seve	mg/L	11/4/01

D.F. - Dilution Factor

ND - Not Detected

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CLIENT: Arctech
PROJECT ID: Actodemil
PROJECT #: 9605

CLIENT ID: **SB-1**
DATE SAMPLED: 10/27/01
NEL SAMPLE ID: R0110114-01

TEST: **TCLP-8 Metals**
MATRIX: Aqueous

PARAMETER	RESULT mg/L	REPORTING LIMIT	D. F.	METHOD	TCLP/STLC EXTRACTION DATE	DIGESTED	ANALYZED
Arsenic	ND	0.1 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Barium	1.1	1. mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Cadmium	ND	0.01 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Chromium	0.069	0.01 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Lead	0.11	0.05 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Mercury	ND	0.002 mg/L	10	EPA 7470A	NA	11/1/01	11/1/01
Selenium	ND	0.1 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Silver	ND	0.02 mg/L	1	EPA 6010	NA	11/1/01	11/1/01

D.F. - Dilution Factor

ND - Not Detected

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CLIENT:	Arctech	CLIENT ID:	**Method Blank**
PROJECT ID:	Actodemil	DATE SAMPLED:	NA
PROJECT #:	9605	NEL SAMPLE ID:	1101-1.1-BLK

TEST: **TCLP Metals**
MATRIX: TCLP Extract

PARAMETER	RESULT	REPORTING LIMIT	D. F.	METHOD	TCLP/STLC EXTRACTION DATE	DIGESTED	ANALYZED
Arsenic	ND	0.1 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Barium	ND	1. mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Cadmium	ND	0.01 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Chromium	ND	0.01 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Lead	ND	0.05 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Selenium	ND	0.1 mg/L	1	EPA 6010	NA	11/1/01	11/1/01
Silver	ND	0.02 mg/L	1	EPA 6010	NA	11/1/01	11/1/01

D.F. - Dilution Factor

ND - Not Detected

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CLIENT:	Arctech	CLIENT ID:	**Method Blank**
PROJECT ID:	Actodemil	DATE SAMPLED:	NA
PROJECT #:	9605	NEL SAMPLE ID:	L10305HG-BLK

TEST: **TCLP Metals**
MATRIX: TCLP Extract

PARAMETER	RESULT	REPORTING LIMIT	D. F.	METHOD	TCLP/STLC EXTRACTION DATE	DIGESTED	ANALYZED
Mercury	ND	0.002 mg/L	10	EPA 7470A	NA	11/1/01	11/1/01

D.F. - Dilution Factor

ND - Not Detected

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Code of Federal Regulations

Title 40 - Protection of Environment

Volume: 28
Date: 2012-07-01
Original Date: 2012-07-01
Title: Section 268.48 - Universal treatment standards.
Context: Title 40 - Protection of Environment. CHAPTER I - ENVIRONMENTAL PROTECTION AGENCY (CONTINUED). SUBCHAPTER I - SOLID WASTES (CONTINUED). PART 268 - LAND DISPOSAL RESTRICTIONS. Subpart D - Treatment Standards.

§ 268.48 Universal treatment standards.

(a) Table UTS identifies the hazardous constituents, along with the nonwastewater and wastewater treatment standard levels, that are used to regulate most prohibited hazardous wastes with numerical limits. For determining compliance with treatment standards for underlying hazardous constituents as defined in § 268.2(i), these treatment standards may not be exceeded. Compliance with these treatment standards is measured by an analysis of grab samples, unless otherwise noted in the following Table UTS.

Universal Treatment Standards

[Note: NA means not applicable]

Regulated constituentcommon name	CAS 1 number	Wastewaterstandard	Nonwastewaterstandard
		Concentration 2 in mg/l	Concentration 3 in mg/kg unless noted as “mg/l TCLP”
Organic Constituents			
Acenaphthylene	208-96-8	0.059	3.4
Acenaphthene	83-32-9	0.059	3.4
Acetone	67-64-1	0.28	160
Acetonitrile	75-05-8	5.6	38
Acetophenone	96-86-2	0.010	9.7
2-Acetylaminofluorene	53-96-3	0.059	140
Acrolein	107-02-8	0.29	NA
Acrylamide	79-06-1	19	23
Acrylonitrile	107-13-1	0.24	84
Aldrin	309-00-2	0.021	0.066
4-Aminobiphenyl	92-67-1	0.13	NA
Aniline	62-53-3	0.81	14
o-Anisidine (2-methoxyaniline)	90-04-0	0.010	0.66
Anthracene	120-12-7	0.059	3.4
Aramite	140-57-8	0.36	NA
alpha-BHC	319-84-6	0.00014	0.066
beta-BHC	319-85-7	0.00014	0.066
delta-BHC	319-86-8	0.023	0.066

gamma-BHC	58-89-9	0.0017	0.066
Benzene	71-43-2	0.14	10
Benz(a)anthracene	56-55-3	0.059	3.4
Benzal chloride	98-87-3	0.055	6.0
Benzo(b)fluoranthene (difficult to distinguish from benzo(k)fluoranthene)	205-99-2	0.11	6.8
Benzo(k)fluoranthene (difficult to distinguish from benzo(b)fluoranthene)	207-08-9	0.11	6.8
Benzo(g,h,i)perylene	191-24-2	0.0055	1.8
Benzo(a)pyrene	50-32-8	0.061	3.4
Bromodichloromethane	75-27-4	0.35	15
Bromomethane/Methyl bromide	74-83-9	0.11	15
4-Bromophenyl phenyl ether	101-55-3	0.055	15
n-Butyl alcohol	71-36-3	5.6	2.6
Butyl benzyl phthalate	85-68-7	0.017	28
2-sec-Butyl-4,6-dinitrophenol/Dinoseb	88-85-7	0.066	2.5
Carbon disulfide	75-15-0	3.8	4.8 mg/l TCLP
Carbon tetrachloride	56-23-5	0.057	6.0
Chlordane (alpha and gamma isomers)	57-74-9	0.0033	0.26
p-Chloroaniline	106-47-8	0.46	16
Chlorobenzene	108-90-7	0.057	6.0
Chlorobenzilate	510-15-6	0.10	NA
2-Chloro-1,3-butadiene	126-99-8	0.057	0.28
Chlorodibromomethane	124-48-1	0.057	15
Chloroethane	75-00-3	0.27	6.0
bis(2-Chloroethoxy)methane	111-91-1	0.036	7.2
bis(2-Chloroethyl)ether	111-44-4	0.033	6.0
Chloroform	67-66-3	0.046	6.0
bis(2-Chloroisopropyl)ether	39638-32-9	0.055	7.2
p-Chloro-m-cresol	59-50-7	0.018	14
2-Chloroethyl vinyl ether	110-75-8	0.062	NA
Chloromethane/Methyl chloride	74-87-3	0.19	30
2-Chloronaphthalene	91-58-7	0.055	5.6
2-Chloropchenol	95-57-8	0.044	5.7
3-Chloropropylene	107-05-1	0.036	30
Chrysene	218-01-9	0.059	3.4
p-Cresidine	120-71-8	0.010	0.66
o-Cresol	95-48-7	0.11	5.6
m-Cresol (difficult to distinguish from p-	108-39-4	0.77	5.6

cresol)			
p-Cresol (difficult to distinguish from m-cresol)	106-44-5	0.77	5.6
Cyclohexanone	108-94-1	0.36	0.75 mg/l TCLP
o,p′-DDD	53-19-0	0.023	0.087
p,p′-DDD	72-54-8	0.023	0.087
o,p′-DDE	3424-82-6	0.031	0.087
p,p′-DDE	72-55-9	0.031	0.087
o,p′-DDT	789-02-6	0.0039	0.087
p,p′-DDT	50-29-3	0.0039	0.087
Dibenz(a,h)anthracene	53-70-3	0.055	8.2
Dibenz(a,e)pyrene	192-65-4	0.061	NA
1,2-Dibromo-3-chloropropane	96-12-8	0.11	15
1,2-Dibromoethane/Ethylene dibromide	106-93-4	0.028	15
Dibromomethane	74-95-3	0.11	15
m-Dichlorobenzene	541-73-1	0.036	6.0
o-Dichlorobenzene	95-50-1	0.088	6.0
p-Dichlorobenzene	106-46-7	0.090	6.0
Dichlorodifluoromethane	75-71-8	0.23	7.2
1,1-Dichloroethane	75-34-3	0.059	6.0
1,2-Dichloroethane	107-06-2	0.21	6.0
1,1-Dichloroethylene	75-35-4	0.025	6.0
trans-1,2-Dichloroethylene	156-60-5	0.054	30
2,4-Dichlorophenol	120-83-2	0.044	14
2,6-Dichlorophenol	87-65-0	0.044	14
2,4-Dichlorophenoxyacetic acid/2,4-D	94-75-7	0.72	10
1,2-Dichloropropane	78-87-5	0.85	18
cis-1,3-Dichloropropylene	10061-01-5	0.036	18
trans-1,3-Dichloropropylene	10061-02-6	0.036	18
Dieldrin	60-57-1	0.017	0.13
Diethyl phthalate	84-66-2	0.20	28
p-Dimethylaminoazobenzene	60-11-7	0.13	NA
2,4-Dimethylaniline (2,4-xylidine)	95-68-1	0.010	0.66
2,4-Dimethyl phenol	105-67-9	0.036	14
Dimethyl phthalate	131-11-3	0.047	28
Di-n-butyl phthalate	84-74-2	0.057	28
1,4-Dinitrobenzene	100-25-4	0.32	2.3
4,6-Dinitro-o-cresol	534-52-1	0.28	160

2,4-Dinitrophenol	51-28-5	0.12	160
2,4-Dinitrotoluene	121-14-2	0.32	140
2,6-Dinitrotoluene	606-20-2	0.55	28
Di-n-octyl phthalate	117-84-0	0.017	28
Di-n-propylnitrosamine	621-64-7	0.40	14
1,4-Dioxane	123-91-1	12.0	170
Diphenylamine (difficult to distinguish from diphenylnitrosamine)	122-39-4	0.92	13
Diphenylnitrosamine (difficult to distinguish from diphenylamine)	86-30-6	0.92	13
1,2-Diphenylhydrazine	122-66-7	0.087	NA
Disulfoton	298-04-4	0.017	6.2
Endosulfan I	959-98-8	0.023	0.066
Endosulfan II	33213-65-9	0.029	0.13
Endosulfan sulfate	1031-07-8	0.029	0.13
Endrin	72-20-8	0.0028	0.13
Endrin aldehyde	7421-93-4	0.025	0.13
Ethyl acetate	141-78-6	0.34	33
Ethyl benzene	100-41-4	0.057	10
Ethyl cyanide/Propanenitrile	107-12-0	0.24	360
Ethyl ether	60-29-7	0.12	160
bis(2-Ethylhexyl)phthalate	117-81-7	0.28	28
Ethyl methacrylate	97-63-2	0.14	160
Ethylene oxide	75-21-8	0.12	NA
Famphur	52-85-7	0.017	15
Fluoranthene	206-44-0	0.068	3.4
Fluorene	86-73-7	0.059	3.4
Heptachlor	76-44-8	0.0012	0.066
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD)	35822-46-9	0.000035	.0025
1,2,3,4,6,7,8-Heptachlorodibenzofluran (1,2,3,4,6,7,8-HpCDF)	67562-39-4	0.000035	.0025
1,2,3,4,7,8,9-Heptachlorodibenzofluran (1,2,3,4,7,8,9-HpCDF)	55673-89-7	0.000035	.0025
Heptachlor epoxide	1024-57-3	0.016	0.066
Hexachlorobenzene	118-74-1	0.055	10
Hexachlorobutadiene	87-68-3	0.055	5.6
Hexachlorocyclopentadiene	77-47-4	0.057	2.4
HxCDDs (All Hexachlorodibenzo-p-dioxins)	NA	0.000063	0.001
HxCDFs (All Hexachlorodibenzofurans)	NA	0.000063	0.001

Hexachloroethane	67-72-1	0.055	30
Hexachloropropylene	1888-71-7	0.035	30
Indeno(1,2,3-c,d) pyrene	193-39-5	0.0055	3.4
Iodomethane	74-88-4	0.19	65
Isobutyl alcohol	78-83-1	5.6	170
Isodrin	465-73-6	0.021	0.066
Isosafrole	120-58-1	0.081	2.6
Kepone	143-50-0	0.0011	0.13
Methacrylonitrile	126-98-7	0.24	84
Methanol	67-56-1	5.6	0.75 mg/l TCLP
Methapyrilene	91-80-5	0.081	1.5
Methoxychlor	72-43-5	0.25	0.18
3-Methylcholanthrene	56-49-5	0.0055	15
4,4-Methylene bis(2-chloroaniline)	101-14-4	0.50	30
Methylene chloride	75-09-2	0.089	30
Methyl ethyl ketone	78-93-3	0.28	36
Methyl isobutyl ketone	108-10-1	0.14	33
Methyl methacrylate	80-62-6	0.14	160
Methyl methanesulfonate	66-27-3	0.018	NA
Methyl parathion	298-00-0	0.014	4.6
Naphthalene	91-20-3	0.059	5.6
2-Naphthylamine	91-59-8	0.52	NA
o-Nitroaniline	88-74-4	0.27	14
p-Nitroaniline	100-01-6	0.028	28
Nitrobenzene	98-95-3	0.068	14
5-Nitro-o-toluidine	99-55-8	0.32	28
o-Nitrophenol	88-75-5	0.028	13
p-Nitrophenol	100-02-7	0.12	29
N-Nitrosodiethylamine	55-18-5	0.40	28
N-Nitrosodimethylamine	62-75-9	0.40	2.3
N-Nitroso-di-n-butylamine	924-16-3	0.40	17
N-Nitrosomethylethylamine	10595-95-6	0.40	2.3
N-Nitrosomorpholine	59-89-2	0.40	2.3
N-Nitrosopiperidine	100-75-4	0.013	35
N-Nitrosopyrrolidine	930-55-2	0.013	35
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9	0.000063	0.005
1,2,3,4,6,7,8,9-Octachlorodibenzofluran (OCDF)	39001-02-0	0.000063	0.005

Parathion	56-38-2	0.014	4.6
Total PCBs (sum of all PCB isomers, or all Aroclors) 8	1336-36-3	0.10	10
Pentachlorobenzene	608-93-5	0.055	10
PeCDDs (All Pentachlorodibenzo-p-dioxins)	NA	0.000063	0.001
PeCDFs (All Pentachlorodibenzofurans)	NA	0.000035	0.001
Pentachloroethane	76-01-7	0.055	6.0
Pentachloronitrobenzene	82-68-8	0.055	4.8
Pentachlorophenol	87-86-5	0.089	7.4
Phenacetin	62-44-2	0.081	16
Phenanthrene	85-01-8	0.059	5.6
Phenol	108-95-2	0.039	6.2
1,3-Phenylenediamine	108-45-2	0.010	0.66
Phorate	298-02-2	0.021	4.6
Phthalic acid	100-21-0	0.055	28
Phthalic anhydride	85-44-9	0.055	28
Pronamide	23950-58-5	0.093	1.5
Pyrene	129-00-0	0.067	8.2
Pyridine	110-86-1	0.014	16
Safrole	94-59-7	0.081	22
Silvex/2,4,5-TP	93-72-1	0.72	7.9
1,2,4,5-Tetrachlorobenzene	95-94-3	0.055	14
TCDDs (All Tetrachlorodibenzo-p-dioxins)	NA	0.000063	0.001
TCDFs (All Tetrachlorodibenzofurans)	NA	0.000063	0.001
1,1,1,2-Tetrachloroethane	630-20-6	0.057	6.0
1,1,2,2-Tetrachloroethane	79-34-5	0.057	6.0
Tetrachloroethylene	127-18-4	0.056	6.0
2,3,4,6-Tetrachlorophenol	58-90-2	0.030	7.4
Toluene	108-88-3	0.080	10
Toxaphene	8001-35-2	0.0095	2.6
Tribromomethane/Bromoform	75-25-2	0.63	15
1,2,4-Trichlorobenzene	120-82-1	0.055	19
1,1,1-Trichloroethane	71-55-6	0.054	6.0
1,1,2-Trichloroethane	79-00-5	0.054	6.0
Trichloroethylene	79-01-6	0.054	6.0
Trichlorofluoromethane	75-69-4	0.020	30
2,4,5-Trichlorophenol	95-95-4	0.18	7.4
2,4,6-Trichlorophenol	88-06-2	0.035	7.4

2,4,5-Trichlorophenoxyacetic acid/2,4,5-T	93-76-5	0.72	7.9
1,2,3-Trichloropropane	96-18-4	0.85	30
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	0.057	30
tris-(2,3-Dibromopropyl) phosphate	126-72-7	0.11	0.10
Vinyl chloride	75-01-4	0.27	6.0
Xylenes-mixed isomers (sum of o-, m-, and p-xylene concentrations)	1330-20-7	0.32	30
Inorganic Constituents			
Antimony	7440-36-0	1.9	1.15 mg/l TCLP
Arsenic	7440-38-2	1.4	5.0 mg/l TCLP
Barium	7440-39-3	1.2	21 mg/l TCLP
Beryllium	7440-41-7	0.82	1.22 mg/l TCLP
Cadmium	7440-43-9	0.69	0.11 mg/l TCLP
Chromium (Total)	7440-47-3	2.77	0.60 mg/l TCLP
Cyanides (Total) 4	57-12-5	1.2	590
Cyanides (Amenable) 4	57-12-5	0.86	30
Fluoride 5	16984-48-8	35	NA
Lead	7439-92-1	0.69	0.75 mg/l TCLP
Mercury—Nonwastewater from Retort	7439-97-6	NA	0.20 mg/l TCLP
Mercury—All Others	7439-97-6	0.15	0.025 mg/l TCLP
Nickel	7440-02-0	3.98	11 mg/l TCLP
Selenium 7	7782-49-2	0.82	5.7 mg/l TCLP
Silver	7440-22-4	0.43	0.14 mg/l TCLP
Sulfide 5	18496-25-8	14	NA
Thallium	7440-28-0	1.4	0.20 mg/l TCLP
Vanadium 5	7440-62-2	4.3	1.6 mg/l TCLP
Zinc 5	7440-66-6	2.61	4.3 mg/l TCLP

Footnotes to Table UTS

1	CAS means Chemical Abstract Services. When the waste code and/or regulated constituents are described as a combination of a chemical with it's salts and/or esters, the CAS number is given for the parent compound only.
2	Concentration standards for wastewaters are expressed in mg/l and are based on analysis of composite samples.
3	Except for Metals (EP or TCLP) and Cyanides (Total and Amenable) the nonwastewater treatment standards expressed as a concentration were established, inpart, based upon incineration in units operated in accordance with the technical requirements of 40 CFR part 264, subpart O or 40 CFR part 265, subpart O, or based upon combustion in fuel substitution units operating in accordance with applicable technical requirements. A facility may comply with these treatment standards according to provisions in 40 CFR 268.40(d). All concentration standards for nonwastewaters are based on analysis of grab samples.
4	Both Cyanides (Total) and Cyanides (Amenable) for nonwastewaters are to be analyzed using Method 9010C or 9012B, found in “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,” EPA Publication SW-846, as incorporated by reference in 40 CFR 260.11, with a sample size of 10 grams and a distillation time of one hour and 15 minutes.
5	These constituents are not “underlying hazardous constituents” in characteristic wastes, according to the definition at § 268.2(i).

6	[Reserved]
7	This constituent is not an underlying hazardous constituent as defined at § 268.2(i) of this Part because its UTS level is greater than its TC level, thus a treatment selenium waste would always be characteristically hazardous, unless it is treated to below its characteristic level.
8	This standard is temporarily deferred for soil exhibiting a hazardous characteristic due to D004-D011 only.

[59 FR 48103, Sept. 19, 1994, as amended by 60 FR 302, Jan. 3, 1995; 61 FR 15654, Apr. 8 1996; 61 FR 33690, June 28, 1996; 62 FR 7596, Feb. 19, 1997; 63 FR 24626, May 4, 1998; 63 FR 28739, May 26, 1998; 63 FR 47417, Sept. 4, 1998; 64 FR 25417, May 11, 1999; 65 FR 14475, Mar. 17, 2000; 70 FR 34590, June 14, 2005; 70 FR 9178, Feb. 24, 2005; 71 FR 40279, July 14, 2006; 75 FR 13008, Mar. 18, 2010; 76 FR 34156, June 13, 2011]

Analytical Report For 911079

for

Arctech

Project Manager: Nand Kaushik

Project Name: McAlister AAP

GPL

Laboratories

GPL Laboratories, LLLP certifies that the test results meet all requirements of the NELAC Standards unless otherwise noted.

Reviewed By,
Project Manager

Approved By,
Laboratory Director

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1	Lab Sample ID:	911079-001-001-1/3
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW3010A
Prepared Date/Time:	11/30/2009 11:00	Analytical Method:	SW6010B_TCLP

# Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time	
1) Arsenic	7440-38-2	BQL	U	2000	2000	1	ug/L	11/30/09	16:28
2) Barium	7440-39-3	BQL	U	10000	10000	1	ug/L	11/30/09	16:28
3) Cadmium	7440-43-9	BQL	U	600	600	1	ug/L	11/30/09	16:28
4) Chromium	7440-47-3	BQL	U	2000	2000	1	ug/L	11/30/09	16:28
5) Lead	7439-92-1	BQL	U	2000	2000	1	ug/L	11/30/09	16:28
6) Selenium	7782-49-2	BQL	U	2000	2000	1	ug/L	11/30/09	16:28
7) Silver	7440-22-4	BQL	U	2000	2000	1	ug/L	11/30/09	16:28

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1	Lab Sample ID:	911079-001-001-1/3
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW7470A_DIG
Prepared Date/Time:	12/01/2009 06:00	Analytical Method:	SW7471A_TCLP

# Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time
1) Mercury	7439-97-6	BQL	U	20	20	1	ug/L	12/01/09 14:07

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1DL1	Lab Sample ID:	911079-001-004-1/7
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW5030B
Prepared Date/Time:	12/01/2009 08:47	Analytical Method:	SW8260B

#	Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time	
1)	1,1,1,2-Tetrachloroethane	630-20-6	BQL	U	510	2500	500	ug/kg	12/01/09	19:20
2)	1,1,1-Trichloroethane	71-55-6	BQL	U	600	2500	500	ug/kg	12/01/09	19:20
3)	1,1,2,2-Tetrachloroethane	79-34-5	BQL	U	200	2500	500	ug/kg	12/01/09	19:20
4)	1,1,2-Trichloroethane	79-00-5	BQL	U	300	2500	500	ug/kg	12/01/09	19:20
5)	1,1-Dichloroethane	75-34-3	BQL	U	390	2500	500	ug/kg	12/01/09	19:20
6)	1,1-Dichloroethene	75-35-4	BQL	U	460	2500	500	ug/kg	12/01/09	19:20
7)	1,2,3-Trichloropropane	96-18-4	BQL	U	350	2500	500	ug/kg	12/01/09	19:20
8)	1,2,4-Trichlorobenzene	120-82-1	BQL	U	130	2500	500	ug/kg	12/01/09	19:20
9)	1,2-Dibromo-3-Chloropropane	96-12-8	BQL	U	320	2500	500	ug/kg	12/01/09	19:20
10)	1,2-Dibromoethane	106-93-4	BQL	U	340	2500	500	ug/kg	12/01/09	19:20
11)	1,2-Dichlorobenzene	95-50-1	BQL	U	200	2500	500	ug/kg	12/01/09	19:20
12)	1,2-Dichloroethane	107-06-2	BQL	U	230	2500	500	ug/kg	12/01/09	19:20
13)	1,2-Dichloropropane	78-87-5	BQL	U	300	2500	500	ug/kg	12/01/09	19:20
14)	1,3-Dichlorobenzene	541-73-1	BQL	U	240	2500	500	ug/kg	12/01/09	19:20
15)	1,4-Dichlorobenzene	106-46-7	BQL	U	200	2500	500	ug/kg	12/01/09	19:20
16)	2-Butanone	78-93-3	BQL	U	200	5000	500	ug/kg	12/01/09	19:20
17)	2-Chloro-1,3-Butadiene	126-99-8	BQL	U	500	2500	500	ug/kg	12/01/09	19:20
18)	2-Chloroethyl Vinyl Ether	110-75-8	BQL	U	1200	5000	500	ug/kg	12/01/09	19:20
19)	4-Methyl-2-Pentanone	108-10-1	BQL	U	240	5000	500	ug/kg	12/01/09	19:20
20)	Acetone	67-64-1	BQL	U	660	5000	500	ug/kg	12/01/09	19:20
21)	Acetonitrile	75-05-8	BQL	U	3500	100000	500	ug/kg	12/01/09	19:20
22)	Acrolein	107-02-8	BQL	U	1100	25000	500	ug/kg	12/01/09	19:20
23)	Acrylonitrile	107-13-1	BQL	U	2100	25000	500	ug/kg	12/01/09	19:20
24)	Benzene	71-43-2	BQL	U	360	2500	500	ug/kg	12/01/09	19:20
25)	Bromodichloromethane	75-27-4	BQL	U	420	2500	500	ug/kg	12/01/09	19:20
26)	Bromoform	75-25-2	BQL	U	260	2500	500	ug/kg	12/01/09	19:20
27)	Bromomethane	74-83-9	BQL	U	660	5000	500	ug/kg	12/01/09	19:20
28)	Carbon Disulfide	75-15-0	BQL	U	1300	2500	500	ug/kg	12/01/09	19:20

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1DL1	Lab Sample ID:	911079-001-004-1/7
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW5030B
Prepared Date/Time:	12/01/2009 08:47	Analytical Method:	SW8260B

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1DL1	Lab Sample ID:	911079-001-004-1/7
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW5030B
Prepared Date/Time:	12/01/2009 08:47	Analytical Method:	SW8260B

# Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time	
29) Carbon Tetrachloride	56-23-5	BQL	U	840	2500	500	ug/kg	12/01/09	19:20
30) Chlorobenzene	108-90-7	BQL	U	290	2500	500	ug/kg	12/01/09	19:20
31) Chloroethane	75-00-3	BQL	U	620	5000	500	ug/kg	12/01/09	19:20
32) Chloroform	67-66-3	BQL	U	380	2500	500	ug/kg	12/01/09	19:20
33) Chloromethane	74-87-3	BQL	U	370	5000	500	ug/kg	12/01/09	19:20
34) Dibromochloromethane	124-48-1	BQL	U	410	2500	500	ug/kg	12/01/09	19:20
35) Dibromomethane	74-95-3	BQL	U	340	2500	500	ug/kg	12/01/09	19:20
36) Dichlorodifluoromethane	75-71-8	BQL	U	600	2500	500	ug/kg	12/01/09	19:20
37) Hexachlorobutadiene	87-68-3	BQL	U	320	2500	500	ug/kg	12/01/09	19:20
38) Iodomethane (Methyl Iodide)	74-88-4	BQL	U	500	2500	500	ug/kg	12/01/09	19:20
39) Isobutyl Alcohol	78-83-1	BQL	U	4300	50000	500	ug/kg	12/01/09	19:20
40) Methacrylonitrile	126-98-7	BQL	U	3300	2500	500	ug/kg	12/01/09	19:20
41) Methyl Methacrylate	80-62-6	BQL	U	160	2500	500	ug/kg	12/01/09	19:20
42) Methylene Chloride	75-09-2	BQL	U	270	5000	500	ug/kg	12/01/09	19:20
43) Naphthalene	91-20-3	BQL	U	220	2500	500	ug/kg	12/01/09	19:20
44) Tetrachloroethylene	127-18-4	BQL	U	650	2500	500	ug/kg	12/01/09	19:20
45) Toluene	108-88-3	BQL	U	500	2500	500	ug/kg	12/01/09	19:20
46) Trichloroethene	79-01-6	BQL	U	470	2500	500	ug/kg	12/01/09	19:20
47) Trichlorofluoromethane	75-69-4	BQL	U	590	2500	500	ug/kg	12/01/09	19:20
48) Vinyl Chloride	75-01-4	BQL	U	640	5000	500	ug/kg	12/01/09	19:20
49) cis-1,3-Dichloropropene	10061-01-5	BQL	U	660	2500	500	ug/kg	12/01/09	19:20
50) m,p-Xylene	136777-61-	BQL	U	500	2500	500	ug/kg	12/01/09	19:20
51) n-Butanol	71-36-3	BQL	U	200000	50000	500	ug/kg	12/01/09	19:20
52) o-Xylene	95-47-6	BQL	U	240	2500	500	ug/kg	12/01/09	19:20
53) trans-1,2-dichloroethene	156-60-5	BQL	U	780	2500	500	ug/kg	12/01/09	19:20
54) trans-1,3-dichloropropene	10061-02-6	BQL	U	500	2500	500	ug/kg	12/01/09	19:20

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1DL1	Lab Sample ID:	911079-001-004-1/7
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW5030B
Prepared Date/Time:	12/01/2009 08:47	Analytical Method:	SW8260B

# Surrogate Parameter	CAS	Percent Recovery	Control Limits	Dil Fact	Analysis Date/Time	
55) 1,2-Dichloroethane-d4	17060-07-0	90 %	65 - 125	500	12/01/09	19:20
56) 4-Bromofluorobenzene	460-00-4	98 %	85 - 120	500	12/01/09	19:20
57) **Dibromofluoromethane**	**1868-53-7**	**1 %**	**85 - 115**	**500**	**12/01/09**	**19:20**
58) Toluene-D8	2037-26-5	98 %	85 - 115	500	12/01/09	19:20

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1DL2RE	Lab Sample ID:	911079-001-004-1/7DL2RE
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW5030B
Prepared Date/Time:	12/02/2009 17:00	Analytical Method:	SW8260B

#	Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time
1)	Cyclohexanone	108-94-1	BQL	U	740	5000	500	ug/kg	12/02/09 22:43

#	Surrogate Parameter	CAS	Percent Recovery	Control Limits	Dil Fact	Analysis Date/Time
2)	1,2-Dichloroethane-d4	17060-07-0	115 %	65 - 125	500	12/02/09 22:43
3)	4-Bromofluorobenzene	460-00-4	98 %	85 - 120	500	12/02/09 22:43
4)	**Dibromofluoromethane**	**1868-53-7**	**1 %**	**85 - 115**	**500**	**12/02/09 22:43**
5)	Toluene-D8	2037-26-5	101 %	85 - 115	500	12/02/09 22:43

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1DL2	Lab Sample ID:	911079-001-005-2/7DL2
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW5030B
Prepared Date/Time:	12/02/2009 10:35	Analytical Method:	SW8260B

#	Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time	
1)	1,1,1,2-Tetrachloroethane	630-20-6	BQL	U	51	250	50	ug/kg	12/02/09	13:23
2)	1,1,1-Trichloroethane	71-55-6	BQL	U	60	250	50	ug/kg	12/02/09	13:23
3)	1,1,2,2-Tetrachloroethane	79-34-5	BQL	U	20	250	50	ug/kg	12/02/09	13:23
4)	1,1,2-Trichloroethane	79-00-5	BQL	U	30	250	50	ug/kg	12/02/09	13:23
5)	1,1-Dichloroethane	75-34-3	BQL	U	39	250	50	ug/kg	12/02/09	13:23
6)	1,1-Dichloroethene	75-35-4	BQL	U	46	250	50	ug/kg	12/02/09	13:23
7)	1,2,3-Trichloropropane	96-18-4	BQL	U	35	250	50	ug/kg	12/02/09	13:23
8)	1,2,4-Trichlorobenzene	120-82-1	BQL	U	13	250	50	ug/kg	12/02/09	13:23
9)	1,2-Dibromo-3-Chloropropane	96-12-8	BQL	U	32	250	50	ug/kg	12/02/09	13:23
10)	1,2-Dibromoethane	106-93-4	BQL	U	34	250	50	ug/kg	12/02/09	13:23
11)	1,2-Dichlorobenzene	95-50-1	BQL	U	20	250	50	ug/kg	12/02/09	13:23
12)	1,2-Dichloroethane	107-06-2	BQL	U	23	250	50	ug/kg	12/02/09	13:23
13)	1,2-Dichloropropane	78-87-5	BQL	U	30	250	50	ug/kg	12/02/09	13:23
14)	1,3-Dichlorobenzene	541-73-1	BQL	U	24	250	50	ug/kg	12/02/09	13:23
15)	1,4-Dichlorobenzene	106-46-7	BQL	U	20	250	50	ug/kg	12/02/09	13:23
16)	2-Butanone	78-93-3	BQL	U	20	500	50	ug/kg	12/02/09	13:23
17)	2-Chloro-1,3-Butadiene	126-99-8	BQL	U	50	250	50	ug/kg	12/02/09	13:23
18)	2-Chloroethyl Vinyl Ether	110-75-8	BQL	U	120	500	50	ug/kg	12/02/09	13:23
19)	4-Methyl-2-Pentanone	108-10-1	BQL	U	24	500	50	ug/kg	12/02/09	13:23
20)	Acetone	67-64-1	BQL	U	66	500	50	ug/kg	12/02/09	13:23
21)	Acetonitrile	75-05-8	BQL	U	350	10000	50	ug/kg	12/02/09	13:23
22)	Acrolein	107-02-8	BQL	U	110	2500	50	ug/kg	12/02/09	13:23
23)	Acrylonitrile	107-13-1	BQL	U	210	2500	50	ug/kg	12/02/09	13:23
24)	Benzene	71-43-2	BQL	U	36	250	50	ug/kg	12/02/09	13:23
25)	Bromodichloromethane	75-27-4	BQL	U	42	250	50	ug/kg	12/02/09	13:23
26)	Bromoform	75-25-2	BQL	U	26	250	50	ug/kg	12/02/09	13:23
27)	Bromomethane	74-83-9	BQL	U	66	500	50	ug/kg	12/02/09	13:23
28)	Carbon Disulfide	75-15-0	BQL	U	140	250	50	ug/kg	12/02/09	13:23

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1DL2	Lab Sample ID:	911079-001-005-2/7DL2
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW5030B
Prepared Date/Time:	12/02/2009 10:35	Analytical Method:	SW8260B

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1DL2	Lab Sample ID:	911079-001-005-2/7DL2
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW5030B
Prepared Date/Time:	12/02/2009 10:35	Analytical Method:	SW8260B

# Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time	
29) Carbon Tetrachloride	56-23-5	BQL	U	84	250	50	ug/kg	12/02/09	13:23
30) Chlorobenzene	108-90-7	BQL	U	29	250	50	ug/kg	12/02/09	13:23
31) Chloroethane	75-00-3	BQL	U	62	500	50	ug/kg	12/02/09	13:23
32) Chloroform	67-66-3	BQL	U	38	250	50	ug/kg	12/02/09	13:23
33) Chloromethane	74-87-3	BQL	U	37	500	50	ug/kg	12/02/09	13:23
34) Dibromochloromethane	124-48-1	BQL	U	41	250	50	ug/kg	12/02/09	13:23
35) Dibromomethane	74-95-3	BQL	U	34	250	50	ug/kg	12/02/09	13:23
36) Dichlorodifluoromethane	75-71-8	BQL	U	60	250	50	ug/kg	12/02/09	13:23
37) Hexachlorobutadiene	87-68-3	BQL	U	32	250	50	ug/kg	12/02/09	13:23
38) Iodomethane (Methyl Iodide)	74-88-4	BQL	U	50	250	50	ug/kg	12/02/09	13:23
39) Isobutyl Alcohol	78-83-1	BQL	U	430	5000	50	ug/kg	12/02/09	13:23
40) Methacrylonitrile	126-98-7	BQL	U	330	250	50	ug/kg	12/02/09	13:23
41) Methyl Methacrylate	80-62-6	BQL	U	16	250	50	ug/kg	12/02/09	13:23
42) Methylene Chloride	75-09-2	BQL	U	27	500	50	ug/kg	12/02/09	13:23
43) Naphthalene	91-20-3	BQL	U	22	250	50	ug/kg	12/02/09	13:23
44) Tetrachloroethylene	127-18-4	BQL	U	65	250	50	ug/kg	12/02/09	13:23
45) Toluene	108-88-3	BQL	U	50	250	50	ug/kg	12/02/09	13:23
46) Trichloroethene	79-01-6	BQL	U	47	250	50	ug/kg	12/02/09	13:23
47) Trichlorofluoromethane	75-69-4	BQL	U	59	250	50	ug/kg	12/02/09	13:23
48) Vinyl Chloride	75-01-4	BQL	U	64	500	50	ug/kg	12/02/09	13:23
49) cis-1,3-Dichloropropene	10061-01-5	BQL	U	66	250	50	ug/kg	12/02/09	13:23
50) m,p-Xylene	136777-61-	BQL	U	50	250	50	ug/kg	12/02/09	13:23
51) n-Butanol	71-36-3	BQL	U	200000	5000	50	ug/kg	12/02/09	13:23
52) o-Xylene	95-47-6	BQL	U	24	250	50	ug/kg	12/02/09	13:23
53) trans-1,2-dichloroethene	156-60-5	BQL	U	78	250	50	ug/kg	12/02/09	13:23
54) trans-1,3-dichloropropene	10061-02-6	BQL	U	50	250	50	ug/kg	12/02/09	13:23

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1DL2	Lab Sample ID:	911079-001-005-2/7DL2
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW5030B
Prepared Date/Time:	12/02/2009 10:35	Analytical Method:	SW8260B

# Surrogate Parameter	CAS	Percent Recovery	Control Limits	Dil Fact	Analysis Date/Time	
55) 1,2-Dichloroethane-d4	17060-07-0	94 %	65 - 125	50	12/02/09	13:23
56) 4-Bromofluorobenzene	460-00-4	96 %	85 - 120	50	12/02/09	13:23
57) Dibromofluoromethane	**1868-53-7**	**1 %**	**85 - 115**	**50**	**12/02/09**	**13:23**
58) Toluene-D8	2037-26-5	98 %	85 - 115	50	12/02/09	13:23

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1	Lab Sample ID:	911079-001-011-1/2
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW3550
Prepared Date/Time:	11/30/2009 09:30	Analytical Method:	SW8270C

#	Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time	
1)	1,2,4,5-Tetrachlorobenzene	95-94-3	BQL	U	110000	950000	1	ug/kg	12/01/09	00:55
2)	1,2-Dichlorobenzene	95-50-1	BQL	U	100000	950000	1	ug/kg	12/01/09	00:55
3)	1,2-Diphenylhydrazine	122-66-7	BQL	U	100000	950000	1	ug/kg	12/01/09	00:55
4)	1,3-Dichlorobenzene	541-73-1	BQL	U	100000	950000	1	ug/kg	12/01/09	00:55
5)	1,4-Dichlorobenzene	106-46-7	BQL	U	88000	950000	1	ug/kg	12/01/09	00:55
6)	1,4-Dioxane (P-Dioxane)	123-91-1	BQL	U	210000	950000	1	ug/kg	12/01/09	00:55
7)	2,3,4,6-Tetrachlorophenol	58-90-2	BQL	U	150000	950000	1	ug/kg	12/01/09	00:55
8)	2,4,5-Trichlorophenol	95-95-4	BQL	U	180000	950000	1	ug/kg	12/01/09	00:55
9)	2,4,6-Trichlorophenol	88-06-2	BQL	U	190000	190000	1	ug/kg	12/01/09	00:55
10)	2,4-Dichlorophenol	120-83-2	BQL	U	180000	950000	1	ug/kg	12/01/09	00:55
11)	2,4-Dimethylphenol	105-67-9	BQL	U	140000	950000	1	ug/kg	12/01/09	00:55
12)	2,4-Dinitrophenol	51-28-5	BQL	U	510000	190000	1	ug/kg	12/01/09	00:55
13)	2,4-Dinitrotoluene	121-14-2	BQL	U	170000	950000	1	ug/kg	12/01/09	00:55
14)	2,6-Dichlorophenol	87-65-0	BQL	U	140000	950000	1	ug/kg	12/01/09	00:55
15)	2,6-Dinitrotoluene	606-20-2	BQL	U	130000	950000	1	ug/kg	12/01/09	00:55
16)	2-Chloronaphthalene	91-58-7	BQL	U	26000	950000	1	ug/kg	12/01/09	00:55
17)	2-Chlorophenol	95-57-8	BQL	U	160000	950000	1	ug/kg	12/01/09	00:55
18)	2-Nitroaniline	88-74-4	BQL	U	120000	950000	1	ug/kg	12/01/09	00:55
19)	2-Nitrophenol	88-75-5	BQL	U	100000	950000	1	ug/kg	12/01/09	00:55
20)	2-methylphenol	95-48-7	BQL	U	250000	950000	1	ug/kg	12/01/09	00:55
21)	4,6-dinitro-2-methyl phenol	534-52-1	BQL	U	160000	190000	1	ug/kg	12/01/09	00:55
22)	4-Bromophenyl-phenylether	101-55-3	BQL	U	140000	950000	1	ug/kg	12/01/09	00:55
23)	4-Chloroaniline	106-47-8	BQL	U	100000	950000	1	ug/kg	12/01/09	00:55
24)	4-Nitroaniline	100-01-6	BQL	U	260000	950000	1	ug/kg	12/01/09	00:55
25)	4-Nitrophenol	100-02-7	BQL	U	630000	190000	1	ug/kg	12/01/09	00:55
26)	4-chloro-3-methylphenol	59-50-7	BQL	U	250000	950000	1	ug/kg	12/01/09	00:55
27)	4-methylphenol	106-44-5	BQL	U	430000	190000	1	ug/kg	12/01/09	00:55
28)	Acenaphthene	83-32-9	BQL	U	88000	950000	1	ug/kg	12/01/09	00:55

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1	Lab Sample ID:	911079-001-011-1/2
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW3550
Prepared Date/Time:	11/30/2009 09:30	Analytical Method:	SW8270C

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1	Lab Sample ID:	911079-001-011-1/2
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW3550
Prepared Date/Time:	11/30/2009 09:30	Analytical Method:	SW8270C

# Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time	
29) Acenaphthylene	208-96-8	BQL	U	60000	950000	1	ug/kg	12/01/09	00:55
30) Acetophenone	98-86-2	BQL	U	120000	950000	1	ug/kg	12/01/09	00:55
31) Aniline (Phenylamine,	62-53-3	BQL	U	110000	950000	1	ug/kg	12/01/09	00:55
32) Anthracene	120-12-7	BQL	U	120000	950000	1	ug/kg	12/01/09	00:55
33) BIS(2-Chloroisopropyl)ether	39638-32-9	BQL	U	95000	950000	1	ug/kg	12/01/09	00:55
34) Benzo[a]anthracene	56-55-3	BQL	U	110000	950000	1	ug/kg	12/01/09	00:55
35) Benzo[a]pyrene	50-32-8	BQL	U	86000	950000	1	ug/kg	12/01/09	00:55
36) Benzo[b]fluoranthene	205-99-2	BQL	U	370000	950000	1	ug/kg	12/01/09	00:55
37) Benzo[g,h,i]perylene	191-24-2	BQL	U	130000	950000	1	ug/kg	12/01/09	00:55
38) Benzo[k]fluoranthene	207-08-9	BQL	U	280000	950000	1	ug/kg	12/01/09	00:55
39) Benzyl Butyl Phthalate	85-68-7	BQL	U	54000	950000	1	ug/kg	12/01/09	00:55
40) Bis(2-chloroethoxy)methane	111-91-1	BQL	U	46000	950000	1	ug/kg	12/01/09	00:55
41) Bis(2-chloroethyl) ether	111-44-4	BQL	U	180000	950000	1	ug/kg	12/01/09	00:55
42) Bis(2-ethylhexyl) phthalate	117-81-7	BQL	U	120000	950000	1	ug/kg	12/01/09	00:55
43) Chrysene	218-01-9	BQL	U	120000	950000	1	ug/kg	12/01/09	00:55
44) Dibenz[a,h]anthracene	53-70-3	BQL	U	97000	950000	1	ug/kg	12/01/09	00:55
45) Diethyl Phthalate	84-66-2	BQL	U	120000	950000	1	ug/kg	12/01/09	00:55
46) Dimethyl Phthalate	131-11-3	BQL	U	120000	950000	1	ug/kg	12/01/09	00:55
47) Fluoranthene	206-44-0	BQL	U	180000	950000	1	ug/kg	12/01/09	00:55
48) Fluorene	86-73-7	BQL	U	100000	950000	1	ug/kg	12/01/09	00:55
49) Hexachlorobenzene	118-74-1	BQL	U	77000	950000	1	ug/kg	12/01/09	00:55
50) Hexachlorobutadiene	87-68-3	BQL	U	46000	950000	1	ug/kg	12/01/09	00:55
51) Hexachlorocyclopentadiene	77-47-4	BQL	U	220000	950000	1	ug/kg	12/01/09	00:55
52) Hexachloroethane	67-72-1	BQL	U	86000	950000	1	ug/kg	12/01/09	00:55
53) Indeno[1,2,3-cd]pyrene	193-39-5	BQL	U	120000	950000	1	ug/kg	12/01/09	00:55
54) N-Nitrosodi-n-propylamine	621-64-7	BQL	U	220000	950000	1	ug/kg	12/01/09	00:55
55) N-Nitrosodimethylamine	62-75-9	BQL	U	68000	950000	1	ug/kg	12/01/09	00:55
56) N-Nitrosodiphenylamine	86-30-6	BQL	U	71000	950000	1	ug/kg	12/01/09	00:55

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1	Lab Sample ID:	911079-001-011-1/2
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW3550
Prepared Date/Time:	11/30/2009 09:30	Analytical Method:	SW8270C

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1	Lab Sample ID:	911079-001-011-1/2
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	SW3550
Prepared Date/Time:	11/30/2009 09:30	Analytical Method:	SW8270C

# Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time	
57) Naphthalene	91-20-3	BQL	U	40000	950000	1	ug/kg	12/01/09	00:55
58) Nitrobenzene	98-95-3	BQL	U	68000	950000	1	ug/kg	12/01/09	00:55
59) Pentachloronitrobenzene	82-68-8	BQL	U	170000	950000	1	ug/kg	12/01/09	00:55
60) Pentachlorophenol	87-86-5	BQL	U	240000	190000	1	ug/kg	12/01/09	00:55
61) Phenanthrene	85-01-8	BQL	U	94000	950000	1	ug/kg	12/01/09	00:55
62) Phenol	108-95-2	BQL	U	250000	950000	1	ug/kg	12/01/09	00:55
63) Pyrene	129-00-0	BQL	U	200000	950000	1	ug/kg	12/01/09	00:55
64) Pyridine	110-86-1	BQL	U	120000	290000	1	ug/kg	12/01/09	00:55
65) di-n-Butyl Phthalate	84-74-2	BQL	U	180000	950000	1	ug/kg	12/01/09	00:55
66) di-n-Octyl Phthalate	117-84-0	BQL	U	240000	950000	1	ug/kg	12/01/09	00:55

# Surrogate Parameter	CAS	Percent Recovery	Control Limits	Dil Fact	Analysis Date/Time	
67) 2,4,6-Tribromophenol	**118-79-6**	**30 %**	**35 - 125**	**1**	**12/01/09**	**00:55**
68) 2-Fluorobiphenyl	321-60-8	92 %	45 - 105	1	12/01/09	00:55
69) 2-Fluorophenol	367-12-4	81 %	35 - 105	1	12/01/09	00:55
70) Nitrobenzene-d5	4165-60-0	95 %	35 - 100	1	12/01/09	00:55
71) Phenol-d5	4165-62-2	87 %	40 - 100	1	12/01/09	00:55
72) p-Terphenyl-d14	1718-51-0	92 %	30 - 125	1	12/01/09	00:55

Analytical Summary Report

Client Name:	Arctech	Sample Matrix:	SOIL
Client Sample ID:	A-HAX-1	Lab Sample ID:	911079-001-013-1/1
Sample Date/Time:	11/24/2009 11:00	Percent Moisture:	NA
Receipt Date/Time:	11/25/2009 11:21	Preparation Method:	NA
Prepared Date/Time:		Analytical Method:	SW9014R

#	Parameter	CAS	Reported Result	Q	Method Detection Limit	Reporting Limit	Dil Fact	Units	Analysis Date/Time
1)	Cyanide, Reactive	REACT-CN	BQL	U	0.02	0.020	1	mg/kg	12/01/09 14:00

TECHNICAL BULLETIN # 5

HUMIC ACID
A REVIEW OF CHARACTERISTICS, PROPERTIES, ANALYTICAL METHODS AND APPLICATIONS

PREPARED BY

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ARCTECH
Preserving tomorrow's world... today

FOREWORD

Humic acid is unique natural organic material with many versatile properties which is now increasingly being utilized for meeting several real world needs. This technical bulletin is a compilation of the available literature on the characteristics, properties, analytical methods and applications of humic acid.

This review is periodically prepared by the ARCTECH Humic Substances Research Team over the past ten years. It presents the state of the art scientific information as well as the overview of the properties and potential applications of humic acid in a number of situations including agriculture and environmental remediation. ARCTECH, Inc. manufactures humic acids under the trade name actosol® - an organic humic biostimulant and fertilizer, HUMASORB® - a multipurpose pollution filter, Actodemil® - for safe destruction and recycling of explosives into fertilizer and 3PM™ - for pollution prevention and profits from manure and wastes. It is developing a number of processes and products to exploit the unique properties of humic acid.

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HUMIC ACID

A REVIEW OF CHARACTERISTICS, PROPERTIES, ANALYTICAL METHODS AND APPLICATIONS

INTRODUCTION

Humic substances (HSs) are naturally occurring, brown and black organic matter. Comprised of humic acid, fulvic acid and humin, they are collectively called "humus." The importance of humus in productive agriculture has been known for a long time. Today, HSs isolated from coals can provide a practical and economic enhancement approach for sequestering large volumes of carbon dioxide resulting from combustion of carbon fuels. Application of HSs in soil results in increased crop yields and tree biomass even in arid, saline, impaired lands which otherwise are lying barren. The HSs applied in the soils become stable and increased biomass uptakes more carbon dioxide.

Humic substances are the largest component of soil organic matter. They also account for up to 95% of the total dissolved organic matter in natural waters. HSs act as buffers and help to counteract the effects of acid rain in lakes, rivers and forests. Most importantly, HSs are the fourth largest storehouse of carbon in our planet, as shown in Table 1.

Table 1. Estimated size of major pools of carbon in the world carbon budget

	Trillion kilograms of carbon
Atmosphere (as CO_2)	700
Land	
Biomass	480
Humic substances (expressed as 50% of soil organic matter)	1500-2500
Waters	
Freshwater	250
Marine dissolved and suspended	4150
Sediments	2,000,000
Fossil fuels	10,000

Sources: B. Bolin *Science*, **196**: 613 (1977); B. Bolin and R. B. Cook (Eds.), *The Major Biogeochemical Cycles and Their Interactions*, Wiley, New York, 1983.

The American Society of Agronomy classifies the three components of HSs based on solubility. Fulvic acids (yellow) are very soluble in water, but brown humic acids (HAs) precipitate when acid is added to HA solutions. Humins (with a brown-black color) are insoluble in water and are believed to consist of humic acid molecules firmly attached to clay (such as kaolinite) or a mineral (such as hematite).

Humic acids are the major fraction of humic substances. They contain more carbon than all living things. HAs exist in plants, soils, water, municipal solid waste, compost and sewage, and they are being isolated from soft coals. HAs strongly retain water and they are the buffer and matrix of chemical and biochemical reactions in soils.

Although the detailed molecular structures of HAs are unknown at present, HAs behave as if they have two main structural features. One feature is chemical functional groups, which help HAs to regulate physical and chemical reactions. Chemical functional groups include carboxylic, phenolic, aliphatic and enolic-OH and carbonyl/quinoid (C=O). An example of a physical reaction is the binding of a plant nutrient such as magnesium (thus concentrating the metal for absorption through the plant roots). Another is binding of a toxic metal such as cadmium (tying up the metal and keeping it out of the water supply). Another physical reaction is retention of water, which is essential for plant growth.

HAs also direct chemical reactions because they can accept and donate electrons. For example, HAs can convert carcinogenic chromate in the water from plating and tanning factories to non-toxic chromic ions. A biochemical example is that HAs act as mediators in the reactions of microbes with iron-containing minerals. The HAs help to transfer electrons produced by the microbes to the minerals as the microbes eat, grow and reproduce. The microbes themselves cannot interact directly with the minerals, but HAs can. Another property is that HAs buffer the pH of soil water and thereby affect microbial and enzymatic activity.

Chemical or biological mineralization and thermal oxidation of any organic material releases carbon dioxide in the air. If all the carbon behaved in this way we would have only plants (grown by photosynthesis) on the land and carbon dioxide in the air, but there would be no organic matter in the soils. (Some carbon dioxide in the air interacts with inorganic compounds such as limestone on the land and in water sediments, and this helps to somewhat reduce the amount of CO_2 in the air). Plants need water, air and soil to grow and reproduce. The fact is that soils exist because humic substances are stable compared to carbohydrates and other plant and animal molecules. Carbon dating indicates that some HSs are 10,000 to 30,000 years old. HUMASORB®, a cross-linked humic acid product created by Arctech for remediation, is almost as stable as coal. HUMASORB ® provides an excellent approach for carbon sequestration, while also of added benefit for removing toxic contaminants from the environment.

As noted above that HSs have functional groups that they use to bind metals and retain water. Their other structural feature is carbon-rich units ("greasy blobs") that give the HA molecules some hydrophobic (water-repellant) character. One HA model has the hydrophilic (water-loving) functional groups on the outside and the hydrophobic groups on the inside of a molecule that looks like a telephone cord. The molecule presumably can "turn itself inside out" as necessary, making the outside hydrophobic.

The scanning electron micrograph below shows a sample of a solid HA and the Figure 1 shows a proposed molecular structure that has a mainly hydrophilic exterior. A hypothetical structure of humic acid is shown in Figures 2 and 3.

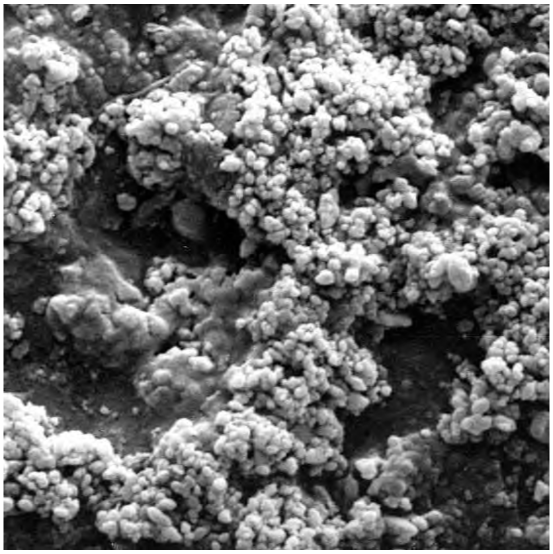


Figure 1. SEM image (approx 2000 times enlarged) of a solid humic acid (www.hagroup.neu.edu).

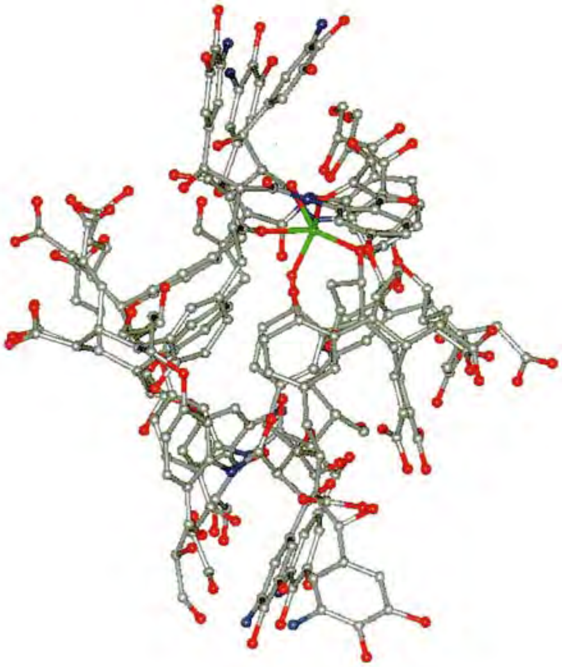
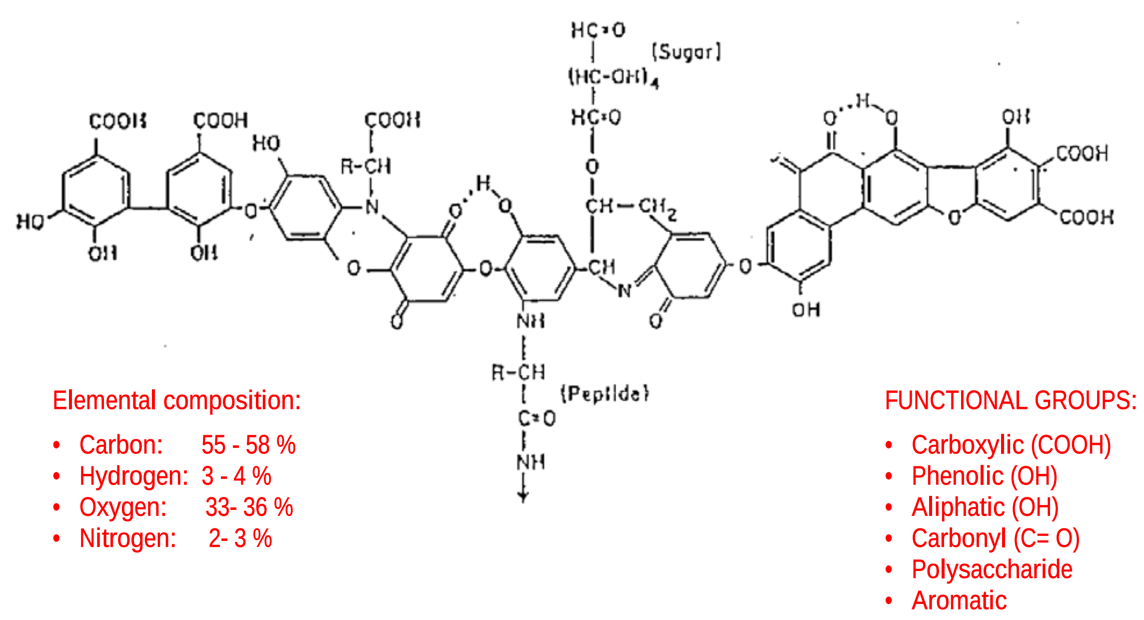


Figure 2. A proposed humic acid building block with a hollow interior for water retention (Davies et al., 1997 [1]).



Elemental composition:

- Carbon: 55 - 58 %
- Hydrogen: 3 - 4 %
- Oxygen: 33- 36 %
- Nitrogen: 2- 3 %

FUNCTIONAL GROUPS:

- Carboxylic (COOH)
- Phenolic (OH)
- Aliphatic (OH)
- Carbonyl (C= O)
- Polysaccharide
- Aromatic

Figure 3. Proposed hypothetical structure of humic acid [2].

SOURCES AND OCCURRENCE OF HUMIC ACID

Humic acid can be derived from a number of sources. The most predominant ones include coal, soil humus and sewage sludge.

Coal: Coal being the most abundant and predominant product of plant residue coalification is a major source of humic acid. All ranks of coal contain humic acid but leonardite, an oxidized form of lignite represents the most easily available and concentrated form of humic acid. Leonardite is a naturally occurring overlay of lignite mines with concentration of humic acid ranging from 30-90 % depending on location.

Soil humus: Humic acid is the major extractable component of soil humic substances. Soil humic acid are of greater ^{14}C age, have higher aromatic carbon and higher polysaccharide content than aquatic humic substances.

Sewage sludge: Sewage sludge contains equal proportions of humic and fulvic acid fractions on average. The sludge typically contains 20 to 30% organic carbon. In contrast to soil humic acid, humic acid obtained from sludge has higher nitrogen content, lower carbon to nitrogen ratio, higher sulfur content, and higher hydrogen to carbon ratio (high aliphatic component). Also, the sludge humic acid is characterized by a lower concentration of carbonyl groups, lower total acidity and contains complex binding sites involving both nitrogen and oxygen ligand systems.

Humic acid is ubiquitous present in several natural materials. Based on its key attribute that it is soluble at pH >2 and precipitate below pH 2. Several natural materials were tested for humic acid contents. Results of these tests are shown in Figure 3.

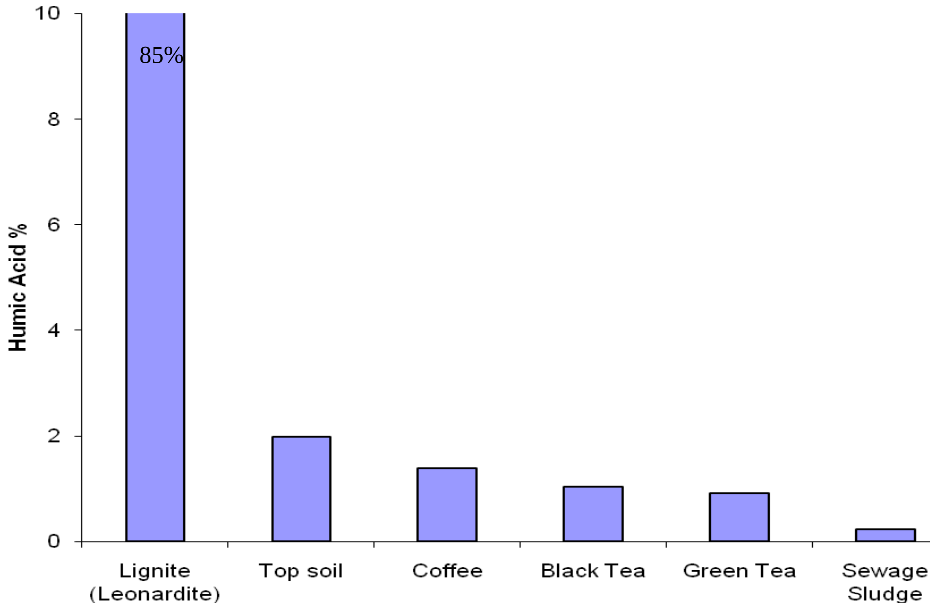


Figure 3. Humic acid contents in various materials.

RECENT ADVANCES IN HUMIC ACID RESEARCH

Humic acids (HAs) are black to brown, naturally occurring, and highly functionalized, carbon-rich biopolymers. They are the most important fraction of the humic substances family, which includes Fulvic acids (FAs) and Humins in addition to HAs. They are anchored by metal binding and attachment to clays and minerals, which decreases their solubility at a given pH. It is hard to distinguish between low $<M_W>$ HAs and FAs because useful ways of estimating polymer molecular mass (e.g. gel permeation chromatography and viscosity measurements) are frustrated by HAs' desire to aggregate.

HAs are the Earth's sponges, thermal buffers and storehouses. As its primary water retainers, metal binders and sorbents, HAs are essential to healthy soils and sediments. HAs' water retention gives the Earth thermal buffer capacity that prevents catastrophic climates. HAs are amorphous, *fractal* materials. Some studies suggest that HAs' density increases from the edge to the centre. New research predicts that HA molecules have hollow centers that normally are filled with water.

HA were thought only to result from plant and animal decay under moist conditions in a process called humification. However, HA has been isolated from a living plant (*Pilayella littoralis*) for the first time. Plants that contain HA and biomass that is easily composted are of enormous interest for soil creation, improvement and remediation.

HA also are found in the gastro-intestinal tract of humans and animals and HA are absorbed by animals. They circulate with the blood and are metabolized in the liver. Oral doses of HA reduce heavy metal absorption in animals and also decrease pesticide toxicity. HA can be administered prophylactically and therapeutically in animals, including pregnant animals, without apparent risk. Some HA control uterine cancer in rats and HA markedly reduce the mutagenic effect of benzopyrene, 3-aminoanthracene, 2-nitrofluorene and 1-nitropyrene. These desmutagenic effects depend on adsorption of mutagens on the HA surface. A recent comprehensive volume clearly links HA properties with human health [2].

Computational Studies of Humic Acid Structure: A complete elucidation of the HAs' structure is not known yet. This fact lead to frontier research on highly purified HAs and the prospects of understanding HAs' roles in the carbon cycle, biomineralization and other life processes.

Because of their polyfunctionality and ability to sorb, bind, fragment, aggregate and be oxidized and reduced. HAs are much more complicated than nucleic acids, polysaccharides and proteins. Their primary, secondary and higher order structures have been debated almost from the day HAs were first isolated. Early proposed HA building blocks were aromatic and "coal-like." Present knowledge indicates a hydrophobic framework of aromatic rings linked by more flexible carbon chains, with alcohol, amine, carboxylic, carbonyl, phenol and quinone functional groups. HAs' existence in live plants suggests they have rational primary and higher order structures resulting from biochemically controlled reactions [3].

Figure 4a shows the lowest energy conformation of the Temple-Northeastern-Birmingham (TNB) HA building block, which has an empirical formula of $C_{36}H_{30}O_{15}N_2 \bullet xH_2O$ ($x = 0 \approx 15$, water not shown) derived after allowance for polysaccharide and protein content from analytical data for HAs isolated with different methods from many different soil sources and from modeling work (3). Biosynthesis of this HA building block from phenylalanine and tryptophan has been rationalized. Figure 4b shows the three dimensional representation of the TNB building block, which resulted from the favorable $3.6A^0$ van der Waals' interaction between rings A and C in Figure 4a. Previous work shows that high purity HAs are chiral as indicated by the R&S configurations (Figure 4a) and contain amide bonds. Figure 4c predicts how the lowest energy TNB HA building blocks link through amide ("peptide") bonds to form a half turn of the hollow helical secondary structure made from two of the same TNB enantiomer (Figure 4d). The helix in Figure 4d is hydrophobic at north and south, has acidic functional groups at east and west, is lined with polar hydrophobic groups and has an elliptical cross section because of favorable ring A--ring C interactions (Figure 4b). This secondary structure likely is terminated by amino acids or carbohydrates that always are found with HAs. It has a central cavity for water, metal and solute binding. HA synthesis is Nature's way of retaining water and solutes within and between HA molecules and the HA helix normally is filled with water. This water-filled helical model is consistent with many HA properties.

Wershaw's membrane-micelle model of aggregated HA molecules has a sausage shape with polar, hydrophilic functional groups (e.g. carboxylic acid) on the ends and sides. Functional groups that are non-acidic or are made less polar by hydrogen bonding and other interactions are in the model's hydrophobic interior. Wershaw's model describes HA aggregation and HA attachment to clay and mineral surfaces through HA functional groups. It accounts for sorption of hydrophobic organic compounds (HOCs) in terms of partition in the hydrophobic HA interior, as when a solute distributes between water and an organic liquid. Polar solutes such as pesticides also interact specifically with HA functional groups or more rigid structural features like stacked aromatic rings (see Figure 4b). Sorption of two solutes by partition should be much less competitive than specific interaction with HA functional groups or rigid structural features. The helix predicted in Figure 4d has the shape anticipated by Wershaw and characteristics that account for partitional and specific solute sorption and metal binding by HAs [3].

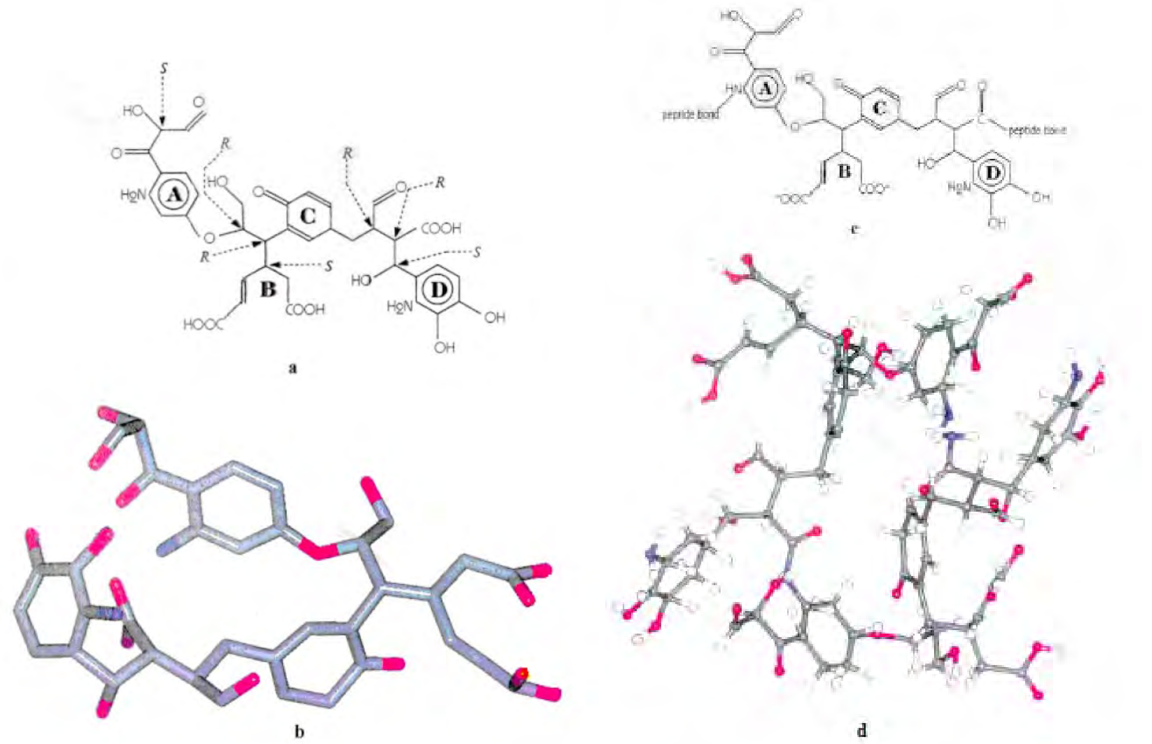


Figure 4. Proposed biosynthetically generated TNB HA building block (a) Lowest energy building block; (b) Three dimensional representation; (c) Building block linkages; (d) One half turn of the HA helix. Color code: C, gray; O, red; N, blue; H, white.

Characterization of Humic Acid: Dry, natural or synthetic humic acids are solids with densities in the range 1.5-1.7 gm/mL. Their surface areas measured by the Brunauer-Emmett-Teller method with adsorbent butane range from 10±3 m^2/gm for natural HA to 45±4 m^2/gm for synthetic HA. Pure HA are dispersed solids with moderately high surface areas. However, they are not highly porous. Most of the interior of humic acid particles is made up of covalently linked carbon, hydrogen, nitrogen and oxygen atoms.

Elemental analysis is one of the more reliable determinations that can be carried out on humic substances. The elements C and H are most frequently determined, with O generally being obtained by difference. Estimating O content by difference can be a serious source of error in many cases because it assumes that humic substances are constituted exclusively of C, H, and O. It has been found that C, H, O, N, P and S generally account for 100 % of the composition of humic substances on an ash-free basis, and it is recommended that six elements be determined where possible. Elemental compositions of typical humic acid derived from different sources are shown in Table 2 [4].

Table 2. Elemental composition of typical humic acid derived from different sources

	C	H	O	N	S	P
Aquatic humic acid$^+$	54.99	4.84	33.64	2.24	1.51	0.06
Soil humic acid$^+$	58.03	3.64	33.59	3.26	0.47	0.10
actocol^R humic acid^{++}	57.2	3.8	36.1	2.9	N.D.	N.D.

+ : From reference 3

++ : From reference 4 (actosol^R derived from leonardite)

The C, H, N and O contents of pure HA and the type (alcohol, amine, carbonyl, carboxylic acid, phenol, quinone), amounts and relative amounts of their functional groups depend on the source but do not vary greatly. The carboxylic acid and phenolic groups are responsible for the total acidity of humic acid. The functional group composition of humic acid obtained from neutral soils is shown in Table 3 [5].

Table 3. Functional group composition of humic acid derived from a neutral soil [5]

Functional group	Concentration meq/100 gm
Total acidity	620-660
COOH	390-450
Acidic OH	210-250
Weakly acidic + alcoholic OH	240-320
Quinone C = O and ketonic C = O	450-560
OCH_3	30

The ultraviolet-visible spectra of humic acids in alkaline solution contain no strong features, although shoulders centered at 260-300 nm are sometimes detected and the absorbance generally increases with decreasing wavelength. However, the ratio Q (E_4 /E_6, where E_4 and E_6 are the absorbances at 465 and 665 nm, respectively) often is in the characteristic range 3 - 6 in 0.05 M $NaHCO_3$.

The infra-red spectra of HA are useful fingerprints. They contain features indicating the presence of oxygen-containing functional groups and aromatic character. Table 4 shows the assignments of different IR features.

Table 4. Assignments of IR absorption bands of HA

Frequency (cm^{-1})	Assignments
3420-3380	O-H or N-H stretching
3000-2920	aliphatic C-H stretching in CH_2 and CH_3
2900-2700	vibration of aldehyde groups
2880-2815	vibration of aldehyde groups, C-O stretching of ethers
1730-1720	C=O stretching of COOH, ketones or aliphatic aldehydes
1650-1630	asymmetric stretching of COO^-, aromatic C=C, C=O in CHO, C=O of quinones or in conjugation with alkenes
1560-1540	aromatic C=C or NH deformation in amides
1420-1320	deformation of aliphatic C-H or OH, stretching of C-O in phenol groups, symmetrical stretching of COO^-
1225-1175	vibration of C=O in Ar-carbonyl groups or deformation of CH_2 in alkyl-carboxyl groups
1100-1060	C-O stretching of polysaccharides or Si-O vibration (impurities)
1050-1020	O-H and C-O stretching in various groups
1000-650	vibration of aromatic >C-H or =C-H groups, vibration of COOH
600-400	aliphatic C-C vibration

Nuclear magnetic resonance is a valuable fingerprint of the functional groups of HA. The ^1H and ^{13}C spectra often are obtained in alkaline $NaOD/D_2O$ solutions. ^{13}CPMAS solid state data are also useful. The peaks are often broad but are still assignable. Functional groups that can be identified and expressed in relative amounts are listed in Table 5. Typical ^{13}CPMAS spectra of HA isolated from soil is shown in Figure 5.

Electron paramagnetic activity is associated with the presence of free radicals (for example, resulting from electron transfer to quinones) and/or paramagnetic ions such as Cu^{2+} and Fe^{3+}.

Other identifying features of highly purified humic acids include broad, low angle X-ray powder diffraction peaks (indicating an amorphous structure) that are sometimes accompanied by sharper peaks associated with residual minerals.

Electron microscopy indicates the characteristic spherical or spheroidal shape of humic acid particles. The spheroids aggregate to form irregularly shaped, elongated particles [3].

Table 5. Nuclear magnetic resonances of humic acids

(a) ^{1}H spectra

d, ppm	Assignment	Relative intensity
0.9-1.08	aliphatic	1.6
3.3	HO-alkyl	0.6
4.8	HO-aryl	1.1
5.1	olefinic	1.0
3.0 -5.5	glycosidic	6.2
6.1- 7.2	aromatic/quinoid	3.1

(b) ^{13}C spectra

120	aryl-C-H	13.0
160	aryl-C-OH	5.0
170	-COOH	1.0
190	quinoidal C	0.1

(c) ^{13}CPMAS spectra

0-40	aliphatic C-H
40-100	aliphatic C-OH
80-105	acetol
110-130	aromatic C-H
140-155	phenol C-OH
176	- COOH

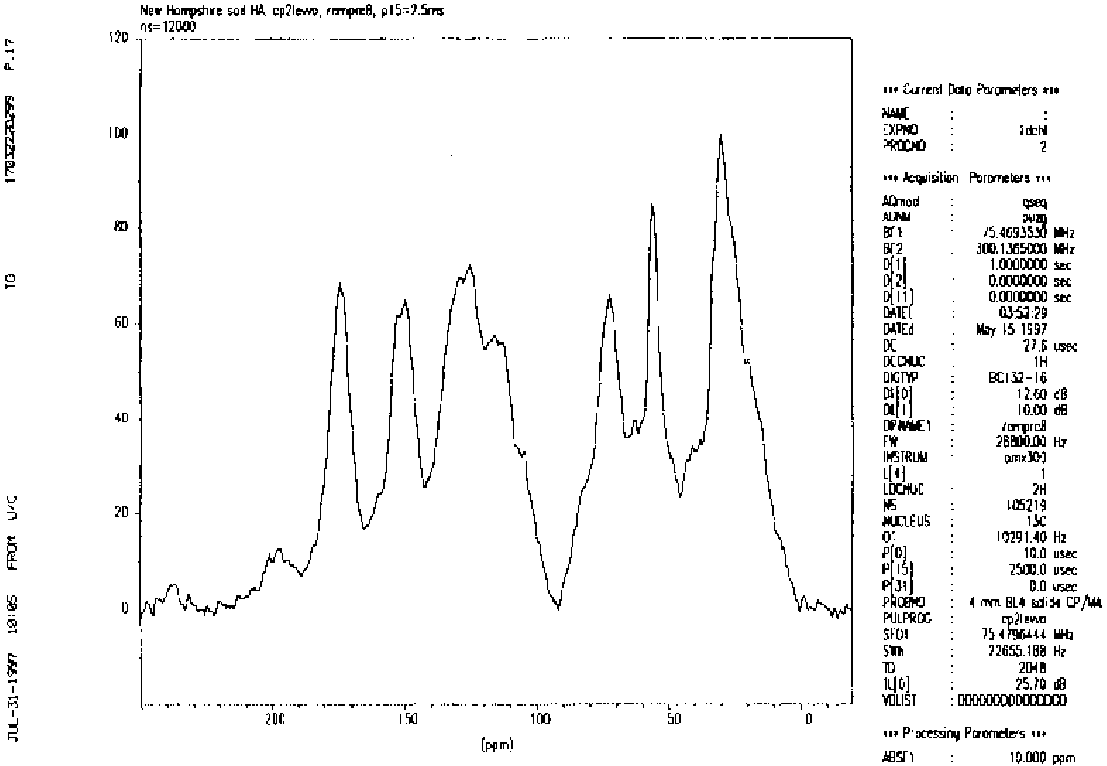


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Figure 5. ^{13}CPMAS Spectra of humic acid.

PROPERTIES

The properties and characteristics of humic acid include:

- High cation exchange capacity,
- Ability to chelate metals,
- Ability to adsorb organics,
- Precipitates easily at high pH in the presence of coagulants,
- Easily combustible due to its organic nature.

Cation Exchange: In comparison to leonardite, humic acid is characterized by high cation exchange capacity. The exchange capacity of leonardite is 50 meq/100 gm, whereas that of humic acid derived from leonardite is 200-500 meq/100 gm. In comparison, the exchange capacity of commercial ion exchange resins is approximately 150 meq/100 gm. The cation exchange capacity of a few soil colloids are shown in Table 6 [6].

Humic acid can help provide slow release of plant macronutrients such as nitrogen, phosphorus, sulfur for agricultural purposes. The ability to form complexes with metal ions and high cation exchange capacity contributes to cation retention. The exchange capacity is useful to retain plant macro- and micronutrients and prevent leaching.

Table 6. Cation exchange capacity of major soil colloids [9]

Soil colloid	Cation exchange capacity, meq/100 gm
Humus	200
Vermiculite	100-150
Montmorillonite	70-95
Illite	10-40
kaolinite	3-15
Sesquioxides	2-4

Chelation of metals: Metals are bound to the carbon skeleton of humic substances through heteroatoms such as nitrogen, oxygen or sulfur. Sulfur is present in low concentrations. Its effect on metal binding, however, is not understood very well. Nitrogen is present in significant concentration and has been shown to have a positive effect on metal binding. According to the evidence in the literature, the most common metal binding occurs via carboxylic and phenolic oxygen. A conceptual view of metal binding by humic acid is shown in Figure 6.

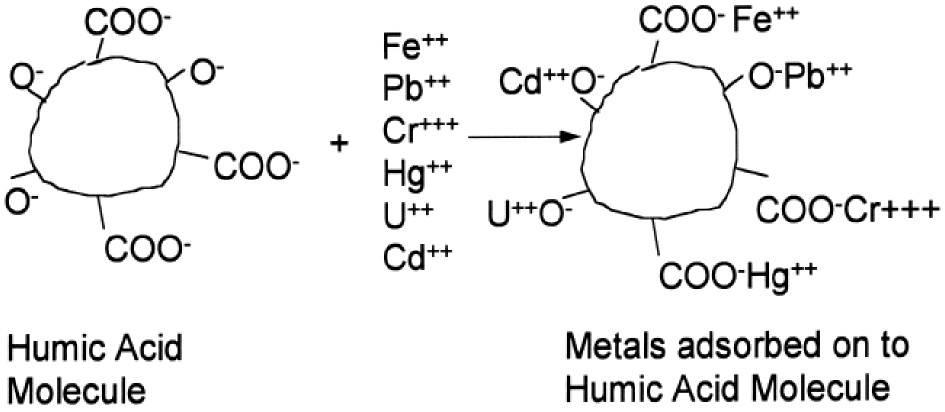


Figure 6. Conceptual view of metal ions attached to humic acid.

Adsorption of organics: Humic acid is an association of molecules forming aggregates of elongated bundles of fibers at low pHs and open flexible structures perforated by voids at high pHs. The voids can trap and adsorb both organic and inorganic particles if the charges are complementary. Humic acid combines with herbicides by electro-static bonding (i.e., attraction of a positively charged organic cation to an ionized carboxylic or phenolic group), hydrogen bonding and ligand exchange. In addition, the high concentrations of stable free-radicals in humic acid are capable of binding herbicides that can ionize or protonate to the cation form. The mechanisms that have been postulated for the adsorption of organic compounds include [7]:

- Van der Waals attractions
- hydrophobic bonding

- hydrogen bonding
- charge transfer
- ion exchange
- ligand exchange

Van der Waals forces are involved in the adsorption of non-ionic and non-polar compounds. These forces result from short range dipole-dipole interactions and are additive in nature. The forces between the atoms of the adsorbate and the adsorbent can result in considerable attraction for large molecules.

Non-polar compounds are also adsorbed by the hydrophobic bonding mechanism. This type of bonding is believed to be responsible for the strong adsorption of compounds such as dichlorodiphenyltrichloroethane (DDT) and organochlorine insecticides. This mechanism is also believed to be responsible for the adsorption of hydrocarbons.

Hydrogen bonding is also a dipole-dipole interaction in which the hydrogen atom serves as a bridge between two electronegative atoms. One of the electronegative atoms is held by a covalent bond and the other by electrostatic forces. The adsorption of anionic herbicides on humic acid is attributed to hydrogen bonding. This mechanism may also explain the ability of soils containing humic acid to retain moisture.

The binding of organic compounds which exist as cations, or are positively charged through protonation on to humic acid can occur by ion-exchange. The adsorption of herbicides such as paraquat and diquat by humic acid occurs by ion-exchange through the carboxylic and phenolic-OH groups.

Ligand exchange involves the replacement of ligands by a stronger chelating molecule. The compounds formed are known as coordination compounds or complexes and contain a central atom or ion (usually a metal) surrounded by a cluster of molecules.

Precipitation and coagulation: Humic acid is present in water as a negatively charged macromolecule in the colloidal size range. Coagulants such as alum can be used to overcome the stability of the molecule in water through two destabilization mechanisms: charge neutralization (adsorption) and precipitation [8].

Charge neutralization occurs due to a chemical interaction between positively charged aluminum species and negatively charged humic colloids. This chemical interaction can be accomplished over a narrow pH range (4-6). Destabilization by precipitation is accomplished by using higher dosage of alum compared to charge neutralization. The precipitation is believed to occur by either coprecipitation of aluminum humate with aluminum hydroxide floc or by incorporation of the humic matter within the aluminum hydroxide floc (sweep coagulation) [8]. In addition, coagulation and precipitation of humic acid can occur by complexation of hydrolyzed soluble aluminum polymer by humic colloids.

Toxicity: Humic acid is less toxic compared to the conventional chelating agents used in agriculture such as ethylenediaminetetraacetic acid (EDTA). The acute oral LD/50 for humic acid is 5.5 gms/kg [9], for EDTA it is 2 gms/kg [10] and as a reference it is 10 mg/kg for potassium cyanide [11]. Humic acid is thus three times less toxic than EDTA and potassium cyanide is 550 times more toxic than humic acid.

ANALYTICAL METHODS FOR HUMIC AND FULVIC COMPONENTS

Humic substances are the naturally occurring brownish black organic multifunctional polymers comprising of aromatic macromolecule with various linkages between the aromatic groups. The different compounds involved in linkages include amino acids, amino sugars, peptides, aliphatic acids and other aliphatic compounds. The various functional groups in humic substances include carboxylic groups (COOH), phenolic, aliphatic and enolic - OH and carbonyl (C=O) structures of various types.

Humic substances traditionally are classified into three main fractions by their aqueous solubility as shown in the following Figure 7:

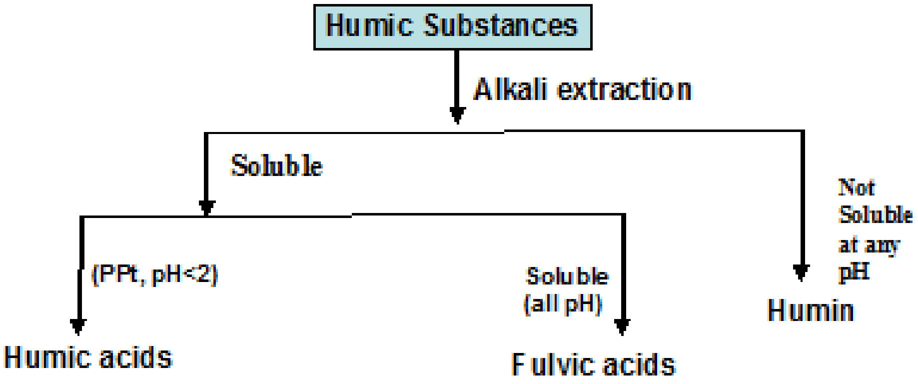


Figure 7. Classification of humic substance.

Professor Geoff Davies of the Northeastern University in Boston, MA, USA, describes that FA's, the smallest molecule as babies, HA's are the adult, and the Humin as the deceased ancestors as they lack any functional groups. Humic acids, the most important member of the humic substances family and they are highly functionalized, carbon-rich biopolymers that stabilize soils as soil organic matters. Almost 70% of the soil organic matter is generally found to be comprised of humic substances. The elemental analysis of the humic acid shows that C, H, O, N, P and S generally account for 100% of their composition. Humic acids are colloids and behave somewhat like clays, even though the nomenclature suggests that they are acids and form true salts. When the cation exchange sites on the humic molecule are filled predominantly with hydrogen ions, the material is considered to be an acid and becomes water insoluble solid. When the predominant cation on the exchange sites is other than hydrogen, the material is called humate. In current commercial literature liquid products are promoted as humic acid, even though they are humate salts of potassium, calcium, iron, ammonium etc.

Several models of the humic acid structure have been proposed based on the observed properties. These models are either based on the fact that the humic acid is a heterogeneous mixture of organic acids, or the humic acid has a definite structure of repeated units.

As a water retainer, metal binder, and absorbent, humic acid is essential to maintenance of fertile soils recognized for centuries for cultivation of lands. The word ‘HUMUS” has its origin in Greek, which referred it to fertile soil. The AJURVEDA from the Vedic literature in Sanskrit from India, which guides the use of various plants to maintain healthy life, and it describes the basis of the plants are soils and the juices of the soils connect the non-living to living. Humic acid’s water retention property gives the earth a thermal buffer capacity that prevents catastrophic climates. The versatile characteristic properties of humic acid include: a high cation exchange capacity, the ability to chelate metals, the ability to adsorb organics, a high water holding capacity, an ease of precipitation at low pH or in the presence of coagulants, and an ease of combustion due to its organic nature. These versatile properties are useful for agricultural and environmental purposes. Humic substances are the third largest storehouse of carbon in our planet, after carbonate rocks/sediments/oceans and fossil fuels. Replenishment of these in soils offers an economic value generating approach for carbon sequestration and combating climate change concerns.

Benefits of humic acids in agriculture: Role of humic acid in growing cycle of the plant--- three ways it helps.

Physical Benefits:

- **Increases moisture holding capacity**
- **Improves soil tilth & infilteration of compacted soils**

Chemical Benefits

- **Increases cation exchange capacity & chelation of plant nutrients**
- **Improves photosynthesis**
- **Converts phosphorus into plant available form**
- **Improves buffering properties of soils**
- **Increases water uptake in high salinity soils by modulating osmotic pressure**

Biological Benefits

- **Accelerates plant cell division and promotes growth**
- **Stimulates hormonal activity as a supplemental auxin**
- **Stimulates growth & proliferation of soil microorganisms**
- **Aids in photosynthesis**.

So even on application of small amounts of humic acid, the first benefits result from the biological activities and then on cumulative additions of humic acid especially in the soil results in imparting physical and chemical benefits. Physical benefits result in agglomerating the soil (improves tilth and improves infiltration of soils) especially soils compacted with high Na and salt build up, by increasing moisture holding capacity- thus resistant to drought, decreases soil erosion. Chemical benefits result by increasing EC of soils, increasing nutrient up take especially P, increasing buffering capacity. It is being recognized that the use of humic acid products in water soluble liquid form provide economical benefits from use of only 2-5 gallons per acre as foliar and in soils then addition of powder/granular humic products in soils which require both right conditions and long periods for providing benefits. Today worldwide the use of HA products are being recognized as excellent natural biostimulant.

These benefits include slow release of the micronutrients for the plants. For example, humic acid increases the availability of phosphate to the plant by breaking the bond between the phosphate ion and iron or calcium. Phosphate is a stimulator of seed germination and root initiation in plants. In addition, humic acid is very effective in conversion of iron to suitable forms to protect the plants from chlorosis, even in the presence of high concentrations of the phosphate ion. Humic acid contributes to mineralization and immobilization of nitrogen in soil. The complexes formed between ammonium ions and humic acid are reported to release nitrogen slowly in to the soil. Humic acid serves as a slow release nitrogen carrier in the soil in this respect.

These properties are of great importance, not only in controlling the uptake of nutrients by the plant and their retention in the soil, but also in suppressing the deleterious effect of soil acidity. Humic acid mitigates the negative effect of high salinity on plants. **The Humic Acid optimum efficacy and its positive effect on increasing yield and quality of plants depends critically on its concentration at the time of application. At high concentration, humic acid has herbicidal effect and can cause phytotoxicity to the plants.** As shown in the following Figure8, application rate ranges from 800 ppm for foliar applications and 1500 ppm for soil applications. Many scientific research studies show that the optimum application rates of HA for plant growth have been reported to range from 50 to 350 ppm.

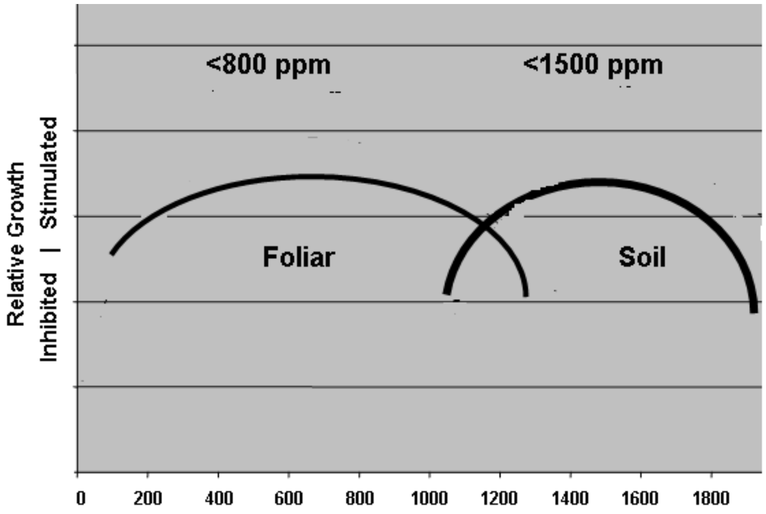


Figure 8. Application rates of humic acid for plant growth.

Another important factor in consideration of humic acid content of the commercial products is requirement of water to ensure its dilution below the phytotoxicity level. Thus the products made with too high a concentration, e.g. 12% will require 150 gallons for every gallon of product applied for foliar application. Many agricultural areas, especially in unirrigated lands, water is scarce. Therefore, it is recommended that these products should be provided at a lower humic acid concentration. The method of analysis and the proper dilution factor are extremely important for achieving beneficial results from the application of humic acid products. Another important factor in considering the humic acid content of the product is that, at a high concentration, it limits the ability to formulate it with other plant nutrients. When nutrients are added to a high concentration of humic acid product, it results in a highly viscous and thick product.

Many researchers are also reporting the importance of maintaining acceptable lower concentration of humic acid in animal feed to obtain desired results. Higher concentration results in decrease in desired stimulation.
Manufacturers all over the world are making earnest efforts to promote the use of humic acid products in agriculture and other markets. These products not only are gaining acceptance by the agriculture community, but also many government institutions are including these products as part of their import specifications that designate humic acid content, as is the practice in the many countries all over the world. In the United States, all the states require registration of products specifying guaranteed analysis to comply with U.S. weights and measures laws.

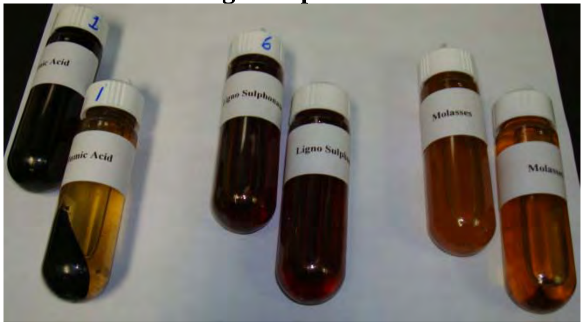
At ARCTECH, a comparative evaluation of three methods was conducted on several commercial liquid humic acid products (product #1 to #10). Three methods are the acid precipitation method, the barium chloride precipitation method, and the optical density method. As shown in the Table 7, the results indicate that the measurements based on barium chloride lead to the highest humic acid content. This anomaly with barium chloride method was also observed for products that contain NPK and micronutrients.

Table 7. Humic acid content of different commercial products determined with different methods

Product	Product Compositions		Acid Precipitation[a]	Barium Chloride[b]	Spectrophotometric[c]
	Claimed HA	Mineral Nutrients			
1	20%	None	4%	9%	7%
2	15%	None	2%	16%	2%
3	15%	None	12%	18%	31%
4	12%	None	8%	14%	15%
5	6%	None	3%	6%	6%
6	5%	None	3%	4%	4%
7	3%	None	4%	7%	5%
8	3%	15-3-5	4%	27%	4%
9	3%	10-10-10	3%	29%	4%
10	3%	2% Fe	3%	14%	4%

a. Acid precipitation method (California method)
b. Barium Chloride method (American colloid Co. method)
c. Spectrophotometric method (North Carolina method)

All over the world currently several different methods are in use by commercial manufacturers, testing labs and in government laboratories for regulating the import/registration and use of the commercial products. Most of the methods are based on the solubility of HA in alkaline solutions and its precipitation when alkaline extracts are acidified. Figure 9 shows the unique property of precipitating HA at pH of 2 while other compounds such as Molasses or Ligno Sulphonate do not precipitate at low pH. Table 8 summarizes different methods for Humic Substances Testing.



Only Humic Acid Precipitate at pH<2

Figure 9. Unique property of precipitating humic acid at pH of 2.

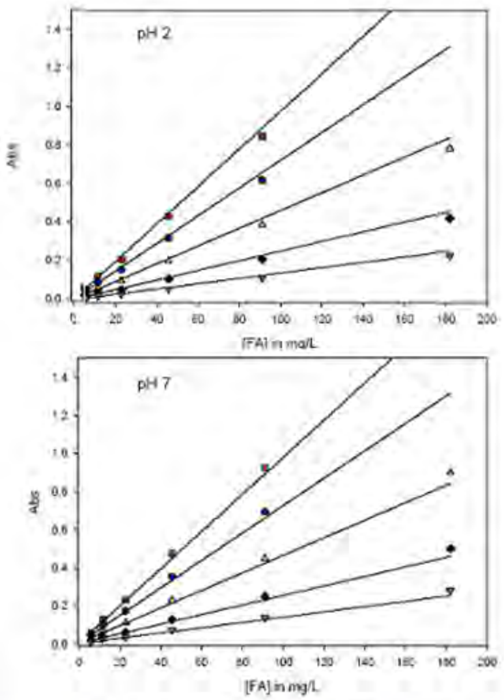
Table 8. Methods for humic substances testing

Methods	Principal of the Method
1. Schnitzer, 1982, Organic Matter Characterization in Methods of Soil Analysis Part 2, American Society of Agronomy Part 9.	Following extracting and fractionation of humic substances using NaOH under an atmosphere of N2 at room temperature, the alkaline extract is acidified and washed to pH < 2 with HCl. Allow to stand 24 hours and then separate the soluble material (FA) from the coagulated HA by centrifugation. Freeze-dry both fractions. Humic acid is then purified by washing several times with a dilute solution of HCl and HF to reduce its ash content to <1%. Fulvic acid is purified by repeated passages over cation exchange resins in H form. The weight of the freeze dried components is calculated as a content of HA and FA.
2.CaliforniaMethod.(CDFA, 1983)	Adopted by The California Department of Food and Agriculture and is based on the modification of the procedure described above by Schnitzer 1982. The method uses 0.5N NaOH to extract humic substances from solid samples. Once extracted, the pH of the extract is adjusted to 2 using concentrated HCl. The precipitated HA is then washed, dried and weighed to determine its concentration.
3. Colorimetric Method (1984)	A commercial reagent grade Aldrich Humic acid sodium salt is used for preparing standard solutions with conc. between 0 to 500 mg. A calibration curve is created from the absorbance measurements at 450 or 650 nm of each of the HA standard solution. Absorbance of diluted test samples from 0.2M NaOH alkaline extracts of HA is measured and used to calculate HA from standard curve.
4. Barium Chloride Method (American Colloid Co. Method) No Date.	12% Barium chloride solution is used to precipitate the HA in alkaline extracts as Barium Humate. Barium Humate is then separated on filter paper, dried, weighed and calculated using the following formula:

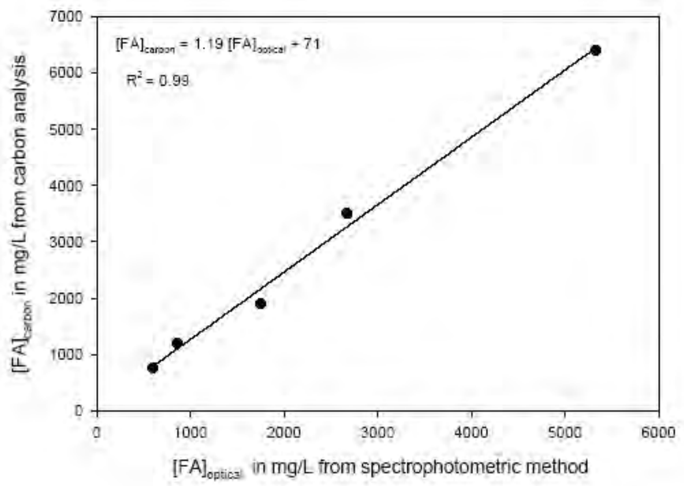
	% HA = Wt. of Dried Barium Humate/ Wt. of sample X 93.7%.
5. International Humic Substance Society Method	The methods is based on using liquid sample of humic substances through DAX-8 column so that HA and FA are absorbed on the column. Wash column with 0.1N HCl and then back elute with 0.1N NaOH to obtain HA and FA. Acidify sample to pH 1 to separate HA from FA. Then % HA or FA are determined by measuring total organic carbon.
6. Chinese National Humic Acid Testing Standard :NY/T 1971-2010	Humic acid is precipitated from the liquid test sample with sulfuric acid. The precipitated humic acid is oxidized with potassium dichromate for determination of organic carbon. The residual potassium dichromate is determined by titration. Based on the amount of organic carbon in the precipitate, humic acid content in the test sample is calculated.
7. Italian Method (2006)	This method is based on alkaline extraction of HA and FA using 0.1 N $NaP_2O_7 \bullet 10H_2O$ plus 0.1 M NaOH for 48 hrs at 65°C (Measure total organic carbon). Acidify sample to pH 2 to Separate HA from FA. Then pass the FA through polyvinylpyrrolidone column. % FA and HA are calculated as organic carbon using the dichromate acid oxidation method.
8. ISO 5073	It is based on alkaline hydrolysis using pyrophosphate and NaOH for extraction of humic acid from brown coals and lignite followed by wet oxidation procedure using potassium dichromate with external heat and back titration to measure the amount of untreated dichromate to determine the total carbon in humic matter and then calculate the total humic content based on a coefficient of 0.59 (avg. C in coals) and subtracting the ash content in the extracted humic acid. ANNEX A includes method for liquid products based on acid precipitation and subtraction of ash content for humic acid measurement. A copy of the ISO 5073 is give below
9. Spanish	In this method, the samples are subjected to an alkaline extraction to obtain the total humic extract, and subsequently the humic acids in this extract are precipitated at pH 1.
10. Russian	Need translation

Fulvic Acid (FA): Humic acid obtained from natural humic rich sources, such as coal, humates, and soils, contain different amounts of FA. Currently there is no standard method for quantifying FA. FA is soluble at all pH compare to HA which uniquely precipitate at acidic pH. Several products such as molasses, lignosulphonate and phenolic compounds are also soluble at all pH levels and have brown and yellow colors. Therefore, it is a challenge to distinguish FA from these products. Humic substances researchers use cation exchange column to isolate and purify FA but these methods are time consuming, requiring specialized research equipment generally not available in commercial testing labs and are expensive.

In an attempt to develop a fast and low-cost practical method, optical absorbance is used for quantifying and analyzing FA. Gan, Kotob and Waila (2007) used linear absorption vs. FA concentration (mg/L) plots at five fixed wavelength in the range of 350-500 nm for solutions of FA standard sample obtained from IHSS. In addition, the authors found linear relationship between FA content and carbon content (analyzed by the Hoffman Labs) as shown in the following Figure 10. Based on this method, four commercial products were determined to be very different than claimed by the manufactures. This data is shown in Table 9.



Calibration curves of IHSS fulvic acid at different wavelengths (350 nm ■: 370 nm ●: 400 nm ▲: 450 nm◆: and 500 nm ▼) in pH 2 and pH 7 aqueous solutions.



The correlation between fulvic acid concentrations obtained from the spectrophotometric method at pH 2.0 and carbon analysis.

Figure 10. Linear absorption vs. FA concentration (mg/L) plots at five fixed wavelength in the range of 350-500 nm and linear relationship between FA content and carbon content.

Table 9. Fulvic acid contents in 4 commercial products with spectrophotometric method

Product	Fulvic Acid Measured (ppm)	Claimed Fulvic Acid
1	1128	2-6 %
2	1200	
3	760	
4	5367	

Recently Ghabbour and Davies (2009)^a supported Gan et. al. (2007)^b findings of the linear correlation of [FA] carbon with [FA]optical for commercial FA sample solution predicts that the average FA molecule contains 52% carbon. They concluded in their studies that absorbance measurements 350 and 370 nm are practical and rapid means of estimating the concentration of FA that has pH independent and offer 1.4 fold advantage in sensitivity with an estimated error in the FA content of ±6%. Figure 11 shows formation of fulvic acid continued after repeated precipitation of humic acid.

a. Ghabbour and Davies, Annals of Environmental Science, 2009, Vol 3, 131-138
b. D. Gan et al., Annals of Environmental Science, 2007, Vol 1, 11-15

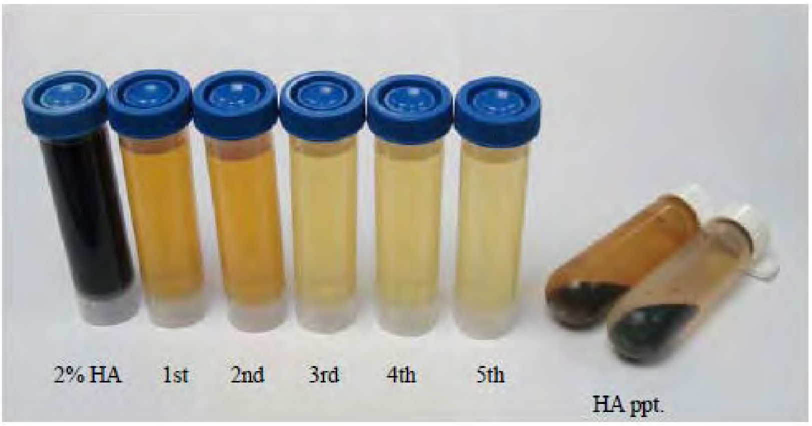


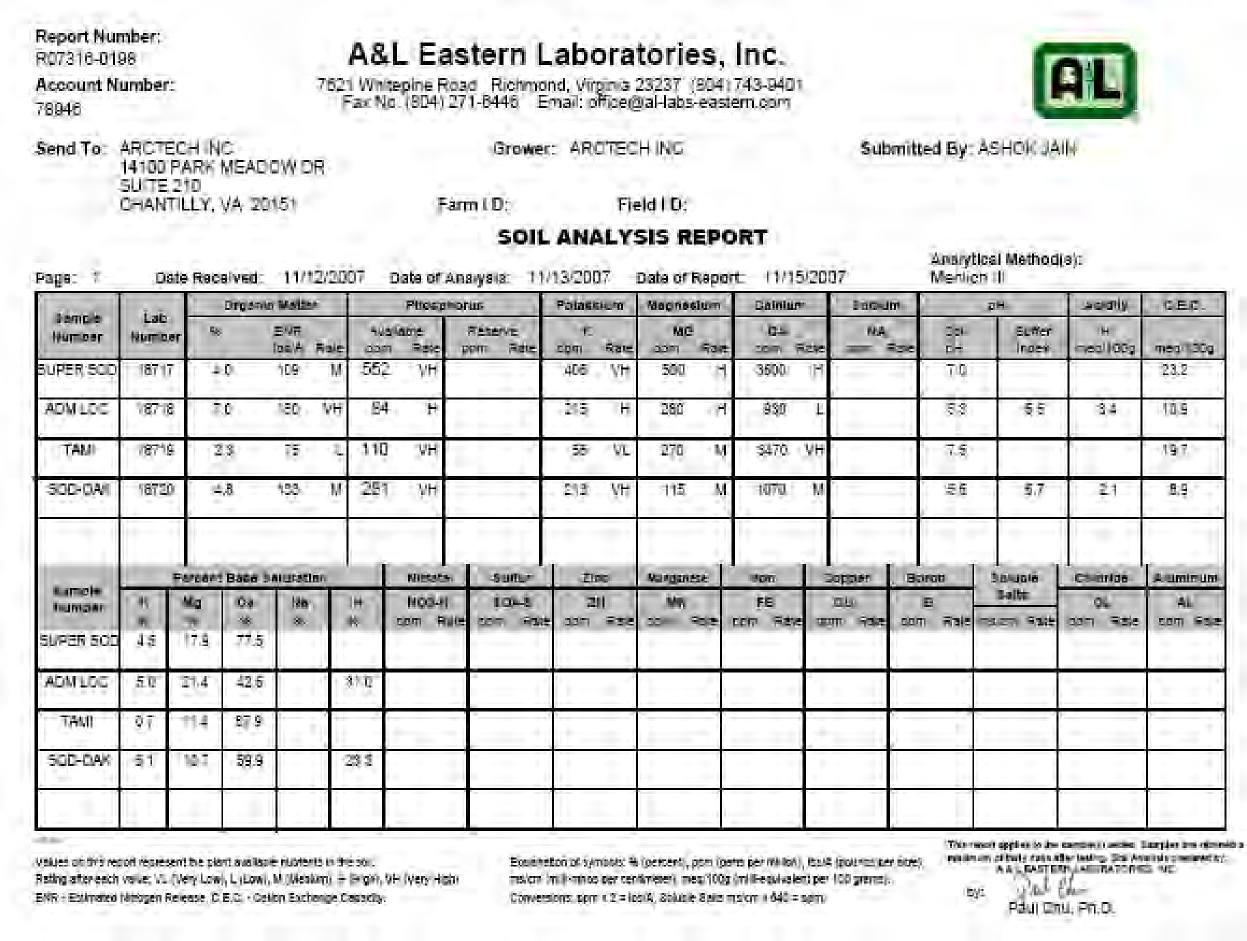
Figure 11. Formation of fulvic acid continued after repeated precipitation of humic acid (60mL of 2% water soluble HA was acid precipitated and re-dissolved in base and reprecipitated multiple times).

Humic substances analysis in soil: Current standard approaches for analysis of soils for organic matters are based on two methods:

1. Loss-On-Ignition (LOI) method based on loss in weight of soil sample on combustion which results in loss in weight not only by combustion of organic matter but also due to dehydration of clays and decomposition of other mineral components in the soil.

2. A modified Walkley-Black method based on chemical oxidation of carbon components in soil.

However, these methods do not give accurate analysis of HA in the soils. Most commonly the commercial labs use Loss in Ignition Method for soil analysis, which generally results in much higher analysis. A typical commercial lab report is as follows (Figure 12).



Report Number:
R07316-0198
Account Number:
78946

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Grower: ARCTECH INC

Submitted By: ASHOK JAIN

Farm I D:

Field I D:

SOIL ANALYSIS REPORT

Page: 1 **Date Received:** 11/12/2007 **Date of Analysis:** 11/13/2007 **Date of Report:** 11/15/2007

Analytical Method(s):
Mehlich III

Sample Number	Lab Number	Organic Matter			Phosphorus				Potassium		Magnesium		Calcium		Sodium		pH		Acidity	C.E.C.
		%	ENR lbs/A	Rate	Available ppm	Rate	Reserve ppm	Rate	K ppm	Rate	MG ppm	Rate	CA ppm	Rate	NA ppm	Rate	Soil pH	Buffer Index	H meq/100g	meq/100g
SUPER SOD	18717	4.0	109	M	552	VH			406	VH	500	H	3600	H			7.0			23.2
ADM LOC	18718	7.0	160	VH	84	H			215	H	280	H	930	L			5.3	6.5	3.4	10.9
TAMI	18719	2.3	75	L	110	VH			56	VL	270	M	3470	VH			7.5			19.7
SOD-OAK	18720	4.8	133	M	251	VH			213	VH	115	M	1070	M			5.6	5.7	2.1	8.9

Sample Number	Percent Base Saturation					Nitrate		Sulfur		Zinc		Manganese		Iron		Copper		Boron		Soluble Salts		Chloride		Aluminum	
	K %	Mg %	Ca %	Na %	H %	NO3-N ppm	Rate	SO4-S ppm	Rate	ZN ppm	Rate	MN ppm	Rate	FE ppm	Rate	CU ppm	Rate	B ppm	Rate	mmhos/cm	Rate	CL ppm	Rate	AL ppm	Rate
SUPER SOD	4.5	17.9	77.5																						
ADM LOC	5.0	21.4	42.6		31.0																				
TAMI	0.7	11.4	87.9																						
SOD-OAK	6.1	10.7	59.9		23.3																				

Values on this report represent the plant available nutrients in the soil.
Rating after each value: VL (Very Low), L (Low), M (Medium), H (High), VH (Very High)
ENR - Estimated Nitrogen Release, C.E.C. - Cation Exchange Capacity.

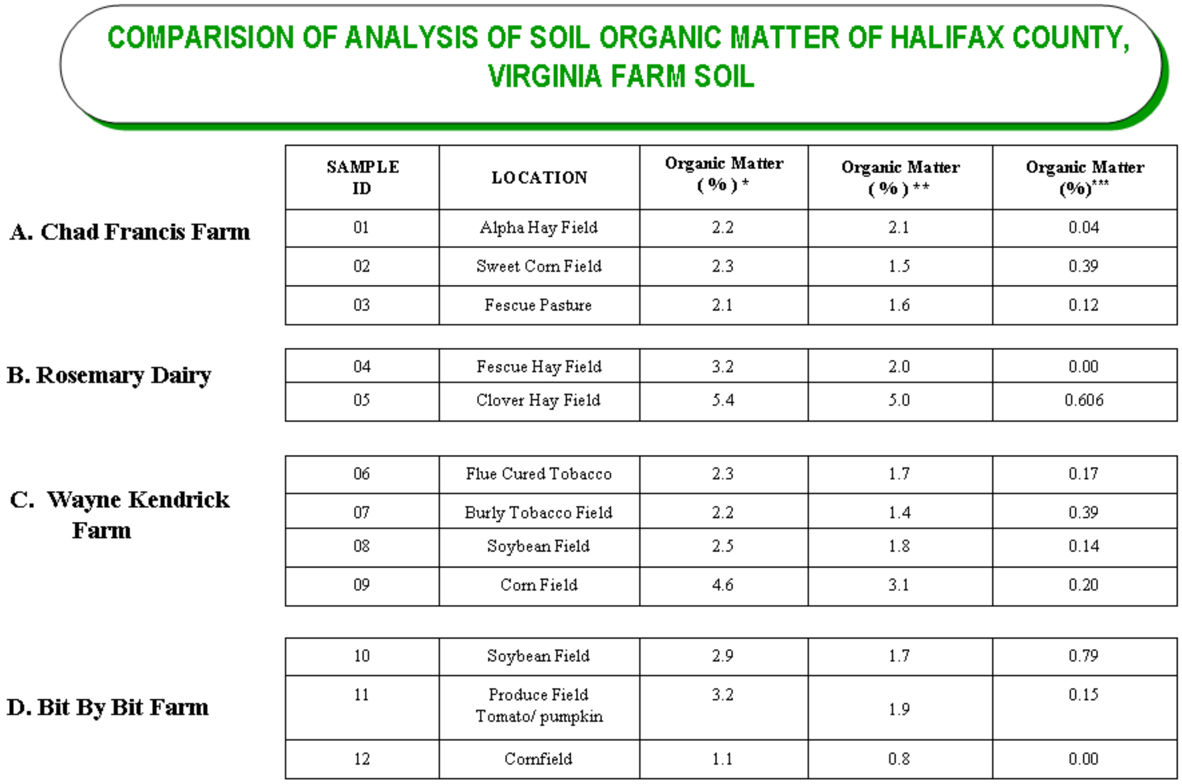
Explanation of symbols: % (percent), ppm (parts per million), lbs/A (pounds per acre), ms/cm (milli-mhos per centimeter), meq/100g (milli-equivalent per 100 grams).
Conversions: ppm x 2 = lbs/A, Soluble Salts ms/cm x 640 = ppm

This report applies to the sample(s) tested. Samples are retained a maximum of thirty days after testing. Soil Analysis prepared by:
A & L EASTERN LABORATORIES, INC.
by:
Paul Chu, Ph.D.

Figure 12. Typical commercial lab report for soil analysis.

ARCTECH collected soil samples from various farm lands in Virginia USA. These samples were analyzed by both of the above mentioned methods and by American Society of Agronomy methods for HA analysis. A comparison of analysis by these methods is given in the following Table 10.

Table 10. Analysis of soil organic matter of Halifax County, Virginia farm soil.



COMPARISION OF ANALYSIS OF SOIL ORGANIC MATTER OF HALIFAX COUNTY, VIRGINIA FARM SOIL

	SAMPLE ID	LOCATION	Organic Matter (%) *	Organic Matter (%) **	Organic Matter (%)***
A. Chad Francis Farm	01	Alpha Hay Field	2.2	2.1	0.04
	02	Sweet Corn Field	2.3	1.5	0.39
	03	Fescue Pasture	2.1	1.6	0.12
B. Rosemary Dairy	04	Fescue Hay Field	3.2	2.0	0.00
	05	Clover Hay Field	5.4	5.0	0.606
C. Wayne Kendrick Farm	06	Flue Cured Tobacco	2.3	1.7	0.17
	07	Burly Tobacco Field	2.2	1.4	0.39
	08	Soybean Field	2.5	1.8	0.14
	09	Corn Field	4.6	3.1	0.20
D. Bit By Bit Farm	10	Soybean Field	2.9	1.7	0.79
	11	Produce Field Tomato/ pumpkin	3.2	1.9	0.15
	12	Cornfield	1.1	0.8	0.00

*Loss-On-Ignition (LOI), a gravimetric, dry oxidation method, was used to estimate the percentage Soil Organic Matter by Virginia Tech.

** A modified Walkley-Black method was used, where dichromate solution oxidizes organic C to CO_2 in acid medium by Virginia Tech.

*** Humic Matter Analysis Method by Alkali Extraction per American Society of Soil Agronomy analysis

There is lack of understanding of the state of soils as far as its humic matter content. So far we have come across only one country- Mauritius, an island in the Indian Ocean, where the French tested the soils for humic content and based on this knowledge turned this rocky island in to major sugar cane producer (Figure 13).

An Example of Country Wide Analysis of Humic Matter in Soils To Improve Agriculture in the Rocky Island of Mauritius

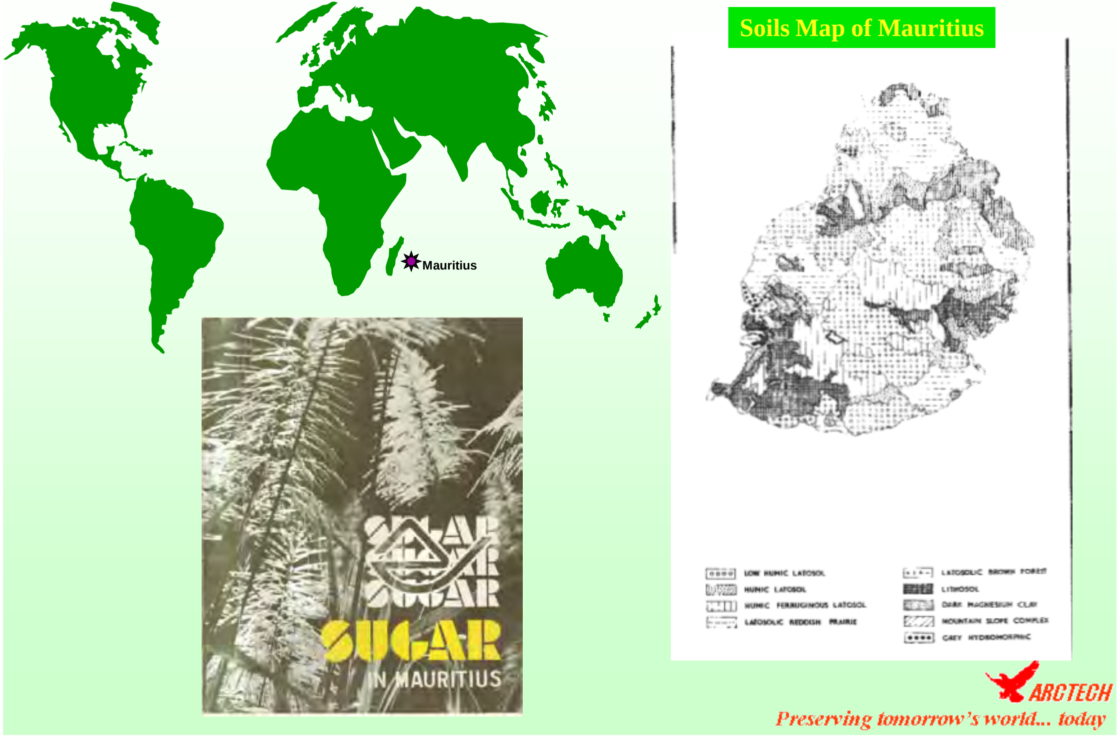


Figure 13. Example of country wide analysis of humic matter in soils.

On November 28, 2011, the UNFAO reported that Global food production is being undermined by the land degradation and shortages of farmland and water resources, making feeding the world's rising population – projected to reach nine billion by 2050 – a daunting challenge (Figures 14 and 15).

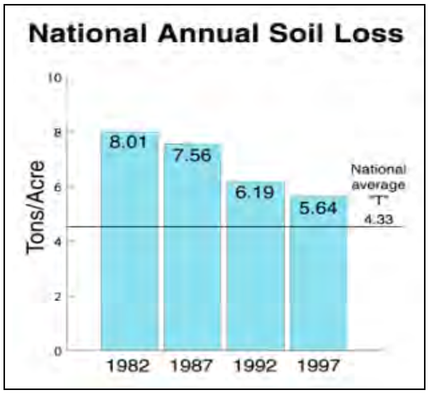


Figure14. National annual soil loss

Figure 15. Land degradation, UNFAO 2011

This is of great ecological concern as one inch of topsoil can take 500 years to form naturally. In USA, a National Soil project is underway by the humic research group at the Northeastern University in Boston to access the state of organic humic matter content of in the farm lands (www.hagroup.neu.org). In their recent research report on 24 agriculture top soil samples from 24 counties in Southern Idaho they reported that samples contain 0.31 to 9.8 % humic acid with a grand average of 1.9 ± 1.1% av. deviation [(55 samples). Excluding the two samples with an average of 9.8% humic acid, the average for 53 samples drops to 1.6 ± 0.8%.

CRITICAL NEED CONTINUES TO EXIST FOR SCIENTIFICALLY SOUND ANALYTICAL METHOD FOR SOILS, ORES AND PRODUCTS AS SOILD AND LIQUID WHICH IS SIMPLE AND COST EFFETIVE

In spite of increasing level of interest in research and as well use in the products especially in the last decade, there continues to be extensive controversy as to how to analyze for humic and fulvic acid. There are two primary needs. One is need for determination in the soils for establishing the state of the soil and in ores such as coals for determining their suitability for use for production of the products. The Second need is to analyze the products being produced by many manufacturers worldwide as soild and as water soluble liquid products.

The underpinning scientific reason for this controversy is that the humic matter occurring in nature is never found in pure state. It contains varying amounts of mineral matter depending up on the source.

Several researchers have reported that the attachment to minerals stabilizes HAs [11, 13]. Coal-derived HAs have a high mineral content (a typical ash content of lignite-derived HA is 34%w/w).

Akim and Bailey of the US National Research Council and US EPA in 1998 reported at the Northeastern University Humic Science and Technology

Conference a strong bonding of the mineral surfaces with humic substances from their computational chemistry approach studies.

Even though as described above the unique property of humic acid component in the humic substances is that it precipitates at pH < 2. But the mineral components remain bound to the humic acid and thus precipitate along with it. Thus depending up on the source mineral component varies and results in giving in accurate amount of humic acid. Among all the ten Standard Methods tabulated above the first method by Schnitzer included a step for correcting for mineral component by leaching out with HCL and HF. This requires long procedure and apparently did not get adopted for routine analysis. Other methods either ignored for the need for removing mineral components or used other ways to get around it by measuring carbon and then calculating humic acid content from it. But these methods lack ability to distinguish the adulterants.

The acid precipitation approach for measuring the humic acid component continues to be the most scientifically sound approach as this is also the basis of the definition of humic acid. However from the precipitated humic acid the correction must be made for mineral matter which remains bound to it. A recent method adopted by European Union as per ISO 5073 for determining humic acid content in the lignite and brown coals included in the Table above gives a guidance for correction for mineral components by determining the ash content of the precipitated humic acid and subtracting it from the humic acid precipitate weight gives a simple and practical way for determining fairly accurately the humic content of the test samples in the laboratory.

For soils and ores it will require to use alkaline or whatever extraction method a humic products manufacturer may have to extract the humic acid. This is followed by acid precipitation at pH <2. The precipitate is separated, dried and then subjected to ash at 850°C by the ASTM Method. Subtract the ash from the precipitate, which will give humic acid content in the test soil or ore test sample. This method will give information on the extractable amount of humic acid in the soil or ore but does not mean that it is in soluble form.

For products as solid and/or liquid form, most important is determine their content of humic acid in available form So for the liquid products which are already made in water soluble form, precipitate the humic acid at pH<2.As described above ash in the precipitate is determined and determine the humic acid content in the liquid product. The solid product should also be analyzed for humic acid by first mixing these with water at near nutral pH and then analyzing for dissolved humic acid by precipitation. This should be followed by ashing as described above for subtracting it for accurate determination of humic acid in the solid product. This procedure will give information on the amount of humic acid available in the products and thus it will allow proper comparison of humic acid in the products and as well as for determining the dilution factor which as described in previous Section as one of the most important factor in ensuring these products are applied below the concentrations at which humic acid becomes phototoxic.

The fulvic acid is the component remaining in the solution after the precipitation of the humic acid. Attempts have been made to quantify this component in the test samples by absorption method and by comparing it with absorption of the IHSS Fulvic acid as standard. However, this method is prone to errors due to incorporation of adulterants such as molasses, lignosulfonates etc. in the products. A scientifically sound and cost effective analytical method is needed for accurate analysis for fulvic acid. One approach for such a method may be to consider developing antibody specific to fulvic acid and using it as analytical method. The production of antibodies unique to a specific molecule and their use as analytical method is now become wide spread for many medical diagnostics and as well as for industrial chemicals.

APPLICATIONS

The properties of humic acid summarized in the preceding paragraphs can be exploited for agricultural purposes and for the treatment and detoxification of hazardous waste streams. In addition, humic acid can be used in the oil well drilling industry and as emulsifiers. The applications of humic acid for the purification of polluted water include the following:

- removal of metals by chelation
- adsorption of organics from water
- neutralization of acidic water streams by exchange of calcium, magnesium or sodium for hydrogen ion, and formation of insoluble pure humic acid
- removal of anions such as phosphates, cyanides, etc. by mixed ligand complexation
- reduction of metal species (e.g. chromium (VI) to chromium (III)) and stabilization by chelation
- combinations of the above can be accomplished simultaneously.

Agricultural applications: The organic molecules in soil such as humic acid have the opportunity to exercise their desirable characteristics due to their resistance to degradation. The biopolymers such as proteins possess certain characteristics and properties similar to humic substances, but undergo rapid decomposition in the soil, compared to the persistent humic substances.

Humic acid increases the availability of phosphate to the plant by breaking the bond between the phosphate ion and iron or calcium. Phosphate is a stimulator of seed germination and root initiation in plants. In addition, humic acid is very effective in conversion of iron to suitable forms to protect the plants from chlorosis, even in the presence of high concentrations of the phosphate ion [12]. Iron is essential for stimulation of initial plant growth, chlorophyll formation and transport of enzymes and elements within the plant.

Humic acid contributes to mineralization and immobilization of nitrogen in soil. The complexes formed between ammonium ions and humic acid are reported to release nitrogen slowly in to the soil. Humic acid serves as a slow release nitrogen carrier in the soil in this respect [13]. Humic acid however, immobilizes 20 to 35 % of the nitrogen added as a fertilizer at the end of the growing season. This residual nitrogen is unavailable for plant uptake during subsequent seasons and attains equilibrium with the native humic matter

[14]. It is postulated that a small fraction of the fertilizer nitrogen applied during a growing season remains in the soil for a very long time [14].

Humic acid promotes rapid and uniform germination of seeds, producing healthier seedlings. This results in increased yields of plants such as tomatoes, peppers, cucumbers, potatoes, corn, etc. In pot culture studies, the use of humic acid with urea resulted in 30% increase in the crop yield [15]. The benefits of humic acid and humic substances for agricultural purposes include [5]:

- Slow release source of N, P, and S for plant nutrition and microbial growth.
- High water-holding capacity to maintain water regime of the soil
- Buffering capacity against continued pH changes of the soil
- Cementing to hold clay and silt particles together to reduce soil erosion
- Binding of micronutrients to prevent leaching
- Plant-growth stimulation.
- Increases tolerance to salinity.

Today the soils have become heavily depleted in organic matter, which is leading to decrease in yields from the gains made during the green revolution. Large tracks of land are become un arable due to droughts and salts build up from use of chemical fertilizers. Recently the UNFAO in December 2011, reported that 30% of soils worldwide are degraded and need exist to increase food production by 60% by 2025 to feed population expected to increase to seven billion.Salinity has become a major challenge due to build up in the soils and use of the ground water with high salinity. Humic acid has unique attributes in negating the adverse impacts of salinity in soils and plants.

High salinity of as much as 2000 ppm in soils and in irrigation water inhibits the uptake of water by the plant due to increased osmotic pressure, which results in water moving from the plant to soil and thus the plants become desiccated and growth is severely inhibited. Humic acid regulates the osmotic pressure and thus assisting movement of the water from soil to the plant. High Sodium in the saline soils exchanges with potash and other cations in the clays and sodium clays being very fine particles result in forming compact soils and severely decreases its infiltration properties and thus limiting the water, air movement in the soil and as well as retard the root growth. Humic acid agglomerates the soil particles and thus resulting in decompacting the tight soils. The adverse impacts of high salinity have become a major challenge in maintaining fertile soils and grow crops and sustain vegetative growth. These unique properties of humic acid and formulated into specific formulation in actosol® are assisting in sustaining robust plant growth in desert land soils in Egypt containing as high as 16,000 ppm salt concentrations.

Removal of metals: Alberts and Geisy [16] investigated the degree of metal binding to oxy-functional groups of humic substances isolated from several streams. They determined the conditional stability constants and number of binding sites for copper, cadmium and lead. They also evaluated the effect of competing ions such as aluminum, calcium and manganese on the binding of Cu, Cd and Pb by humic substances.

Aluminum was very effective in blocking the binding sites of divalent metals such as cadmium, copper and lead. Calcium was the least effective and manganese was intermediate in its ability to block binding sites. This data supports the lower stability constant for the calcium complex relative to cadmium and lead. In general, trivalent ions have higher stability constants than divalent metals [16].

Pettersson et al. [17] studied the speciation of metals such as Al, Fe, Cu, Zn and Cd in water streams that were rich in humic and fulvic acids. They also characterized these metals with respect to their cationic and anionic exchange properties. Al and Fe were found in both anionic and cationic forms when excess Al and Fe were present in relation to the total exchange capacity of humic and fulvic acids. Both Al and Fe were present as complexes with humic and fulvic acids, pure inorganic species and possibly as colloids. However, Cu and Cd and Zn were predominantly present in cationic forms as complexes with humic and fulvic acids. The stability constants for the copper and zinc complexes with the humic substances increased with pH, but the increase was not significant for cadmium.

Musani et al [18] studied the chelation of radionuclides such as ^{65}Zn, ^{109}Cd and ^{210}Pb by humic acid isolated from marine sediments. The chelation of metals by humic acid was significant. The binding mechanism was found to be different depending on the physical state of the humic acid. Binding was stronger with precipitated humic acid than with dissolved humic acid. The chelation effect was stronger for the metals in the absence of calcium and magnesium. The effect of humic acid concentration on binding of ^{210}Pb is shown in Figure 16. The order of binding was determined to be Pb>Zn>Cd [18].

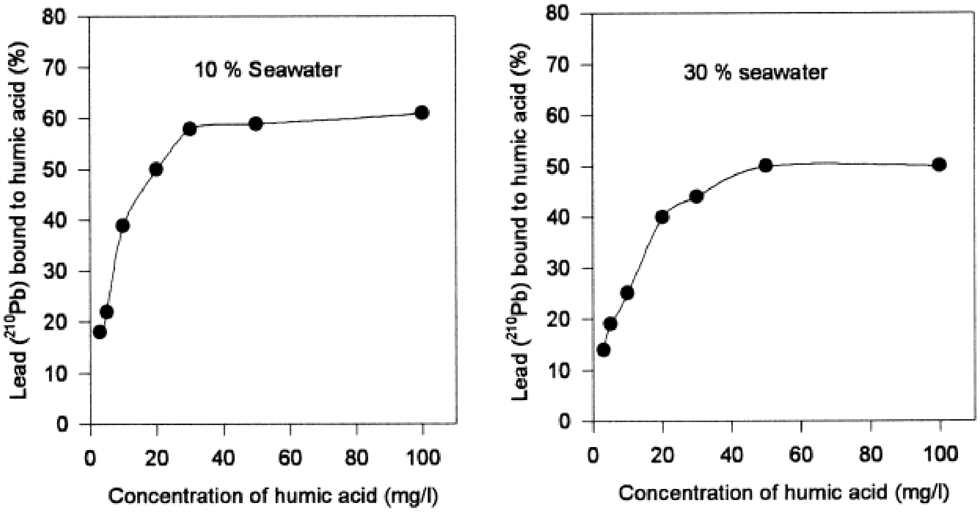


Figure 16. Effect of humic acid concentration on binding of lead (^{210}Pb) (Adapted from Musani, LJ., et al. Estuarine and Coastal Marine Science, II, 639, 1980).

Pahlman and Khalafalia [19] used humic acid to remove heavy metals from process waste streams. The efficiency of heavy metal removal by humic acids derived from lignite, a sub-bituminous coal and peat were evaluated. The effect of pH on metal removal was determined. Humic acid was very effective in removal of toxic metal ions. The pH range of 6.5 to 9.5 was determined to be the optimal range for complete removal of heavy metal ions by humic acids derived from lignite and subbituminous coal. The effect of pH on metal removal by humic acid is shown in Figure 17. The efficiency of heavy metal removal by humic acid was higher compared to the conventional lime treatment even at lower concentrations of metals. Humic acids were very effective in the removal of the most toxic metals such as cadmium, mercury and lead. The removal of these toxic metals by lime is incomplete, particularly at near neutral pH.

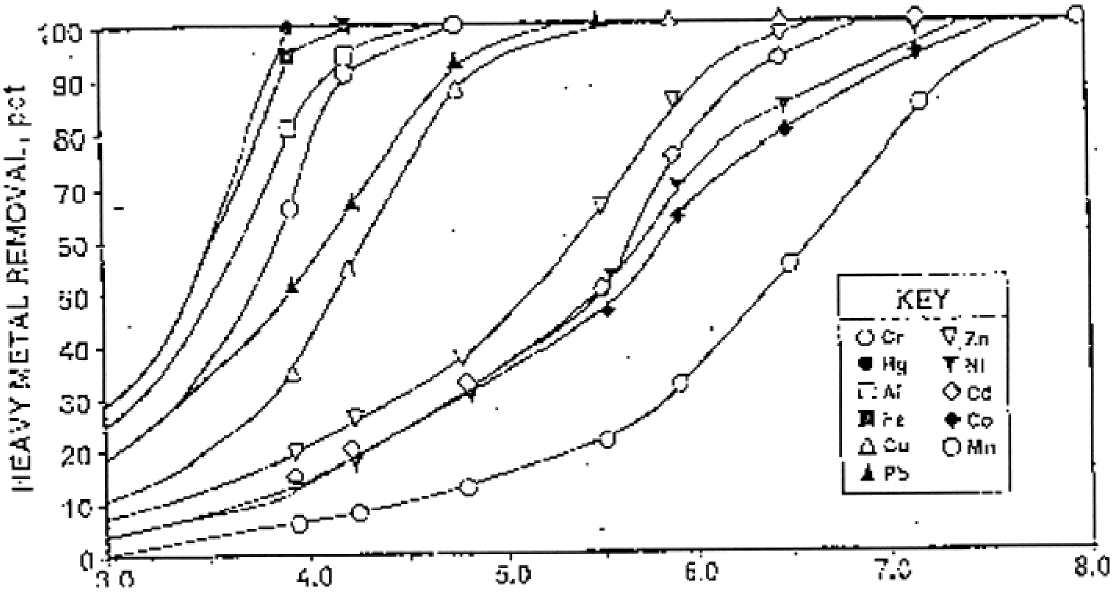


Figure 17. Effect of pH on metal removal by humic acid (Adapted from Pahlman, J.E., Khalafalia, S.E., U.S. Bureau of Mines, RI 9200, 1988).

Adsorption of organics: The adsorption of organic chemicals onto humic substances such as humic acid have been studied extensively. The reported investigations on adsorption of organic compounds by humic acid include studies on:

- non-ionic organics such as benzene, halogen substituted benzene, and chlorinated hydrocarbons such as 1,1,1-trichloroethane,
- nitrogen compounds such as ureas and anilines,
- polychlorinated biphenyls (PCB),
- fumigants such as Telone and insecticides such as DDT,
- herbicides such as paraquat, diquat, triazines,
- organophosphorous compounds such as parathion.

The adsorption of benzene, halogen substituted benzenes, and chlorinated hydrocarbons such as 1,1,1-trichloroethane, and similar nonionic organic compounds on soil containing different amounts of soil organic matter has been reported by Chiou [20]. The adsorption on soil organic matter of various nonionic organic compounds from water was attributed primarily to solute partitioning into the organic adsorbent. The partitioning theory was supported by experimental observations of linear adsorption isotherms up to concentrations approaching saturation. In addition, the absence of competitive effects between solutes and low equilibrium heats support the partition approach. The presumed partition was also analyzed in relation to the equilibrium properties of organic compounds in solvent-water mixtures.

Humic acid has been shown to adsorb considerable amounts of nitrogen compounds such as urea, anilines, etc. The stable free radicals in humic acid are believed to play a significant role in urea-humic acid interaction [21]. In addition, it has been postulated that urea forms an addition complex with humic acid through the carboxyl and phenolic hydroxyl group [22]. It has been determined that the complex formed is very stable and that the decomposition of urea is inhibited in the presence of humic acid. The adsorption of aniline on soil organic matter is directly related to the concentration of the humic acid. The adsorption of aniline on humic acid follows both the Freundlich and Langmuir relations.

Adsorption of PCB's from aqueous streams has been reported by Haque and Schmedding [23]. The adsorption on humic acid increased with the increase in the number of chlorine atoms in the PCB. Adsorption isotherms of PCB's on humic acid followed the Freundlich equation and the constant K (measure of adsorptive capacity) increased from di- to hexa-chloro PCB. The high K value on humic acid was attributed to a combination of high surface area and the number of functional groups present in humic acid.

Chlorinated fumigants such as telone and insecticides such as DDT are readily adsorbed by humic acid. The adsorption of telone on bentonite increases significantly in the presence of humic acid. The functional groups on humic acid such as carboxyl and phenolic groups on dissociation participate in exchange reactions to adsorb telone. The mechanism for telone (206) adsorption by humic acid has been postulated as [24]:

$$\text{Cl-CH=CH-CH}_2\text{-Cl} + \text{ROH} \longrightarrow \text{Cl-CH=CH-CH}_2\text{OR} + \text{HCl}$$

Herbicides such as paraquat and diquat dissociate in water to form divalent cations. They can react with more than one negatively charged site on humic acid. The adsorption is accompanied by the release of significant amounts of hydrogen ions indicating an ion-exchange mechanism. In the presence of metal ions such as calcium (Ca^{2+}), it has been shown that the herbicides are preferentially adsorbed at low pH (4-5); however, at slightly higher pH (6-7), the metal ion is adsorbed preferentially [25]. The adsorptive capacity of cation-saturated humic acid for these herbicides is inversely proportional to the stability of the metal-humic acid complex [26].

Herbicides which are less basic such as triazines are protonated by hydrogen during adsorption or in the soil solution. The reactions leading to adsorption include complexing by the functional groups present in humic acid and ion exchange. The following reactions are postulated for adsorption of triazine [27].

$T + H_2O \Leftrightarrow HT^+ + OH^-$
$RCOOH + H_2O \Leftrightarrow R\text{-}COO^- + H_3O^+$
$R\text{-}COO^- + HT^+ \Leftrightarrow R\text{-}COO\text{-}HT$
$RCOOH + T \Leftrightarrow R\text{-}COO\text{-}HT$

where R is the humic acid organic core, and T is the triazine molecule.

Hydrogen bonding between the amino group of triazine and phenolic hydroxyl or carbonyl group of the humic acid has also been suggested as a possible mechanism for adsorption. This mechanism is illustrated in Figure 18 for atrazine [28]. The adsorption of atrazine follows the Langmuir relation as shown in Figure 19 [29].

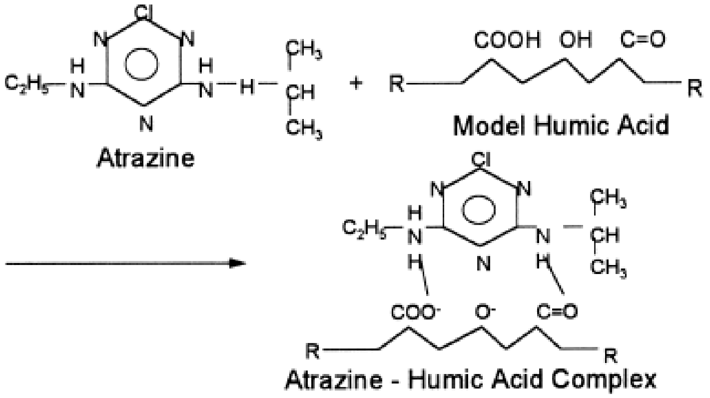


Figure 18. Proposed mechanism of atrazine adsorption by humic acid (Adapted from Sullivan, J.D. and Felbeck, G.T., Soil Sci., 106, 42, 1988).

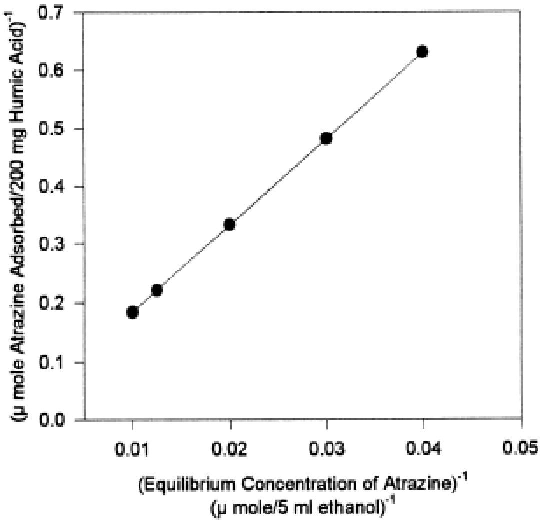


Figure 19. Langmuir Isotherm for atrazine adsorption on humic acid (Adapted from Toxicological and Environmental Chemistry, Vol. 6, 127, 1983).

Anionic herbicides and other organic anions exhibit relatively insignificant adsorption on humic acid. The adsorption of picloram, an anionic herbicide on humic acid occurs in the unionized form at pH values below its pKa values (1). The suggested mechanism is hydrogen bonding, physical adsorption (Van der Waals forces) and ligand exchange.

Humic acid has a high affinity for organophosphorus compounds such as parathion and dyfonate. The adsorption of these compounds follows the Freundlich isotherm relation [30]. The adsorptive capacity is dependent on the cation with which the humic acid is associated. The adsorbate molecules are held by weak forces on the humic acid surface to dyfonate-humic acid complexes.

Reduction of metal species: Humic substances influence metal speciation through oxidation-reduction reaction. Humic acid functions as a reducing agent with an oxidation-reduction potential of 0.70 V. Humic acid can influence oxidation-reduction of metal species and also stabilize the reduced cationic form by chelation. An unchelatable oxoanion such as $Cr_2O_7^{2-}$ is reduced to chelatable Cr^{3+}. This shifts the reaction to the right in the presence of humic acid reducing more of the oxoanion [31].

Humic acid has been shown to be an effective reducing agent for hexavalent actinides such as neptunium and plutonium. Neptunium(VI) was readily reduced to Np(V) by humic acid and the reaction was complete within a few hours under all conditions. Plutonium(VI) was also reduced to Pu(IV) by humic acid, but the contact time required for complete reduction was in the order of a few days. In addition, humic acid complexes the IV and V valence states of these actinides strongly [32]. The reduction of different metal species such as mercury, vanadium, iron and plutonium by humic acid has been reported by a number of investigators [33-36].

Drilling industry: Humic acid is used in muds used for oil well drilling. Leonardite, containing high concentrations of humic acid is commercially used for its sequestering capabilities in the oil well drilling industry. The sodium present in a salt dome encountered during drilling combines with the clays used as lubricants for the drill bit, to form a solid mass and freezes the drill bit. The addition of leonardite sequesters the sodium and prevents the reaction. This characteristic is also used for agriculture in sodic or saline soils to make them more friable and prevent formation of a thick mass that prevents plant roots from penetrating [37].

Demilitarization of explosives: ARCTECH has developed a unique and innovative method for converting propellants and explosives into usable, non-hazardous, environmentally-benign fertilizer materials. The ARCTECH technology involves the use of its actosol® humic acid product for denitration of explosive compounds by hydrolysis and conversion of the hydrolysis products to fertilizers. The denitration reaction releases nitrogen, which are complexed by humic acid and are available to plants as a slow release nitrogen source [38].

The technology is applicable to single, double, and triple base propellants, and explosive materials such as nitrocellulose, HMX, RDX, NG, and other nitrate ester-type materials. Reaction times potentially vary from 4-6 hours for triple base to 16-20 hours for single base propellants. The resultant product is permanently non-explosive, non-toxic, and environmentally friendly. It is composed of NO_2 and NO_3 ions, and hydrocarbons, which are adsorbed into the humic acid matrix as nitrogen and organic matter. These adsorbed materials are essential for plant growth, and the product therefore, can be sold for use as fertilizer material. The process economics are favorable, and depending upon the price at which the product is sold, can actually generate positive revenue. The entire process can be mounted on a mobile platform and shipped to the facility where the explosive materials are stored.

ARCTECH was granted U.S. Patent Number 5,538,530 for its actosol® denitration process on 25 July 1996.

Air pollution control: Humic acid products are proving out to be effective in control of air pollutants such as sulfur dioxide, nitrogen oxides, toxic metals and even carbon dioxide. A few studies have been conducted using humic acid-fly ash mixtures and sodium humates for sulfur dioxide removal. The major mechanism for sulfur dioxide removal is postulated as the formation of hydrogen sulfite (HSO_3^-) at high pH and formation of a humate complex of sulfur dioxide at low pH [31].

CONCLUSIONS

Humic acid and its interaction with environmental chemicals has been studied extensively. Humic acid has several properties that can be exploited for the treatment and detoxification of hazardous waste streams. The properties that have a potential to be exploited for environmental purposes include the ability to chelate metals, reduce oxidized metal species, and adsorption of organic compounds from wastewater systems. The available literature clearly indicates a promise for the use of humic acid based technology for various applications. However, further research is needed to develop humic acid based detoxification processes for specific applications.

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