Utilization of Alkaline Coal Ash in the Treatment of Municipal Sludge – Producing Agricultural Soil Amender

Robert S. Reimers[1], Kari B. Fitzmorris-Brisolara[2],
Terry J. Logan[3] and Yue Xu[4]

[1]Texas A&M University, College Station, Texas
[2] Louisiana State University, New Orleans, Louisiana
[3] Ohio State University, Columbus, Ohio
[4] Tulane University, New Orleans, Louisiana

International Work Shop on Agricultural Coal Ash Uses
May 27, 2014

History of Alkaline Processes

- Alkaline Stabilization was first developed to control odors in the 1930s.
- Advanced Alkaline Stabilization either pasteurizes biosolids by heating to70^0C develop in Sweden in the 1070s or heat to 55^0C where ammonia assists in the disinfection patented in the 1080s.
- The heating process is due the exothermic reactions of water with quicklime, which can be greatly enhanced with acid trimming initiated in the mid 1990s.
- Alkaline treated biosolids creates enough ammonia to inactivate soil plant pathogens, which the N-Viro processed biosolids were certified in Canada in the 1990s.

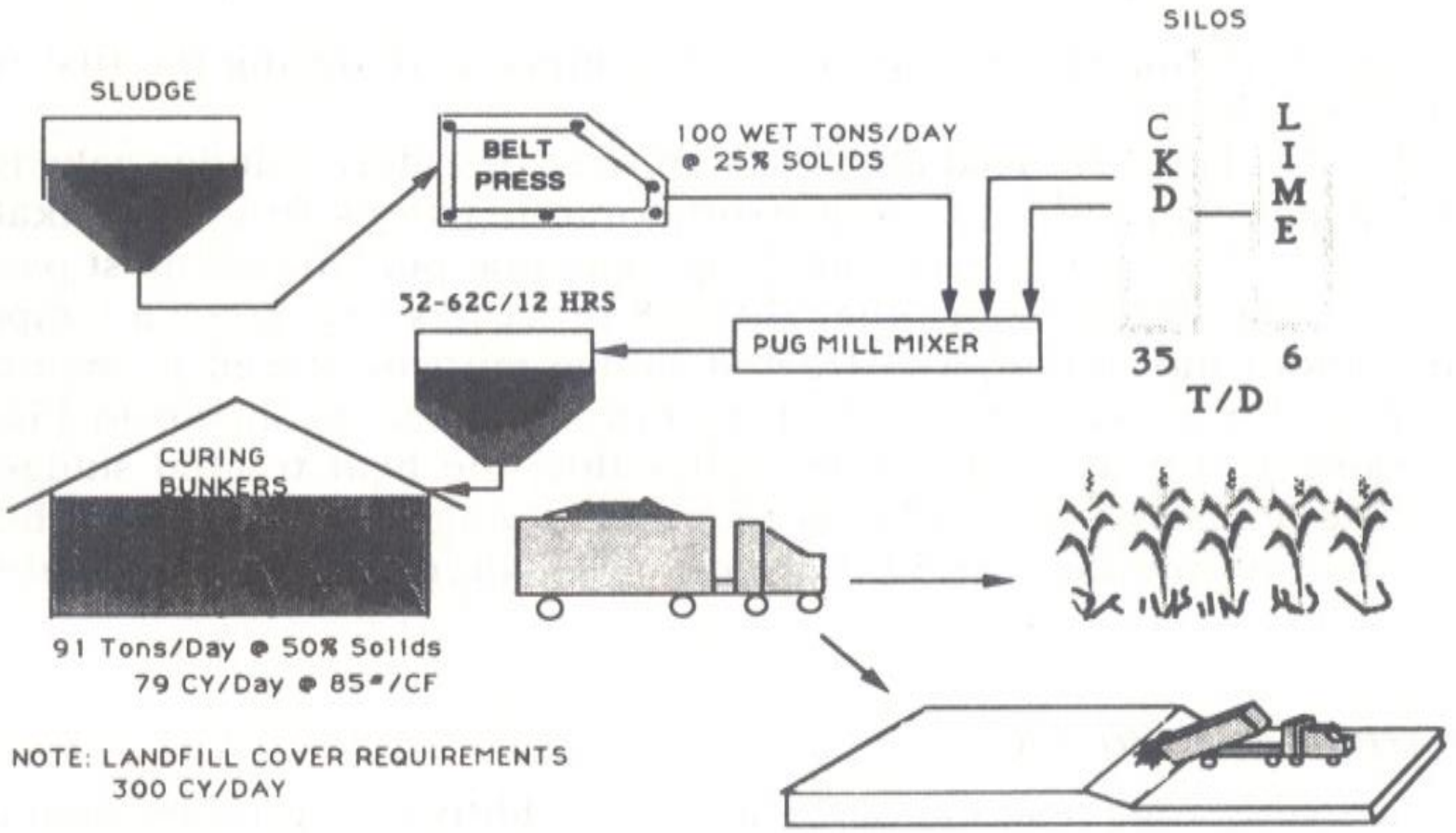
Background of N-Viro Process

The first alkaline treatment of municipal sludge was developed by N-Viro Corporation in the 1980s by Dr. Jeffrey C. Burnham of then Medical College of Ohio.

This process was patented by N-Viro in the late 1980s.

It was called Advanced Alkaline Stabilization with Subsequent Accelerated Drying or AASSAD Process.

Diagram of the N-Viro Process illustrating the addition of alkaline admixture following the dewatering of municipal sludge. Following the mixing, 12 hours heating period (52 to 62°C) in conjunction with a pH of 12 accomplishes disinfection. The process them employs three mixings of the curing windrows prior to storage of the soil amender product for stabilization.



Advanced Alkaline Stabilization Mixing Process

- Chemical process – Not biological
- Elevate pH, produce heat, dry, deodorize, granulate.
- Fly Ash, Cement & lime kiln dust, wood ash.
- High surface area provides for immediate odor control.
- Admixtures are effective in granulation, ignition profile.

Process Components

- Admixture Storage (Silo)
- Sludge Receiving (Live Bottom Bin)
- Proportional Mixer
- Direct Dryer
- Product Storage
- Complete Odor Control

Process Flexibility

- N-Viro Processes Under One Roof
- System Allows 24 Hour Operation
- Facility Control is Fully Automated
- Change Process by Flip of a Switch

N-Viro Process Structure

Advanced Alkaline Stabilization

Proportional Mixer

Subsequent Accelerated Drying

Subsequent Accelerated Drying

- Direct heat rotary dryer
- Sized based upon lbs of water evaporated/hr
- Simple rugged proven technology
- Optimal efficiency from N-Viro Fuel particulate size
- Continuous operation (not a batch dryer)
- Full automated within system integration

In the past 25 years, the Disinfection Mechanisms of Alkaline Stabilization have been elucidated

- Lagoon treatment enhancing of the alkaline stabilization process.
- Low alkaline dosing enabling disinfection in 2 to 3 months.
- Usage of enclosed alkaline systems, which has enhanced the disinfection process and control odorous emissions

Table 3: Chemicals Used for Disinfection of Biosolids

Alkaline Agents	Acid Trimming Agents	Oxidation Reduction Control Agents	Non-Charged Disinfectants
Lime Cement Kiln Dust	Sulfuric Acid Nitric Acid	Ozone Peroxide	-Ammonia (Alkaline Treatment)
Portland Cement Alkaline Fly Ash	Phosphoric Acid Sulfamic Acid	Ferrate Chlorine Dioxide	-Amines (Alkaline Treatment/Composting)
Silicates Spent Bauxite Hydroxide anions	Sodium Bisulfate	Chlorite Chlorate Hypochlorite Hypochlorous Acid	-Organic Acids, Aldehydes, and Ketones (Anaerobic Digestion and Composting)
			-Nitrous Acid (Acidic Treatment) Peracetic Acid Methyl Isothiocyanate N-methyl dithiocarbamate

Factors/Stressors Controlling Disinfection in Alkaline Stabilization Processes

1. Ammonia due to alkaline hydrolysis of amines.
2. Heat produced by exothermic of quicklime with water Influencing volatilization of ammonia, increase concentration of ammonia by a magnitude (pKa)
3. Increased solids content increasing the available amine content for hydrolysis
4. Increased ionic strength and dissolved solids, which reduce the heat capacity of the biosolids.
5. Enclosing the reactor will increase the ammonia content and higher capacity due Henry Gas Law.

Ammonia Concentration to Inactivate Helminth Eggs with respect to Temperature
a pH of 12

Temperature (C°)	Ammonia Dosage (mg/L)	Inactivation Time
20	170-240	230 days
20	5,200	25 days
25	1,000	180 days
25	10,000	10 days
30	170-240	24 days
30	5,200	4.8 days
35	1,000	10 days
35	10,000	3 days
40	170-240	3.4 days
40	5,200	0.39 days

Ammonia Concentration to Inactivate Pathogens

Temperature (C^o)	Pressure (pisg)	NH_3 Concentration (mg/L)	Sludge Matrix	Inactivation Time (minutes)	Reference
40	---	170 -200	Raw Municipal Sludge (RMS)	4,896	Pecson et. al., 2007
50	---	170 – 240	RMS	110	Pecson et. al., 2007
53	17	775	Anaerobic Municipal Sludge	40	Bioset PEC Study 2011
55.3	17/25	335	Aerobic Municipal Sludge	40	Bioset PEC Study 2011
56.7	20	130	RMS	40	Bioset PEC Study 2011

Ammonia Level to Disinfect

Temperature (°C)	Time in minutes for Inactivation	Comments
40	4,896	
50	110	44.5 times less than at 40°C
55	40	2.75 times less than at 50°C

Stabilization of Alkaline Processes

1. The basic stabilization is defined as holding the pH at 12 for 2 hours and at 11.5 for 22 hours. In general, the pH can be held for a period of a few weeks to months.
2. In the N-Viro process, the product is stabilized biologically by alkaline windrow composting.
3. As a result of this stabilization aging process, the calcium hydroxide is converted to calcium carbonate and the pH of the amender drops to around a pH of 8.5.

Toxicity Assessment Criteria

1. **Tier I** – Assumes that all the constituent analyzed in the soil, sediment, biosolids or slurry is released 100% to the environment. This is an conservative assessment.
2. **Tier II** – Assesses the potential of the adsorbed constituents situations to release under specific to the aquatic environment (extraction testing).
3. **Tier III** - Assesses the potential biological impact of a constituent to bioaccumulate or effect the biota/organisms.

U.S. Army Corp of Engineers

1. **Tier I** – Alert levels for potential toxicity concentration in dredged sediments.
2. **Tier II** – The elutriation extraction to determine the availability of sediment contaminants to release to the aquatic environment in dredging operations.
3. **Tier III** – Bioassay for accumulation utilizing worms for freshwater and clams for marine water environments.

Potential 503 Pollutants

Constituents	Land Applied	Surface Disposal
Barium and Manganese	Aquatic Community	Adults and Children
Beryllium	Aquatic Community	
Silver	Aquatic Community, Aquatic Invertebrates, Fish, Adults and Children	
Flouranthene and Pyrene	Aquatic Community, Sediment, Soil and Biota	
4-Chloroaniline	Aquatic Invertebrates,	Adults and Children
Nitrate and Nitrite		Adults and Children

Additional Emerging Chemicals of Concern

Chemicals	Basis of Inclusion/Use
14 metals	The ten 503 metals and 4 target metals (barium, beryllium, manganese and silver)
Benzo(a)pyrene	Fossil fuels, tobacco, wood, charbroiled foods and toast combustion byproducts
2-methylnaphthalene	Caulking compounds/sealants, synthetic resins, rubber adhesives and wall coverings
bis (2-ethylhexyl) phthalate	Plasticizers used in cosmetics, toys, tools and laboratory equipment
Fluoride	Used to prevent tooth decay and other uses.
Water- extractable phosphorus (WEP)	Phosphorus concentration in runoff from land application sites

Additional Emerging Chemicals of Concern

Chemicals	Basis of Inclusion/Use
11 polybrominated diphenyl ethers (PBDEs)	Four of the PBDEs were of most interest because of available human health information that may be useful for future risk evaluations. PBDEs are used as flame retardants in a wide array of products, including building materials, electronics, furnishings, motor vehicles, plastics, polyurethane foams and textiles.
97 pharmaceuticals steroids and hormones	These are included because there has been a broad emerging interest in these compounds. They have had a major impact on the aquatic life in Europe and Southeastern United States.

United States Agencies' Alert Levels

1. **USEPA Excellent Quality Biosolids with respect to metals**
2. **AAPFCO Association of American Plant Food Control Officials AAPFCO SUIP #25 Heavy Metal Rule ppm per 1% P_2O_5**
3. **AAPFCO Association of American Plant Food Control Officials AAPFCO SUIP #25 Heavy Metal Rule ppm per 1% micronutrients**
4. **Soil Screening Test REPO determines if a soil is contaminated or not contaminated from State of Louisiana**
5. **Dredged Sediment Criteria Alert level if a sediment is contaminated or not contaminated from the US Corps of Engineers**

Comparison of N-Viro Soils to Different US Agencies Criteria for Metals

Metal	1990	1994	2013	EPAEQ[1]	APFCO[2]	APFCO[3]	SST[4]	CORPS[5]
As	---	**7.6**	**33.5**	41	13	78	12	70
Cd	**9.0**	**0.83**	**0.24**	39	10	60	3.4	9.6
Cr	**120-20**	---	**22.3**	1,200	---	---	23	370
Cu	**80**	**134**	**76.5**	1,500	---	---	310	270
Hg	---	---	**0.39**	17	1.0	6.0	23	0.71
Mo	---	**1.38**	**9.1**	75	42	252	---	---
Ni	**137-35**	**55**	**72.1**	420	250	1,500	16	51.6
Pb	**120-100**	**48**	**20.8**	300	61	366	100(400)	218
Se	---	**1.69**	**12.7**	36	26	156	20	---
Zn	**433-350**	**186**	**84.3**	2,800	420	2,520	2,300	410

Comparison of N-Viro Soil to Different European Criteria or Alert Levels for Metals

Metal	1990	1994	2013	European Council Directive for Sewerage (86/278/EEC)	Canada
As	---	**7.6**	**33.5**	---	75
Cd	**9.0**	**0.83**	**0.24**	20-40	20
Cr	**120-20**	---	**22.3**	1,000-1,500	---
Cu	**80**	**134**	**76.5**	1,000-1750	---
Hg	---	---	**0.39**	16-25	5
Mo	---	**1.38**	**9.1**	---	20
Ni	**137-35**	**55**	**72.1**	300-400	180
Pb	**120-100**	**48**	**20.8**	750-1,200	500
Se	---	**1.69**	**12.7**	36	14
Zn	**433-350**	**186**	**84.3**	2,500-4,000	1,850

Tier II Testing
Extraction Procedures (Maximum Potential)

These methods were initiated in the late 1960s to determine the availability of toxins for the environment

Elutriation Test

- Developed by the Corps of Engineers in the late 1960s.
- The procedure for the Standard Elutriate Test was extracted from TR EPA/CE-81-1 “Procedure for Handling and Chemical Analysis of Sediment and Water Samples.”

Sediment Analysis (Determine Polluted Sediments)

- History (Bulk Density – 1968)
- Elutriation Analysis (Developed in 1970s)
  - Assess polluted sediments quickly.
- This was developed by the Corps of Engineers for dredge sediment assessment.

Synthetic Acid Precipitation Leach Test (USEPA SW-846 Method 1312)

- This test is to determine if a soil is contaminated or not.
- This test can take a waste residual from a solid waste to none waste or out of the solid waste classification.
- The synthetic acid precipitation test simulates acid rain as opposed to simulation a leachate in a sanitary or municipal landfill

Definition of Solid Waste or Not

- If the extracting solution is above the Regulatory Limit, the residual is defined as a solid waste or a contaminated soil.
- If the extracting solution is below the Regulatory Limit, then the residual is defined as a non-waste or a non-contaminated soil.

Acid Rain Extraction Protocol

- There are 140 metals and organic constituents (semi-volatile and volatile)
- Regulatory limit (RL) is based on 20 times groundwater or human health criteria (MCL) which is lower.

After passing the extraction test, the enduse of the residual can be ascertained

- If below the residential bulk density limit, the residual can be used as *residential soil*.
- If between the residential and industrial limit, then the residual can be utilized as an *industrial soil*.
- If above the industrial bulk density limit, then the residual is defined as a *solid waste*.

Tier III Testing on the Biota

Bioassays to measure impact on plants and animals

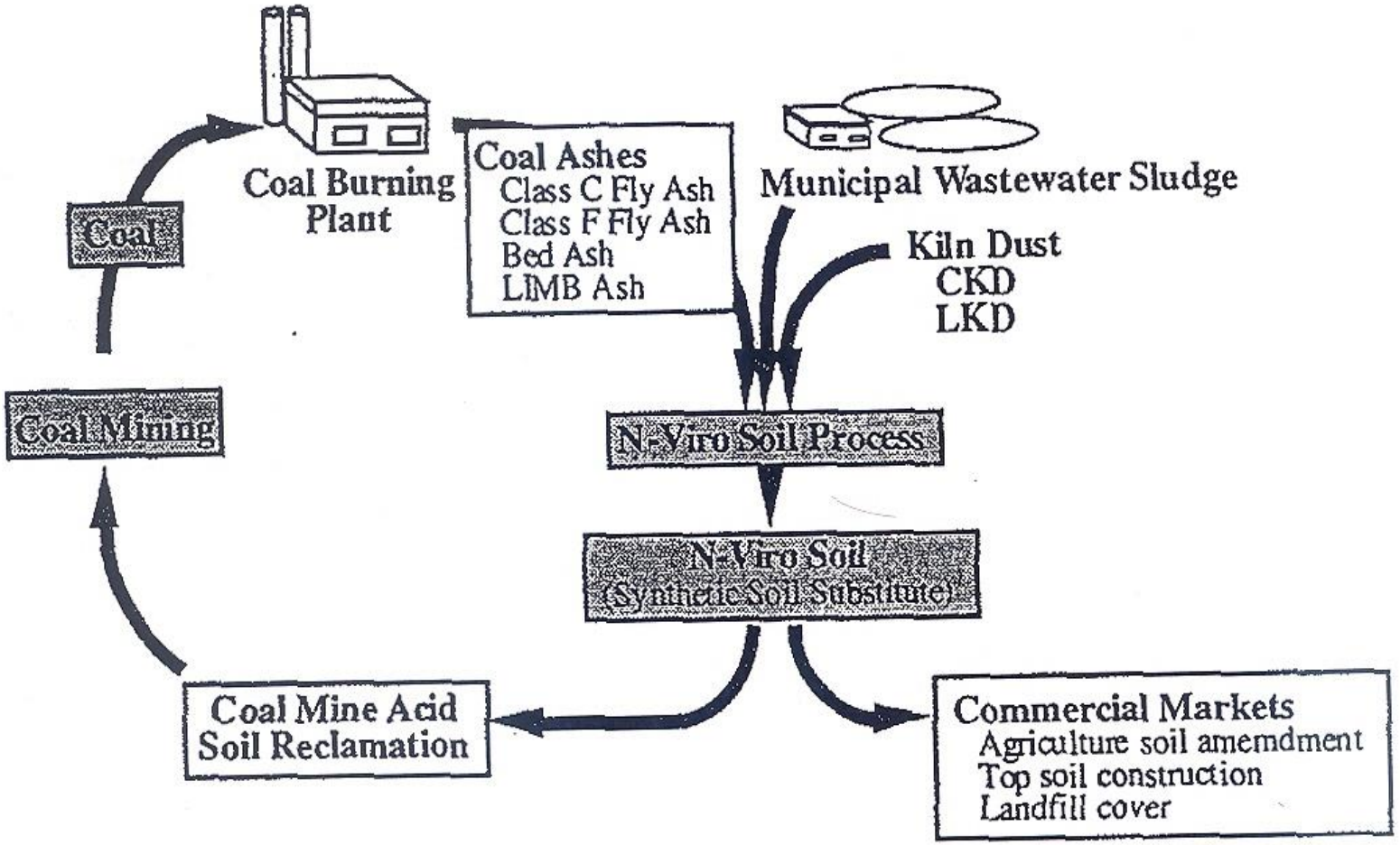
1. Bioassays assessing bioaccumulation, acute toxicity, and sublethal toxicity.

2. Impact of biochemical impact such as estrogenic activity, mutagenic activity and dioxin impact.

Usage of Molecular Assays

- There are 50 to 300 PPCPs in wastewaters.
- Similarly, there are 30 to 100 EDCs.
- Chemical analysis can determine if these compounds are impacting or toxic.
- The usage of yeast and human hormonal cells can determine if there is a health or environmental impact.

Schematic Diagram of the Cycle of Spent Coal Ash Products Producing Commercial Agriculture Soil Amenders, Reclamation Soil and Biocidal Agent



The Future Direction of the Application of Coal Ash as a Sustainable Agriculture Soil Amender

The application of Coal Ash, Kiln Dust, Spent Bauxite and other industrial ashes will be used in developing and developed countries. This ash makes:

1. Remediation soil amender for acid mine drainage
2. Biocidal soil agent for parasite infested soils due to its high ammonia content
3. Agriculture aglime agent for increasing the pH of acidic soils
4. Landfill cover
5. Soil amender and partial fertilizer

This is due to its low expense in producing this product for developing countries at a cost of under 50 US dollars per dry ton. The cost of disposal to a landfill in US is 200 US dollars per dry ton.

From here...

...To here

In Summary

- The application of coal ashes have been utilized to produce beneficial products.
- Disinfection is a function of ammonia, temperature, solids content, dissolve solids and enclosed systems.
- Stabilization is due to high pH, alkaline composting and aging
- Low levels of toxins with appropriate monitoring has been observed in US.

UPDATE

Our Changing View of Beneficial Use

1991:

"Beneficial Use means any application of sludge on land specifically designed to take advantage of the nutrient and other characteristics of this material to improve soil fertility or structure and thereby further some natural resource management objective."

Source: NEBRA, 2007

December 2011:

"The Water Environment Federation (WEF) supports a comprehensive approach to wastewater treatment and solids management that ensures the recycling and recovery of valuable resources including water, nutrients, organic matter, and energy."

Source: WEF, 2011

United Nations Endorsement

SHAFDAN (Israel) Wastewater Treatment Plant uses the N-VIRO process technology.
Diverts up to 40% of the untreated sludge from the Mediterranean Sea.

Wastewater Treatment facility with N-VIRO process was selected by the United Nations as a notable installation.
One of thirty exemplars of environmental sustainability.

This list was published in a special report of the UNEP (United Nations Environment Program) and the ICLEI (Local Governments for Sustainability) adjacent to the RIO +20 United Nations Conference on Sustainable Development that took place between 13-22 of June, 2012.

Thank you

Are there any questions?