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Utilization of Alkaline Coal Ash in the Treatment of Municipal Sludge - producing an Agricultural Soil Amender

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Abstract

The first application of spent coal ash was developed by N-Viro International Corporation (Toledo, Ohio). The process was developed by Dr. Jeffrey C. Burnham of then Medical College of Ohio. The process was patented in the 1980s and formulated two alternatives (USEPA, 2003):

1. Fine alkaline materials (cement kiln dust (CKD), quicklime fines (CaO), hydrated lime and or alkaline coal ash (ACA)) uniformly mixed into a liquid or dewatered sludge to raise the pH to > 12 for 7 days. If the sludge is liquid, it is dewatered. The stabilized sludge cake is air dried for 30 days until the cake is > 65 % solids. The solids concentration of > 60% before the pH drops below 12. The mean temperature of the air in the windrow aeration is 5^{o}C (41^{o}F) for the first 7 days.

2. Fine alkaline materials as noted in the first alternative are uniformly mixed to raise the pH to 12 for 72 hours. If the sludge is liquid, it is dewatered. The sludge cake is then heated in the lime stage of the process, which is raising the pH to 12 by the addition of CaO, reactive CKD and or reactive ACA that causes an exothermic reaction with water with the possible addition of heat. The sludge cake is then heated, while the pH is > 12, using exothermic reactions or heat to 52^{o}C (126^{o}F) throughout the sludge matrix for > 12 hours. The stabilized is then dried by windrow aeration, while the pH is > 12 for 3 days, to 50% solids. The process is shown in the below Figure 1.

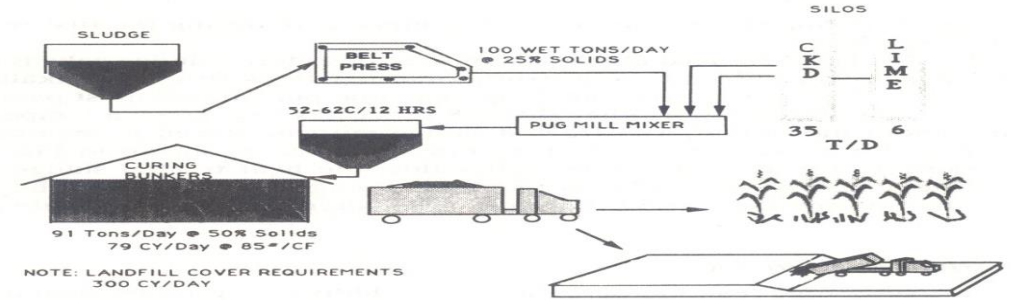

Figure 1: Diagram of the N-Viro process illustrating the addition of alkaline admixture following the dewatering of municipal sludge. Following the mixing, 12 hours heating period in conjunction with a pH of 12 accomplishes disinfection. The process then employs three mixings of the curing windrows prior to storage of the soil amender product (Burnham, et.al., 1992)

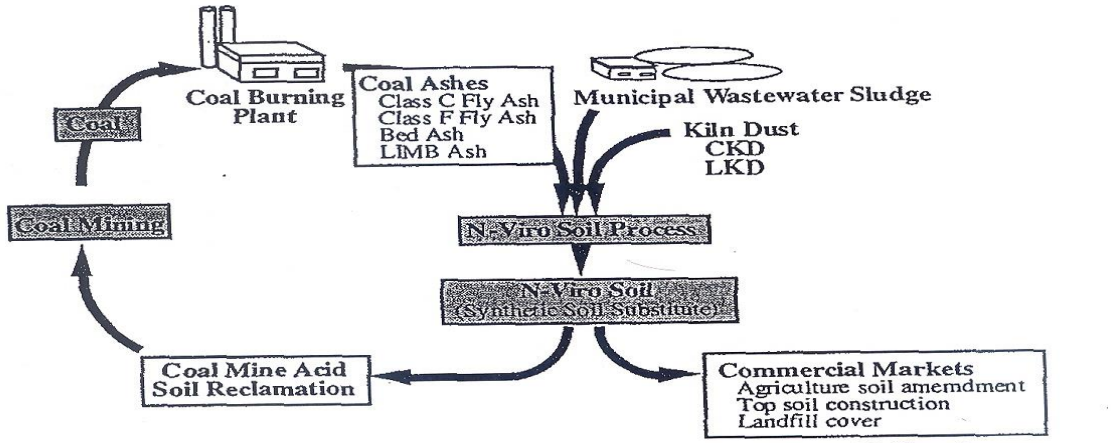

Figure 2: Schematic Diagram of the Cycle of Coal Product Utilization (Faulmann, et.al., 1995)

The N-Viro process utilizes coal ash in their process related to the end uses of the product and quality of the coal ash (Burnham, 1993) as noted in Figure 2.

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Over the past 25 years, research has been delineated the mechanisms and process refinements in the N-Viro process (Yamakawa and Logan, 2000) and other alkaline stabilization processes. As a result, the usage of lagoon systems for developing countries (Reimers et.al., 2001), ditching of the alkaline treated municipal sludge (Abu-Orf et.al., 2003) and usage of close systems have been implemented utilizing physical, chemical and biological mechanisms noted for disinfection, stabilization and value-added product refinement (Fitzmorris et. al., 2007).

The disinfection process is related to multi-stressors as noted by Dr. Burnham in his first articles on the N-Viro process (Burnham et.al., 1992). After many years of research, the main stressors in alkaline processes are discussed below (Fitzmorris-Brisolara et.al, 2013):

1. **Ammonia** is a disinfectant, which is an excellent biocide that is produced in the alkaline hydrolysis of the amines.
2. **Heat** from the exothermic reaction of quicklime and or reactive alkaline ashes with water along with possible outside heating will assist in pathogen disinfect due to deactivation DNA as a result of the increased temperature, volatilization of the ammonia and ammonia concentration due to the lowering the pKa, which increases the ammonia concentration by an order of magnitude.
3. **Increased solids content** will enhance the disinfection process since the ammonia concentration is produced by the alkaline hydrolysis reaction so the higher the solids content produces a high ammonia concentration.
4. **Enclosing ionic strength and chloride content** will assist the heating process and effect the inactivation of microbes such as fecal coliforms.

This phenomena is noted in the below table, which denotes the effectiveness of ammonia in inactivation of helminth eggs, which is the critical pathogen.

Table 1: Ammonia Concentration to Inactivate Helminth Eggs with respect to Temperature a pH of 12

Temperature (^oC)	**Ammonia Dosage (mg/L)**	**Inactivation Time** (days)
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

Table 2: Ammonia content for disinfection in alkaline disinfection processes

Temperature (C^o)	**Pressure (pisg)**	**NH_3 Concentration (mg/L)**	**Sludge Matrix**	**Inactivation Time (minutes)**
40	---	170 -200	Raw Municipal Sludge (RMS)	4,896
50	---	170 – 240	RMS	110
53	17	775	Anaerobic Municipal Sludge	40
55.3	17/25	335	Aerobic Municipal Sludge	40
56.7	20	130	RMS	40

Stabilization for alkaline systems has been delineated by USEPA as 2 hours at pH 12 and 22 hours at a pH 11.5(USEPA, 2003). If the pH drops below 10.5, purification will begin thereby releasing odors as a result of release of mercapitans and hydrogen sulfide. In the N-Viro process, stabilization is controlled by pH, biological activity, moisture content and mineral electron buffer capacity. This noted by the longer pH control, biological windrow process, conversion of calcium hydroxide the calcium carbonate as noted by research conducted by both Drs. Burnham and Logan (Burnham, 1993) (Yamakawa and Logan, 2000). The only problem is related to release of mercapitans at the processing at 53^{o}C to 55^{o}C. This can be controlled by having a closed system.

The first criteria of toxicity are bulk density levels which assume the tier I criteria as 100% release of the toxin from the soil, sediment and sludge (Reimers et. al., 2013). In the United States, the metals concentrations at equivalent (EQ) levels or lower are not restrictive at any loading rate, whereas in other countries or in the food industry the allowable levels are much more restrictive (Reimers et.al., 2008). The soil screening criteria have organics, metals, pesticides, PAHs, THM and some inorganics, which elucidates the categories of 147 compounds regulated by the criteria. There are 16 metals, 15 types of pesticides, three kinds of inorganics, 43 and 11 of PAHs and THMs, respectively, of concern. In fact, when assessing contaminated soils, the metals limits are very restrictive for residential soils but not as limiting for industrial soils. These criteria are used to determine whether a soil or an industrial residual is a solid waste or a non-contaminated soil. Assessment of the potential usage of ash and biosolids for the wetlands utilizes criteria coming from the Corps of Engineers Dredge Sediment Alert Levels for these metals (Reimers et.al., 2013). Assessment of the N-Viro soil is shown in Table 3.

Table 3: Comparison of N-Viro Soils to Different US Agencies

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

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 Engineerings.

Tier II testing assess availability of the toxins that released from the solids to the environment (Reimers et. al., 2013). In the United States, coal ash is considered a solid waste and must fall into solid waste arena. By using the ash as an ingredient in alkaline waste process, the product can be assessed under the 503 regulations. For ashes and sludges for application in the wetlands, the levels of metals will have to meet the soil screening testing protocol plus pass the synthetic acid precipitation leaching test (USEPA SW-846 Method 1312), which assimilates acid rain level in the United States. This test will determine whether an ash and sludge could be contaminated; if the test shows that the soil and sludge is not contaminated, these residuals can be taken out of the solid waste category. In these testing, two tests are being utilized. The first determines the solids can be classified as a contaminated or non-contaminated soil. Typical test is synthetic acid rain test "designed to determine the mobility of both organic and inorganic analyzes present in liquids, soils, and wastes". For soils, depending on where the sample site is located, the extraction fluid employed is a function of the region of the country. If the soils are considered waste, the extraction fluid used is a pH of 4.2 east of the Mississippi River and a pH of 5.0 west of the Mississippi related to acid rain in the United States. The collected extraction fluid is then being tested for constituents of concern. The other assessment extraction test is the Elutriation Test developed by the Corps of Engineers and EPA to provide a technically more appropriate alternative to the bulk chemical criteria approach for evaluating dredged sediments for their potential adverse effects on water quality. This test was to determine if the dredging sediments are contaminated or not.

The Tier III test assesses the availability of the toxins in the biota (Reimers et. al., 2013).. For EDCs the below two tests are going to be utilized (. With respect to EDCs and PPCPs, there are possibly 200 to 300 of these compounds in the ng/kg range, and the measurement of the concentration of a few EDCs would be meaningless so it recommended utilizing molecular assays. The organic compounds described in the section on emerging chemicals of concern could perform as carcinogens or bind with certain gene receptors. MVLN/MCF-7 cell proliferation assays and yeast estrogen screen (YES) cell assays have been used for endocrine screening. In addition, bioaccumulation assays can be preformed. Work in Canada and United States has observed little accumulation.

Conservation of man-made waste by transformation into a consumable product has evolved from alkaline processes. Again, there has been a movement from incineration and heat drying to advanced alkaline stabilization, innovative chemical processes and/or thermophillic processes. This progression must ensure disinfection, stabilization, and the destruction/biodegradation of refractory organics. These treated municipal waste residuals are further refined to fabricate a beneficial use. The specific factors in assessing beneficial use products include:

1. Optimizing heat/chemical stabilization/disinfection processes for municipal waste, manures and other waste residuals;
2. Developing cost effective processes to convert municipal waste, manures and other waste residuals and other residuals to value-added products, such as landfill cover, soil amender, engineered soils, ornamental horticultural fertilizer, and turf grass;
3 Evaluating value-added products against comparable commercial products on an economic and risk assessment basis;
4. Developing engineering, economic, and outreach plans to utilize the beneficial use products in the marketplace.

An area that has not been assessed with fertilizer/soil amender utilization of municipal waste residuals, manures and other waste residuals is the nature of crop yields, crop qualities, and nutrient value. Therefore, this area has to be addressed in the near future. Additional variables are elucidated below:

- Inactivation emerging pathogens such as prions, helminth eggs, and bacterial spores,
- Stabilization of these treated residuals chemically by use of oxidants along with alkaline agents and microbes,
- Destruction or altering chemicals of emerging concern (CEC) that they are mineralized or in a form that is degradable.

As the liability begins to rise, then the movement to beneficial use products or value-added products has moved out of arranger liability arena.

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