



Alkaline industrial by-product effects on plant growth in acidic-contaminated soil systems
by Joel Thomas Mehlenbacher

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation

Montana State University

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Abstract:

In some regions of the United States the near proximity of alkaline industrial byproducts to acidic-contaminated landscapes in concert with low acquisition cost, make these by-products an attractive option for soil remediation projects. The objective of this research was to determine whether acidic-contaminated soil systems amended with alkaline industrial by-products enable plant growth equivalent to that attained with a commercial grade mixture of CaCO_3 and CaO . In addition, it was determined whether an alkaline by-product dosage threshold existed, above which plant growth was impaired.

Three types of cement kiln dust (CKD), three types of lime kiln dust (LKD), and two other alkaline by-products (Dicalcium Silicate, Carbide Lime) were evaluated in this investigation. These alkaline by-products, and the standard treatment composed of a commercial grade CaCO_3/CaO mixture, were applied to metalliferous tailings (pH 1.8), and metal contaminated soil (pH 5.0) and plant growth was evaluated.

All alkaline products produced a desired soil pH (7.0 - 8.4) in the root zone during plant growth tests. Following a 111 day plant growth period with Basin Wildrye and Redtop all alkaline industrial by-products tested had plant growth equal to-or greater than- the CaCO_3/CaO mixture. This was the case in tailings and the contaminated soil for above ground plant biomass, plant height, root biomass, root depth, and number of roots at the 5 cm and 10 cm soil depths.

When alkaline by-products, including the CaCO_3/CaO mixture, were added to the Plant Growth Center soil, the greater the application rate the less was plant growth. Across the alkaline product dosage range of 0 % to 12 % (soil dry weight basis) the loss in aboveground plant biomass was 65 % for Basin Wildrye and 88 % for Redtop.

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency and is ready for submission to the College of Graduate Studies.

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Abstract

In some regions of the United States the near proximity of alkaline industrial by-products to acidic-contaminated landscapes in concert with low acquisition cost, make these by-products an attractive option for soil remediation projects. The objective of this research was to determine whether acidic-contaminated soil systems amended with alkaline industrial by-products enable plant growth equivalent to that attained with a commercial grade mixture of CaCO_3 and CaO . In addition, it was determined whether an alkaline by-product dosage threshold existed, above which plant growth was impaired.

Three types of cement kiln dust (CKD), three types of lime kiln dust (LKD), and two other alkaline by-products (Dicalcium Silicate, Carbide Lime) were evaluated in this investigation. These alkaline by-products, and the standard treatment composed of a commercial grade CaCO_3/CaO mixture, were applied to metalliferous tailings (pH 1.8), and metal contaminated soil (pH 5.0) and plant growth was evaluated.

All alkaline products produced a desired soil pH (7.0 - 8.4) in the root zone during plant growth tests. Following a 111 day plant growth period with Basin Wildrye and Redtop all alkaline industrial by-products tested had plant growth equal to-or greater than- the CaCO_3/CaO mixture. This was the case in tailings and the contaminated soil for above ground plant biomass, plant height, root biomass, root depth, and number of roots at the 5 cm and 10 cm soil depths.

When alkaline by-products, including the CaCO_3/CaO mixture, were added to the Plant Growth Center soil, the greater the application rate the less was plant growth. Across the alkaline product dosage range of 0 % to 12 % (soil dry weight basis) the loss in aboveground plant biomass was 65 % for Basin Wildrye and 88 % for Redtop.

CHAPTER 1

INTRODUCTION

History has many lessons; not the least of which points to the importance of foresight. Mining practices that occurred in the United States prior to Federal and State legislation utilized all existing resources to extract the relevant mineral often without regard or respect for the land which harbored it. The advent of the industrial revolution in the United States brought with it the ability to strip the earth of resources crucial to the development, if not the integrity, of this nation.

The Butte-Anaconda region of Montana has a long history of mining, primarily hard rock mining. The processing required to extract and purify the relevant mineral produces a waste stream of material enriched in metals, primarily, Al, Cd, Cu, Pb, Zn, the metalloid As, and metal sulfides. The final processed ore is sent to a smelting operation where further impurities are volatilized. The waste or "mill tailings" are slurried into an impoundment where the excess water is extracted. Upon exposure to O_2 and H_2O , the metal sulfides present in the tailings produce hydrogen ions acidifying the soil and mobilizing metals that contaminate water resources and deter any vegetative establishment.

The waste impoundments cover many square kilometers and pose a health risk to both humans (U.S. EPA 1998) and wildlife (U.S. EPA, 1999). In addition to waste impoundments, many tens of square kilometers has been impacted by stack emissions emanating from the smelting process. It is assumed that dry deposition of metals and sulfates have decreased the pH of the soil impacting all but deeply rooted vegetation;

subsequently, erosion of the topsoil can be severe in these areas. The result is the largest Environmental Protection Agency (EPA) Superfund site in the country. Remedial strategies based upon the best available technology consist of a thin lime layer underlying a 46 cm coversoil cap and/or an in situ treatment of soil with a 60 %/40 % mixture of commercial grade CaCO_3/CaO respectively (RRU *et al*, 1987). The rationale depicted is establishing a suitable plant root zone and prevention of upward migration of contaminants and acidity into the coversoil and establishing a suitable plant root zone by raising the pH of the soil to a range of 9 - 11 s.u. to precipitate metals of concern after which plant growth can be established when pH falls below 8.5 s.u.. Regions in the state of Montana that require this type of reclamation are frequently limited by financial resources. The scale of the site and frequently, the lack of a responsible party, create a cost prohibitive scenario.

Alkaline Industrial By-Products

Due to absence of a market, many types of alkaline industrial by-products have historically been landfilled in the United States. Cement kiln dust (CKD) and lime kiln dust (LKD) are two of the most common alkaline by-products, but there are many others. In some regions of the United States, the near proximity of these alkaline by-products to acidic-contaminated landscapes in concert with low acquisition cost, make these by-products an attractive option for land reclamation projects. The U.S. EPA estimated that in 1990 the

cement industry produced approximately 14 million tons (12.7 metric tons) of cement kiln dust from 111 plants in 38 states (EPA, 1999). The industry disposed of 3.6 million metric tons of CKD in 1995 (EPA, 1999). Lime kiln dust, a by-product of calcium oxide production, is produced at 114 plants in 32 states (USGS, 1999).

Sources of Contamination

These alkaline products are in the strictest sense a waste stream and liability of the manufacturer. They are discarded due to impurities that are introduced via:

- i) the type of fuel used in the kiln process
- ii) the limestone ore body chemistry (or dolomite in the case of Dicalcium Silicate)
- iii) chemical inputs required for the final product
- iv) the degree of recirculation of the dust within the kiln

The type of fuel utilized in the kiln process can be coal, coke, petroleum, heat oil, natural gas or a combination of fuels. All fuel except natural gas leave an ash residue with an inherent metal and salt content. This "fly ash" becomes part of the kiln dust and directly affects the utility of the kiln dust for reclamation projects. Natural gas, which does not introduce new contaminants into the kiln can have the potential to concentrate the kiln dust relative to the burning of coal and coke. The introduction of coal and coke into the kiln is accomplished through forced air due to the extreme temperatures present. This input effectively dilutes the kiln dust several magnitudes by increasing the amount of kiln dust

created. A natural gas-fired kiln will not require this forced air input and relative to a coal and coke fueled kiln will have a increased concentration of contaminants (Holnam, 2000).

Companies that use kilns to produce burnt lime (CaO) typically input the highest grade of limestone available. Therefore, ore bodies associated with this industry are typically 95 % or greater limestone resulting in a low potential to introduce impurities into the LKD. Cement production in a kiln requires additional constituents to reach the desired output. The manufacturing of cement requires iron, aluminum and silica inputs in addition to limestone. When the ore body does not contain these materials, they must be added to the kiln. This has the potential to increase the metal and salt content of the resulting kiln dust compared to lime production.

Kiln dust, although impure, contains amounts of the original materials and can be recirculated into the kiln for continued processing. This results in highly enriched kiln dust but overall, the amount of kiln dust produced decreases which is beneficial to the manufacturer. A study by the Portland Cement Association (1992) chemically analyzed CKD at most cement manufacturing facilities in the United States. The only samples of CKD that failed to pass the Toxicity Characteristic Leaching Procedure (TCLP) test, which is used to determine whether a material is a hazardous waste, were those from kilns where the kiln dust was recirculated. The study concluded the single most important parameter in determining the level of trace metals in CKD is the degree of recirculation of the CKD in the kiln system.

Efforts to Characterize Kiln Dust Physicochemical Traits

Haynes and Kramer (1982) analyzed kiln dust samples from 102 cement plants in the United States. Concentrations of aluminum (Al), chloride (Cl^-), fluoride (F^-), sulfate (SO_4^{2-}), strontium (Sr), and titanium (Ti) were consistently greater than 500 mg/kg. Lead (Pb) concentrations ranged as high as 2500 mg/kg and 8000 mg/kg for zinc (Zn) while median values were 148 and 167 mg/kg, respectively. They determined CKD was not a hazardous waste as defined by the Resource Conservation and Recovery Act (RCRA).

The Portland Cement Association (1992) sampled kiln dust from 79 plants in the United States. All but two samples passed the TCLP test used to identify a hazardous waste. Total concentrations of 12 metals were determined and enrichment was greatest for barium (Ba) (mean 280 mg/kg) followed by chromium (Cr), nickel (Ni), arsenic (As), and Pb.

Dollhopf (1996a, 1996b, 1997a, 1997b) and Dollhopf and Juntunen (1995) analyzed both CKD and LKD from several facilities located in the northwest United States. All CKD and LKD evaluated had high calcium carbonate equivalence and contained desired compounds (CaCO_3 , $\text{Ca}(\text{OH})_2$, CaO) for neutralization of acidic-metalliferous mine waste. Some kiln dusts formed a notable quantity of coarse particles (>0.25 mm diameter) due to having been weathered in outdoor storage areas, a physical trait that is not desired for neutralization of acidic soil, but most materials were fine textured. Both LKD and CKD contained enriched levels of metals compared to concentrations present in natural soils in the United States. However, copper (Cu), manganese (Mn), Pb, Zn, and other metals were very enriched in some CKD samples. In addition, sodium adsorption ratio (SAR) in CKD

was typically very high (20 - 60) which could exacerbate a preexisting sodic condition in a soil. The soluble salt content in LKD was low but this trait was not analyzed in CKD. These investigators found both LKD and CKD were capable of neutralizing acidic-metalliferous mine waste, but did not have the opportunity to evaluate these industrial by-products with plant growth tests.

May (1999) evaluated whether representative trace metal data in CKD could be obtained from a single grab sample. More than 20,000 samples were collected from two cement kilns. Results indicated that variation between samples was sufficiently large that multiple samples should be collected to accurately determine chemical traits of CKD.

Kiln Dust use in the Soil - Plant System

Redente and Richard (1998) conducted plant (Redtop, *Agrostis alba*) growth tests in the greenhouse in acidic waste rock from the Summitville Superfund Site amended with LKD, quicklime (CaO), and limestone (CaCO₃). They found limestone supported significantly greater plant shoot and root biomass compared to LKD. This result was attributed to the high pH produced in the root zone when LKD was applied compared to that attained with limestone. However, the authors did not allow the LKD to attain a suitable pH <8.5 for plant establishment.

Gitt and Dollhopf (1991) treated acidic coal waste with agriculture grade limestone and CKD at a field site in central Montana that was seeded to a mixture of grasses and forbs. They found both amendments neutralized the acidic nature of the coal waste, but limestone treatment resulted in significantly more (3 fold) plant production compared to treatment with CKD.

Dollhopf and McDaniel (1997) studied alkaline industrial by-products (Dicalcium Silicate and Flux Bar Residue) produced from a kiln during the manufacture of magnesium from dolomite. Bench top column test indicated these alkaline by-products effectively neutralized acidic mine wastes and precipitated metals of concern. However, when these by-products were used to treat acidic wastes, above ground plant (*Agropyron intermedium*, Intermediate wheatgrass) production attained with a mixture of agriculture grade limestone and a commercially produced calcium hydroxide was 20-fold that produced with Dicalcium Silicate, and no plant growth was attained with Flux Bar Residue. Mine waste application rates for Dicalcium Silicate and Flux Bar Residue were very high, 190.6 t/1000t and 129 t/1000t respectively.

ARCO Environmental Remediation, L.L.C (1999) reported LKD had been used on eight sites in the Upper Clark Fork River Basin in Montana where the landscape had become acidic and contaminated with metals due to historical overland flooding containing mine waste and/or fallout from smelter emissions. These authors indicated vegetation measurements had not been completed on all sites, but some locations exhibited notable plant establishment and growth following treatment with LKD.

Winking and Dollhopf (2000) amended acidic-metalliferous tailings with LKD at an application rate of 9.8 % (dry weight basis), Dicalcium Silicate at an application rate of 9.5 %, and a mixture of commercial grade limestone with calcium hydroxide at a 8.5 % application rate. All amendments successfully neutralized the acid conditions in the tailings. Above and below ground growth of *Thinopyrum intermedium* (Intermediate wheatgrass, var. Tegmar) and *Elymus trachycaulum* (Slender wheatgrass, var. Pryor) were the same for tailings amended with the commercial grade limestone/calcium oxide mixture and LKD, but Dicalcium Silicate amended tailings had significantly less plant growth.

Investigators reported loss in plant growth when soils were treated with CKD. Saravanan and Appavu (1998) measured decreased root length, shoot length and seedling vigor index for crops grown in soils treated with CKD. Investigators determined plants grown in a solution treated with CKD had a decreased mitotic index which was related to plant chromosome damage and it was suggested CKD acted as a mutagen to the plant system (Ignacimuthu and Muraleytharan 1994, Kaushik 1996).

Numerous investigators reported deposition, i.e. dusting, of CKD onto plant leaves impaired growth of various plant species (Chitralkha and Dhakshinamoorthy 1998, Rao and Narayanan 1998, Durge and Phadnawis 1994, Durge and Phadnawis 1998, Hegazy 1996, Prasad and Inamdar 1990, Uma and Ramana 1994, Uma and Ramana 1993). This result may be a function of the caustic ($\text{pH} > 9$ s.u.) nature of kiln dusts. It is likely that any caustic amendment (i.e. CKD, LKD, CaO or $\text{Ca}(\text{OH})_2$) transferred by wind onto adjacent lands could cause impaired plant growth.

Gutenmann et al. (1994) found enriched levels of selenium in CKD resulted in significantly higher concentrations of this element in plant parts when the soil had been treated with CKD compared to commercial grade CaCO_3 and CaO .

Investigators reported LKD and CKD improved plant growth when applied to soils at rates comparable to fertilizer application or in combination with sewage sludge treatments (Simpson and Stopes 1991, Christie et al. 2001, Lafond and Simard 1999, Luo and Christie 1997).

Alkaline Industrial By-product Chemical Enrichment

Alkaline industrial by-products often contained metal contaminants at concentrations that may produce phytotoxic responses in plant growth. However, phytotoxic concentrations may be mitigated when applied to soils at an application rate of 2 - 10 % of the soil mass which facilitates dilution of the amendment metal chemistry, and the change in amendment pH from a range of 9.6 - 13.7 to the soil pH of 7.0 - 8.4 results in decreased contaminant solubility in the soil solution.

The water soluble metal content of an alkaline by-product at its pH, which ranged from 9.6 to 13.7, may be significantly different compared to an amended soil where the final pH will be in a target range of 7.0 - 8.4. It was predicted that water soluble metal concentration in alkaline by-products would be at lower concentration in an amended soil (pH 7.0 - 8.4) compared to its water soluble metal concentration at pH 9.6 - 13.7. As will be

discussed below, certain water soluble metal concentrations of alkaline industrial by-products had the potential for phytotoxicity, however, no toxicity appeared to be in the amended soil system having a pH of 7.0 - 8.4.

Alkaline industrial by-products will be applied to acidic-contaminated soil systems at various application rates ranging up to 10 %, i.e. 100 tons amendment/1000 tons soil. Often a by-product contained a total metal concentration that had the potential for phytotoxicity. However, amendment incorporation into the soil profile results in notable dilution that decreases the risk of a phytotoxic response.

By-product dilution during soil incorporation and a decrease in metal solubility following treatment implementation generally led to interpretations that these alkaline products would not produce phytotoxic symptoms in the plant root zone. Uncertainty associated with these interpretations is present, thus plant growth tests presented later in this thesis provide additional information regarding by-product phytotoxicity.

Vanadium

Vanadium (V) is a ubiquitous element and is naturally present in surface soils in the United States which are reported to contain 7 - 300 mg/kg V and sedimentary rocks such as limestone typically contain 10-45 mg/kg V (Kabata-Pendias and Pendias, 1984) Gough et al. (1979) reviewed the topic of V phytotoxicity and stated that there are no reports indicating V toxicity under field conditions. However, he stated under experimental conditions, V concentrations as high as 0.5 ppm in the nutrient solution, and 140 ppm in the soil solution,

may be toxic to plants. Kaplan et al. (1989) reported dosages of 3 and 6 mg/l V were applied in a hydroponic study that induced visual toxicity symptoms in beans that increased with V concentration. He stated part of the toxicity effect of V on plants was related to the depression of calcium and possibly manganese uptake by the plant which leads to nutrient deficiency. In 1990, Kaplan et al. reported on a study where both sand and loamy sand soils were prepared with 1, 20, 40, 60, 80, and 100 mg/kg total V. At the two highest concentration of V, the sand soil had significantly less plant biomass of *Brassica oleracea*, but the loamy sand soil showed no effect on plant growth. These investigators also evaluated seed germination as a function of V in soil solutions that ranged from 0-75 mg/l. Low concentrations of V (1 mg/l) stimulated radicle elongation while slightly greater concentration (3 mg/l) caused severe toxicity. These investigations suggest high concentrations of V in soil systems have potential to impair plant growth. The concentration of V that will cause impaired plant growth is dependent upon the plant species present and the soil physicochemical characteristics.

Aluminum

Natural soil solutions contain approximately 0.4 mg/l Al (Kabata-Pendias and Pendias (1984), and Munshower (1994) reported water extractable concentrations of 1 - 5 mg/kg may be phytotoxic. When Dicalcium Silicate is used as a soil amendment, all water soluble aluminum in Dicalcium Silicate (464 mg/l) must transform into a solid phase precipitate that is unavailable for plant uptake. If a portion of the by-product Al remains in solution in the plant root zone, phytotoxic conditions would likely be present.

Barium

Kabata-Pendias and Pendias (1984) indicate the total Ba content of surface soils in the United States average 400 to 835 mg/kg depending on soil type and range from 10 to 3000 mg/kg. In soil systems, Ba is relatively insoluble since it tends to form precipitates with sulfates and carbonates, and is strongly adsorbed by clays. Therefore, Ba enrichment measured in kiln dust is not expected to impair plant growth.

Boron

Kabata-Pendias and Pendias (1984) indicate total boron (B) content of surface soils in the United States average 20 - 55 mg/kg depending on soil type. Holnam (CH₄) CKD had a water extractable B concentration of 5 mg/l while all other alkaline products were below the detection limit. Soil water extractable B concentrations >5 mg/l may impair growth and reproduction of some plant species (Eaton 1944, Munshower 1994). The 5 mg/l B measured in the water extract from the Holnam CKD where the kiln was fired with natural gas (CH₄), was at a solution pH of 13.7. Adsorbed (or fixed) B, as opposed to B in the soil solution is highly pH dependent, with maximum adsorption occurring in a pH range of 7 - 9 (Barth et al. 1987). At soil pH >9.2, B(OH)₄⁻ predominates in solution and was likely the species measured in CKD. Nonionized B(OH)₃ predominates in soil solution in the pH range 7 to 9. Therefore, the amount of B in solution would be less in a pH range of 7.0 - 8.5 compared to a pH of 13.7. Given the solubility characteristics of B, and anticipated

alkaline product application rate of less than 10 % of the soil dry weight mass, the enriched levels of water soluble B measured at pH 13.7 are not expected to impair plant growth in an amended soil system having a pH in the range of 7.0 - 8.3.

Selenium

The primary concern with enriched soil Se levels is that it may facilitate enriched Se concentrations in plant tissues that cause toxic symptoms in livestock as a result of grazing on these plants. Munshower (1994) reported a soil water extractable Se concentration $>0.5 \mu\text{g/g}$ is considered very enriched (Note $1 \mu\text{g/g} = [1 \text{ mg/l}]/\text{relative density}$). Certain plant species accumulate sufficient Se to be toxic to animals if soluble soil selenium (selenate, SeO_4^{2-}) concentrations were only a few tenths of a $\mu\text{g/g}$ (Lakin, 1972). AB-DTPA extractable soil Se concentrations of $< 0.2 \mu\text{g/g}$ produced plant tissue Se levels greater than levels recommended for prolonged consumption by livestock (Producers and Munshower 1991).

Selenate is the predominant form of Se in calcareous soils and selenite is the predominant form in acid soils (Sims et al. 1986). Selenate is highly mobile (i.e. soluble) in alkaline soils. Griffen and Shimp (1978) showed that selenite solubility decreased from a pH of 2 to 9. Therefore, use of CKD to treat acidic-metalliferous soil should be done with caution pertaining to use of selenium accumulating plant species and livestock grazing issues.

Zinc

The soil solution concentration of Zn that can cause a phytotoxic response is uncertain. Total Zn concentrations in soil that produce phytotoxic response are usually in the 250 to 650 mg/kg range (Munshower 1994). Kabata-Pendias and Pendias (1984) reviewed results from several investigations and found total soil Zn concentrations of 70 - 400 mg/kg caused phytotoxicity. Kiln dust application rates in the range of 2 - 10 % (dry weight basis) will increase the total Zn concentration in the tailings approximately 1 % to 50 % and in contaminated soil < 1 % to 15 %. It is not known whether increased Zn concentration in the soil system due to kiln dust application will exacerbate the phytotoxicity issue, but the risk of impaired plant growth is increased by producing a higher contaminant concentration in the soil system

Arsenic, Cadmium, Chromium, Copper, Lead, Manganese, Nickel

Although the degree of enrichment for these chemical elements in the by-products was often notable, the final concentration in an amended soil (assuming a 2 - 10 % amendment application rate, dry weight basis) would be relatively low and is not expected to produce a phytotoxic response. However, use of kiln dust will generally increase the level of these contaminants in the amended soil system and the impact, if any, to plant growth is not known. Given these circumstances, plant growth tests are appropriate to better understand phytotoxicity issues.

In summary, the toxicity of these elements when applied as an amendment to a soil system is nebulous. The texture of the soil, resulting pH of the root zone, and the plant species present greatly affect the degree of impairment. The literature cited for all elements reported that levels of plant growth impairment were less as a function of increased levels of calcium (Ca^{2+}) and magnesium (Mg^{2+}) present in the soil matrix. This indicates that, to a certain degree, the effects of introduced contaminants in the plant root zone can be mitigated by the alkaline inputs of these industrial by-products.

Objectives of Research

The goal of this research was to determine whether acidic-contaminated soil systems amended with alkaline industrial by-products enable plant growth equivalent to that attained with a commercial grade mixture of CaCO_3 and CaO .

Alkaline by-products with enriched concentrations of metals and/or soluble salts may provide the means for good plant growth when applied at low soil application rates, but a threshold dosage rate may exist that impairs plant growth. This investigation was conducted to better understand these concerns.

Three types of CKD, three types of LKD, and two other alkaline by-products (Dicalcium Silicate, Carbide Lime) were evaluated in this investigation. These alkaline by-products, and the standard treatment composed of a commercial grade CaCO_3/CaO

mixture, were applied to acidic-metalliferous soil matrices and an optimal soil matrix and plant growth was evaluated. Specific objectives of this investigation were as follows.

- Determine the physicochemical traits of alkaline industrial by-products.
- Determine plant growth characteristics in acidic-metalliferous soil matrices amended with alkaline by-products and a CaCO_3/CaO mixture.
- Determine whether an alkaline by-product dosage thresholds exist, above which plant growth is impaired.
- Identify those alkaline by-products that are suitable for in-situ treatment of acid soil systems.

CHAPTER 2

METHODS AND MATERIALS

Tailings, Contaminated Soil, Plant Growth Center Soil Bulk Sample Collection

A bulk composite tailings sample of approximately 680 liters (180 gallons) was collected from the D-2 cell of the Opportunity pond site near Anaconda, MT. Stainless steel tools were used to place tailings into clean plastic cans. The sample was collected to a depth of 45 cm avoiding the initial 0 - 7 cm depth increment which contained some limestone. Similarly, a bulk composite contaminated soil sample of approximately 680 liters was collected from the east end of Stucky Ridge near Anaconda, Montana within the 0 - 10 cm depth increment. The MSU Plant Growth Center soil was composed of 33 % Bozeman silt-loam, 33 % sand and 33 % sphagnum peat (volume basis). This soil was sterilized with forced steam and used as an optimal potting medium to support maximum plant growth of the test species.

Alkaline Industrial By-Products Bulk Sample Collection

These following nine alkaline industrial products were collected for this investigation.

CaCO₃/CaO

Limestone (CaCO₃) was provided by Montana Limestone, Bridger, MT. Burnt lime (CaO) was provided by Greymont, Inc. (formerly Continental Lime Company), Townsend, MT.

Greymont LKD

This LKD was produced by Greymont, Inc. Townsend, MT. A composite bulk sample, consisting of 10 subsamples, was collected from a stockpile of this LKD located in Anaconda; Montana, owned by Atlantic Richfield Company. This LKD was produced in a kiln heated with a fuel mixture of 70 % coal and 30 % coke. The kiln process did not include recirculation of the LKD.

Tacoma LKD

This LKD was produced by Tacoma Lime, Inc. Tacoma, WA. The company referred to this LKD as "Econolime". Limestone is shipped to Tacoma where the kiln is located. Atlantic Richfield Company purchased this LKD and had it transported by rail to Rocker, Montana where it was stockpiled. A composite bulk sample, consisting of 6 subsamples, was collected from this stockpile in Rocker, MT.

MT Limestone LKD

This LKD was produced by Montana Limestone, Bridger, MT. The limestone pit and kiln are located in Frannie, WY. This LKD was produced in a kiln heated with a fuel mixture of coal and coke. Montana Limestone staff collected the bulk LKD sample and shipped it to Montana State University.

Holnam (CH₄) CKD

This CKD was produced by Holnam, Inc., Three Forks, MT. The limestone pit and kiln are located in Trident, MT. The CKD was produced in a kiln heated with methane gas (CH₄). In addition to limestone, amounts of shale, sand, glass and iron ore were placed in the kiln to produce cement. The kiln process did not include recirculation of the CKD. A single bulk sample of CKD was collected from the storage silo.

Holnam (Coal, Coke) CKD

This CKD was produced by Holnam, Inc., Three Forks, MT. The limestone pit and kiln are located in Trident, MT. The CKD was produced in a kiln heated with a mixture of 75 % coal and 25 % coke. In addition to limestone, amounts of shale, sand, glass and iron

ore were placed in the kiln to produce cement. The kiln process did not include recirculation of the CKD. A single bulk sample of CKD was collected from the storage silo.

Ash Grove CKD

This CKD was produced by Ash Grove Cement Company, Clancy, MT. The limestone pit and kiln are located in Montana City, MT. The CKD was produced in a kiln heated with a mixture of 70 % coal and 30 % coke. In addition to limestone, amounts of shale, silica, and slag iron were placed in the kiln to produce cement. Approximately one-third of the CKD was recirculated through the kiln. A single bulk sample of CKD was collected from the storage silo.

Dicalcium Silicate

This kiln dust was produced by Northwest Alloys, Addy, Washington., where magnesium is produced from dolomitic limestone. The limestone pit and kiln are located in Addy, WA. Staff from Northwest Alloys collected a bulk sample and shipped it to Montana State University.

Carbide Lime

This alkaline by-product was produced by Liquide Air, Missoula, MT. The by-product stockpile was located on Liquide Air properties in Missoula, MT. Carbide Lime is a by-product in the production of acetylene gas. Coke is combusted in the presence of calcium oxide to produce calcium carbide, which is then treated with water to yield acetylene and Carbide Lime. A composite bulk sample, consisting of 10 subsamples, was collected from a stockpile in Missoula, MT

Analytical Methods for Soil and Alkaline Industrial By-Products

The soil samples collected from the field (tailings and contaminated soil) were mechanically homogenized prior to analysis. Samples were placed in a rotating tractor driven cement mixer at the MSU Plant Growth Center for five minutes with the tractor set at 1200 rpm. Subsamples were then collected and dried for analysis of physicochemical parameters listed in Table 1.

In addition to the standard bench top pH glass electrode method, a stainless steel pH probe (Scientific Instruments Model IQ150) was used to measure root zone pH during the plant growth period. The probe was periodically pushed into the pot substrate to the 2.5 cm soil depth and pH measured with the calibrated instrument.

Table 1. Analytical testing methods for soil and alkaline industrial by-products.

Analysis	Note	Method
pH, s.u.		Agron. Soc. Amer., Monograph No. 9, Methods of Soil Analysis, 1965, Method 62-1.3.2.1, p. 935.
Electrical Conductivity ² , dS/m		Agron. Soc. Amer., Monograph No. 9, Methods of Soil Analysis, 1965, Method 62-2.2.3, p. 938.
Total Metals ¹	Ag, Al, As, Ba, Be, B, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Ni, P, Pb, Se, Sn, V, Zn	Test Methods for Evaluating Solid Waste, 1986. Method 3050 (HNO ₃ and H ₂ O ₂ digestion).
Water Soluble Metals ¹	Al, As, B, Cd, Cl, Cu, Fe, Mn, Pb, Se, SO ₄ , Zn,	Agron. Soc. Amer., Monograph No. 9, Methods of Soil Analysis, 1965, Method 62-1.3.2.1, p. 935
Toxicity Characteristic Leaching Procedure (8 RCRA metals) ¹	As, Ba, Cd, Cr, Pb, Hg, Se, Ag	EPA, SW 846, Method 1311
Calcium Carbonate Equivalence (CCE) ¹ , %		Agron. Soc. Amer., Monograph No. 9, Methods of Soil Analysis, 1965, Method 91-4.2., p. 1387.
Loss on Ignition ¹ , %		ASTM (1980) C25-90, Section 21
Sodium Adsorption Ratio ²	$[\text{Na}]/([\text{Ca}] + [\text{Mg}]/2)^{1/2}$, meq/l	Agron. Soc. Amer., Monograph No. 9, Methods of Soil Analysis, 1965, Method 62-1.3.2.1, p. 935
Acid-Base Account ¹		Modified Sobek Method (RRU <i>et al.</i> , 1987) (Sobek <i>et al.</i> 1978)
Lime Requirement (SMP Buffer) ¹	Lime requirement tons/1000 tons	Method 12-3 (ASA, 1982), Part 2
Particle Size Analysis ²	% sand, silt and clay	Modified Day, Method 15-5 (ASA, 1982), Part 1
Textural Classification ²	USDA Textural Triangle	Soil Survey Staff (1975)
% Rock Fragments ²	≥ 2 mm diameter	ASTM (1993) D421-85
% Saturation ²		Method 27a (U.S. Salinity Lab Staff, 1969)

¹ Energy Laboratories, ² RRU Laboratory

Table 2. Characteristics of plant species used in this investigation (Munshower, 1998).

Plant Specie	Plant Common Name	Salinity Tolerance	Acid Tolerance	Metal/Non-metal Tolerance	Seeding Depth (cm)
<i>Leymus cinereus</i> , Magnar	Basin Wildrye	good to very good	acid to alkaline	Elevated heavy metals, very tolerant of water soluble arsenic in soil	1.25
<i>Agrostis alba</i> , Streaker	Redtop	moderate	acid	some	1.25

Plant Species

Plant species selected for this investigation were based on their relevance to disturbed land reclamation and tolerance to saline and acidic-metalliferous soils. Perennial grasses selected are listed in Table 2.

Table 3. Alkaline amendment application rates for tailings, contaminated soil, and Plant Growth Center soil.

Treatment	Application Rate, Tons Amendment/ 1000 Tons Soil		
	Tailings	Contaminated Soil	Plant Growth Center
1) Control	0	0	0
2) CaCO ₃ /CaO	29.16 CaCO ₃ + 11.23	4.36 CaCO ₃ + 1.87 CaO	29.16 CaCO ₃ + 11.23
3) Greymont LKD	75.15	12.55	75.15
4) Tacoma LKD	116.60	19.47	116.60
5) MT Limestone LKD	91.25	6.24	91.25
6) Holnam (CH ₄) CKD	53.31	8.90	53.31
7) Holnam (Coal, Coke)	55.15	9.21	55.15
8) Ash Grove CKD	68.70	11.47	68.70
9) Dicalcium Silicate	42.35	7.07	42.35
10) Carbide Lime	73.84	12.33	73.84

Soil Treatments for Tailings, Contaminated Soil and Plant Growth Center Soil

Nine alkaline products were applied to three difference soil types (Table 3). The tailings had a lime requirement of 47.43 t CaCO₃/1000 t, the contaminated soil had a lime requirement of 7.92 t CaCO₃/1000 t, and the Plant Growth Center soil had no lime requirement and was included to evaluate the effects of the lime products in an optimal plant growth medium. The total lime requirement for these three soil types was calculated according to Equation 1.

$$\begin{aligned} \text{t CaCO}_3 / 1000 \text{ t soil} = & (\% \text{ HNO}_3 \text{ Extractable S} + \% \text{ Residual S}) 31.25 + 23.44 \\ & (\% \text{ HCl Extractable S}) + \text{SMP Lime Requirement, t CaCO}_3 / 1000 \text{ t soil} \quad [\text{Equation 1}] \end{aligned}$$

A control treatment served to evaluate plant growth in each soil type without addition of an alkaline product. The application rate was different for each alkaline product for tailings and for the contaminated soil since physicochemical traits of each product are different. An alkaline product application rate for a soil was a function of the calcium carbonate equivalence, particle size < 60 mesh (0.25 mm), and gravimetric water content. The Plant Growth Center alkaline product application rate was set the same as that required for tailings as the contaminated soil requirement was very low and higher application rates would provide a better comparison. All treatments were replicated 8 times into a randomized complete block experimental design. This constituted 480 experimental pots (8 replications x 10 soil treatments x 3 substrates x 2 plant species). Plant growth containers

were round plastic pots with dimensions of approximately 15 cm in diameter and 15 cm deep. Plants were watered at a rate of 100 ml per day. The plant growth period was 111 days.

Soil Treatments for The Alkaline Product Dosage Sequence Plant Growth Tests

Nine alkaline products were applied to the Plant Growth Center soil at seven different application rates that ranged from 0 % (0 t alkaline amendment / 1000 t) to 12 %

Table 4. Alkaline amendment application rates for variable dosage rate research using the Plant Growth Center soil.

Treatment	Alkaline Amendment Dosage Sequence						
	0 %	2 %	4 %	6 %	8 %	10 %	12 %
	Tons Amendment/ 1000 Tons Soil						
1) CaCO ₃ /CaO	0	20	40	60	80	100	120
2) Greymont LKD	0	20	40	60	80	100	120
3) Tacoma LKD	0	20	40	60	80	100	120
4) MT Limestone LKD	0	20	40	60	80	100	120
5) Holnam (CH ₄) CKD	0	20	40	60	80	100	120
6) Holnam (Coal, Coke) CKD	0	20	40	60	80	100	120
7) Ash Grove CKD	0	20	40	60	80	100	120
8) Dicalcium Silicate	0	20	40	60	80	100	120
9) Carbide Lime	0	20	40	60	80	100	120

(120 t alkaline amendment / 1000 t) in 20-ton increments (Table 4). All treatments were replicated 5 times a randomized complete block experimental design. This constituted 630 experimental pots (5 replications x 9 soil treatments x 7 application rates x 2 plant species).

Plant growth containers were square plastic pots with dimensions of approximately 11 cm in diameter and 10 cm deep. Plants were watered at a rate of 50 ml every other day. The plant growth period was 90 days.

Plant Growth Conditions

Initially, all soil materials treated with alkaline products had a pH >8.5 due to the presence of CaO and Ca(OH)₂. In order to reduce this pH, carbonation of these oxides and hydroxides of calcium was facilitated with CO₂ gas piped through each substrate in the presence of applied water. The carbonation treatment process required a several month period to complete. When all substrate pH levels were below 8.5, seeding was instituted. A seed stock viability test was performed to determine the percent live seed for Basin Wildrye and Redtop. Ten seeds of each species were placed on paper towels in a petri dish and kept moist. This procedure was replicated 4 times. Percent of the seeds that germinated was recorded. Live seed was 92.0 ± 5.4 % for Basin Wildrye and 92.0 ± 4.8 % for Redtop. Fifteen seeds of the same plant species were planted in each pot. Following 14 days of post-emergence plant growth, several growth characteristics were measured and then plants were thinned to five per pot. Plants were grown with 18 hours of light per day at 21° C (69.8° F). Night temperatures were maintained at 18° C (64° F).

Plant Growth Measurements

Nine types of plant growth measurements were made and are described in Table 5. Measurement of below ground biomass, i.e. root biomass, was facilitated with a water

Table 5. Plant Growth Measurements

Measurement	Procedure
Time To Emergence	Number of days for seedling to emerge from date of seeding.
14 Days After Emergence	
Germination	Given the 15 seeds per pot, the number that germinated and emerged.
Survival	Number of viable seedlings of those that emerged.
Shoot Height	Distance from ground to the end of the longest leaf for each plant.
Plant Harvest	
Aboveground Height	Distance from the ground to the end of the longest leaf for each plant.
Maximum Root Depth	The maximum root length in each growth pot measured a maximum of the depth of pot.
Root Distribution	The number of roots at 5 cm and 10 cm soil depth.
Aboveground Biomass	The aboveground biomass of all plants measured after drying at 50° C for a minimum of 48 hours.
Belowground Biomass	The belowground biomass of all plants measured after drying at 50° C for a minimum of 48 hours.

washing procedure that separated soil from the root. Maximum Root Depth and Root Distribution at 10 cm was not measured in plant growth tests associated with alkaline

product dosage sequence investigation.

Statistical Analyses

Plant growth measurements were statistically analyzed using Sigmastat® statistical software version 2.03 (SPSS 1997). Statistical analyses for soil pH were performed using $[H^+]$. Normally distributed data were analyzed using a two-way ANOVA to determine if treatment means were significantly different ($p < 0.05$). If treatment means were found to be significantly different, then the means were separated using the All Pairwise Multiple Comparison Procedures (Student-Newman-Keuls Method). Data that were not normally distributed were transformed and analyzed using a two-way ANOVA to determine if treatment means were significantly different ($p < 0.05$). Data that were not normally distributed and could not be normalized through transformation were analyzed using the nonparametric one-way Kruskal-Wallis ANOVA on ranks to determine whether significant differences were present

($p < 0.05$).

Data Quality Control

Laboratory analyses were conducted on tailings, soil, and alkaline industrial products.

Statements pertaining to laboratory data accuracy, precision and completeness are presented in Appendix C.

CHAPTER 3

RESULTS AND DISCUSSION

Physicochemical Characteristics of Tailings and Contaminated Soil

Opportunity Tailings

Tailings material was collected from the D2 Opportunity Impoundment near Anaconda, MT. No plant growth was present at the field site. It contained no coarse fragments (> 2 mm diameter) and had a sandy loam particle size distribution (Table 6). Tailings were acidic (pH 1.8) and saline (electrical conductivity 9.7 ds/m) with a low sodium adsorption ratio of 0.03. Water soluble concentrations of aluminum were very enriched (976 mg/l), and associated concentrations of copper, manganese, and zinc were also enriched.

In tailings, 19.2 t CaCO_3 /1000 tons of tailings was required to neutralize the active acidity. Potential acidity emanating from sulfide minerals (0.51 %) required 15.9 t CaCO_3 /1000 tons of tailings to neutralize this source of acidity. It was assumed that relatively insoluble sulfate minerals were present, e.g. jarosite, which had the potential to produce acidity that required an additional 3.8 t CaCO_3 /1000 tons of tailings. The total CaCO_3 requirement was 47.43 t/1000 t (Table 6).

Table 6. Physicochemical characteristics of tailings and contaminated soil.

Sample Type	SMP Active Acidity analysis tCaCO ₃ /1000t	Lime Requirements (%)											
		HCl Extractable S	HNO ₃ Extractable S	Residual S	H ₂ O Extractable S	Total S	Neut. Pot. t/1000t as CaCO ₃	Acid Pot. t/1000t as CaCO ₃	Acid Base Pot. as CaCO ₃	Non-Sulfate Sulfur	H ₂ O by Weight	Substrate >2 mm	Total Lime Requirement tCaCO ₃ /1000t
Contaminated Soil	5.4	0	0.01	0.02	0.01	0.04	<1	1	-1	0.03	1.38	23.0	7.92
Tailings	19.2	0.12	0.44	0.07	0.51	1.14	<1	20	-20	0.63	6.01	0	47.43

Sample Type	Water Saturated Paste Extract (mg/l)												
	pH	EC ds/m	Sodium Adsorption Ratio	Ca meq/l	Mg meq/l	Na meq/l	Al	As	Cu	Pb	Mn	Zn	
Contaminated Soil	5.0	0.60	0.32	2.84	0.48	0.42	1	0.36	22.5	<1	4.6	10.5	
Tailings	1.8	9.7	0.03	27.6	23.3	0.14	976	6.8	99.0	<.01	183	81.4	

Sample Type	Total Concentration (mg/kg)					
	Al	As	Cu	Pb	Mn	Zn
Contaminated Soil	11400	443	1400	138	241	311
Tailings	2680	76	162	273	93	94

Sample Type	% Passing Dry Sieve Size		Calcium Carbonate Equivalence	Loss on Ignition	Particle Size Analysis			Textural Class	Saturation Percentage %
	10 mesh 2.0 mm	60 mesh 0.25 mm			% Sand	% Silt	% Clay		
Contaminated Soil	77	ND	0.1	ND	73.4	16.6	10	sandy loam (sl)	24.1
Tailings	100	ND	0.1	ND	58.4	30	11.6	sandy loam (sl)	36.0

ND = Not Determined

Contaminated Soil

The contaminated soil was collected from the east end of Stucky Ridge near Anaconda, MT. Contamination in this natural soil emanated from smelter emissions of sulfates and metals. There was no grass growth at this field site, but Canadian thistle constituted approximately a 5% plant cover. This soil had a coarse fragment content of 23 %, i.e. particles not passing a sieve with 2 mm openings, and a sandy loam particle size distribution (Table 6). The contaminated soil was acidic (pH 5.0) but was neither saline nor sodic. Total soil concentrations of arsenic (443 mg/kg) and copper (1400 mg/kg) were very enriched while lead, manganese and zinc were enriched to a lesser degree. Water soluble concentrations of arsenic (0.36 mg/l) were low in the pH 5.0 soil matrix, while copper (22.5 mg/l) and zinc (10.5 mg/l) were the most enriched metals in the soil solution.

In order to neutralize the active acidity in this contaminated soil, 5.4 t CaCO₃/1000 tons of soil would be required. Potential acidity emanating from sulfide minerals was small (0.03 %) and required 0.9 t CaCO₃/1000 tons of soil to neutralize this source of acidity. The total CaCO₃ requirement was 7.92 t/1000 t (Table 6).

Physicochemical Characteristics of Alkaline Industrial By-Products, Calcium Carbonate and Calcium Oxide

That portion of an alkaline amendment passing a 60 mesh sieve (0.25 mm) is chemically reactive for neutralization of soil acidity (Tisdale et al, 1966). This is true for

CaCO_3 . However, both CaO and Ca(OH)_2 are each approximately 100 times more soluble in water compared to CaCO_3 . Thus the coarse particles (>60 mesh) of an alkaline amendment that pass a 60 mesh sieve following a 16 hour period of shaking in a beaker of water are considered reactive CaO and Ca(OH)_2 .

All alkaline amendments passed the 60 mesh screen except for Greymont Lime Kiln Dust (LKD), Tacoma LKD, and Carbide Lime (Table 7). Following dry and wet sieving procedures, 19.2 % of the Greymont LKD failed to pass the 60 mesh sieve, while 55.1 % of

Table 7. Physicochemical Characteristics of Alkaline Industrial By-Products and Commercial Grade Lime.

Sample Type	% Passing Dry Sieve Size		% Passing Wet Sieve 60 mesh 0.25 mm	% 60 mesh minus material Wet + Dry	Calcium Carbonate Equivalence %	Loss on Ignition %
	10 mesh 2.0 mm	60 mesh 0.25 mm				
Greymont LKD	ND*	68.7	38.5	80.75	78.4	26.3
Tacoma LKD	ND	15.3	35.0	44.90	90.6	37.2
MT Limestone LKD	ND	100	ND	100	127	9.33
Holnam (CH_4) CKD	ND	100	ND	100	89	26.3
Holnam (Coal/Coke) CKD	ND	100	ND	100	86	21.7
Ash Grove CKD	ND	100	ND	100	69.1	23.3
Dicalcium Silicate	ND	100	ND	100	112	0.99
Carbide Lime	ND	30.2	52.0	66.49	96.6	38.3
CaCO_3	ND	100	ND	100	97.6	ND
CaO	ND	19.0	100	100	169	ND

ND = Not Determined

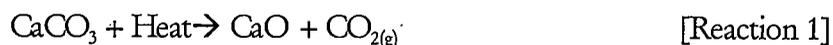
the Tacoma LKD failed and 33.5 % of the Carbide Lime failed. Portions of an alkaline amendment failing to pass a 60 mesh sieve are considered inert, and must be accounted for during calculation of an application rate to neutralize an acidic soil system.

Gravimetric water content of alkaline by-products ranged from 0.0 – 34.3 % (Table 7). By-products stored in silos typically had a very low water content, while those stockpiled

outdoors and not covered had higher water contents and >60 mesh material.

The calcium carbonate equivalence (CCE) of an alkaline by-product is a measure of its acid neutralization capability compared to pure CaCO_3 . The CCE of these alkaline by-products ranged from 69.1 – 127 % (Table 7). The loss on ignition test results ranged from 0.99 to 38.3 % (Table 7) which by calculation means the CaCO_3 content of these by-products ranged from 2.2 to 87.0 %. It was estimated that the CaO and Ca(OH)_2 content of these alkaline by-products ranged from 3.4 – 80.7 %.

The loss on ignition (LOI) laboratory test is used to determine the CaCO_3 content of a alkaline amendment. If a material is pure CaCO_3 , it will lose 44 % of its mass after ignition in accordance with Reaction [1]. If the alkaline amendment loses less than 44 % of its mass after



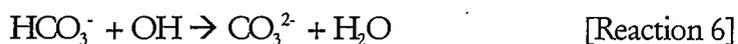
ignition, then proportionately less CaCO_3 is present. The interpretation of the LOI test can be complicated by the presence of Ca(OH)_2 . If Ca(OH)_2 is present, the LOI test will remove its molecular bound water in accordance with Reaction 2. Therefore this loss in mass as water could mistakenly be interpreted as CO_2 loss [Reaction 1], which would cause



an overestimation of CaCO_3 content. Given the mass of Ca(OH)_2 , it has the potential to lose 24 % of its weight during LOI. In the laboratory, ignition of these by-products was

performed in a furnace with an air atmosphere. In addition to error associated with water loss from $\text{Ca}(\text{OH})_2$ during ignition, the air atmosphere in the furnace may cause analytical error. The CO_2 in air may contribute to carbonation of CaO instead of CO_2 release from CaCO_3 [Reaction 1], causing an overestimation of CaCO_3 content and associated underestimation of CaO and $\text{Ca}(\text{OH})_2$ contents.

Data presented in Table 7 indicate each alkaline industrial by-product contained the compounds CaCO_3 , $\text{Ca}(\text{OH})_2$ and CaO which are important for treatment of acidic-metalliferous soil substrates. Additional neutralizing compounds may be present, such as MgO , but are assumed to be in very small concentrations. It is important that the hydroxide (OH) and oxide (O) compounds of calcium be present to raise the amended soil pH up into the 10 - 12 range such that metal contaminants can effectively precipitate out of the soil solution, and consequently not be available for plant uptake. Both $\text{Ca}(\text{OH})_2$ and CaO in alkaline by-products must undergo carbonation [Reactions 3 - 7] to form CaCO_3 in the soil system to facilitate a suitable soil pH for plant growth. A soil system containing CaCO_3 , as opposed to $\text{Ca}(\text{OH})_2$ and/or CaO , will have a soil pH less than 8.4.



All alkaline by-products passed the U.S.E.P.A. Toxicity Characteristic Leaching Procedure that determines whether a material fits the criteria for a hazardous waste (Table 8). The alkaline industrial by-products tested at this time passed the TCLP and therefore are not considered hazardous waste.

Table 8. Toxicity Characteristic Leaching Procedure for Alkaline Industrial By-Products and Commercial Grade Lime.

Sample Type	Toxicity Characteristic Leaching Procedure (TCLP)							
	As	Ba	Cd	Cr	Pb	Hg	Se	Ag
Greymont LKD	<0.5	<10	<0.1	<0.5	<0.5	<0.02	<0.1	<0.5
Tacoma LKD	<0.5	<10	<0.1	<0.5	<0.5	<0.02	<0.1	<0.5
MT Limestone LKD	<0.5	<10	<0.1	<0.5	<0.5	<0.02	<0.1	<0.5
Holnam (CH ₄) CKD	<0.5	<10	<0.1	<0.5	<0.5	<0.02	<0.1	<0.5
Holnam (Coal/Coke) CKD	<0.5	<10	<0.1	<0.5	<0.5	<0.02	<0.1	<0.5
Ash Grove CKD	<0.5	<10	<0.1	<0.5	<0.5	<0.02	<0.1	<0.5
Dicalcium Silicate	<0.5	<10	<0.1	<0.5	<0.5	<0.02	<0.1	<0.5
Carbide Lime	<0.5	<10	<0.1	<0.5	<0.5	<0.02	<0.1	<0.5
CaCO ₃	ND	ND	ND	ND	ND	ND	ND	ND
CaO	ND	ND	ND	ND	ND	ND	ND	ND
TCLP Regulatory Limit	5	100	1	5	5	0.2	1	5

ND = Not Determined

Alkaline Industrial By-Product Soluble Salt Content – Salinity and Sodicity

The soluble salt content of an alkaline by-product refers to the inorganic constituents that are appreciably soluble in water. In general, the growth of salt sensitive plant species may be impaired when the soil electrical conductivity is > 4 ds/m (Firman, 1955). Soil dispersion and associated loss of structure and decreased water permeability rate may occur

when the sodium adsorption ratio[†] is > 10 for fine textured soils and > 20 for coarse textured soils.

Cement kiln dust (CKD) samples were both saline (66.8 – 97.3 ds/m) and sodic (SAR 28.5 – 40.1) (Table 9). Conversely, lime kiln dust (LKD) samples, Dicalcium Silicate and Carbide Lime were neither saline (0.2 – 2.2 ds/m) nor sodic (0.02 – 1.8). CKD salinity may emanate from high concentrations of water soluble SO_4^{2-} (15300 – 48100 mg/l) and Cl^- (1070 – 1180 mg/l) in association with the cations Ca^{2+} , Mg^{2+} , Na^+ and K^+ . These sulfate and chloride salts were either added during the manufacturing of cement or were a component of the fuel ash remaining in the kiln. CKD salinity is sufficiently high that an

Table 9. pH, salinity and sodicity characteristics of alkaline industrial by-products and commercial grade lime.

Sample Type	pH s.u.	EC ds/m	Ca meq/l	Mg meq/l	Na meq/l	SO_4 mg/l	Cl mg/l	SAR	H_2O by Weight %
Greymont LKD	9.6	2.2	69.8	<0.01	2.47	1380	160	0.41	0.32
Tacoma LKD	10.1	0.91	28.4	<0.01	6.8	7	22	1.8	15.5
MT Limestone LKD	10.0	1.2	81.3	<0.01	1.69	1680	279	0.26	0
Holnam (CH_4) CKD	13.7	97.3	3.35	<0.01	51.9	15300	1070	40.1	0.03
Holnam (Coal/Coke) CKD	13.7	66.8	12.1	<0.01	103	28100	1050	41.8	0
Ash Grove CKD	13.5	79.2	6.09	<0.01	49.9	48100	1180	28.5	0.1
Dicalcium Silicate	10.4	0.2	20	<0.01	0.14	<1	3	0.04	0
Carbide Lime	11.9	1.64	41.9	<0.01	0.09	5	87	0.02	34.3
CaCO_3	8.0	0.56	6.79	0.58	0.74	59	43	0.38	0
CaO	12.3	4.9	50.9	<0.01	0.57	134	6	0.11	0

[†]Sodium Adsorption Ratio = $[\text{Na}]/([\text{Ca}]+[\text{Mg}])/2)^{1/2}$, meq/l.

Table 10. Electrical conductivity of Plant Growth Center potting soil as a function of alkaline amendment application rate.

Amendment	Soil Electrical Conductivity, ds/m						
	Alkaline Amendment Application Rate (dry weight basis)						
	0 %	2 %	4 %	6 %	8 %	10 %	12 %
Greymont LKD	0.94 ¹	2.01	2.22	2.70	2.46	3.02	3.35
Tacoma LKD	0.87	0.94	1.55	2.03	1.20	1.32	1.70
MT Limestone LKD	0.65	2.38	2.75	2.78	3.74	2.72	3.00
Holnam (CH ₄) CKD	0.89	1.38	1.87	2.68	4.45	5.82	7.08
Holnam (Coal, Coke) CKD	0.75	1.64	2.30	3.17	3.36	4.10	5.54
Ash Grove CKD	0.68	3.23	5.09	8.13	10.66	12.94	16.63
Dicalcium Silicate	0.54	1.24	1.02	1.39	0.86	1.35	0.98
Carbide Lime	0.76	1.71	1.53	2.22	1.30	2.63	1.10
CaCO ₃ /CaO	0.74	1.26	1.46	1.05	2.00	1.32	1.35

¹ n = 1. Plant Growth Center potting soil was analyzed in replication number five.

amended soil may be elevated into a range that could impair plant growth of salt sensitive species. Assuming the CKD field application rate will range from 2 – 10 % of the soil mass, the soil salinity could be increased 1.3 – 9.7 ds/m. Given these same assumptions, the soil sodium adsorption ratio (SAR) could be increased 0.4 – 4.0 units. Most acidic soils are not sodic, so an increase of 0.4 – 4.0 SAR units when CKD is applied may not notably impair either the soil physical condition or plant growth. However, the potential increase in soil salinity from CKD may be sufficient to impair plant growth during periods when water availability is not abundant. In plant growth tests discussed later in this document, alkaline amendments were mixed into Plant Growth Center potting soil at application rates that ranged from 0 % to 12 % (dry weight basis). Following a 90 day plant growth period the soil electrical conductivity was measured in one replication of the experiment (Table 10). All alkaline products increased soil salinity across the application rate range of 0 - 12 %. Soil

salinity increases associated with the amendments CaCO_3/CaO , Dicalcium Silicate and Carbide Lime ranged from 0.32 - 1.87 ds/m, while increases for LKD ranged from 0.07 - 3.09 ds/m, and increases for CKD ranged from 0.49 - 15.95 ds/m. The three CKD amendments elevated the soil EC to a range of 5.54 ds/m to 16.63 ds/m for the 12 % amendment application rate. Soil treatment with CKD resulted in a saline soil, defined as having an electrical conductivity > 4 ds/m, for application rates low as 4 % (40 tons CKD/1000 tons soil). Under conditions of abundant plant available water, these measured increases in soil salinity with alkaline amendment use will likely not impair plant growth. However, under conditions of plant water stress, these increases in soil salinity may impair plant growth due to the osmotic potential created between salt and water within the soil matrix. The plant has to expend greater energy to uptake water from the salt enriched soil matrix compared to a soil system not enriched in salt, which can cause a loss in plant growth.

Alkaline Industrial By-Product - Chemical Enrichment

CKD by-products were enriched 12.2 to 25.9 times for total zinc (Zn), while LKD enrichment was 1.3 to 3.8 compared to the control (CaCO_3 and CaO , Table 12). Dicalcium Silicate and Carbide Lime were not enriched in Zn. Ash Grove CKD contained the greatest concentration of total Zn (467 mg/kg), and had the highest water extractable concentration 1.9 mg/l at pH 13.5 (Table 11).

Total selenium (Se) was not enriched in alkaline industrial by-products, but the water extract from a saturated paste was enriched several hundred times in CKD compared to the

control. Holnam and Ash Grove CKD contained 3.31 and 1.30 mg/l Se, respectively,

Table 11. Water soluble metal concentrations of Alkaline Industrial By-Products and Commercial Grade Lime.

Sample Type	Water Saturated Paste Extract (mg/l)									
	Al	As	B	Cd	Cu	Fe	Pb	Mn	Se	Zn
Greymont LKD	<1	<0.01	<1	<0.01	<0.01	<0.1	<0.01	<0.01	0.05	<0.1
Tacoma LKD	<1	<0.01	<1	<0.01	<0.01	<0.1	<0.01	<0.01	<0.01	<0.1
MT Limestone LKD	<1	<0.01	<1	<0.01	<0.01	<0.1	<0.01	<0.01	0.09	<0.1
Holnam (CH ₄) CKD	<2	0.55	5	<0.01	<0.02	0.4	0.7	<0.02	3.31	1.3
Holnam (Coal,Coke)CKD	<2	0.03	<2	<0.01	<1	<1	0.02	<1	0.1	<1
Ash Grove CKD	<1	0.36	<1	<0.1	0.10	<0.1	0.2	<0.01	1.3	1.9
Dicalcium Silicate	464	<0.01	<1	<0.01	0.20	<0.1	<0.01	<0.01	0.01	<0.1
Carbide Lime	<1	<0.01	<1	<0.01	<0.1	<0.1	<0.01	<0.01	0.01	<0.1
CaCO ₃	<1	<0.01	<1	<0.01	<0.1	0.2	<0.01	<0.01	<0.01	<0.1
CaO	<1	<0.01	<1	<0.01	<0.1	<0.1	<0.01	<0.01	<0.01	<0.1

compared to control materials (CaCO₃ and CaO) which had <0.01 mg/l Se (Table 11). At issue is whether 1.30 – 3.31 mg/l Se water extractable measured at a pH of 13.5 – 13.7 in CKD increases- or decreases- in concentration when applied to a soil system and a pH of 7.0 – 8.3 is produced in the plant root zone.

Total boron (B) was enriched in Greymont LKD (137 mg/kg) and Montana Limestone LKD (130 mg/kg) approximately 50 times compared to control materials (CaCO₃ and CaO, Table 12).

Total barium (Ba) was enriched in most kiln dusts by as much as 33 times compared to CaCO₃ and CaO (Table 12). Montana Limestone LKD had the greatest total Ba content, 862 mg/kg.

Table 12. Total Metal Concentration of Alkaline Industrial By-Products and Commercial Grade Lime.

Sample Type	Total Concentration (mg/kg)										
	Al	Ag	As	B	Ba	Be	Cd	Ca	Cr	Cu	Fe
Greymont LKD	16300	<5	5	137	475	<5	4	309000	<5	19	4290
Tacoma LKD	2810	<5	11	7	23	<5	<1	281000	<5	20	4210
MT Limestone LKD	16300	<5	<5	130	862	<5	1	416000	42	13	5310
Holnam (CH ₄) CKD	12000	<5	13	16	77	<5	4	295000	59	11	10700
Holnam (Coal/Coke) CKD	11200	<5	9	<1	161	<5	2	294000	83	10	10100
Ash Grove CKD	9380	<5	15	20	131	<5	5	237000	33	45	7270
Dicalcium Silicate	67100	<5	<5	<5	24	<5	<1	345000	<5	<5	335
Carbide Lime	3070	<5	<5	6	11	<5	<1	272000	<5	<5	197
CaCO ₃	794	<5	<5	<5	17	<5	<1	347000	<5	<5	1140
CaO	1100	<5	<5	<5	26	<5	<1	556000	78	5	856

Table 12. Total Metal Concentration of Alkaline Industrial By-Products and Commercial Grade Lime - Continued.

Sample Type	Total Concentration (mg/kg)										
	Hg	K	Mg	Mn	Ni	P	Pb	Se	Sn	V	Zn
Greymont LKD	<1	860	9700	325	129	280	107	5	<5	454	49
Tacoma LKD	<1	191	2790	96	7	179	18	<5	<5	15	68
MT Limestone LKD	<1	1720	13800	228	<5	414	9	<5	<5	18	23
Holnam (CH ₄) CKD	<1	40600	7350	278	<5	131	205	<5	<5	25	219
Holnam (Coal/Coke) CKD	<1	25100	7920	276	11	219	94	<5	<5	60	115
Ash Grove CKD	<1	73200	9230	247	13	117	117	6	<5	43	467
Dicalcium Silicate	<1	39	29100	7	<5	94	<5	<5	<5	<5	<5
Carbide Lime	<1	<50	179	<5	<5	10	<5	<5	<5	5	<5
CaCO ₃	<1	368	1470	85	<5	61	<5	<5	<5	7	10
CaO	<1	129	9590	159	<5	101	<5	<5	<5	6	18

Total aluminum (Al) was enriched 2-30 times in alkaline industrial by-products compared to the control (CaCO₃ and CaO). Dicalcium Silicate contained the greatest

concentration of total Al (67,100 mg/kg). The associated water saturated paste extract for Dicalcium Silicate contained 464 mg/l Al, while all other alkaline industrial by-products contained <2 mg/l (Table 11).

Following the 111 day plant growth period discussed later in this thesis, the 8 replicated pots amended with Dicalcium Silicate were composited for tailings, contaminated soil, and Plant Growth Center soil, and the extract from a water saturated soil paste was analyzed for Al (Table 13). Following the carbonation process (Reactions 3 - 7) that produced a soil pH in the range of 7.0 - 8.3 and 111 day plant growth period, the amount of Al in the soil solution was relatively low, ranging from < 0.5 - 2.0 mg/l. As will be discussed below, plant growth in these pots was good and was not impaired by an Al phytotoxicity issue.

Table 13. Water soluble concentrations of aluminum (Al) following a 111 day plant growth period in tailings, contaminated soil, and Plant Growth Center soil amended with Dicalcium Silicate.

Sample Type	Dicalcium Silicate Application Rate tons/1000 tons	Aluminum	
		Total Concentration mg/kg	Water Saturated Paste Extract mg/l
Tailings	42.35	ND	<0.5
Contaminated Soil	7.07	ND	1.3
Plant Growth Center Soil	42.35	ND	2.0

ND = Not Determined

Dicalcium Silicate will infuse a large quantity of Al into the soil solution when applied as an amendment. During the 4 - 12 month period following application the soil

