

Predicting the Efficacy of Fly Ash as a Soil Ameliorant

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1. INTRODUCTION AND BACKGROUND

South African cropping soils are of limited extent, infertile shallow, extremely vulnerable to degradation and of low resilience (recovery potential)⁽¹⁾. Only about 13% (14 million ha) of the country's land is considered to be arable. To exacerbate the situation, low and highly variable rainfall often results in marginal crop yields.

Inappropriate land-use practices have aggravated this parlous state of affairs⁽²⁾. Root penetration is stunted by soil compaction while crusting limits water ingress, and acidification has altered the chemical and physical properties of the soil. Remediation is urgently required if the country is to feed its burgeoning population.

However, the results of several years of research indicate that this situation can be remediated by the responsible use of coal ash as a soil ameliorant.

2. COAL ASH AS AN AMELIORANT FOR DEGRADED SOIL

The use of fly ash to counteract or limit some of the aforementioned problems has been extensively investigated and shown to be remarkably effective^{(3) - (8)}. Fly ash amends nutritional limitations, textural characteristics and leaching behaviour which leads to an increase in soil productivity.

Being rich in essential and trace elements but poor in nitrogen, organic matter and, to a lesser degree, potassium and phosphorus fly ash should be seen as an ameliorant or soil amendment rather than as a fertiliser. Nevertheless its efficacy in improving plant metabolism and growth is widely reported.

Field experiments have shown that fly ash (either on its own or in conjunction with biological materials and/or fertiliser) can improve soil quality and increase crop yield under a variety of climatic conditions, plant species and soil types. The addition of fly ash is particularly beneficial on acidic soils. This is primarily due to improved soil texture, water retention and the contribution of fly ash itself to the nutrient status of the soil by changing the pH regime, influencing the cation exchange capacity and supplying trace minerals.

One outstanding salient feature of soil amendment with fly ash is the longevity of the effect. Although the initial dosage may seem somewhat excessive the amendment lasts for several (5-7) years before supplementary addition may be required⁽³⁾. This would seem to indicate that the addition of fly ash leads to a sustainable improvement of the biological status of the soil.

Despite being an effective soil ameliorant it is, however, difficult to predict the efficacy of fly ash in improving soil conditions and plant growth. Given the disparity of the soils and differences in the nature and composition of the fly ashes available, it is not surprising to find that some fly ashes have been shown to be more effective than others. The degree of improvement is, however, uncertain and the ability to predict performance remains elusive.

3. THE RHIZOSPHERE

Across all ecosystems from the tundra to the savannah, complex biological communities thrive in the top few centimeters of the soil, constantly facilitating the exchange of carbon and the uptake of nutrients. This process is concentrated in hotspots of activity around the roots of plants (rhizosphere) where microbes feed on sugars and organic acids exuded from the roots⁽⁹⁾. The bacteria and fungi break down complex molecules into simpler structures, mineralise them into inorganic forms, such as nitrates, which the plants are then able to assimilate.

Several of low molecular weight (LMW) organic acids are present in the soil. The source of these has been identified as exudates from the roots of plants as well as from cell lysis by soil micro organisms. Even in a pristine environment such as Antarctica, soils from penguin rookeries contain LMW acids like citric, oxalic, formic, acetic, lactic, propionic, and succinic acid.

Low molecular weight organic acids play a crucial role in nutrient assimilation and plant growth. Due to their chelating properties root exudates are able to alter nutrient availability and stimulate microbial activity⁽¹⁰⁾.

Soil solutions contain a diverse range of LMW organic acids with concentrations from 0.1 to 50 μ moles⁽¹¹⁾. Jones, et al identified thirteen organic acids in quackgrass rhizosphere that carry out specific functions in soil, including nutrient acquisition by the roots, mineral weathering and microbial chemotaxis⁽¹²⁾. Van Hees, et al found a variety of LMW organic acids present in various soil profiles⁽¹³⁾. It has been demonstrated that the concentration and diversity of LMW organic acids in root exudates and soils varied with plant species^{(14) – (15)}.

The interaction of LMW organic acids and the microbial community in the rhizosphere depends upon their spatial concentration in this zone and the concomitant adsorption and desorption processes⁽¹⁶⁾. Certain organic acids show strong affinity for specific mineral surfaces which further enhances dissolution⁽¹⁷⁾.

While there is a lack of understanding about the exact nature of the reactions taking place it has been shown that LMW organic acids in the rhizosphere may affect metal mobilisation, either directly through ligand exchange or sorption processes, or indirectly through a symbiotic utilisation of the soil microbial communities present in the rhizosphere. For example, it is thought that ectomycorrhizal fungi are important in the weathering of soils⁽¹⁸⁾.

These acids mobilise poorly soluble plant nutrients (Mn, Cu, Zn, Fe, P) and detoxify specific metals (Al, Cd) while also acting as efficient weathering agents to promote the dissolution of primary minerals. While the concentration of the LMW organic acids influences all these reactions the ability of the divalent and trivalent acids (citrate, oxalate) to form organo-metallic complexes is an important factor in soil fertility.

4. AIM OF INVESTIGATION

At present it is difficult to predict the effect of fly ash as a soil amendment without carrying out extensive field trials. The paedogenesis of the new more fertile substrate probably involves interaction between those LMW organic acids present and the fly ash particles. Dissolving fly ash in LMW organic acids may, therefore, provide insight into its reactivity, the leachability of minerals and thus its potential to improve soil conditions.

5. EXPERIMENTAL – EFFECT OF ACID

In this investigation, 6 different LMW carboxylic acids of various carbon chain length and protic groups as well as a weak mineral acid (H_3BO_3), a strong mineral acid (HCl), and water were utilised to leach a Class F fly ash (Ke). Their properties, including the first dissociation constant (pK_1), is given in Table 1.

Table 1. The properties of the acids used for leaching fly ash

Acid	Formula	pK1	Carboxylic status
Oxalic	$C_2H_2O_4$	1.27	Diprotic
Acetic	$C_2H_4O_2$	4.76	Monoprotic
Propionic	$C_3H_6O_2$	4.87	Monoprotic
Lactic	$C_3H_6O_3$	3.86	Monoprotic
Ascorbic	$C_6H_8O_6$	4.17	Triprotic
Citric	$C_6H_8O_7$	3.15	Triprotic
Boric	H_3BO_3	9.24	Triprotic
Hydrochloric	HCl	-8.00	Monoprotic

The interaction between these LMW organic acids and fly ash (Ke) was studied by mixing 20 g with 100 ml of the respective acids (1 M). Distilled water served as the reference lixivant.

The various ash-acid mixtures were kept at room temperature and periodically stirred during the test period of 6 weeks. Upon conclusion, the residues were filtered, thoroughly washed with distilled water and dried prior to examination in a scanning electron microscope (SEM). Images of the surface were studied for visual evidence of changes in texture which could be interpreted as indicative of leaching.

The spent acids were analysed for specific elements. The use of glassware precluded analysis for silica. The concentration of major components as well as elements required for plant vitality was determined. The pH of the spent acids was also measured.

6. RESULTS

6.1 Particle size

Laser diffraction was used to measure the particle size distribution of the fly ash before and after leaching (Table 2). The only marked decrease in average particle size occurred when it was exposed to oxalic, propionic, and boric acid. All other lixivants had little or no effect on the particle size.

Table 2. Average particle size (μm) of the fly ash (Ke) before and after leaching

Lixivant	Particle size	Lixivant	Particle size	Lixivant	Particle size
Water	52.46	Propionic	42.93	Citric	53.08
Oxalic	40.13	Lactic	57.93	Boric	40.74
Acetic	57.22	Ascorbic	56.37	Hydrochloric	51.66

6.2 Scanning Electron Microscopy (SEM)

Images of the fly ash, taken on an electron microscope, reveal the diverse effect of the various lixivants with each exhibiting its own particular characteristics. All the acids etched the surface of the fly ash spheres to a greater or lesser degree. Not all particles are affected to the same extent; some are only partially leached while others appear to be essentially unaltered (Images 1 - 2). This diversity reiterates the micro-heterogeneity of fly ash. The reason why particular spheres are more susceptible to dissolution is probably as a result of the composition of the amorphous phase which differs from sphere to sphere.

Compared to the starting material secondary minerals appeared to have deposited on the surface of some spheres (Images 3 - 4). It is unclear whether these deposits are associated with trace elements known to be enriched on the surface. Due to their extremely low concentration it would be very difficult to quantify these deposits by transmission electron microscopy.

The greatest change in the appearance of the fly ash occurred when it was leached by oxalic acid (Images 5 - 6). In Image 5 the selective nature of the dissolution of the individual spheres is again apparent.

6.3 Elements leached

All solutions (except water) were still acidic at the end of 6 weeks (Table 3). The degree of removal of elements by oxalic acid is comparable to and generally exceeds that of HCl. This is not surprising since, from its pKa value, oxalic acid should be considered a strong acid.

Table 3. pH of lixivants at the end of tests (6 weeks of leaching)

H ₂ O	Oxalic	Acet	Prop	Lact	Asc b	Citr	Boric	HCl
11.0	0.8	1.4	2.5	1.0	3.3	2.2	6.2	0.6

The varied appearance of the leached fly ash particles suggests that the acids differ in their ability to solubilise elements. The fraction of elements dissolved from the fly ash matrix for the various acids is given in Table 4.

Table 4. Mass fraction of elements solubilised in water and the LMW carboxylic acids (1 M) (All values % x100)

Element	H ₂ O	Oxalic	Acet	Prop	Lact	Asc b	Citr	Boric	HCl
Al	-	3.22	0.20	-	0.61	1.55	2.25	-	2.51
Fe	-	11.04	0.52	0.31	1.01	4.13	2.82	-	2.71
Ca	0.57	0.34	10.51	11.36	11.08	9.39	19.01	3.69	19.82
Mg	-	35.04	18.03	14.11	10.11	26.24	29.13	12.11	29.03
P	-	41.93	10.00	11.39	30.02	35.04	39.20	1.62	30.11
K	0.09	2.03	0.49	0.16	0.21	0.80	1.10	0.19	1.29

(Only values in excess of .001% actual i.e. 0.1% tabulated figure are given)

As can be seen from this data, oxalic acid was the most aggressive lixivant and leached a greater amount of the elements than the other acids. The figure for the dissolution of Ca with oxalic acid can be misleading. Most of the calcium leached from the fly ash will, due to the insoluble nature of the compound ($K_{sp} 10^{-8}$), precipitate as calcium oxalate.

Energy Dispersive X-ray analysis (EDX) of various regions shown in Image 6 revealed that both the needle-like and platelet particles are rich in calcium and are probably calcium oxalate.

More of the trace elements were solubilised by oxalic acid than by the other lixivants (Table 5). The functionality of LMW organic acids is largely dependant on their ability to complex metal cations. Consequently, it is expected that the presence of divalent and trivalent acids would be more effective for the assimilation of trace metals by plants.

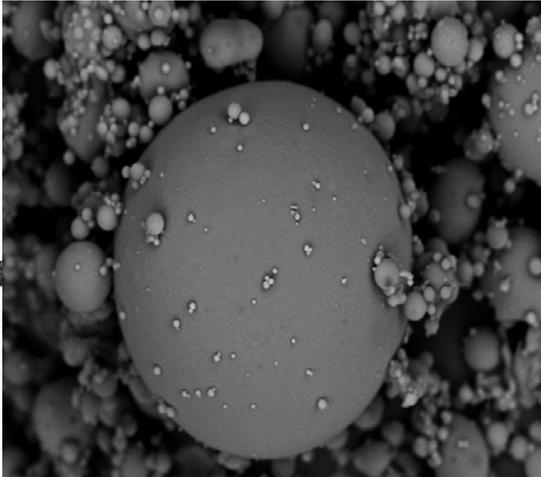


Image 1. Sphere in propionic acid (unaltered)

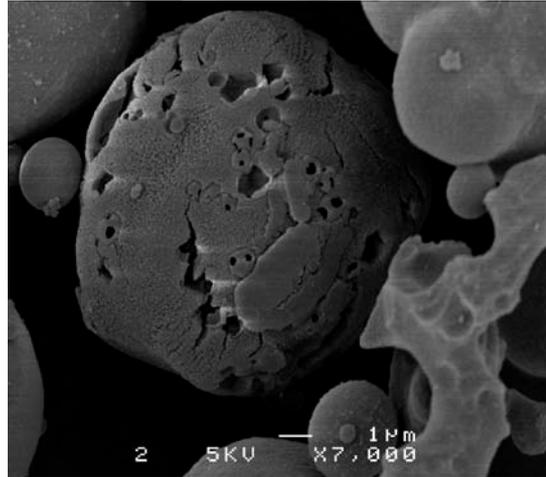


Image 2. Sphere leached by propionic acid

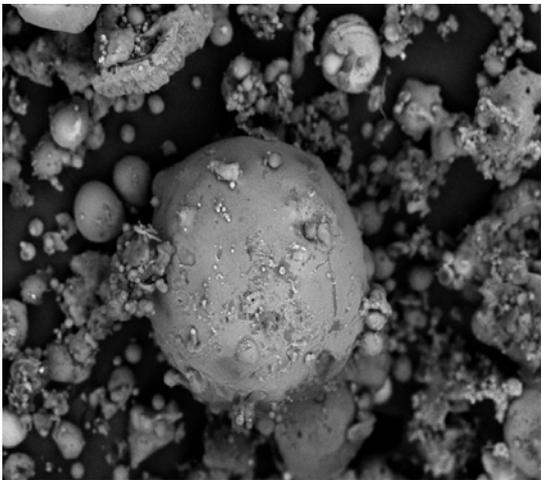


Image 3. Surface deposits on sphere (citric acid)

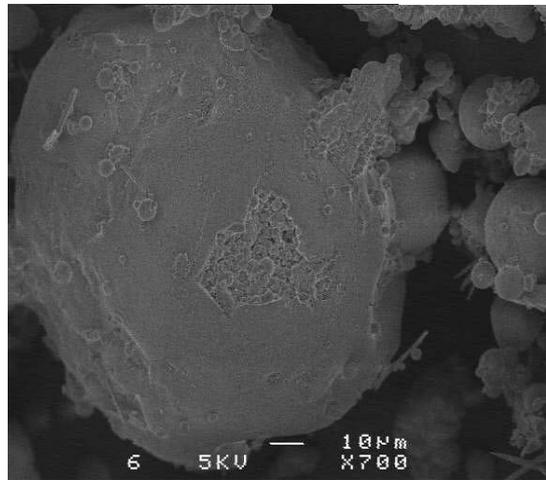


Image 4. Surface deposits on sphere (ascorbic acid)

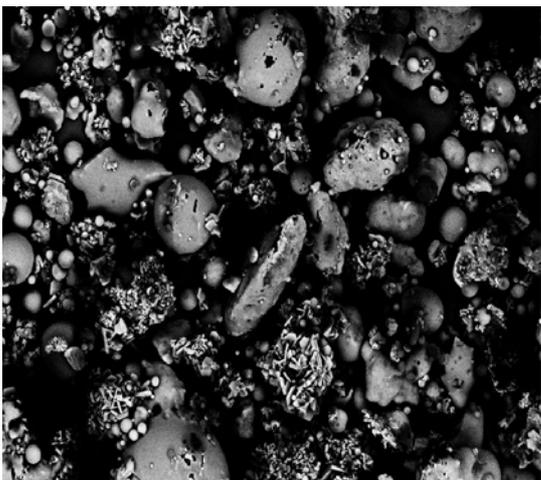


Image 5. Extensive and varied leaching by oxalic acid

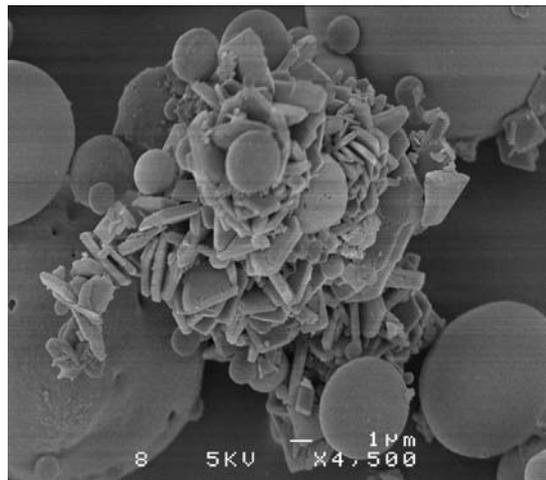


Image 6. Sphere leached in oxalic acid showing oxalate crystals

Table 5. Mass of minor elements solubilised in water and the LMW carboxylic acids (1 molar) (All values µg/g)

Element	H ₂ O	Oxalic	Acetic	Prop	Lact	Ascb	Citr	Boric	HCl
Na	151	790	223	498	514	662	728	196	722
Cu	ND	19	7	ND	ND	ND	8	ND	12
Mn	ND	354	168	103	102	264	294	44	309
Zn	ND	26	12	14	5	19	18	ND	17

(ND = Not detected)

7. EXPERIMENTAL – EFFECT OF FLY ASH

Following on from the tests on fly ash (Ke) three other fly ashes (Le, Ma, Lo) of different composition were leached under the same conditions in propionic and oxalic acid to determine to what degree the composition of the fly ash influences dissolution. The results are presented in Tables 6 and 7. Irrespective of the fly ash leached oxalic acid once again proved to be the most aggressive lixiviant.

Table 6. Mass fraction of elements solubilised from fly ashes (Le, Ma, Lo) after 6 weeks exposure to a 1 molar solution of oxalic and propionic acids (All values % x100)

Element	Oxalic Acid			Propionic Acid		
	Le	Ma	Lo	Le	Ma	Lo
Al	2.91	1.86	4.89	0.08	0.10	0.23
Fe	6.32	4.46	6.61	0.26	0.38	0.92
Ca	0.33	0.15	1.26	8.78	2.14	12.78
Mg	25.51	4.38	10.90	4.78	0.63	2.73
P	31.25	6.98	25.57	8.44	0.45	4.80
K	1.80	1.08	6.07	0.73	0.22	0.42

Table 7. Concentration (µg/g) of minor elements solubilised from fly ashes (Le, Ma, Lo) after 6 weeks exposure to a 1 molar solution of oxalic and propionic acids

Element	Oxalic Acid			Propionic Acid		
	Le	Ma	Lo	Le	Ma	Lo
Na	225	437	2778	140	197	740
Cu	14	-	-	-	-	8
Mn	211	104	353	50	37	141
Zn	12	6	6	4	5	30

8. DISCUSSION

The solubility of elements differs along with both the LMW acid used as well as the specific fly ash being leached. The greater degree of dissolution by oxalic acid, shown in Images 1 – 6, is confirmed by greater solubilisation of both major and trace elements in all the fly ashes tested.

The composition of the four fly ashes used was determined by X-ray fluorescence (XRF) and the crystalline components by X-ray diffraction (XRD). The amorphous phase was calculated by subtracting the total crystalline content from 100. The results are given in Table 8.

Table 8. Oxide composition for selected elements and amorphous content of the four fly ashes evaluated

Constituent	Ke	Le	Ma	Lo
Amorphous	47.90	51.40	52.50	68.00
% SiO ₂	54.40	55.75	53.69	55.10
% Al ₂ O ₃	29.45	30.87	31.01	19.72
% CaO	5.25	4.75	6.10	3.07
% Fe ₂ O ₃	5.13	4.16	2.90	7.49
% MgO	0.63	0.46	2.01	1.42
% Na ₂ O	0.14	0.12	0.60	1.15
% K ₂ O	0.92	0.75	0.86	1.84
% P ₂ O ₅	0.67	0.42	0.51	0.50

Compared to the other fly ashes Lo has a substantially different composition in terms of alumina content and amount of amorphous phase (Table 8). The higher amorphous content does not necessarily imply an increase in the solubility of all elements (Tables 6 and 7). Sometimes more of an element is leached, sometimes less. For example propionic acid solubilised less Mg, P and K but more Al, Fe and Ca from Lo. The amount of alumina leached from all samples was minor (less than 0.05%).

Fly ash (Ma) did, however, exhibit different leachability compared to the others. Less Al, Fe, Ca, Mg, P and K was solubilised in both oxalic and propionic acid. There was no apparent difference in the chemical composition which could account for this result.

Table 9. Estimated composition of amorphous phase

Constituent	Ke	Le	Ma	Lo
% SiO ₂	30.14	33.44	34.61	47.09
% Al ₂ O ₃	4.66	7.47	8.53	12.34
% CaO	4.69	4.12	4.43	2.26
% Fe ₂ O ₃	3.70	3.26	1.43	4.90
Other	2.32	1.77	2.98	3.45

In Table 9 the XRF and XRD data was used to estimate the composition of the amorphous phase. Perusal of this data suggests that the lower leachability of fly ash (Ma) could be caused by its relatively low amorphous Fe₂O₃ content. Iron is known to modify glass structure. A low iron content implies a more structured silicate network which would be less susceptible to acid dissolution. The lower leachability of Al, Mg, Ca, K and P, all of which will modify glass structure, is supportive of this theory.

9. CONCLUSION

The research reported here is the first exploratory phase of work aimed at predicting the efficacy of fly ash as a soil ameliorant. Leaching fly ash with LMW organic acids showed disparate dissolution efficiency. Being the most aggressive lixiviant oxalic acid would probably provide some measure of insight into the interaction between fly ash and the LMW organic acids present in the rhizosphere. This would, however, require auxiliary tests (mineralogical analysis, microscopy) if the efficacy of fly ash as a soil ameliorant is to be predicted.

Future work to assess the effect of time and temperature is planned. Allied to the current microbiological study¹⁹ this data will be used. Comparative agricultural field trials are envisaged to ascertain whether leaching behaviour is a potential predictive tool for soil amelioration with fly ash.

10. ACKNOWLEDGEMENTS

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