CHEMICAL FRACTIONS OF Al IN VOLCANIC SOIL AMENDED WITH CELLULOSE WASTE

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ABSTRACT

The cellulose industry generates a great volume of organic and inorganic waste, one of these wastes are called dreg (D) and grits (G). These residues have a high content of calcium carbonate, positioning them as potential bleachers in acid soils. Due to the important content of Al in the residues, a sequential extraction was done to establish the metal chemical fractions such as exchangeable, adsorbed, organic carbonated, and the ones associated to sulfurs, in incubated samples (2, 4, 8, and 32 days at 60ºC) of an Andisol amended soil with Grits, Dregs + Grits and lime in 1, 2 and 3 ton/ha doses. The results revealed that there was a significant increase in the amount of Al in all fractions, in comparison to the control soil. On the other hand the incorporation of these residues through a Dregs (70%) + Grits (30%) mixture provoked a pH increase, always higher than the commercial lime.

Finally, the Al present on amended soils was mostly distributed in the residual and carbonated chemical fractions, which would constitute less labile chemical forms to the soil-solution.

Keywords: sequential extraction, chemical fractions, cellulose waste (*Dregs*, *Grits)*, volcanic soil, waste disposal.

INTRODUCTION

The cellulose industry generates organic and inorganic waste, especially in the bleached and causticizing process, known as *Dregs* (D) and *Grits* (G) [1]. These wastes have an alkaline character, since *D* are generated in a clarification process called green liquor ($Na_2CO_3 + Na_2SO_4 + Na_2S + Fe(OH)_2$), while *G* are solid inorganic wastes. Both have high $CaCO_3$ and heavy metals content, due to the different processes of paper manufacturing [2, 3]. Consequently, these wastes have already been considered as possible soil bleaching agents. In this context, preliminary studies of the waste application on acid soils have evidenced that the toxicity and dangerousness of *D* and *G* are above the EPA (Environmental Protection Agency) regulations [4] and above the limits established for forestry utilization [5]. Besides, it was observed that the use of these wastes in soil amendment improves the chemical availability of nutrients through pH increase and also increases the water retention in soils used for *Pinus radiate* growing [6]. In Brazil the wastes from this industry are used for forest plantations of the country, using dregs and grits mixtures as a replacement of lime to improve soil pH [7]. On the other hand, the use of waste such as sludge or biosolids from the paper and cellulose industry as pH improvers in acid soils has proved to be useful [8]. Also, studies exist that attempt to assess the use of these wastes in the cement and structural concrete industry, using waste from the bins, as well as in composting [9, 10].

In Chile previous studies exist concerning the use of these wastes from the Kraft cellulose fabrication process for the vegetal productivity in Chile, where a pH improvement in amended soils was observed [11].

Considering the geographic zone of the cellulose plants in Chile, volcanic materials derived soils are considered as optimal candidates to dump this kind of waste. These soils are around the 70% of the arable land in Chile. Also, these are acid and show considerable quantities of iron oxides and organic matter, while its variable charge, which is pH and ionic strength dependent, is one of its singular features. Furthermore, they possess a high cationic exchange capacity (CEC) and a high accumulation of P as phosphate [12]. As mentioned above, these soils present acidity problems. One primarily responsible is Al^{3+} released to the soil-solution with a consequent acid-base equilibrium shift in aqueous solution, product of climatologic factors and agricultural management. Despite the importance of Al presence, scarce studies exist [13] regarding this kind of soil amended with these wastes, particularly Al, related to its incorporation and possible associations due to the content of this metal in cellulose residuals.

Consequently, it is necessary to study the different fractions or association of Al in amended soils with different cellulose residuals, establishing the importance of the use of these wastes as pH improver or bleacher in agricultural soils.

MATERIALS AND METHODS

Sampling

Samples of the surface horizon (0-0.15 m) of one volcanic soil located in southern Chile were used. The Andisol (Santa Barbara, *Ashy, medial, mesic Typic Dystrandept*) was collected at 2 mm, and stored at field moisture content. The industrial residues from a cellulose plant near to Santa Fe city were used. The residues were dried, crushed, and sifted through a 0.250 mm (60 mesh) sieve to improve soil interaction. The residues considered in this study were Grits (G) and Dregs (D). In addition, commercial lime was included in this study to be used as a comparison parameter in contrast to the rest of the amendments. The used amendments were i) Grits (G); ii) Mix of *D* and *G* in 70%-30% proportion, respectively (D-70 + G-30). The quantity of residue and lime added to the soil was worked out considering an equivalent amendment of 1, 2 and 4 ton ha^{-1} of $CaCO_3$. Four different conditions were considered: (a) control soil, (b) control soil with G (1, 2 and 4 ton ha^{-1}), (c) control soil with D-70 + G-30, (1, 2 and 4 ton ha^{-1}), and (d) control soil with lime (1, 2 and 4 ton ha^{-1})

Incubation procedure

A "fast incubation" procedure was utilized [14]. All the amended samples were packed and wetted up to 50% of its water-holding capacity. Then, the samples were taken to the incubator in the darkness at 60ºC during 2, 4, 8 and 32 days. All the samples were taken in triplicate, according to the conditions and dose described above.

Characterization

Santa Barbara soil was characterized for organic matter (OM) content using the Walkley-Black method (Allison 1965) adapted to Chilean soils [15], pH, electrical conductivity (1:2.5 w/v soil:water). The CEC was estimated as a total amount of Ca-Na-K-Mg exchanged in soil. Besides, the sand-lime-clay distribution, using the pipette method [16], and the bulk density were established [17]. In all incubated samples the pH was determined using the aforementioned method.

Al chemical fractions

The chemical fraction of Al was obtained utilizing the Sposito et al. (1982) sequential extraction procedure [18] carried out in triplicate. Al fractionation involves exchangeable, adsorbed, organic, carbonate, and residual fractions. Samples (2 g) were sequentially treated with 25 mL of the following reagents: 0.5 mol L^{-1} KNO$_3$ maintained in contact for 16 h (F1); deionized water for 2 h (3 times, the extracts are combined) (F2); 0.5 mol L^{-1} NaOH for 16 h (F3); 0.05 mol L^{-1} Na$_2$EDTA for 6 h (F4); and 4 mol L^{-1} HNO$_3$ at 80 ºC for 16 h (F5). After each extraction the suspension was centrifuged and the supernatant filtered through a 0.45 mm membrane filter. The Al content in each extract was determined by ICP-OES spectrometry on an Optima 2000 DV Perkin Elmer instrument.

RESULTS AND DISCUSSION

Characterization

The soil used for the assay belongs to the Andisol series, which is classified as a volcanic soil with silty-loam texture. The pH of this soil has acid characteristics with low electric conductivity and density, and low quantities of exchangeable Ca, Na, K, and Mg (see Table 1).

The OM content was important. Andisols are rich in OM and its accumulation is probably associated with mineralogy, dominated by low crystalline compounds [19]

Table 1. Santa Barbara soil chemical and physical properties

Characteristics	Santa Barbara
Soil Order	Andisol
Soil Class	*Ashy, medial, mesic Typic Dystrandept*
Latitude	71º55´W
Longitude	36º50´S
Altitude (m)	400-1100
Rainfall (m/year)	1.5-2.0
Annual mean temp. (ºC)	13.5
Bulk density (g/mL)	0.79
EC (mS/cm)	0.15
OM(wt%)	16.2
pH-H_2O	5.58
Sand (%)	23.4
Lime (%)	56.0
Clay (%)	20.6
Exchangeable cations (mEq/100 g)	
Ca	5.98
Na	0.04
K	0.78
Mg	0.44
Exchangeable Al (mEq/100 g)	0.21

The pH of the residues has alkaline characteristics, with similar contents of CaO in D and G, which are lower than in commercial lime. Comparatively, D has a higher MgO content, *i.e.* is advantageous to use this residue in Mg-low-content soils and in those with acidity problems. The Al content in D and G residues was high, and therefore, this analyte deserves a more in-depth study. The chemical features of commercial lime are those reported by the manufacturer, showing a minimum and maximum content for CaO and MgO. Table 2 shows the characteristics of residues and commercial lime.

Table 2 – Chemical characteristics of residues and commercial lime.

Characteristics	Dregs	Grits	Commercial lime
pH-H_2O	12.69	12.96	---
CE [mS cm^{-1}]	39.00	27.9	---
CaCO$_3$ [%]	79.52	75.05	91.0-93.5
CaO [%]	44.53	42.03	50.4-52.4
MgO [%]	2.10	0.43	0.8 – 1.1
Al [mg/kg]	6877[1]	7077[1]	---

[1] Chemical analysis from cellulose plant

Since both residues and commercial lime have alkaline pH, their addition to soils caused a pH increase as compared to the soil control, it is directly proportional to the applied dose of any of the used bleaching materials. In general, for equivalent doses of 1, 2 and 4 ton CaCO$_3$/ha, the pH increase is higher when the mixture D+G is used rather than G and lime. As for pH variations, related to incubation time, for all the amended samples pH stabilization occurs after 16 days of incubation. Soils amended with G, show a similar behavior as those amended with lime. However, when the D+G mixture is utilized a higher initial increase than the observed in other amendments

occurred. Hence, when pH variation is analyzed in relation to the doses and incubation days; as for residues, Fig 1 shows that the use of the D+G mixture is the most appropriate.
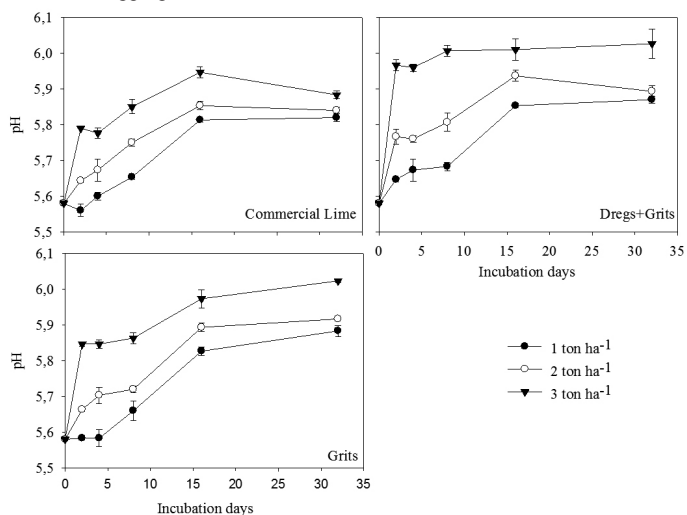

Figure 1 – pH variation of Santa Barbara amended soil – Dose and incubation

An important consequence of this pH change is the likely increase of the negative superficial charge, considering the isoelectric point of this soil (IEP: 3.4). In soils with variable surface charge, when pH increases the negative surface charge increases and, consequently, the CEC of soils; thus, the adsorption of metals (Al) may be also enhanced, as a consequence of the amendment process. According to the well-known buffer capacity of volcanic soils, the pH of amended samples goes down to the control soil pH after an incubation period of 2 months. Therefore, in amended Chilean volcanic soils, after some time the CEC or the excess of previously adsorbed metals may be released to the soil solution [12].

Al chemical fractions

Following Sposito et al. 1982, the exchangeable, sorbed, organic, carbonate, and sulfide fractions of trace metals are assumed to correlate well with the amount extracted by KNO$_3$, H$_2$O, NaOH, EDTA and HNO$_3$. Nevertheless, in this study the Al fractionation will be reported according to the extracting reagent employed, instead of the expected soil solid-phase fraction.

From the analysis of different chemical fractions of Al obtained for the control soil using no incubation, it was found that Al was mostly distributed in the residual fraction than in the fraction associated to organic components, *i.e.* Al would be found mostly as oxide and sulfide with a minor number of forms associated to carbonates. Finally, the more labile fractions that would reveal how leachable or exchangeable the analyte is, are the lowest, being not detectable in its soluble form (see Fig. 2).
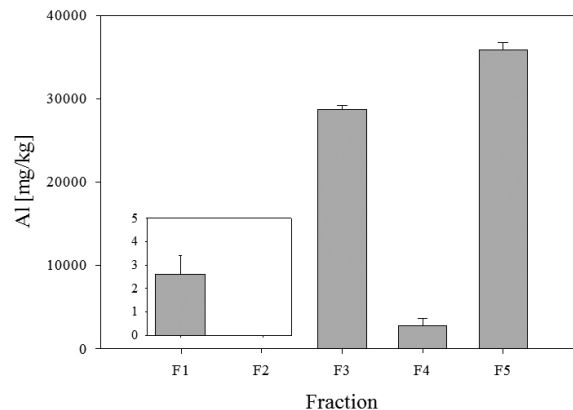

Figure 2 – Chemical fractionation of Al in Santa Barbara soil (no incubation)

Lime

Samples amended with commercial lime, after two days of incubation, the control soil presented higher levels of Al in the adsorbed and organic fraction as compared to soils amended with lime (see Fig. 3). Although in non-incubated soil Al was not detected in F2, in F3 28742,82±455,91 mg kg^{-1} was found, a lower value than 49362,60±545,36 mg kg^{-1} found in F3 of the control soil after two days of incubation. However, the values of Al that were determined in these two fractions stabilize through incubation time, which would imply that this sudden Al increase in the mentioned fractions, is because of the applied temperature during the incubation procedure. This Al content in F2 and F3 decreased due to lime amendment in the three applied doses, exhibiting lower values than the control soil. On the other hand, F1, F4, and F5 bleached soil fractions have no important changes as compared to the control soil. Then, after 4 days, a stabilization of the five fractions was observed, with respect to control soil and soil amended with lime using different doses.
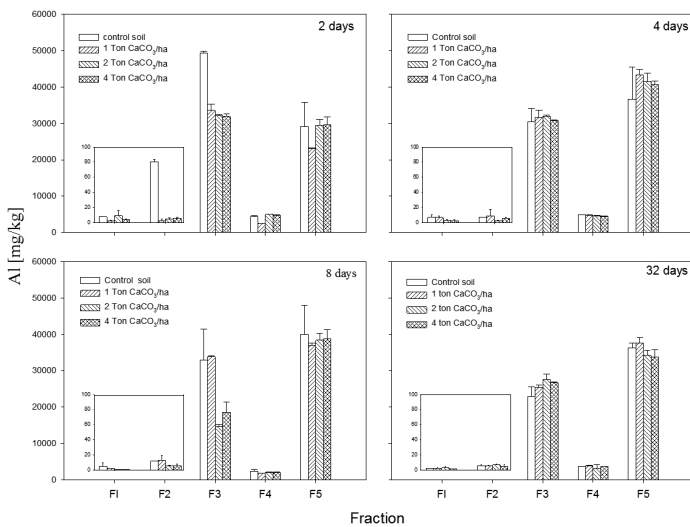

Figure 3 – Commercial lime: Al chemical fractions based on days of incubation and dose.

Only in F1 and F4 it is observed a slight diminution of exchangeable and carbonated Al because of pH increase that lime amendment causes in large doses. Lime amendment exhibits not Al incorporation in significant amount since not increases or decrease occurred after four days of incubation.

After eight days of incubation, an Al change is observed associated to organic components in soils amended with 2 and 4 ton, probably caused by pH increase to 5,85±0,02. The rest of the fractions remained unchanged, with Al levels of bleached soils, similar to previous days.

In general, it is observed that once the procedure of incubation is accomplished, the Al levels in different fractions are slightly increased after commercial lime addition to the initial doses. However, the Al content decreases as the bleacher dose increases, due to pH change (5.88±0.01) in the highest doses, that would be generating an Al deactivation responsible for soil acidification. It is noteworthy that the Al is mostly distributed in the labile soils, therefore, Al has not a high impact in soil-solution.

Grits

Aluminium distribution in different fractions of soils amended with G is depicted in Fig.4.

After two days of soils bleached with G, no considerably changes occur in the fractions, as compared to the control soil. If the fractions of G-amended soils are compared with those amended with commercial lime, no decrease was observed for F2 and F3. Therefore, no initial dampening effect, as occurred with commercial lime, exists.

Then, after 4 days no significant difference between a control soil and a soil with G in the exchangeable, adsorbed, organic and carbonated fractions was observed. Only F5 exhibited a decrease of *ca.* 9000 mg kg^{-1} with respect to the control soil when a 1 ton of CaCO$_3$/ha dose was applied. However, as the dose increases, so does the Al amount. When the fractions of this residue are compared, only in F5 a lower average value was observed, approximately 1000 mg kg^{-1}, in the determined Al in amended soils with G, behaviour that is opposite to that observed in lime amendments in this fraction.
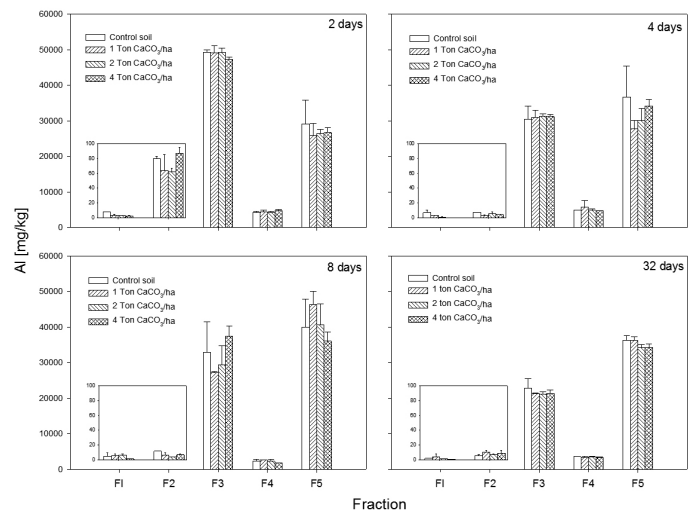

Figure 4 – Grits: Al chemical fractions based on days of incubation and dose

After 8 days of incubation of the G-amended soil, there are no important differences in F1, F2 and F4 as compared to the control soil, while in the organic and residual fractions a decrease and increase, respectively, took place. The G dose increases in F3 increases the Al content, however in F5 the behavior is just the opposite. If Al fractions in lime amended soils are compared, no great variations are obtained, because Al levels in soils with G do not markedly exceed those found in the control soil.

Then, once the incubation with G is accomplished, the Al levels in the five fractions do not exceed that of the control soil, hence the pH increase brought about by G is compensated by no addition of Al. From an environmental viewpoint, this is an important issue to be considered, since no Al addition in its toxic forms to the different chemical fractions takes place, taking into account that in a previous work (data not showed) high levels of Al was found in these residues. If a comparison of these fractions with the corresponding lime amended soil is made, it is demonstrated that soils with G exhibit a lower Al content, ascribed to organic components.

Dregs+Grits

Aluminum content in different fractions of three applied doses is shown in Fig. 5.

After two days of incubation, the control soil exhibited high levels of Al in the adsorbed and organic fractions, where the residual mixture decreases the Al that is present in these fractions due to its initial bleaching effect, similar to what happens when lime is applied. The rest of the fractions exhibit lower levels of Al than the control soils, with a trend to decrease its Al content in the different fractions, being more pronounced in F2 and F3. After 4 days of incubation, the Al in different fractions is equilibrated in the control soil. No considerable increase was obtained when the residual mixture dose is increased. In comparison to that with lime, a similar Al distribution in its five fractions is observed.

After 8 days, the F1, F2, F4 and F5 soil fractions of G in three doses resemble the content of Al extracted in the control soil, with no significant variations. Just a change of Al distribution in the organic fraction was found, with an increase of Al present in this fraction due to D+G addition. However, when the precision of Al content is considered, associated to the control soil, the Al levels are similar to those found in the soil with cellulose residues (D+G).

Finally, after 32 days of incubation, the Al chemical fractions in D+G-amended soils showed similar content in comparison as compared to the control soil, with no considerable addition of Al to each fraction. Consequently, the bleaching effect due to D+G is favorably considered advantageous since there is no important addition of Al to the labile fractions of the soils, with a minimum increase of Al, occurs. In this regard, sequential extractions (European Community Bureau of Reference, BCR) applied to green liquor waste have shown that the potentially bioavailable Al fractions are very low with values of 6.6 mg kg^{-1} (Makela et al., 2012). Likewise, for the fractions associated to species such as sulfides (Filgueiras et al., 2002), Cu and Al exhibited the highest values with 53.5 and 330 mg kg^{-1}, respectively. Heavy

metal extractability studies using artificial gastric fluids have been performed in order to set the human health risk, showing a high degree of extractability of species such as Zn (1290 mg kg^{-1}), Ba (770 mg kg^{-1}) and Al (730 mg kg^{-1}).

Finally, in this study, independent of the added dose of bleaching mixture, a trend exists pointing at a higher Al content in the residual fraction at the end of the incubation as compared with the other fractions.
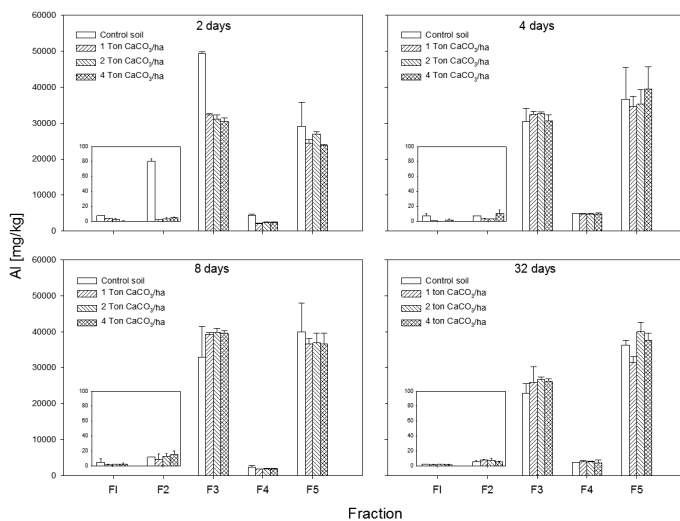

Figura 5 – *Dregs+Grits*: Al chemical fractions based on days of incubation and dose.

CONCLUSIONS

The addition of residues such as G and D+G in the studied proportion, would be a valid option to use in bleaching processes, since the experimental pH increases, enhancing thus the bleaching effect, being the D+G mixture better than commercial lime or G.

Aluminum incorporation in soil owing to cellulose residues is minimal and, at the same time, is compensated by pH increase as a result of the utilized bleachers, distributed in the less available fractions, *e.g.* residual, organic and carbonated; while in more available fractions, the adsorbed fraction is more important than the exchangeable one.

Finally, it was established that there is no significant Al distribution changes in the studied chemical fractions from Santa Barbara amended soil, using either commercial lime or cellulose residues.

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