The use of volcanic soil as mineral landfill liner - I. Physicochemical characterization and comparison with zeolites

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The use of volcanic soil as mineral landfill liner – I. Physicochemical characterization and comparison with zeolites

The main physicochemical characteristics of the volcanic soil of Southern Chile, with allophane as the main pedogenic mineral phase were analysed and compared with common zeolites (clinoptilolite) of the European market. The ultimate goal of this study was to test volcanic soil for the use as mineral landfill liner. The main results indicated that the clay and silt fractions together of the volcanic soil were between 38 and 54%. The buffering capacity of the volcanic soil was higher compared with the studied zeolites, whereas the cationic exchange capacity of the volcanic soil (between 5.2 and 6.5 cmol+ kg^{-1}) is of the same order of magnitude of the studied zeolites (between 9.7 and 11.4 cmol+ kg^{-1}). Moreover, the anionic exchange capacity of the volcanic soil was higher compared to the zeolites analysed. The hydraulic conductivity of the volcanic soil, measured in the laboratory at maximum proctor density, ranges between 5.16×10^{-9} and 6.48×10^{-9} m s^{-1}, a range that is comparable to the value of 4.51×10^{-9} m s^{-1} of the studied zeolite. The Proctor densities of the volcanic soil are in a lower range (between 1.11 and 1.15 g ml^{-1}) compared with zeolites (between 1.19 and 1.34 g ml^{-1}). The volcanic soil physicochemical characteristics are comparable to all the requirements established in the Austrian landfill directive (DVO, 2000). Therefore, the use as mineral landfill basal sealing of the analysed volcanic soil appears reasonable, having a pollutant adsorption capacity comparable to zeolites. It is of special interest for Southern Chile, because there are no alternative mineral raw materials for basal liners of landfills.

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Introduction

Sanitary landfills are commonly designed under the 'multibarrier system' concept in which clay mineral layers play an important role as constituents of landfill barriers, preventing the breakthrough of leachate with hazardous contaminants. The multibarrier system consists normally of a subsoil barrier (geological barrier), a mineral sealing layer, a geomembrane, a protective layer, a drainage blanket and a transition layer underneath the waste body itself (Holzlöhner *et al.* 1999).

The so-called composite liner is the combination of successive natural clay liners with a total thickness of 0.5–1.5 m and a superficial geomembrane 2.5–3.0 mm thick, depending on the type of waste to be disposed and on the environmental regulations of each country (Pavlov *et al.* 2002). The geomembrane itself is made of a high-density polyethylene (HDPE) or polypropylene (PP), and is covered with a geotextile sheet in order to protect it against damage caused by the overlying coarse gravel drainage layer (Holzlöhner *et al.* 1999). Therefore, in order to prevent the leaching of environmental pollutants into the subsoil and groundwater bodies under landfills, the basal liner is constructed with a redundant design: if the geomembrane fails after years or decades of operation, the clay liner should still be able to take over its task of retaining the pollutants (which might be a problem due to desiccation fissures in the clay liner).

Clay minerals have a high capability for sorbing leachate pollutants such as heavy metal ions because of their large specific surface area and their high number of negatively charged bonding sites. Other reactive components in clays that can fix heavy metals are Fe and Mn oxides and hydroxides, carbonates and the organic matter (Roehl & Czurda 1998).

In the absence of impervious natural soils, compacted mixtures of bentonite and sand have been use to form barriers for liquids (Kenney *et al.* 1992), as well as bentonite-zeolite mixtures (Tuncan *et al.* 2003, Kaya & Durukan 2004). Bentonite serves as a pore sealant yielding low hydraulic conductivity, whereas the high cation exchange capacity (CEC) of the zeolite is utilized in purifying the contaminants present in the leachate (Tuncan *et al.* 2003).

The objective of this work is to establish the physicochemical characteristics of the natural volcanic soil of Southern Chile compared to zeolites (a common natural adsorber for pollutants in environmental technology), with the ultimate goal of a possible use of this volcanic soil as a landfill basal sealing. This is of special interest for Southern Chile, as there are no alternative mineral raw materials for basal landfill liners.

Materials and methods

Studied materials

The volcanic soil chosen for this study was collected in the farm 'Estación Las Encinas', Temuco, IX Region, Chile, and it is known as an allophanic soil called Trumao. The mentioned farm is owned by the University of La Frontera and is used as an agricultural experimental station.

The zeolites samples, consisting essentially of clinoptilolite, are common commercial products. They are produced from the same raw material with different particle size distributions.

Total organic carbon

The total organic carbon (TOC) determination was based on the methodology described in the ÖNORM EN 13137 (2001). The TOC value is determined indirectly from the difference between the total carbon (TC) and the total inorganic carbon (TIC) content of the soil sample.

Cationic exchange capacity

The cationic exchange capacity determination was based on the methodology described in DIN ISO 11260 (1997). The effective cationic exchange capacity (CEC_{eff}) is the exchange capacity of the soil at its natural pH value. Therefore, the CEC_{eff} as well as the exchangeable cations Na, K, Ca, Mg, Mn, Fe and Al were measured at the pH value of the soil sample. For the determination of CEC_{eff} and exchangeable cations, 2.5 g dry soil were weighed in centrifuge tubes and saturated with a 0.1 M $BaCl_2$ solution. For a successful barium (Ba) saturation of the soil samples, the mixtures were stirred for 1 h in a shaking chamber and after that centrifuged at 15 000 rpm. The supernatant was decanted and collected in a 100-mL flask. This procedure was repeated three times until the soil was completely saturated with barium. After that, the 100-mL flask was levelled with 0.1 M $BaCl_2$ solution. This liquid sample served also for determining the exchangeable cations by flame atomic absorption spectroscopy (AAS). The exchange equilibrium from the soil was then started with a 0.0025 M $BaCl_2$ solution. The samples were shaken overnight and then centrifuged at 15 000 rpm. The supernatant was decanted while the soil was mixed with 30 ml of a 0.02 M $MgSO_4$ solution and shaken overnight. This procedure allows for the total barium, present in the liquid phase as well as adsorbed in the soil, to precipitate in the form of barium sulfate; while magnesium occupies the free exchangeable cation places. After this procedure, the samples were centrifuged at 15 000 rpm again. The collected supernatant was then filtered through a paper filter in an Erlenmeyer flask. A blank sample was also measured by doing the procedure already described in a sample tube without soil. The determination of the CEC_{eff} was performed through the measurement of the magnesium concentration in the filtered supernatant solution by flame-AAS in a GBC Avanta equipment.

Anionic exchange capacity

The determination of the anionic exchange capacity (AEC) was based on the procedure described by Rowell (1994). Syringes fitted with a capillary hose were filled with 4 g of dry soil samples. The soil sample was secured in between cotton-wool walls, to avoid sample losses during the extraction procedure. After the compaction of the sample with the syringe piston, 5 mL of a 0.002 M NH_4Cl solution was added to the system. With the valve closed, the system was left under these

conditions overnight. The soil-solution mixture was expected to be in equilibrium by the next day. Then, during the next day, the sample was cleaned up to 10 times with 5 mL of 0.002 M NH_4Cl solution, for a total time of 3 h. Thus the soil sample became saturated in chloride. The syringe with the humid sample was then weighed, to determine the water fraction of the humid sample. After that, the sample was washed 10 times with 5 mL of a 0.02 M KNO_3 solution for 3 h. The chloride present in the saturated sample was then displaced. This extraction solution was weighed and analysed by ion chromatography for its chloride content.

pH value

The determination of the pH value of the soil was based on the methodology described in EN 12176 (1998). Basically, 10 g of dry soil were weighed for the pH value determination in 90 mL of distilled water and in 25 mL of a 0.01 M KCl solution. The suspension was mixed with a magnetic stirrer for about 10 min. After calibrating the pH-meter with standard buffer solutions, the measurement was performed taking the average pH value for every three measurements.

Buffer capacity

The determination of the buffer capacity of the soil was based on the methodology described by Rowell (1994). Ten grams of dry soil and 25 mL of a 0.1 M KCl solution were put in a 100 mL glass beaker. The suspension was mixed with a magnetic stirrer and after that, the pH value was measured. Then, 0.5 mL of a 0.1 M HCl solution were added and the suspension was stirred again. The new pH value was measured. The HCl dosage was repeated until the desired acid pH range was covered. The same experiment was repeated adding NaOH (0.1 M solution) for covering the alkaline pH range.

Particle size distribution

The determination of the particle size distribution of the soil was based on the methodology described in DIN 18123 (1983). The particle size distribution was performed by means of wet sieving and sedimentation. The wet sieving procedure was used for determining the particle size distribution for particles with a size larger than 0.063 mm, whereas the sedimentation method produced a particle size distribution smaller than 0.063 mm. The size limit for the sedimentation procedure was established at 0.001 mm. In the first step, the wet sieving process took place with the following sieve disposition: 4, 2, 1, 0.5, 0.25, 0.125 and 0.063 mm. For each measurement the sample mass was about 150 g. Before the wet sieving, the samples were deliberately not dried at 105°C in the drying oven to avoid changes in the clay fraction of the samples. Such changes could make the complete separation of the fraction under 0.063 mm very difficult, and thus, the subsequent sedimentation process almost impossible. Therefore, the determination of the dry mass was based on the water content of another portion of the samples, which was determined previously at 105°C for 24 h in the oven. Before the wet sieving, the samples were treated in an ultrasound bath for 15 min, to disintegrate the particle aggregates. The wet sieving process was subsequently carried out using a Retsch sieve machine in intervallic operation. The sieving duration was established based on the turbidity of the particle size fraction less than 0.063 mm passage and took approximately 25 min for each sample. After finishing the wet sieving, the remnants of each particle size fraction were dried until constant weight was obtained at 105°C. The particle size fraction less than 0.063 mm was caught in receptacles and was then analysed by a sedimentation procedure in test tubes.

Loss on ignition

The loss on ignition (LOI) of a soil sample is a measurement of the total soil organic matter (SOM). It is the difference between the initial and the final (after ignition) soil sample mass. The procedure was made according to DIN EN 12879 (2001). A dry soil sample of about 2 g was weighed in a platinum pan and completely burned in the oven at 1000°C for 1 h (with this procedure, other components such as crystalline water, OH^- and CO_2 contribute to the LOI). The sample was then cooled in a desiccator and the mass after ignition was registered. Thereafter the sample was burned for another hour, to secure a final constant mass, and weighed again. Samples were treated in duplicate.

Proctor density

The Proctor density is the highest possible dry bulk density of a soil sample under defined experimental conditions. Its determination was based on the methodology described in DIN 18127 (1993). According to this methodology, the sample compaction was performed in a steel cylinder. The diameter of this cylinder depends on the maximum particle size fraction of the soil sample. In this case, for volcanic soil and zeolites the maximum particle size fractions are 2 and 4 mm, respectively. This means that the 100 mm cylinder is the most suitable for the Proctor density determination. The sample quantity also depends on the maximum particle size fraction of the sample, as well as on the Proctor cylinder diameter. The sample has to be compacted between the half and the quarter part of the original volume. Therefore, 2 kg samples were used for the Proctor density determinations. First, the samples were dried at 80°C until of constant mass. Then, a known water quantity was added. The initial water quantity chosen was far below the supposed optimal water content. After that, the samples were put into the Proctor cylinder in three separate layers of the same thickness. Each

layer surface was then slightly pressurized with a steel-mortar, and subsequently compacted with 25 beats of a 2.5 kg fall-weight from a height of 30 cm in a circular manner of compression. The initial sample layer thickness chosen allowed the compacted sample to completely fill the Proctor cylinder, with a maximum of 10 mm level difference to the covering ring. The beats were completed without any break (2 s between each beat). When the three layers were compacted, the covering ring was removed and the remaining sample material above the Proctor cylinder was carefully taken away. Then, the sample surface was exactly levelled to the Proctor cylinder top level with a steel ruler. Finally, the cylinder was weighed with the sample. After this first experiment, the other experiments with increasing water content were performed in the same way. To obtain an homogeneous water content in the soil sample, the humid sample on which the water was sprayed, was left for 10 min in the covered Proctor cylinder and mixed afterwards. The water content was determined after each experiment, by weighing the humid mass and after drying of each sample.

Hydraulic conductivity

The hydraulic conductivity (K_f) value describes the resistance of a particular soil (or rock) to the flow of a certain fluid and can be determined exactly only in the Reynolds range between 1 and 10. The K_f value of a water-saturated soil can be determined using Darcy's law, which allows only an approximation of the K_f value for soils with low permeability. Under the simplifying condition that the water flow through the soil is laminar, equation (1) can be applied.

$$\frac{Q}{A} = K_f * i \qquad (1)$$

where Q is the water flow rate ($m^3\ s^{-1}$), A is the cross-sectional area of the soil (m^2), K_f is the measured hydraulic conductivity ($m\ s^{-1}$) and i is the hydraulic gradient ($m\ m^{-1}$). Measuring the flow rate that passes through the soil sample (Q) and knowing the cross-sectional area of the soil sample (A) and the i value, the K_f value can be determined from equation (1). In addition, the standardized K_f values at 10°C (K_{f10}) were calculated using the K_f values determined at the measured water temperature (T) with the Poiseuille formula (DIN 18130 1989) presented in equation (2).

$$K_{f10} = \frac{1.359}{1 + 0.0337 * T + 0.00022 * T^2} * K_f. \qquad (2)$$

The determination of the hydraulic conductivity of the soil was based on the methodology described in DIN 18130 (1989). A hydraulic conductivity cell with changeable i gradient was chosen for determination of the K_f values. Three standing glass tubes with 4, 6 and 8 cm internal diameters were used for the supply of different water flow rates and hydraulic gradients. The highest input water level of the standing tubes was 220 cm. For the determination of the water flow rate, the water level in the tubes was measured through the experiment time. In all the experiments the samples were completely saturated. To achieve this aim, water was supplied until the input and output flow rates were equalized. The changeable hydraulic gradient (i) was obtained by making experiments with different water levels in the input glass tube. The level difference in the input glass tube was measured through a certain time for the flow rate calculation. The water temperature was also measured in each experiment and each trial was repeated four times.

X-ray fluorescence spectrometry

X-ray fluorescence spectrometry (XRFS) analyses were made for the quantitative determination of chemical elements with an atomic number higher than 5 until the trace range. The XRFS method is mainly used to determine the content of principal and secondary elements such as Si, Al, Mg, Ca, Fe, K, Na, Ti, S, P and Mn in silicate rocks, as well as trace compounds such as the heavy metals Pb, Zn, Cd and Cr. The XRFS is a quick and non-invasive method that is appropriate for the evaluation of solid and liquid samples. The used equipment was a Philips PW 1410 with dispersive wavelength X-ray fluorescence spectrometry technique for its determinations.

Results and discussion

Particle size distribution

The particle size distribution is an important physical parameter that characterizes a soil sample. Normally, the most important particle size fractions of soils concerning pollutant retention and permeability reduction are in the smaller than 63 μm range, especially clay and fine silt with a particle size smaller than 0.006 mm (DIN 4022 1991).

In Figure 1, the particle size distributions are presented for volcanic soil (three profiles) and two commercial zeolites from the European market (Agro Clino and Nat Min 9000), for comparison purposes. The grain size distribution of the zeolites was the result of the milling process. They are of significance concerning pollutant retention in landfill liners (Tuncan *et al.* 2003) but are obviously not used for sealing purposes. It is clearly stated that the volcanic soil is relatively rich in clay and silt fractions. These fractions ranged between 38% (40–60 cm profile) and 54% (5–20 cm profile). This result clearly showed that the volcanic could be important for both purposes of mineral landfill liners, namely pollutants retention and impermeabilization. In allophanic soils, the clay and silt fractions together normally range between 27

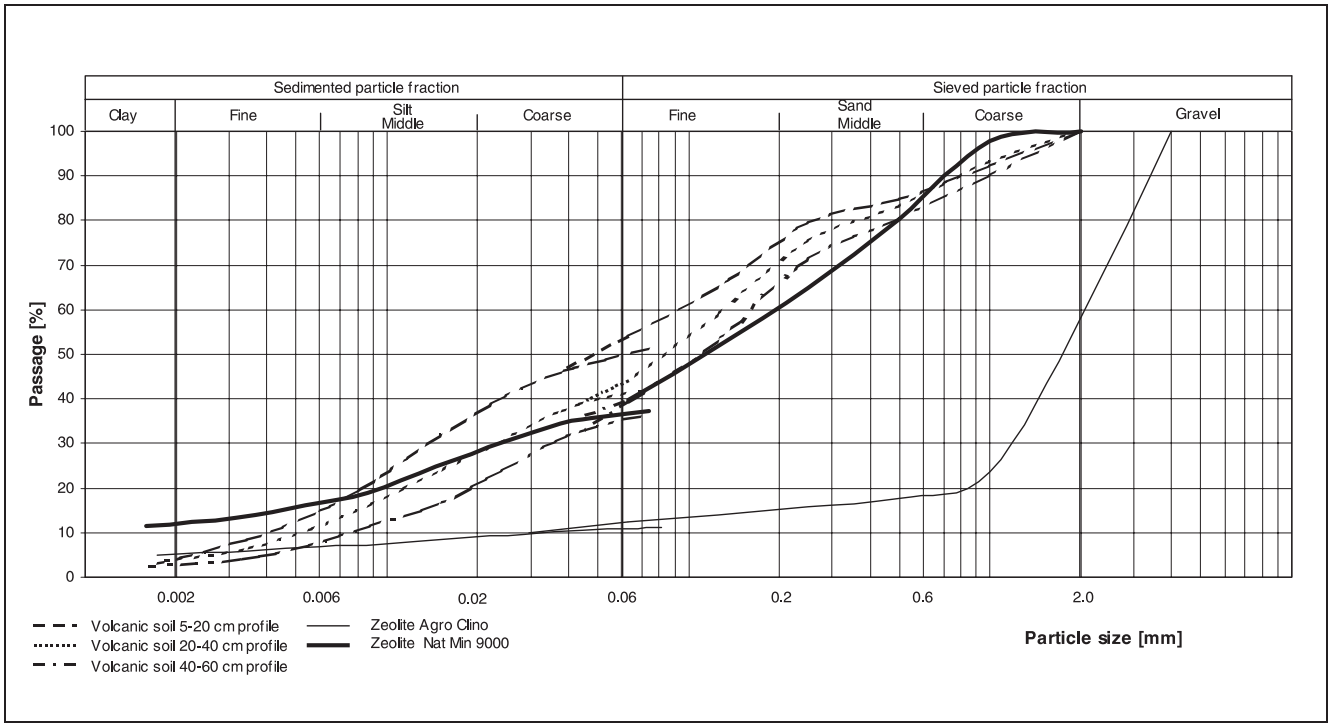

Fig. 1: Volcanic soil and zeolites particle size distribution.

Table 1: Total carbon (TC), total inorganic carbon (TIC), total organic carbon (TOC) and soil organic matter (SOM) content in volcanic soil and zeolite samples.

Sample	TC (%)	TIC (%)	TOC (%)	SOM (%)
Volcanic soil 5–20 cm profile	8.5	< 0.08	8.5	20.2
Volcanic soil 20–40 cm profile	4.6	< 0.08	4.6	14.6
Volcanic soil 40–60 cm profile	2.6	< 0.08	2.6	11.1
Zeolite Agro Clino	< 0.08	< 0.08	< 0.08	6.7*
Zeolite Nat Min 9000	< 0.08	< 0.08	< 0.08	7.0*

*Loss on ignition.

and 78% (Joergensen & Castillo 2001), while the clay and silt fractions content in mineral landfill liners usually range between 52 and 92% (Roehl & Czurda 1998, Mimides & Perraki 2000). This means, the clay and silt fractions of the investigated allophanic volcanic soil samples are near the average value of allophanic soils and near the lower ranges of mineral landfill liners.

Total organic carbon

The total organic carbon (TOC) and soil organic matter (SOM) are also important parameters for characterizing a soil sample. The TOC content in the volcanic soil samples decreased with the depth; this occurred with the SOM as well (Table 1), since both values are directly related. This is an expected result, as in the upper soil profile (5–20 cm) decomposed and non-decomposed matter (roots and plants) increases this value. This effect is less important in the deepest volcanic soil level. No significant values for total inorganic carbon (TIC) were found in the volcanic soil samples (below detection limit). This result indicates that there was no measurable amount of carbonate, bicarbonate and soluble carbon dioxide in the samples. These results are comparable with other allophanic soils, were the SOM content varies between 15 and 34% (Dubroeucq *et al.* 2002). In the case of the zeolites samples, no TIC and no TOC were detected. The absence of TOC was expected, as these zeolites are the result of the transformation of thick beds of glass-rich volcanic ashes under special lacustine conditions (Hay & Sheppard 2001). The loss on ignition (LOI) of 6.7 and 7.0%, obtained for the zeolite Agro Clino and Nat Min 9000 samples, respectively, is attributed to the loss of water present in the zeolites lattice.

X-ray fluorescence spectrometry

As mentioned before, specific elements (metals) and metal oxides were also determined for the volcanic soil characterization with X-ray fluorescence spectrometry (XRFS). The zeolite Nat Min 9000 sample was selected for comparison purposes. The results obtained by XRFS are presented in Table 2. They confirmed the expected composition of the volcanic soil, presenting a high content of SiO_2, Al_2O_3, and Fe_2O_3, with an allophane-like composition.

It was observed that the content of the mentioned metallic elements (i.e., Si, Al and Fe) increased with the soil

Table 2: Specific metals and metal oxides present in volcanic soil and zeolite samples measured by means of X-ray fluorescence spectrometry (XRFS).

(%)	Volcanic soil profile			Zeolite
	5–20 cm	20–40 cm	40–60 cm	Nat Min 9000
SiO_2 (Si)	41.6 (19.4)	43.7 (20.4)	45.0 (21.0)	71.5 (33.4)
Al_2O_3 (Al)	18.6 (9.8)	20.8 (11.0)	21.6 (11.4)	12.3 (6.5)
Fe_2O_3 (Fe)	10.5 (7.3)	11.7 (8.2)	12.4 (8.7)	1.4 (0.9)
CaO (Ca)	3.4 (2.4)	3.3 (2.4)	3.6 (2.6)	2.0 (1.4)
MgO (Mg)	1.8 (1.1)	2.0 (1.2)	2.3 (1.4)	0.9 (0.5)
Na_2O (Na)	1.5 (1.1)	1.6 (1.2	1.8 (1.3)	0.3 (0.2)
TiO_2 (Ti)	1.3 (0.8)	1.5 (0.9)	1.6 (1.0)	0.1 (0.05)
P_2O_5 (P)	0.8 (0.4)	0.6 (0.3)	0.5 (0.2)	0.01 (0.005)
K_2O (K)	0.5 (0.4)	0.4 (0.35)	0.4 (0.35)	3.7 (3.1)
MnO (Mn)	0.3 (0.2)	0.2 (0.15)	0.2 (0.15)	0.04 (0.03)
LOI	20.2	14.6	11.1	7.0
Total	100.5	100.4	100.5	99.3

LOI, Loss on ignition.

depth. This increase is related with the decrease in the soil organic matter (SOM) and water content with the soil depth, which made the mineral content to increase respectively. Typical values for the Si, Al and Fe contents in some andisols in Costa Rica range between 7.4 and 14.4% for Si, 8.9 and 20.1% for Al and 2.5 and 5.5% for Fe (Jongmans *et al.* 1995), showing that the Chilean allophanic soil is richer in Si and Fe. Regarding the zeolite Nat Min 9000 sample, the SiO_2 content was found to be very high, reaching a value of 71.5% compared with values between 41.6 and 45.0% for the volcanic soil profile samples. This SiO_2 content of the zeolite sample corresponds to the upper range of the data for clinoptilolites (Gottardi & Galli 1985). On the other hand, as expected for allophanes, the Al_2O_3 content was much higher in the volcanic soil samples (between 18.6 and 21.6%) compared with only a 12.3% (lower range of the data for clinoptilolites; Gottardi & Galli 1985) in the zeolite Nat Min 9000. In addition, the Fe_2O_3 content was much higher in the volcanic soil samples (10.5 to 12.4%) compared with this metal oxide in the zeolite Nat Min 9000 sample (only 1.4%). In allophanic soils the reactive sites for pollutants retention are mainly related with Si, Al and Fe oxides/hydroxides. Therefore, these parameters became a key point when analysing the volcanic soil ions exchange capacity. The content of all the other metal oxides was found to be very similar when comparing the volcanic soil and zeolite samples. Concerning the pollutants retention, only the K_2O content (3.7%) appears to be important in the case of the zeolite Nat Min 9000 sample.

Effective cationic exchange capacity

The effective cationic exchange capacity (CEC_{eff}) is an interesting parameter for evaluating the possible adsorption mechanisms and capacity of the volcanic soil, compared with zeolites (Table 3). The volcanic soil profile's average CEC_{eff}, decreased with the soil depth, namely from 6.5 cmol+ kg^{-1} for the 5–20 cm profile to 5.2 cmol+ kg^{-1} for the 40–60 cm profile. This result is a consequence of the decrease in the SOM, as the cation exchange capacity of humic substances is much greater, per unit mass, than that of clay (Hillel 1998). The CEC_{eff} is also related with the specific surface area of the soil, which was determined in a previous work to range between 173 and 223 $m^2\ g^{-1}$ for this volcanic soil and was therefore considered as high (Navia *et al.* 2003). Andisols derived from volcanic ashes in Nicaragua, show higher CEC_{eff} values:

Table 3: Anionic exchange capacity (AEC), effective cationic exchange capacity (CEC_{eff}) and exchangeable cations in volcanic soil and zeolite samples.

		Volcanic soil profile			Zeolite	
		5–20 m	20–40 cm	40–60 cm	Agro Clino	Nat Min 9000
AEC (cmol kg^{-1})		2.7	1.6	0.5	0.6	0.6
CEC_{eff} (cmol+ kg^{-1})		6.5	6.1	5.2	11.4	9.7
Exchangeable cations (cmol+ kg^{-1})	Ca^{2+}	10.5	8.0	6.5	13.6	14.8
	Mg^{2+}	0.71	0.66	0.64	2.7	2.1
	K^+	0.85	0.20	0.12	7.3	8.4
	Na^+	0.06	0.08	0.11	4.5	4.7
	Al^{3+}	0.10	0.0	0.0	0.0	0.0
	Fe^{3+}	0.0	0.0	0.0	0.0	0.0
	Mn^{2+}	0.0	0.0	0.0	0.0	0.0

Table 4: pH values of volcanic soil and zeolites.

Sample	pH-value (H_2O)	pH-value (KCl)
Volcanic soil 5–20 cm profile	5.9	5.3
Volcanic soil 20–40 cm profile	6.7	5.7
Volcanic soil 40–60 cm profile	6.8	5.9
Zeolite Agro Clino	7.6	6.2
Zeolite Nat Min 9000	7.8	6.7

between 15.4 and 44.4 cmol+ kg^{-1} (Joergensen & Castillo 2001), whereas in andisols from the Azores Islands (Portugal) the CEC_{eff} values range between 0.71 and 21.3 cmol+ kg^{-1} (Madeira *et al.* 2003). Regarding the zeolites studied, the CEC_{eff} obtained were slightly higher than that of the volcanic soil profiles, but in the same order of magnitude. In clay landfill liners the CEC normally varies between 4 and 80 cmol+ kg^{-1} (Mimides & Perraki 2000, Kugler *et al.* 2002), showing higher values only for clayey materials rich in expandable clay minerals like smectite or smectite-illite.

The main exchangeable cations measured in the volcanic soil profiles were Ca^{2+}, Mg^{2+} and K^+, while in zeolites Na^+ was added to these three cations. On one hand, in acid soils (such as the studied volcanic soil, see Table 4), the main exchangeable cations are normally Ca^{2+}, Mg^{2+}, K^+ and Na^+. On the other hand, in acid mineral soils of very low pH, predominantly Al^{3+} and H^+ occupy the exchange sites. Dubroeucq *et al.* (2002), Madeira *et al.* (2003) and Armas-Espinel *et al.* (2003) corroborated this finding in different andisols from Azores Islands (Portugal), Mexico and Tenerife (Spain). In fact, the same cations, namely Ca^{2+}, Mg^{2+}, K^+ and Na^+, were determined to be the main exchangeable ones. In volcanic soil and zeolites the different cations compete for the exchangeable sites and therefore the properties of the cations and the material will influence the final CEC. In general, the effect of the exchange capacity will depend mainly on the cation valence and diameter. Cations with higher valence will have a stronger exchange force (tendency) and by the same valence, this exchange force will increase with increasing cation diameter (Scheffer & Schachtschabel 2002). Naturally, depending on the soil pH, these properties can change, as presented in the case of acid volcanic soil.

Anionic exchange capacity

The anionic exchange capacity (AEC) is only important in soils with variable charge, with the presence of allophanes and Fe- and Al-oxides/hydroxides. The non-variable surface charge of minerals such as zeolites is mainly negative, being essentially able to exchange cations. The zero point charge pH (pH_{ZPC}) of the volcanic soils of Southern Chile was determined to range between 3.2 and 6.2 (Mora *et al.* 1994), with an average value of 5.5 for the present samples. As the pH values of the volcanic soil profiles are near the pH_{ZPC}, a partially positively charged soil surface was expected. This fact may result in an enhanced anion exchange capacity compared with zeolites. This assumption was confirmed by the obtained experimental data (Table 3). Typical exchangeable anions are Cl^- and NO_3^-, as well as PO_4^{2-}, SO_4^{2-} and HCO_3^-. AEC values for different andisols from the Azores Islands (Portugal) were determined to range between 1.44 and 7.04 cmol kg^{-1} (Madeira *et al.* 2003), values that are quite comparable with those obtained for the Chilean volcanic soil.

pH value

The pH values of the volcanic soil profiles and zeolites are presented in Table 4. The volcanic soil profiles presented an acid pH range. The upper profile (5–20 cm) had an average pH value of 5.9 (in water) and 5.3 (in KCl), while the deepest profile presented an average value of 6.8 (in water) and 5.9 (in KCl). The more acidic pH value in the upper part of the soil profile can be essentially explained by the influence of acidic precipitations and the liberation of H^+ protons during the cation exchange processes in plant roots. In addition, the possible hydrolysis from Al^{3+} ions in the soil solution can contribute to the soil acidity. Acidic volcanic soils of Chile have normally pH values between 4.8 and 6.0 (Aguilera *et al.* 2002, Borie *et al.* 2002), which is the pH range of the volcanic soil samples measured in KCl solution. Zeolites presented higher pH values from 6.2 and 6.7 for the Agro Clino and Nat Min 9000 samples, respectively.

Buffer capacity

The buffer capacity of a natural adsorption material is an important parameter, especially in the case of very acidic or alkaline leachates. Different buffering systems can participate in the soil for binding H^+ and/or OH^- ions, in a reversible or irreversible manner. The pH value is therefore maintained at a relatively constant level until the buffering substance of the soil has completely reacted. The buffering capacity of the volcanic soil profiles and zeolites is presented in Figure 2. The buffering capacity of the three volcanic soil profiles was considerably higher than the one of the zeolite samples. For the volcanic soil profiles the pH value changed up to a maximum value of only 9.6 (40–60 cm profile), whereas the zeolites pH changed up to 11.2 (Agro Clino), when adding 22 mL of a 0.1 M NaOH solution. On the other hand, when adding 16 mL of a 0.1 M HCl solution, the volcanic soil profiles pH values decreased to a minimum of 3.0 (5–20 cm profile), whereas the zeolite samples reached a minimum pH value of 2.1 (Agro Clino). In addition, the shape of the zeolite-buffering capacity curves showed a strong change when

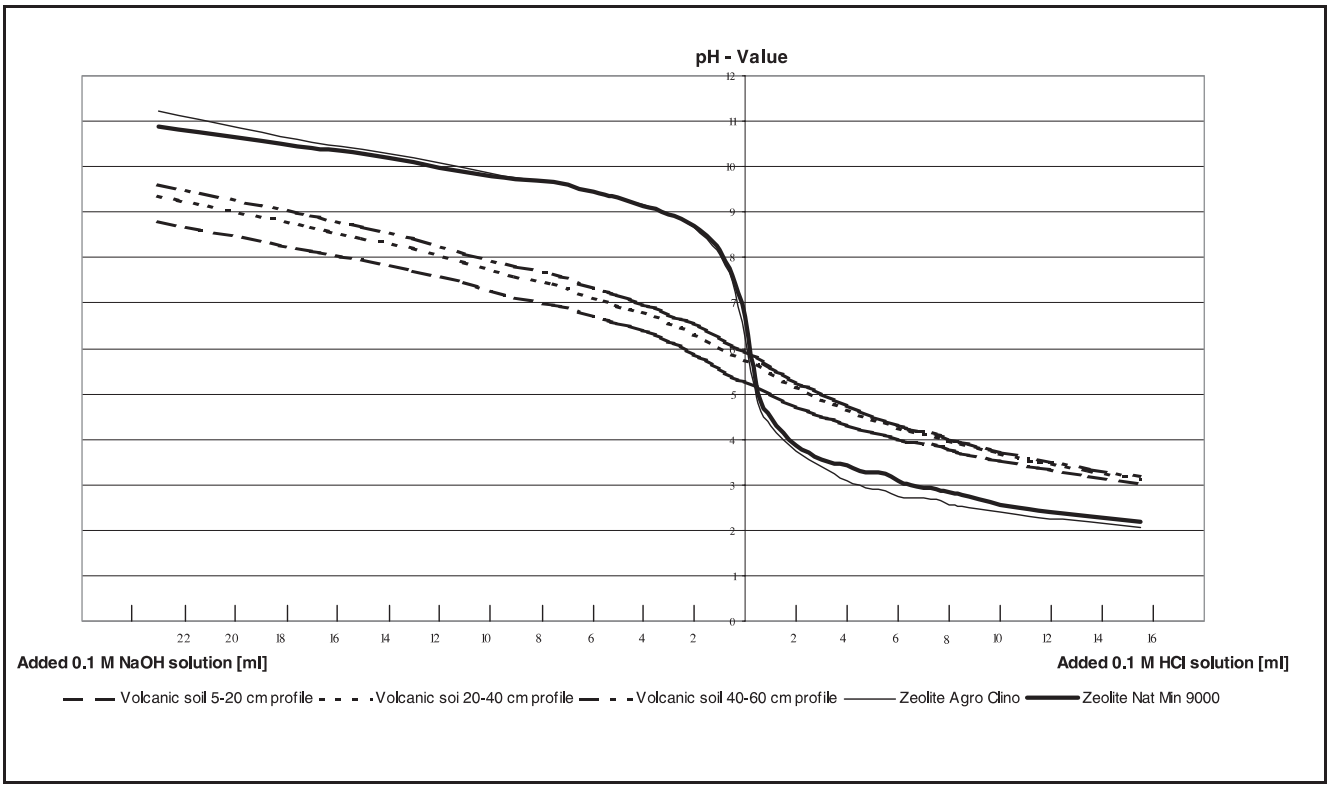

Fig. 2: Volcanic soil and zeolites buffer capacity.

adding only small amounts (< 2 mL) of the acid and the alkaline solutions, indicating that there were no sufficient buffering compounds balancing these acidic and alkaline initial loads present in this material. The volcanic soil profile's buffering capacity curves showed a slightly change under acidic and alkaline initial loads. This fact would suggest that sufficient buffering substances were present in the volcanic soil, neutralizing the H^+ (from the HCl solution) and OH^- (from the NaOH solution) ions until almost the end of the experiment.

The presence of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) is not relevant in the case of volcanic soil and zeolites, as no inorganic carbon was found in either of the natural adsorbents. The contrast in the buffering capacity between volcanic soil and zeolite can be related to the very different mineralogy and the presence of a considerable amount of humus in the case of the volcanic soil.

Proctor density

The Proctor densities were also determined in all of the volcanic soil profiles and, for comparison, in the zeolite samples. Zeolites are not thought to be used as a single compound in landfill liners, but will be of increasing significance for future landfill technology. The results are presented in Figure 3. The different volcanic soil profiles had a similar Proctor density (between 1.11 and 1.15 g ml^{-1}), which is a relatively low range compared with other unconsolidated sedimentary materials. It is in contrast to the relatively high grain density (2.45 to 2.66 g cm^{-3}) determined by Schöffmann (2004) for the samples used in the present Proctor tests. The lowest Proctor density reported for instance by Prinz (1997) is 1.62 g cm^{-3} for silty clay. The low Proctor density of the volcanic soil studied here must be due to the allophane-rich soil aggregates. The Proctor densities of these volcanic soil samples correlate with the grain density. The maximum Proctor density was obtained for the sample with the highest grain density (2.66 g cm^{-3}, volcanic soil 40–60 cm profile), and the lowest Proctor density for the lowest grain density (2.45 g cm^{-3}, volcanic soil 5–20 cm profile).

The zeolite samples (grain density near 2.2 g cm^{-3}) show Proctor densities that seem to be influenced by the particle size distribution. The sample with better grain sorting, namely a higher content in coarse grains and very little fine fractions (Agro Clino) showed a Proctor density of 1.19 g cm^{-3}. This is a considerably lower value in comparison with the Proctor density of 1.34 g $cm^{-3}$of sample Nat Min 9000, which is poorly sorted, having a much larger proportion of fine-grained particles (see Figure 1).

Hydraulic conductivity (K_f)

The hydraulic conductivity (K_f) of the three volcanic soil profiles and zeolite Nat Min 9000 were also determined. The zeolite Nat Min 9000 was chosen because of its similar particle-size distribution compared with volcanic soil.

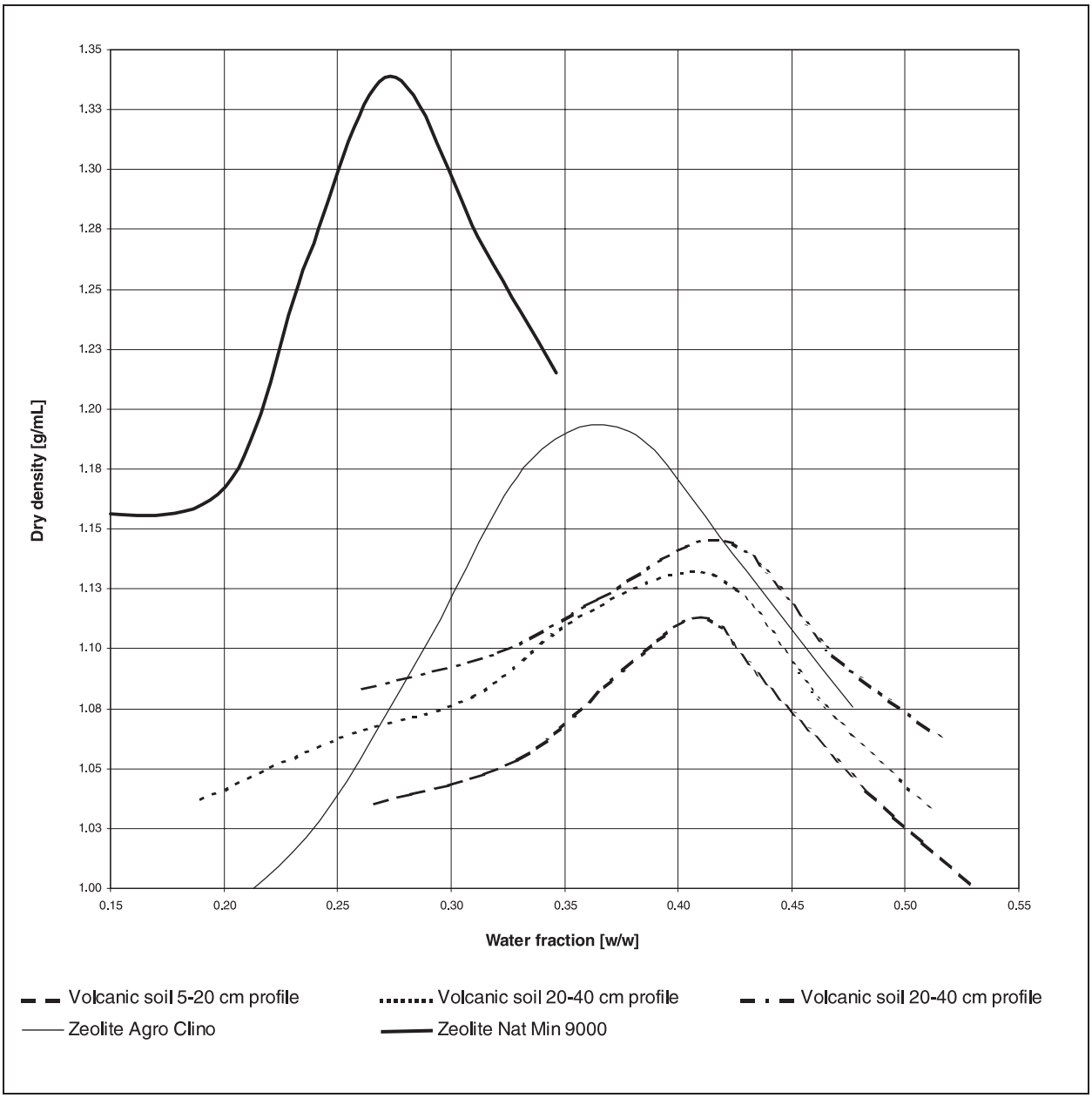

Fig. 3: Proctor density curves of volcanic soil and zeolites.

Table 5: K_f values for volcanic soil and zeolites.

Sample	Water temperature (°C)	K_f (m s^{-1})	K_{f10} (m s^{-1})
Volcanic soil 5–20 cm profile	23.0	$7.18 \cdot 10^{-9} \pm 4.27 \cdot 10^{-11}$	$5.16 \cdot 10^{-9} \pm 3.32 \cdot 10^{-11}$
Volcanic soil 20–40 cm profile	20.5	$7.76 \cdot 10^{-9} \pm 2.22 \cdot 10^{-11}$	$5.91 \cdot 10^{-9} \pm 1.83 \cdot 10^{-11}$
Volcanic soil 40–60 cm profile	26.0	$9.66 \cdot 10^{-9} \pm 2.89 \cdot 10^{-11}$	$6.48 \cdot 10^{-9} \pm 2.06 \cdot 10^{-11}$
Zeolite Nat Min 9000	21.3	$6.03 \cdot 10^{-9} \pm 2.38 \cdot 10^{-11}$	$4.51 \cdot 10^{-9} \pm 2.06 \cdot 10^{-11}$

K_f, Hydraulic conductivity (average and standard deviation of three samples).

The results are presented in Table 5. It is clearly stated that the volcanic soil K_f values are quite similar to the K_f value of the zeolite Nat Min 9000. For the volcanic soil profiles, the K_f values increased with the soil depth, correlating with the higher proportion of fine fraction in the upper part of the soil profiles. The high proportion of fine fractions explains the case of zeolite Nat Min 9000, for which a slightly lower K_f value was obtained.

Table 6: Mineral basal sealing physicochemical requirements and comparison with volcanic soil.

Parameter	Requirements (DVO, 2000)	Volcanic soil
Hydraulic conductivity (K_f)	$5 \cdot 10^{-10}$ m s^{-1} (laboratory test) $5 \cdot 10^{-9}$ m s^{-1} (in-situ test)	$5.16 \cdot 10^{-9}$–$6.48 \cdot 10^{-9}$ m s^{-1} (laboratory test)
Particle size distribution	Residual waste landfills Fines (< 2 µm): 20% w/w Clay minerals (from fines): 50% w/w	Fines (< 2 µm): 1–23% w/w
Total organic carbon (TOC)	< 5% w/w	2.6–8.5% w/w

The main physicochemical technical requirements for mineral-basal sealings in landfills are described in Table 6 (DVO 2000). The volcanic soil characteristics seem to be near all of the requirements presented. Although the volcanic soil K_f values are almost an order of magnitude higher than the stated technical requirements, the analyses of other four different volcanic soil sites in the surroundings of Temuco (Schöffmann 2004, Navia 2004) indicate a maximum clay fraction up to 23% in the samples (as indicated in Table 6), suggesting even lower values for the hydraulic conductivity with a corresponding sealing potential.

Conclusions

The natural volcanic soil of Southern Chile is an interesting material for possible use as a landfill mineral basal sealing, having physicochemical characteristics with respect to pollutant retention that are comparable with zeolites. With about two-thirds of the agricultural land in Chile (approximately 0.4 million km^2) derived from volcanic ash, it can be viewed as an important soil liner resource for future landfill projects. Sufficient quantities could be obtained readily from urban building activities. This natural material warrants further consideration by designers and regulators.

References

Aguilera, M., Mora, M.L., Borie, G., Peirano, P., & Zunino, H. (2002) Balance and distribution of sulphur in volcanic ash derived soils in Chile. *Soil Biology and Biochemistry*, **34**, 1355–1361.

Armas-Espinel, S., Hernández-Moreno, J.M., Muñoz-Carpena, R., & Regalado, C.M. (2003) Physical properties of 'sorriba'-cultivated volcanic soils from Tenerife in relation to andic diagnostic parameters. *Geoderma* **117**, 297–311.

Borie, G., Peirano, P., Zumino, H., & Aguilera, S.M. (2002) N-pool in volcanic ash-derived soils in Chile and its changes in deforested sites. *Soil Biology and Biochemistry*, **34**, 1201–206.

DIN 18123 (1983) Untersuchung von Bodenproben – Korngrößenverteilung.

DIN 18127 (1993) Versuche und Versuchsgeräte – Proctorversuch.

DIN 18130 (1989) Versuche und Versuchsgeräte – Bestimmung der Wasserdurchlässigkeit, Laborversuche.

DIN 4022 (1991) Benennen und Beschreiben von Boden und Fels (Teil 1).

DIN EN 12879 (2001) Charakterisierung von Schlämmen – Bestimmung des Glühverlustes der Trockenmasse.

DIN ISO 11260 (1997) Bestimmung der effektiven Kationenaustauschkapazität und der Basensättigung unter Verwendung von Bariumchloridlösung.

Dubroeucq, D., Geissert, D., Barois, I., & Ledru, M.P. (2002) Biological and mineralogical features of andisols in the Mexican volcanic highlands. *Catena*, **49**, 183–202.

DVO-Deponieverordnung (2000) *Verordnung des Bundesministers für Umwelt über Ablagerung von Abfällen*, BGB1 1996/164, Kodex Abfallrecht, Austria.

EN 12176 (1998) Bestimmung des pH-Werts in Schlämmen.

Gottardi, G. & Galli, E. (1985) *Natural Zeolites*. Springer-Verlag, Berlin, Heidelberg, Germany.

Hay, R.L. & Sheppard, R.A. (2001) Occurrence of zeolites in sedimentary rocks: An overview. In: Bish, D.L. & Ming, D.W. (eds.), *Reviews in Mineralogy and Geochemistry Vol. 45, Natural Zeolites: Occurrence, Properties, Applications*, pp. 217–234. Mineral Society of America.

Hillel, D. (1998) *Environmental Soil Physics*. Academic Press, San Diego, CA, USA.

Holzlöhner, U., Meggyes, T., & Seeger, S. (1999) Landfill technology in Germany. *Land Contamination and Reclamation*, **7**, 109–119.

Joergensen, R.G. & Castillo, X. (2001) Interrelationships between microbial and soil properties in young volcanic ash soils of Nicaragua. *Soil Biology and Biochemistry* **33**, 1581–1589.

Jongmans, A.G., Verburg, P., Nieuwenhuyse, A., & van Oort, F. (1995) Allophane, imogolite and gibbsite in coatings in a Costa Rican andisol. *Geoderma* **64**, 327–342.

Kaya, A. & Durukan, S. (2004) Utilization of bentonite-embedded zeolite as clay liner. *Applied Clay Science* **25**, 83–91.

Kenney, T.C., Van Veen, W.A., Swailow, M.A., & Sungalia, M.A. (1992) Hydraulic conductivity of compacted bentonite-sand mixtures. *Canadian Geotechnical Journal*, **29**, 638–649.

Kugler, H., Ottner, F., Froeschl, H., Adamkova, R., & Schwaighofer, B. (2002) Retention of inorganic pollutants in clayey base sealings of municipal landfills. *Applied Clay Science*, **21**, 45–58.

Madeira, M., Auxtero, E., & Sousa, E. (2003) Cation and anion exchange properties of andisols from the Azores, Portugal, as determined by the compulsive exchange and the ammonium acetate methods. *Geoderma*, **117**, 225–241.

Mimides, T. & Perraki, T. (2000) Evaluation of the attenuating properties of selected Greek clays for toxic inorganic elements in landfill sites. *The Science of the Total Environment*, **253**, 1–13.

Mora, M.L., Escudey, M., & Galindo, G. (1994) Síntesis y caracterización de suelos alofánicos. *Boletín de la Sociedad Chilena de Química*, **39**, 237–243.

Navia, R., Levet, L., Mora, M.L., Vidal, G., & Diez, M.C. (2003) Allophanic soil adsorption system as a bleached Kraft mill aerobic effluent post-treatment. *Water, Air and Soil Pollution*, **148**, 323–333.

Navia, R. (2004) *Environmental Use of Volcanic Soil as Natural Adsorption Material*. PhD Thesis, Department of Sustainable Waste Management and Technology, University of Leoben, Austria.

ÖNORM EN 13137 (2001) Charakterisierung von Abfall; Bestimmung des gesamten organischen Kohlenstoffs (TOC) in Abfall, Schlämmen und Sedimenten.

Pavlov, P., Navia, R., Draganov, L., & Lorber, K.E. (2002) Chemische Stabilität von Abfallteer und mögliche Anwendung als Dichtungsschich-

tkomponente von Deponien. *Berg- und Hüttenmännische Monatshefte*, **147**, 370–372.

Prinz, H. (1997) *Abriss der Ingenieurgeologie*. Ferdinand Elke Verlag, Stuttgart, Germany.

Roehl, K.E. & Czurda, K. (1998) Diffusion and solid speciation of Cd and Pb clay liners. *Applied Clay Science*, **12**, 387–402.

Rowell, D.L. (1994) *Bodenkunde - Untersuchungsmethoden und ihre Anwendungen*. 1. Auflage, Springer Verlag, Berlin, Germany.

Scheffer, F. & Schachtsschabel, P. (2002) *Lehrbuch der Bodenkunde*. 15. Auflage, Spektrum Akademischer Verlag, Heidelberg, Germany.

Schöffmann, E. (2004) *Geologisch-mineralogische Characterisierung einer Vulkanerde aus Chile zur umwelttechnischen Bewertung*. Diplomarbeit, Institut für Prospektion und Angewandte Sedimentologie, Montanuniversität Leoben, Austria.

Tuncan, A., Tuncan, M., Koyuncu, H., & Yucel, G. (2003) Use of natural zeolites as a landfill liner. *Waste Management and Research*, **21**, 54–61.