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Chronosequence of Technosols at the Peña Colorada mine in Colima, Mexico: a short-term remediation alternative

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Abstract

Purpose The objective of this study was to examine the pedogenetic evolution occurring in technic hard materials from an iron mine through the characterization of a chronosequence of 0-, 15-, and 40-year-old Technosols and an older natural soil.

Materials and methods Samples were taken from Technosols of different ages (0, 15, 40 years) which had developed after a layer of crushed conglomerate was placed over the top of the mine tailings, as well as from a natural soil developed on conglomerate which represented the most advanced evolutionary stage in the chronosequence. Analyses of soil micromorphological, physical, chemical, and mineralogical properties included grain size distribution; pH; electric conductivity (EC); organic matter; exchangeable bases; N-NO_3; available P, Fe, Zn, Mn, Cu, and B micronutrients; and clay mineralogy (by X-ray diffraction).

Results Results showed that 15- and 40-year-old Technosols already displayed an advanced structural development and nutrient contents comparable to those in the studied natural soil. Such a rapid pedogenesis was due to the high clay content found within the conglomerates which can be easily incorporated into the soil and reordered within the soil groundmass. The tailings were characterized by a neutral pH (6.9) and a high EC (0.188 S m^{-1}), which decreased in the upper horizons of the 15-year-old Technosols, conforming thionic horizons. Generally, similar clay mineral assemblages dominated by smectite were observed in the conglomerate, the natural soil, and the 40-year-old Technosol.

Conclusion This study confirms the possibility of rehabilitating iron mine tailings with a layer of conglomerate, which mitigates against the adverse effects of mining. Results showed that the conglomerate can easily evolve into a soil within a relatively short period. However, the conglomerate cover should be thick enough to avoid acidification of the topsoil.

Keywords Technosols · Mining · Chronosequence · Pedogenesis · Hydrothermalism · High clay content

1 Introduction

In many cases, the improper use of natural resources has led to their degradation. Soil is a slow-developing resource with natural formation rates in the order of 10^2 to 10^6 years (Targulian and Krasilnikov 2007, being classified as a non-renewable resource on a human life scale (Doran 2002; Blum 2005). That is why there is a need to stimulate soil formation within deteriorated areas and studies have focused on generating suitable soil-forming substrates and evaluating their effects on the environment (Huot et al. 2013; Rodríguez-Vila et al. 2017; Lomaglio et al. 2017). Such substrates designed to support natural soil functions are made of technic materials such as trash, urban waste, concrete, landfill, sludge, slag or mine rock, and ashes which have properties that differ from those of natural materials (IUSS Working Group WRB 2015). Due to the high number of studies and direct and indirect attempts to understand soil formation on man-made substrates, the World Reference Base for Soil Resources (WRB) has included the Technosols group, whose properties and

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pedogenesis are dominated by materials of technical origin or that are sealed by a technic hard material (IUSS Working Group WRB 2015).

One aspect that draws the attention of specialists is related to the treatment and recovery of areas that have been affected or contaminated by mining activity (Kuter et al. 2014; Toktar et al. 2016). Here, Technosols can have a very important role in mitigating the effects of potentially toxic elements (PTEs) (Huot et al. 2015; Ahirwal and Maiti 2018; Krechetov et al. 2019; Santos et al. 2019). Another relevant aspect in the use of Technosols in areas affected by mining activity is their potential long-term effects, given the pedogenetic trends that these technic materials follow once they have been adapted to environmental conditions. These include the organic matter dynamics and its effects on biological activity, the development of porosity and soil structure, changes in pH and element mobility, and the weathering of minerals (Daniell and Van-Deventer 2018). This problem has been addressed by Watteau et al. (2018), who studied the micromorphological changes in a Technosol with man-made materials (such as sludge from the iron and steel industry) abandoned for a 60 year-long period. In addition, Ahirwal and Maiti (2018) evaluated the effect of revegetation on carbon storage in degraded coal mining sites and calculated an improvement of 33% after 16 years. These studies show the importance of the subsequent Technosol transformation and management. Studies of mining site soil chronosequences have proved to be an adequate approach for tracing the evolution of pedogenic and biotic processes as well as soil quality and carbon sequestration dynamics at yearly to decadal timescales (Akala and Lal 2000; Frouz et al. 2001; Scalenghe and Ferraris 2009; Zhao et al. 2013; Uzarowicz 2013; Mukhopadhyay et al. 2014).

The Peña Colorada mine in Mexico has extracted iron oxides (magnetite) since 1975 and has left vast tracts of land with tailings dams of varying ages. This situation inspired this research, since those dams have been remediated with surrounding materials. In particular, the Guasimas dam was built up over several stages and covered with hydrothermalized conglomerates of volcanic origin taken from Cerro León Dormido. The earliest fill is 40 years old, and the subsequent fill is 15 years old. They both represent the company's successful rehabilitation efforts. However, there were no follow-up studies on the pedogenic changes in these materials, and interactions between these conglomerates and the substrate (tailings dam). Therefore, this research aimed to evaluate the degrees of development of the Technosols, to assess their physicochemical properties that allow for the establishment of stable vegetation, and to identify the perspective of pedogenetic evolution.

2 Materials and methods

2.1 Study area

The Peña Colorada mine is located in the extreme northwest of the state of Colima, in the municipality of Minatitlán; 19°23′18″N and 104°02′51″W and 1200 masl (Corona et al. 2009). The iron deposits extracted at this mine are from the Upper Cretaceous-Middle Paleocene (Tritlla et al. 2003) and form part of the Sierra del Mamey within the sub-province of the ranges of the Sierra Madre del Sur. The rocks containing the iron mineral bodies belong to the Tepalcatepec Formation (Albian-Cenomanian) and the conglomerates of the Cerro la Vieja Formation (Tritlla et al. 2003; Corona and Henríquez 2004). The Tepalcaltepec Formation consists of a volcanic-sedimentary sequence (andesites, limestones, sandstones, tuffs, and limolites), which underlies strongly cemented, polymictic conglomerates, green in the base, and red in the top, of the Cerro la Vieja Formation (Tritlla et al. 2003). These two formations are intruded by Late Cretaceous diorites and gabbros. The origin of the Fe-mineralization has been associated to a multi-stage, skarn-related, magmatic-hydrothermal process (Zürcher et al. 2001; Tritlla et al. 2003; Camprubí and Canet 2009; Camprubí et al. 2018). The ore is mainly constituted of magnetite (more than 85%) and, to a lesser degree, martite, hematite, chlorite, pyroxene, and carbonates; its main mineral is pyrite, with lower proportions of chalcopyrite.

The region is characterized by a semi-warm, sub-humid climate with rainy summers. Average precipitation over the past 10 years in the Minatitlán region falls between June and October with a total average of 1604 mm and an average temperature of 26.3 °C (CONAGUA 2019).

The dominant species in the semi-deciduous medium-dry forest are *Rosimum alicastrum*, *Annona purpurea*, *Ficus insípida*, *Bursera grandifolia*, *Enterolobium ciclocarpum*, *Sloanea terniflora*, and *Sapium pedicellatum*. In the low deciduous forest, the dominant species are *Ficus insipida*, *Annona purpurea*, *Enterolobium ciclocarpum*, *Psidium sartorianum*, and *Guazuma ulmifolia* Rzedowski (2006).

2.2 Sampling

Sampling was based on the fill ages in the Guasimas dam located at the Peña Colorada mine. It is important to note that the fill was made with hydrothermalized conglomerate from Cerro León Dormido (identified as the conglomerate of the Cerro la Vieja formation). The ages of the sites were calculated starting from the time when the conglomerate fills were applied, according to technical maintenance reports, and validated by estimating the height of the trees that developed on the Technosols. This led us to select two sampling areas: one within the 40-year-old fill and the other within the 15-year-old fill. In addition, to complete the chronosequence, hydrothermalized conglomerate and tailings dam material, which both represented Age 0, were also sampled (Fig. 1). The natural soil that developed on the conglomerate (pedogenic evolution over several thousand years) was considered as the chronosequence's final point.

The 15-year-old Technosol profiles were in the southeast section of the mine above the dam curtain (Fig. 2). As a part of restoration work, this site had been planted with deciduous species from the semi-arid zone, such as *Acacia farnesiana* and *Pithecellobium dulce*. The fill was divided into Section A and Section B, according to their position on the slope; thus, two 15-year-old profiles were studied. The 40-year-old Technosol profile was located in the northeast section of the mine at the curtain base.

The soil profiles and technic materials were described following the criteria of the World Reference Base (IUSS Working Group WRB 2015). Sampling was undertaken in each horizon and layer, taking two types of samples: one in a polyethylene bag for physicochemical analyses and the other in aluminum foil and polyethylene containers for micromorphological analysis.

2.3 Micromorphological and physicochemical characterization

Undisturbed samples were used for the preparations of thin sections at the Institute of Geology (UNAM), where they were dehydrated at 40 °C for 3 days and underwent vacuum impregnation at 24 micro-atmospheres. Polyester resin was used as a consolidation agent. Once the sample was consolidated, it was cut and polished to a thickness of 30 µm. The micromorphological analysis was performed at the Microscope Laboratory in the Department of Environmental Science and Soils in the Institute of Geology, using an Olympus BX51 microscope. The image acquisition and the micromorphological analysis were done using Image Pro Plus 7.0 software. The observations were made using plane polarized light (PPL), crossed polarized light (XPL) and reflected light (RL) which helps to discriminate the Fe oxide minerals. The descriptions were based on the criteria established by Stoops (2001) and Loaiza et al. (2015).

For the physical and chemical analyses, the samples were air-dried and sieved through a #10 mesh (2-mm aperture). The grain size distribution was determined using the pipette method according to Dane and Topp (2002). The pH and electrical conductivity were measured in a 1:2.5 soil: water suspension in all sampled materials.

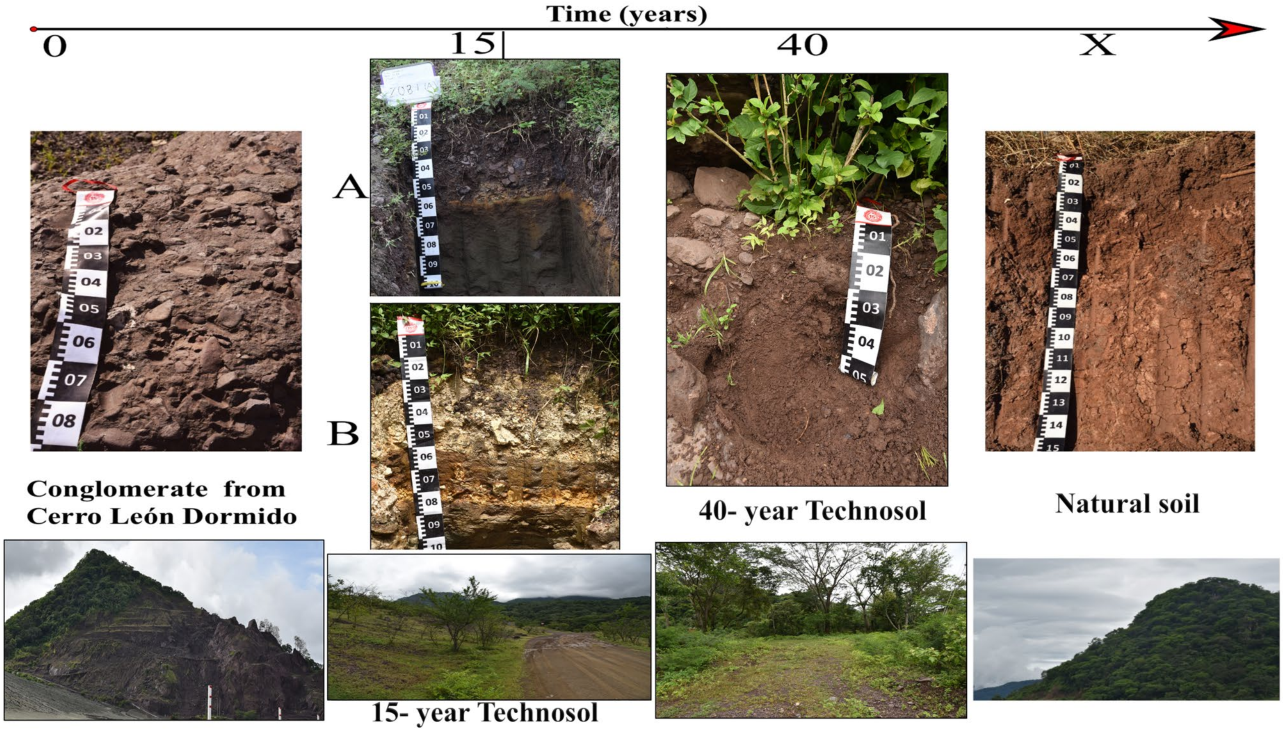

Fig. 1 View of the soil profiles and landscape at the Peña Colorada mine, following the timeline from 0 to several thousand years. Letters A and B denote the two studied sections for the 15-year-old Technosols

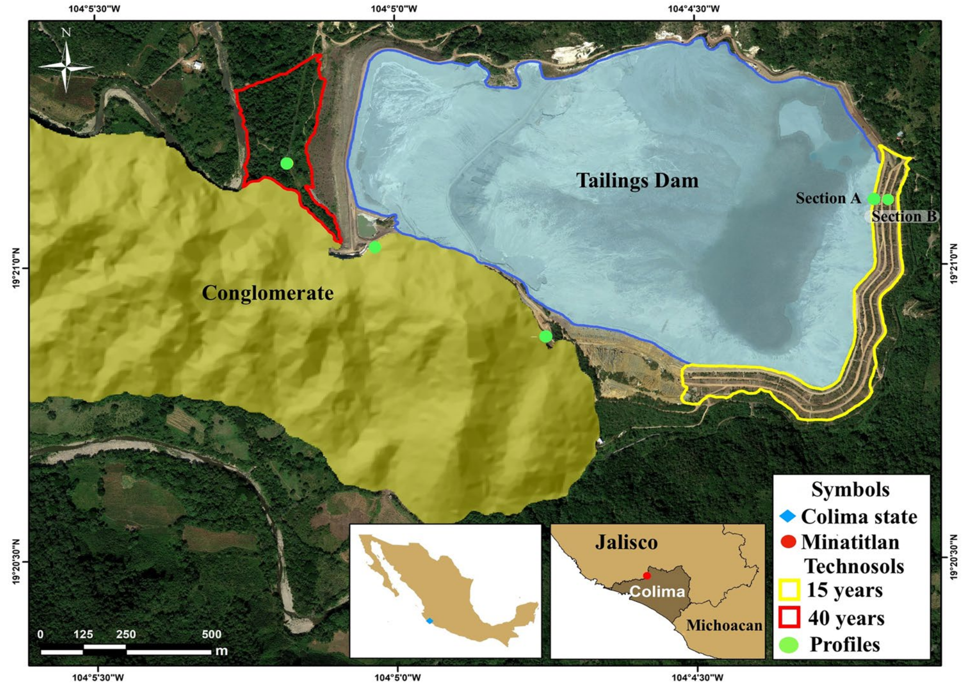

Fig. 2 View of the landscape at the Peña Colorada mine showing the technogenic, lithological, and pedological areas

Some chemical parameters, interpreted as soil quality indicators, were evaluated only in the surface horizons of the studied profiles and technic materials. These analyses were performed at the INIFAP-Celaya laboratory, certified by Standard ISO 9001:2008, NMX-CC-9001-IMNC-2008. The determinations included the following: soil organic matter using the Walkley and Black wet oxidation method; N-$N0_3$ using colorimetry; available P- through the Bray and Kurtz method; the exchangeable bases (K, Ca, Mg, Na) were calculated using extraction with ammonium acetate, and the Fe, Zn, Mn, Cu, and B micronutrients through extraction with DTPA-Sorbitol at pH 7.

2.4 Mineralogical composition of the clay fraction

We selected three samples for clay fraction extraction and mineralogical composition analysis. The samples included the conglomerate from Cerro Leon Dormido and the A horizons of 2 profiles: the natural soil developed on conglomerate and the 40-year-old Technosol. Clay fraction (< 2 μm) was separated by gravity sedimentation in the samples dispersed in distilled water. X-ray diffraction patterns were obtained using an EMPYREAN XRD diffractometer operating with an accelerating voltage of 45 kV and a filament current of 40 mA, using CuKα radiation, nickel filter, and PIXcel 3D detector. For each sample, 3 oriented specimens were analyzed: air-dried (AD), saturated with ethylenglycol (EG) and after heating at 550 °C. Qualitative identification of the most abundant clay minerals was based on the positions of basal diagnostic peaks.

3 Results

3.1 Morphological and physicochemical characterization of Technosols and technic materials (conglomerate and tailings dam sediment)

3.1.1 Conglomerate from the Cerro León Dormido, age 0 years (Fig. 1)

The conglomerate that outcrops within the mine area was used to fill in the tailings dam (Table 1). The sampling site is located at 19°20′52.39″N and 104° 5′4.65″W (Fig. 2). The laboratory analysis revealed a high proportion of sand (78%) and a low clay content (< 10%), a slightly acid pH and a low electric conductivity (EC) (Table 2). The organic matter (OM) content is very low (< 0.03%). The concentrations of macronutrients (Mg, Ca, Na, K, and P) are high, but there are micronutrient deficiencies (Table 2).

3.1.2 Tailing sediment in the Guasimas dam, age 0 years

The sediment found at the dam surface has a gray-brownish color. Its texture is loamy sand (> 80% sand) with a low proportion of clay. The pH is neutral (6.9), but the EC reaches 0.188 S m^{-1} (Table 2). These sediments have low contents of all nutrients, except for sulfur and calcium with concentrations of 2424.0 and 5187.0 mg kg^{-1}, respectively, being the highest in all studied materials.

Table 1 Morphological characteristics of the studied materials

Sampling site	Site description	Residue type	Description	Age years
Cerro León Dormido	Hill	Rock	Conglomerates are mainly constituted by andesitic rocks with evidence of hydrothermal alteration. The color is dominantly grayish red, but there are areas with greenish and more grayish color	0
Guasimas Dam	Tailings dam	Sediments	Superficial sediments with gray-brownish color. The texture is loamy sand with a low proportion of clay	0
Technosol, Section A	The northeast curtain of the tailings dam	Soil formed on the conglomerate and tailings dam	The Technosol is constituted by A-2Bw-2C horizons: A horizon (0–55 cm) presents abundant fine to medium roots, subangular blocky structure, abundant fragments of weathered rocks (> 50%), and sandy loam texture. It has an abrupt contact with the lower horizon. The 2Bw horizon (55–65 cm) is yellow-orange, sand, massive, and cemented. The 2C horizon (> 65 cm) is a grayish-green tailings sediment, with sand texture, structureless and very loose, and laminated	15
Technosol, Section B	The northeast curtain of the tailings dam	Conglomerate and tailings dam	The Technosol is constituted by AC-C-2Bw-2C horizons. AC horizon (0–20 cm) presents abundant fine roots, with subangular blocky structure that breaks into granular, with abundant fragments of weathered rocks, the texture is sandy loam. It has abrupt contact with the underlying C horizon (20–50 cm), which is a loam regolith that is yellowish-white, and contains fragments of saprolites from 1 to 15 cm. The 2Bw horizon (50–75 cm) presents a yellow-orange coloring, with a sandy loam texture and is cemented. The 2C horizon (> 75 cm) is dark gray tailings with a sandy loam texture, and laminations are observed	15
40-year Technosol	At the edge of the tailings dam	Conglomerate and tailings dam	The Technosol is constituted by A–C horizons The A horizon (0 to 10 cm) is dark reddish-brown with abundant fine and medium roots. It presents rounded rock fragments up to 10 cm and rock fragments with angular shapes. The texture is sandy clay loam with a subangular blocky structure that breaks into granular. The first 5 cm are compacted; the following 5–10 cm show abundant vesicular and tubular pores with evidence of high biological activity in the shape of termite and ant galleries. The transition to the lower horizon C is gradual. It has a reddish-brown color and includes rounded and angular rock fragments measuring up to 10 cm. The texture is sandy loam with a subangular blocky structure where abundant vesicular and tubular pores are observed	40
Natural soil	At the Cerro León Dormido	Soil developed on conglomerate	The Ap horizon (0–30 cm) has subangular blocky structures that are very firm. The texture is clay loam, with a reddish-brown color and rock fragments smaller than 1 cm. There is a tubular porosity and the presence of medium and thick roots. The roots have a horizontal development at 30 cm, due to the compaction of the underlying horizon. The BC horizon (30–80 cm) has a subangular blocky structure that is very firm with a prismatic structural trend. It has a reddish color with brown specks. The texture is clay loam and has light-gray zones associated with weathered rock fragments. The C horizon (80–170 cm) shows dark rock fragments, which are covered by a reddish patina. The fine material has a clay loam texture	Nd

Nd not determined

Table 2 Physico-chemical and mineralogical properties of the sediments and the different age Technosols

Horizon	Sand	Silt	Clay	pH	EC	OM	Fe	Al	Zn	Cu	B	Mn	S	Ca	Mg	Na	K	$N\text{-}NO_3$	P-Bray
	%			1:2.5	S m^{-1}	%	mg kg^{-1}												
Ap	30.2	36.1	33.6	6.7	0.0140	3.60	32.5	ND	0.8	1.5	0.3	36.1	1.4	3644	377.0	32.2	158.0	6.7	14.5
BC	28.5	32.2	39.2	6.9	0.0060	nd													
C	29.5	39.7	30.8	6.8	0.0070														
A	64.1	24.7	11.2	3.5	0.0530	0.30	15.1	182	1.18	4.3	0.3	75.9	624.0	2717	465.0	25.5	34.0	3.86	41
2Bw	77.2	15.2	7.6	2.3	0.0004														
2C	84.1	9.9	6.0	7.0	0.1880														
A	66.7	15.7	17.6	5.1	0.0110	4.10	97.8	165	2.23	7.6	0.3	28.7	52.3	1757	535.0	15.6	38.0	70.8	32.8
C	46.0	38.8	15.2	4.4	0.0120														
2Bw	57.4	24.4	18.2	4.1	0.0400														
2C	66.7	28.1	5.2	6.7	0.2560														
A	61.8	7.3	30.9	7.2	0.0370	4.70	50.0	ND	0.65	2.4	0.6	30.5	ND	5238	1431.6	34.0	159.8	0	27.6
AC	65.8	20.6	13.6	6.3	0.0070														
C	78.3	14.1	7.6	6.3	0.0020	0.02	11.8	ND	0.28	0.1	0.1	18.55	ND	2138	968.1	74.9	44.5	0	15.1
C	84.1	9.9	6.0	6.9	0.188	0.03	9.74	ND	0.66	7.6	0.3	2.42	2424	5187	52.6	27.2	72.4	18.2	3.13

EC electric conductivity, *OM* organic matter, *nd* not determined

Technosol, Section A, age 15 years (Fig. 1). This profile is located at the following coordinates: 19°21′9.5″ N and 104°4′10.25″ W, at an altitude of 668 masl (Fig. 2). This section is located in the northeast curtain of the tailings dam on a slope of 30–35°. The soil development began 15 years ago, after the conglomerate from Cerro León Dormido was laid down on these slopes. This Technosol is composed of the following horizons: A-2Bw-2C. The A horizon is a sandy loam with an extremely acid pH (3.5) and an EC of 0.053 S m^{-1}. The 2Bw and 2C horizons have a similar texture (sand). The 2Bw horizon is the most acid with a value of 2.3, but the EC value is very low with 0.0004 S m^{-1}. The underlying 2C horizon has the pH value of 7 and the EC of 0.188 S m^{-1}. The percentage of OM in the A horizon is very low, but the concentrations of macro- and micronutrients are high, with the highest value of P (41 mg kg^{-1}). However, the $N\text{-}NO_3$, K, and Fe contents are very low (Table 2). This profile has been classified as Leptic Spolic Technosol.

The 15-year Technosol, Section B (Fig. 1). This profile is located at the following coordinates: 19°21′9.5″ N and 104°5′10.28″ W, at an altitude of 637 masl, in the northeast tailings dam curtain (Fig. 2). The restoration that took place at this site is similar to the one in Section A. This profile consists of the following horizons: AC-C-2Bw-2C. The AC horizon has a sandy loam texture; it has a pH of 5.1 and the EC value of 0.011 S m^{-1}. The C horizon is loam with the pH of 4.4 and the EC of 0.012 S m^{-1} (Table 2). The 2Bw horizon is sandy loam, more acid (4.1), with an increased EC (0.040 S m^{-1}). The 2C horizon has a sandy loam texture and has a neutral reaction (6.7), but the EC value (0.256 S m^{-1}) is the highest of all studied soils. The A horizon of this Technosol in Section B shows significant increases in OM, $N\text{-}NO_3$, and in macro- and micronutrients, except for P, in comparison to the Section A. This profile is classified as Leptic Spolic Technosol.

The 40-year Technosols profile is the oldest and most developed within the study area and support the of abundant tree growth (Fig. 1). It should be noted that the filling used in the construction of these Technosols was more than 1 m in thickness. The studied profile was located at the following coordinates: 19°21′2.62″ N and 104°5′5.92″ W, at an altitude of 650 masl, at the edge of the tailings dam (Fig. 2). This Technosol is composed of A-AC horizons. The A horizon has a sandy clay loam texture, with a neutral pH (7.2) and an EC value of 0.037 S m^{-1}. The AC horizon (10 to 50 cm) is more silty (Table 2) and has a pH of 6.3 and a low EC value (0.007 S m^{-1}). The highest values (4.7%) of OM are found in the A horizon of this Technosol, with high proportions of Ca, Na, Mg, and K. However, it shows deficiencies in $N\text{-}NO_3$, P, S, and B (Table 2). The soil was classified as a Leptic spolic Technosol.

The natural soil (Fig. 1) is located at Cerro León Dormido at the following coordinates: 19°20′38.19″N and 104° 5′0.73″ W at an altitude of 627 masl (Fig. 2). This profile consists of the following horizons: Ap-BC-C. The natural soil has a clay loam texture and nearly neutral pH values throughout the profile (Table 2); in terms of electrical conductivity, the highest value of 0.014 S m^{-1} was observed in the surface A horizon. This horizon shows high values of OM and adequate concentrations of nearly all the micro and macro elements, although it shows clear deficiencies in N-NO_3, P, S, and B (Table 2). This soil is classified as Leptic Stagnic Cambisol.

3.2 Micromorphological features developed in the Technosols

To understand the modifications of the Technosols within this chronosequence, it is necessary to identify the properties of the original materials: the tailings and the conglomerate, and to compare these with those observed in the Technosols of different ages.

The conglomerate-C horizon is constituted by rock fragments with plagioclases which are coated with iron oxyhydroxides and clay (Fig. 3a). There are also saprolite fragments, showing a high degree of alteration, evidenced by the near-total substitution of the primary minerals by fine clay material with ferruginous pigment (Fig. 3b).

In the tailings-C horizon, a very fine and homogenous groundmass is observed, with fragments of primary carbonates (Fig. 4a), neoformed gypsum within the groundmass (Fig. 4b), and fresh primary minerals combined with iron oxyhydroxide fragments (Fig. 4c). These iron oxyhydroxides also impregnate and cement the groundmass of the 2Bw horizons of the 15-year Technosol (Fig. 4d). In turn, the A horizon of the 15-year Technosol shows plant remains at various stages of decomposition, with rounded, fresh rock fragments (Fig. 5a). An incipient aggregation is observed in the form of dark pellets (Fig. 5b). In addition to the formation of granular aggregates, there are also areas of moderately developed subangular blocky structure impregnated with organic matter (Fig. 5d).

The AC horizon of the 40-year Technosol shows a formation of subangular aggregates (Fig. 6a), with root remains in the pores (Fig. 6b). Those aggregates have thick coatings of iron oxyhydroxides and clay (Fig. 6c) and oxide impregnation in the groundmass (Fig. 6d).

Finally, the natural soil-BC horizon has a more developed angular blocky structure with a fine groundmass (Fig. 7a). The blocks are surrounded with oriented clay, with a porostriated b-fabric pattern (Fig. 7b). In the Ap horizon, an intense biogenic activity is evidenced by the abundance of charcoal fragments (Fig. 7c) and coprolites in pores (Fig. 7d).

3.3 Clay mineral composition

The clay fraction of the Cerro Leon Dormido conglomerate is completely dominated by only one mineral: well crystallised smectite. It produced a strong maximum at ~ 1.4 nm in the air-dry specimen which shifted to ~ 1.6 nm on glicolation and shrinked to 1 nm after heating. The possible presence of kaolinite is indicated by a modest 0.7 nm peak, which completely disappears at 550 °C (Fig. 8a). The clay mineralogy of the A horizon of the natural soil resembles that of its parent material (conglomerate), with the dominant smectitic component being accompanied by minor amounts of kaolinite. The difference was shown in the configuration of the smectite peaks: they are much lower and broader, pointing to a weaker crystallinity of this component (Fig. 8b). In the clay fraction of the A horizon of the 40-year-old Technosol, the same two clay minerals are accompanied by illite, identified by the 1 nm maximum which stayed unchanged under all applied pre-treatments (Fig. 8c).

4 Discussion

The soils and current ecosystems of the technogenic landscape within the study area of the mine are developed on two prevalent materials, i.e., the mining tailings and the conglomerate from Cerro León Dormido. The latter has been used to construct Technosols on the top of the tailings. The features and properties of the profiles that formed upon these two types of materials indicate very distinct pedogenetic trends, controlled by their composition.

The mining tailings are little altered; they have a loamy sand texture and a high content of gypsum (Fig. 4b), primary minerals (plagioclases), and calcite (Fig. 4a), identified under the microscope. These gypsum neoformations are produced by the interaction between the primary calcium carbonates and the acidity generated by the oxidation of sulfide minerals (Santomartino and Webb 2007; Rivera-Uria et al. 2019). The soluble sulfates produced by this interaction account for an increase in the EC values, up to 0.188 S m^{-1}. In certain cases, such as the 2C horizon of the 15-year Technosol, it is as high as 0.2560 S m^{-1} (Table 2). However, the pH value in this horizon is still basic (7.9), due to the fact that primary carbonates have still not exhausted their capacity for acid neutralization. Observations of samples from the unmanaged tailings under the microscope showed hardly any structural development and a sandy groundmass of loose grains. This lack of structure is due to the absence of fine binding agents such as organic matter and mineral clay. In addition, the contents of nutrients, especially phosphorus, are very low (Table 2). Therefore, the brackish tailings have a low physical and chemical quality and do not have an adequate capacity to support plant development.

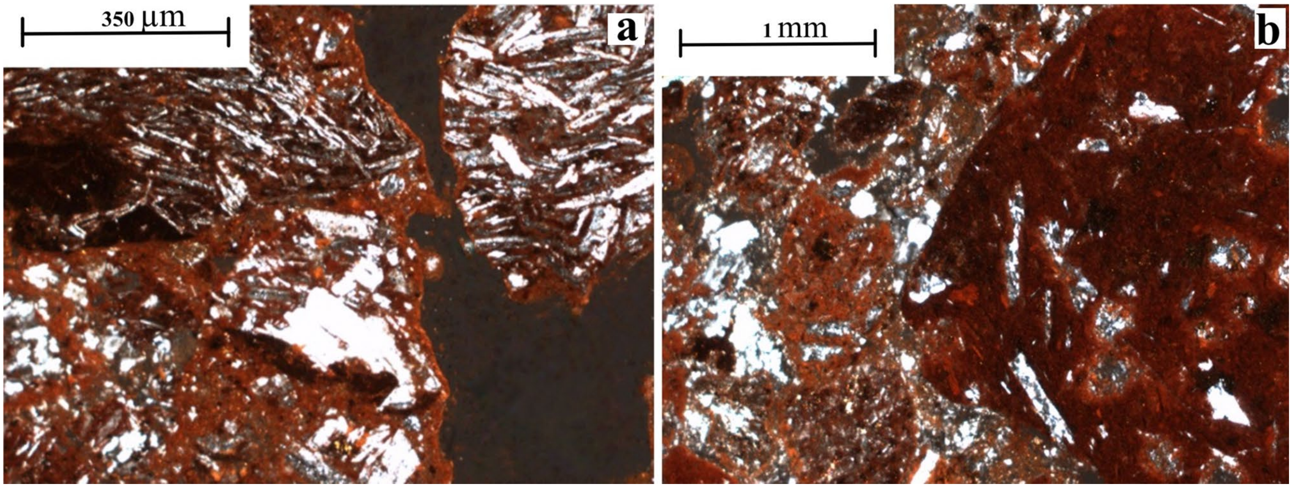

Fig. 3 Micromorphological features of the conglomerate-C horizon: **a** rock fragments with plagioclase minerals and a coating of iron oxyhydroxides and clay (XPL, RL); **b** saprolite fragments with a high degree of weathering (XPL, RL)

Pedogenetic evolution was observed in the rehabilitated tailings, especially, in the 2C horizon of the 15-year Technosol underlain by the tailing material. The results show that tailings exposed to weathering suffer oxidation of sulfide minerals generating rapidly a reduction in pH (down to 2.29). In addition, the thin section of the tailings shows cementation and coating of the sand grains by secondary products, formed by the same oxidation of the sulfide minerals such as iron oxyhydroxides and minerals from the jarosite group (Fig. 4d) (Nordstrom and Alpers 1999). Therefore, in the initial phase when the mining tailings have been freshly deposited, there are loose materials with the potential to support vegetation. However, once the tailings undergo weathering, oxidation, and cementing processes begin, which limits plant establishment. Consequently, the results obtained show that pedogenesis in the tailings produces substrates that are not very favorable for the development of plant cover. The tailings are characterized by a low physical and chemical quality, a lack of structure, and salination problems at the initial stage and an extreme acidity and cementation by iron-rich minerals (as observed in the 2Bw horizon) during the advanced stages (Fig. 4d). That is why, it is necessary to create artificial soils above the tailings using various materials. In this sense, the construction of a Technosol using the local rock from Cerro León Dormido has been successful.

In contrast to the mining tailings from the Guasimas dam, the natural pedogenesis on conglomerate within the undisturbed area has formed a fertile soil that has a clay loam texture, a high content of organic matter, and a moderate content of available phosphorus and N-NO_3 (Table 2). Its neutral pH and low EC indicate the absence of salinity problems. Its structure is well-developed at the macro- and micromorphological levels, indicating a high physical quality. These natural soil properties are beneficial for the development of deciduous forests in the region.

The upper layers of the 15-year-old Technosols derived from Cerro León Dormido conglomerates overlaying the tailings are similar to the natural soil, despite the short period of pedogenesis. The pH of the A horizon (Section B) is 5.1. In contrast, the Technosol of the same age in Section A has an extremely acid pH (3.5) due to the acidification resulting from oxidation of the underlying tailings, as mentioned previously. Its 2Bw horizon also has a very low pH value (2.2), which suggests that the acidification of the upper horizons in this profile is due to the ascent of acidic solutions by capillary action during the dry season. This process has also caused an increase in EC in 2C horizons in Sections A and B (0.188 and 0.256 S m^{-1}), due to the movement of soluble salts through the soil solution. However, all the other horizons have a low electrical conductivity, which do not indicate the salinization process. In contrast, in the 40-year Technosols, the pH of the technic material (AC horizon) remains stable, close to 6.3, which is similar to natural soil values.

Surprisingly, the highest values of available phosphorus were encountered in the 15-year-old Technosol, whereas 40-year Technosol and natural Cambisol showed lower values. The explanation of these differences is challenging, taking into account that the younger Technosols are quite acid, whereas the older Technosol and the natural soil both have a neutral reaction. It is commonly known that a slightly acid to near neutral soil medium is optimal for phosphorus availability (Lindsay 1979). However, Barrow (2017) argued for “a much lower pH optimum” for phosphorus uptake. Penn and Camberato (2019) considered dependency of the phosphorus availability upon pH as an interplay of various chemical mechanisms having sometimes opposite effects. Assuming that Al and Fe phosphates are the main forms of P precipitation in the acid soils, these authors state that on the one hand

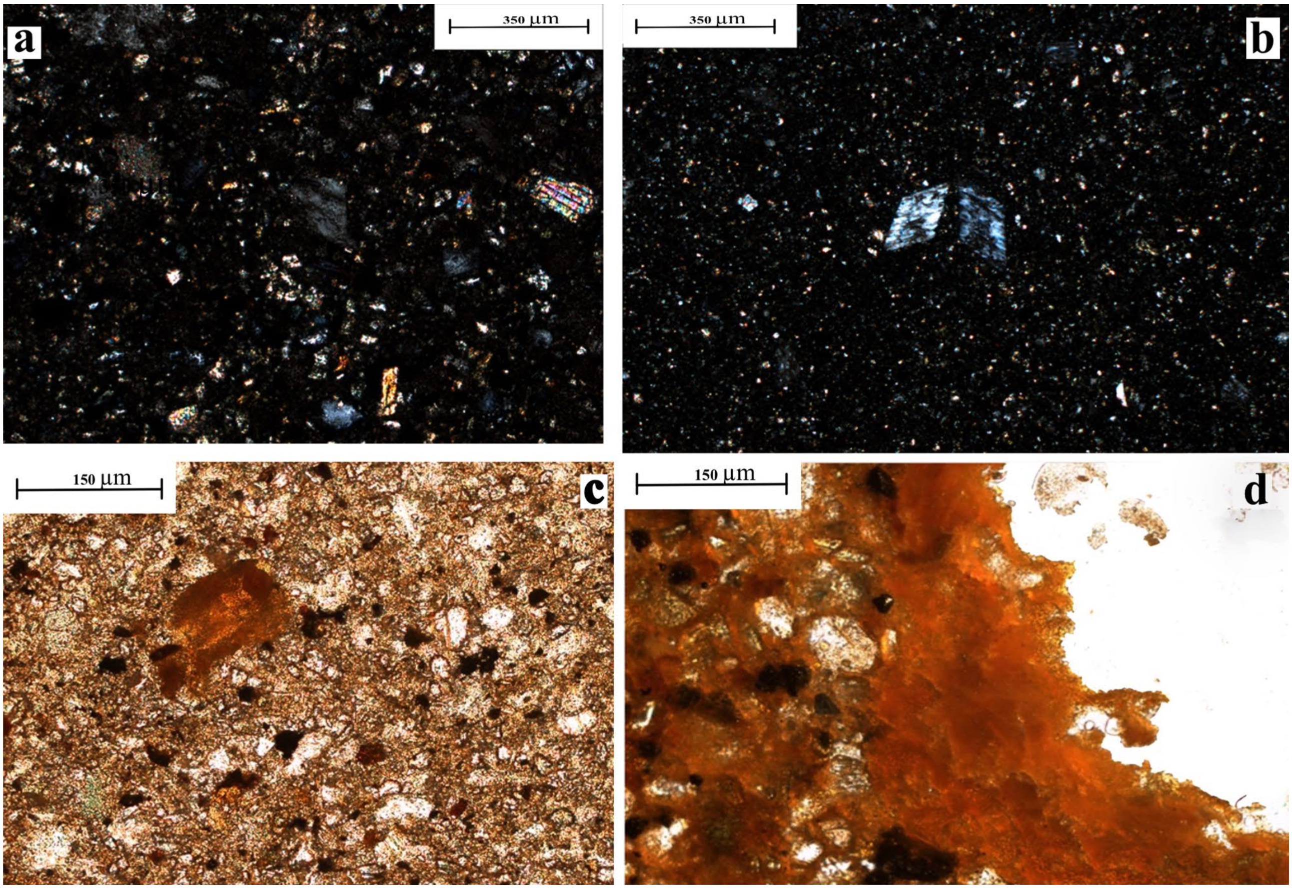

Fig. 4 Micromorphological features of the Tailings at the Guasimas dam; **a** primary carbonate fragments (XPL); **b** neoformed gypsum within the fine groundmass (XPL); **c** iron oxyhydroxide fragment (PPL); **d** iron oxyhydroxides coating and cementing the groundmass observed in the 2Bw horizon of the 15-year Technosol (PPL, RL)

lowering of pH supports dissolution of phosphates; however, on the other hand, it also increases dissolution of Al and Fe hydroxides, providing more Fe^{3+} and Al^{3+} cations for phosphate precipitation. The second mechanism could be more potent and result in an overall increase of phosphate precipitation in cases of abundant Al and Fe hydroxides (Penn and Camberato 2019). This could be valid for deeply weathered acid soils with high accumulations of secondary minerals, e.g., tropical ferrallitic soils. However, in our case, despite the presence of some hydrothermal ferruginous components, primary minerals still dominate in the soil matrix of Technosols. This is clearly indicated by the particle-size analysis, which shows the dominance of coarse (silt and especially sand) fractions. Under such conditions the phosphate dissolution due to the higher acidity could become more important and cause the increase of phosphorus availability.

Penn and Camberato (2019) highlighted one more important factor affecting phosphorus immobilization at low pH, i.e., "exchangeable Al^{3+} and Fe^{3+} must be able to enter the solution phase in order to precipitate with P." Conglomerate contributes smectites to the Technosols; these clay minerals are characterized by high cation exchange capacity and thus can provide exchangeable sites for Al^{3+} and Fe^{3+} ions deviating them from interaction with phosphate anions.

Finally, the amount of soil organic matter could also play an important role in phosphorus availability. Walker and Syers (1976) relying on the soil chronosequence studies stated that increases in organic/bound forms and related decreases in labile fraction of phosphorus take place during soil evolution. In the studied chronosequence, the young 15-year Technosol with maximum of available phosphorus (Section A) has the lowest organic carbon content. We speculate that in this case, soil organic matter has a very low capacity to retain phosphorus in the organic-bound form, and thus, a larger portion of this element could persist in the available fraction.

More detailed pedochemical research is needed to identify the particular reasons for the unusual phosphorus behavior in the Technosols of Peña Colorada.

The 40-year-old Technosol presents the highest structural development and a greater incorporation of organic matter in the soil groundmass; its nutrient properties are similar

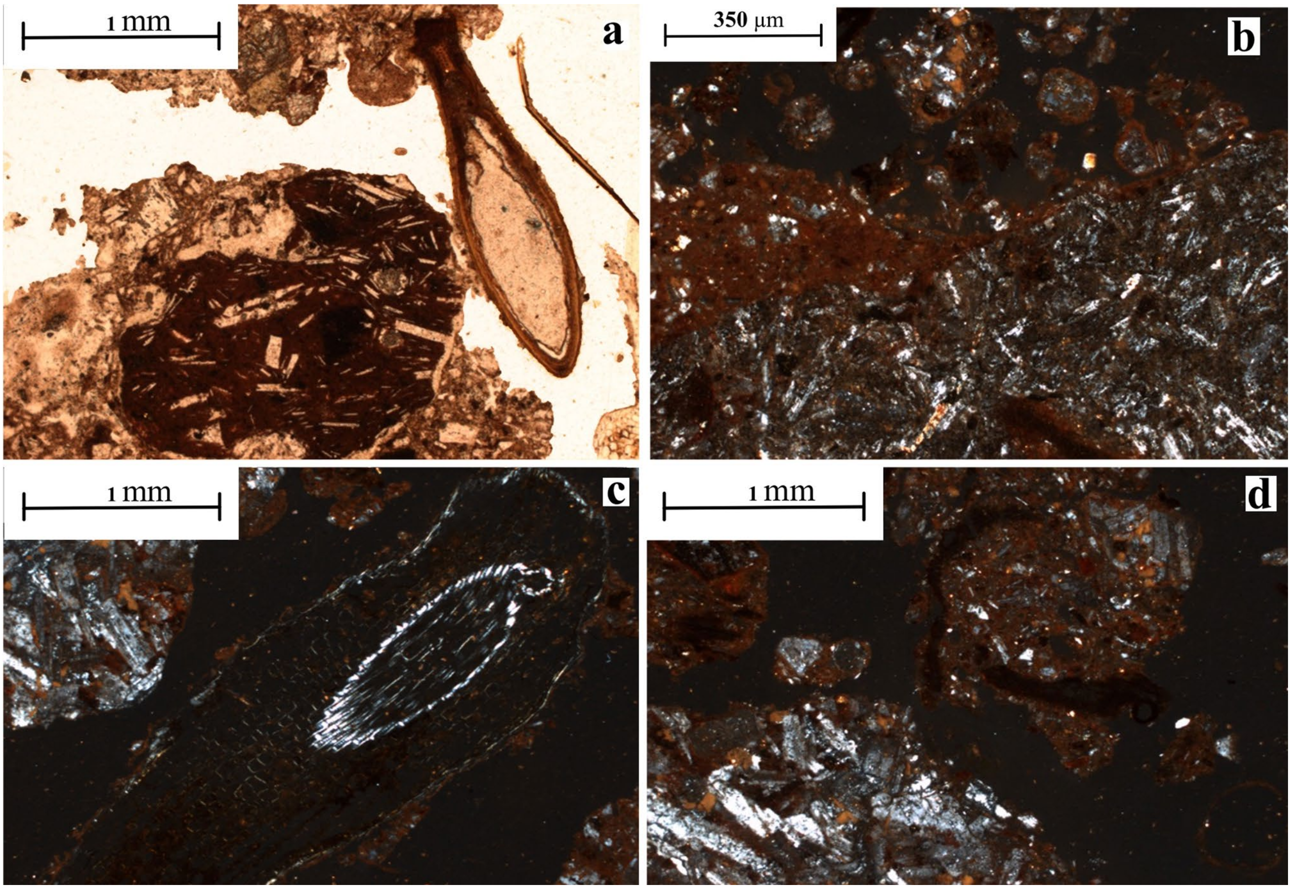

Fig. 5 Micromorphological features of the A horizons of the 15-year Technosol: **a** plant tissue in a pore (PPL); **b** formation of granular aggregates (XPL); **c** fresh root in a pore (XPL); **d** subangular aggregates with organic matter (XPL)

to those present in the natural soil at Cerro León Dormido. The macromorphological and micromorphological observations show a structural development, formed by the granular aggregates and subangular blocks (Fig. 6a, d).

It is assumed that to a large extent, the beneficial properties of the soils (both natural and artificial) derived from the conglomerate largely depend on the accumulation of fine mineral components such as clay, with moderate quantities of iron oxides. The clay content ranges from 11.2 to 17.6% in the Technosols in Sections A and B (Table 2), which exceed the value of 7.6% found in the recently extracted conglomerate (Fig. 5b). This indicates that a lot of clay was formed over the 15 years when the conglomerate material has been on the surface. Likewise, the silt shows a similar tendency as it increases from 14.1% in the conglomerate up to 24.7% in the Technosol in Section A. In contrast, the sand tends to drop from 78.3% in the recently extracted conglomerate to 66.1% and 64.1% in the Technosols. In fact, the A horizon from the 40-year-old Technosol has a clay content of 30.9%, similar to the C horizon from the natural soil at Cerro León Dormido, which has 30.8%. It should be noted that smectite is the dominant clay mineral in the fine fraction of A horizons in the natural soil and 40-year-old Technosol and it seems to be directly inherited from the conglomerate (Fig. 8). The smectite transformation in soil is limited to fragmentation, partial loss of crystallinity, and (probably) interaction with organic matter, which was detected from lowering and broadening of smectite diagnostic peaks in diffractograms. The smectite is known to be the most beneficial clay mineral for the soil biological quality, due to its high cation exchange capacity and its ability to interact with organic substances; the resulting organo-mineral compounds play an important role in soil aggregation. Illite present in the clay fraction of the 40-year-old Technosol could be derived from the micaceous component of tailing material mixed with the conglomerate during the Technosol construction.

The formation and accumulation of clay and iron oxides as products of chemical weathering is a common process within humid tropical forest ecosystems, where they reach the maximum rates of development (Coward et al. 2017). The speed at which clay accumulated in the studied Technosols is of special interest. In the 40-year profile, its content reached the values similar to those in of the natural soil.

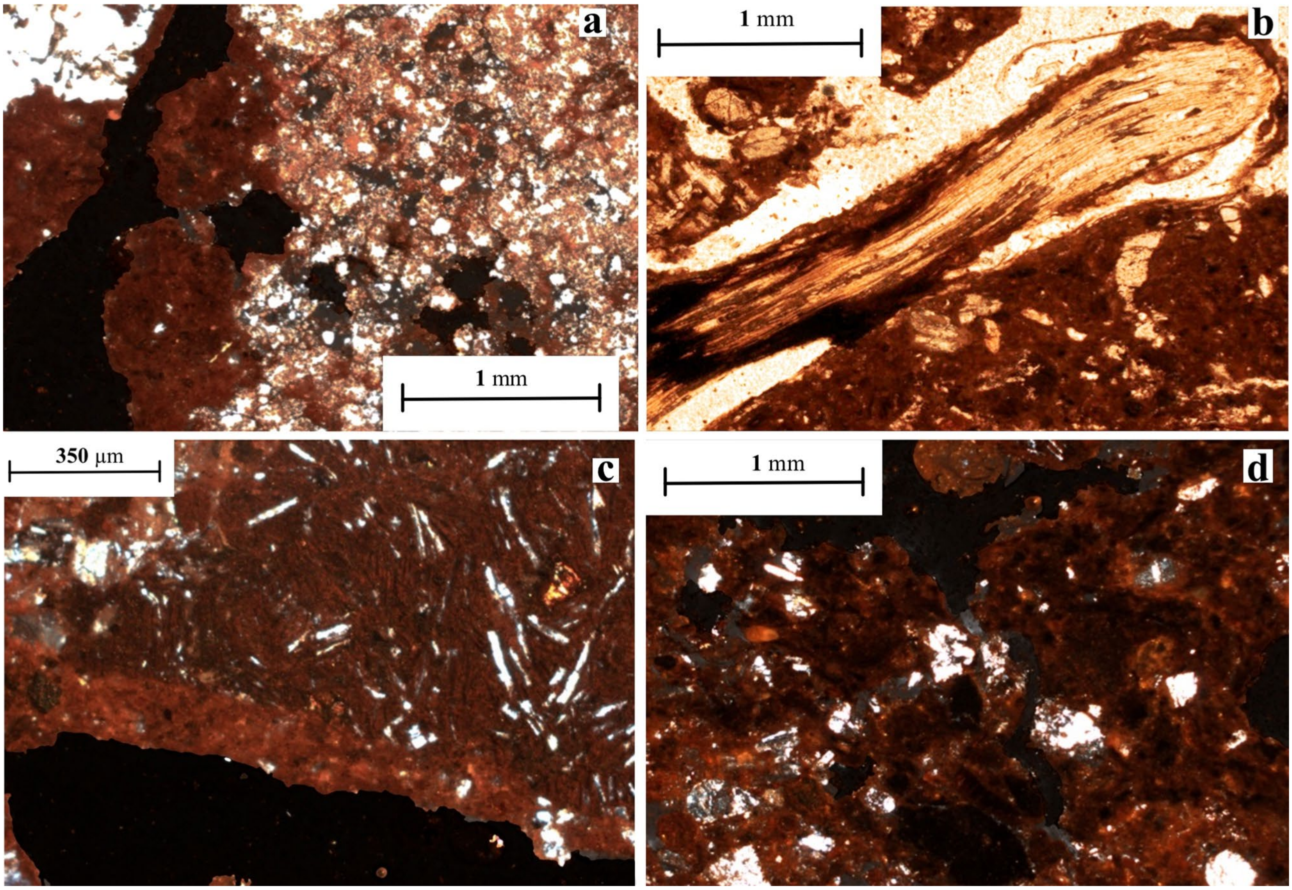

Fig. 6 Micromorphological features of the AC horizon of the 40-year Technosol: **a** aggregates with a subangular blocky structure (XPL); **b** root in a pore (PPL); **c** patina of iron oxyhydroxides and clay (XPL, RL); **d** subangular aggregates with organic matter (XPL, RL)

In the classification of pedogenetic processes, according to their characteristic speeds and times, the weathering producing clay components is between medium and slow processes; that is, its development requires between 1000 and 10,000 years (Targulian and Krasilnikov 2007) even under most favorable conditions of humid tropics.

The difference between clay contents in the 15-year Technosols and the conglomerate is due to the formation of aggregates and the presence of patinas around the clasts. This is interpreted as a reordering of the clay and silt, which form part of the active fraction of the soil. We assume that accumulation of clay and iron oxides promoted the stabilization of the organic matter in the organic-mineral compounds. Thus, in the 40-year Technosol, the content of organic matter is even higher than in the natural soil, showing much higher rates of recovery than in the majority of other reported case studies (Akala and Lal 2000; Brown et al. 2017). This means that the use of the pre-weathered clay-rich geological materials for mine site Technosol design could have important consequences for carbon sequestration in these soils.

All obtained results support the conclusion that in the studied case, the use of hydrothermally altered rock for constructing Technosols played a key positive role in the rapid generation of active soil mineral components, organo-mineral interactions, and overall acceleration of soil development. This role is pre-determined by the specific mineralogical effects, which certain hydrothermal processes produce in the silicate substrate, especially in the intermediate and basic volcanic rocks. In the case of the Peña Colorada mine, the multi-stage magmatic-hydrothermal processes (Zürcher et al. 2001; Tritlla et al. 2003; Camprubí and Canet 2009; Camprubí et al. 2018) produce large amounts of clay minerals, i.e., fine grained 1:1 and 2:1 phyllosilicates (Camprubí et al. 2018). In particular, these processes quite frequently generate smectites (Pirajno 2010), which are highly valuable for soil development due to their high cation exchange capacity and capability to form stable organo-mineral compounds, as discussed above. Sometimes in the transformed rocks, clay minerals are accompanied by fine iron oxihydroxides and carbonates (Pirajno 2010). Those components are beneficial for the development of soil structure and neutralization of acidity. The hydrothermally altered rocks are associated with volcanic environments where a source of water is present. Argillization is one of the processes observed in

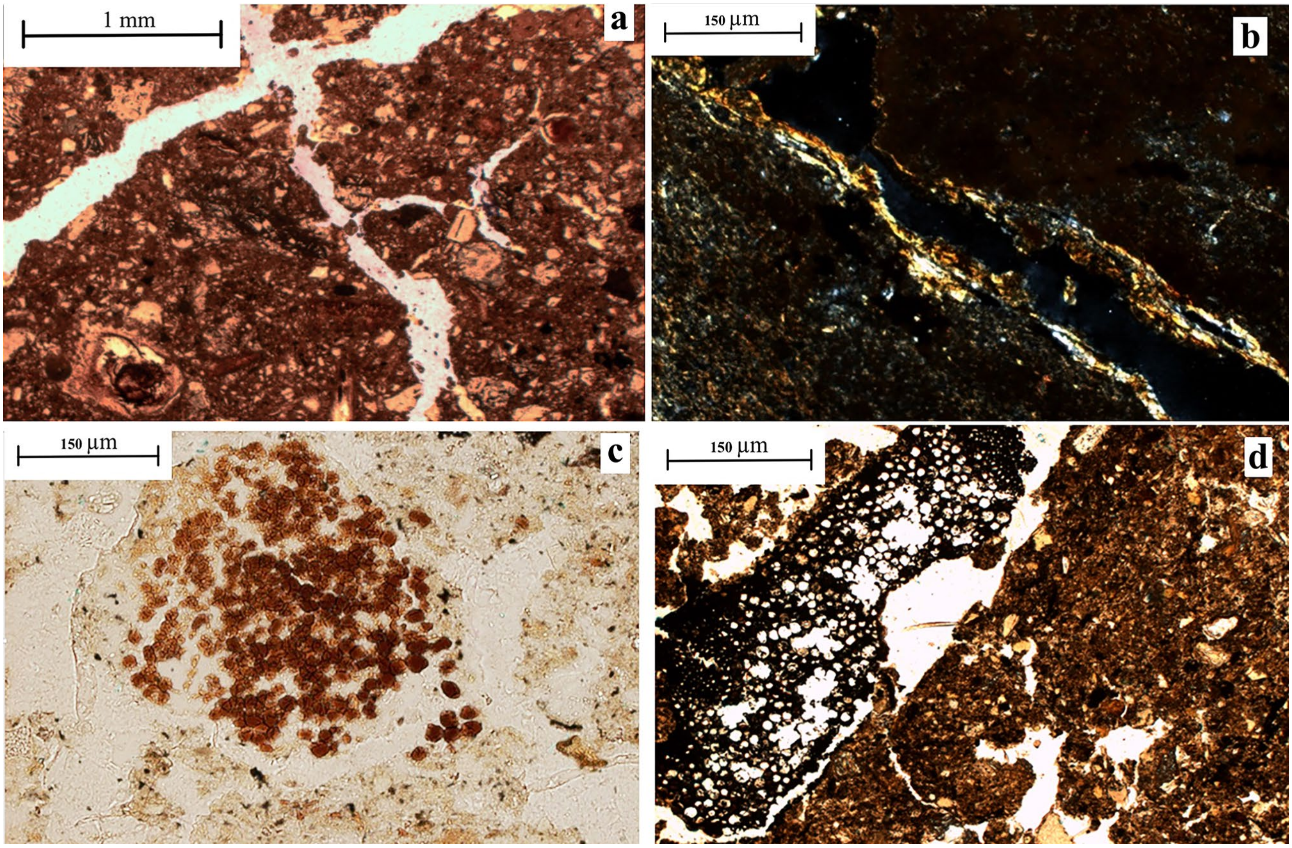

Fig. 7 Micromorphological features of the natural soil at León Dormido; **a** angular blocky structure in the BC horizon (PPL); **b** oriented clay in the BC horizon (XPL); **c** charcoal fragments in the Ap horizon (PPL); **d** coprolites in a pore of the Ap horizon (PPL)

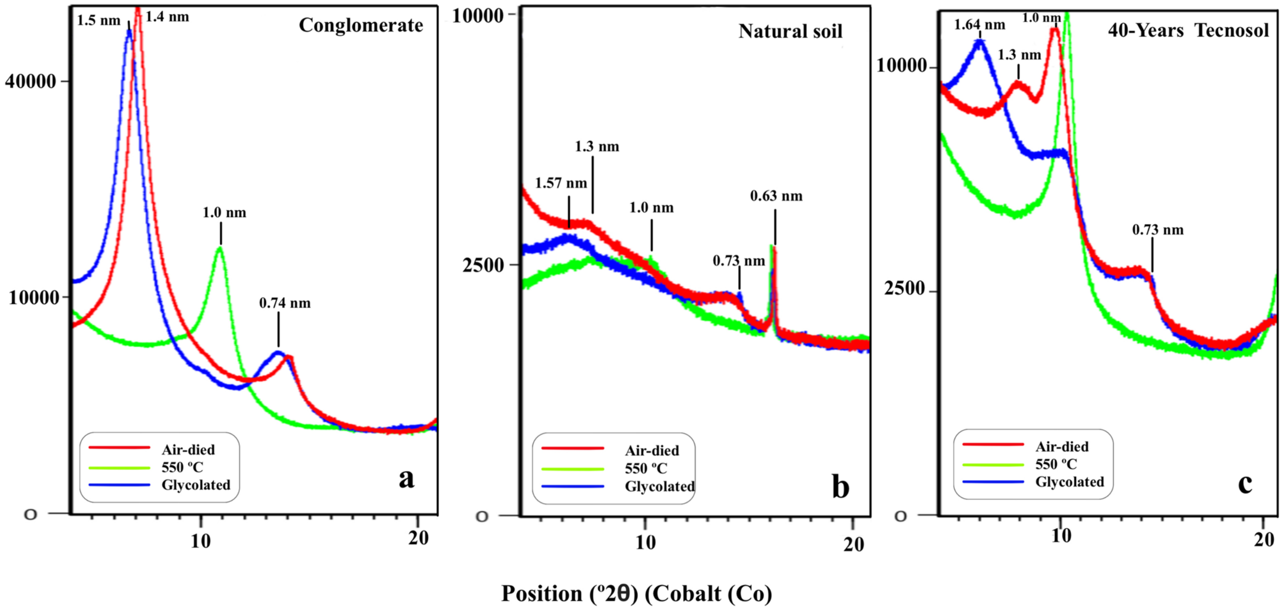

Fig. 8 X-Ray diffractograms of clay fractions from three selected samples as follows: **a** conglomerate; **b** Ap horizon of the natural soil; **c** A horizon of the 40-year-old Technosol

various types of metal ore deposits (Lang and Baker 2001). This means that, in many cases, the hydrothermal clay-rich materials are easily available for Technosol construction at a short distance from the mine sites.

The observation of the natural weathering and pedogenesis on the hydrothermally altered rocks show that the clays already present within them are easily incorporated into soil material and, in general, the formation of soil and weathering profile occurs rapidly. This specific trend of supergene transformation accounts for the separation of these rocks into a special class in the classification of weathering crusts by Chernyakhovsky et al. (1976). Even under the severe climatic conditions of the Siberian boreal forests pedogenesis on the hydrothermally altered basic rocks produce loamy substrates in which clay accumulation and illuviation are the dominant soil forming processes (Belousova et al. 1992; Sedov et al. 1989). Hydrothermal alteration is the main source of 2:1 clay minerals in the tropical (Jongmans et al. 1994) and temperate (Sedov et al. 1993) soils formed on volcanic rocks. In the modern surface soil and buried paleosols in the vicinities of the large polymetallic deposit of the Buenavista del Cobre mine (Sonora, Mexico), the major part of clay material and, in particular, smectitic components are derived from the hydrothermally altered andesites exposed in the area (Ibarra-Arzave et al. 2019; Romero-Lázaro et al. 2019). All these data support our proposal that hydrothermal rocks could be considered as adequate and promising materials to be used for Technosol creation in mine site recultivation projects worldwide.

5 Conclusions

In this study, the successful development of Technosols confirms the possibility of rehabilitating iron mine tailings by use of local conglomerates. The evolution of Technosols, despite their young ages (15- and 40-year-old), was characterized by the same pedogenetic trends as the local natural soil. It was evident that clay and OM contents increased with the age of the Technosols, as the structure improved, and clayey coatings developed. This was due to the fact that the parental material for all of the soils was the conglomerate found in an altered state with preformed clays, which accelerates the processes of pedogenesis. However, it is important to note that the thickness/depth of this conglomerate cover must be taken into consideration in order to prevent the acidification, compaction and cementation of Technosols under the impact of ascending solutions from the underlying tailings. Such an effect was observed in the lower horizons (2C and 2Bw) of the 15-year Technosols that had direct contact with tailings materials.

This study emphasizes the importance of using hydrothermalized rocks, which can provide fine materials as well as clay minerals within shorter periods, in order to accelerate the pedogenesis.

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Author contribution All authors of this manuscript made substantial contributions to the manuscript and qualify for authorship, and no authors have been omitted.

Declarations

If any of the sections are not relevant to your manuscript, please include the heading and write “Not applicable” for that section. We declare all data are shown into the main document.

Conflict of interest The authors declare no competing interests.

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