Geochemical and geophysical techniques application to characterize a mining silt pond from Cartagena- Union (Murcia): potential pollution pathways

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ABSTRACT

According to the I.T.G.M.E. (1999), there are 85 mining silt ponds coming from the treatment and exploitations of metallic sulphurs in Murcia Province. Those silt ponds are potential focuses of environmental pollution. The Technical University of Cartagena is carrying out an integral study of these structures from 2003 to the present time. The results obtained from the geochemical and geophysical techniques carried out in the "Brunita" silt pond (The Union-Murcia) are presented. The aim of this study is to characterize the mining silt pond and to establish the potential contamination pathways.

The data show that the electric tomography 2D and 3D is a effective technique to cube the volume of these mining silt ponds and to visualize these areas that show high concentration of heavy metals (Pb, Zn, Cu, Cd) and sulphates; this fact has been corroborated with the physical-chemical analysis, since those areas showed low values of resistibility through geophysics, around 2-4 ohm-m.

Finally, both techniques allow characterizing the silt pond and the estimation of the potential mobility of heavy metals through the determination of soluble heavy metals.

INTRODUCTION

In Murcia Province, there are 85 mining silt ponds due to intensive mining activities that occurred during last century, especially in the Sierra de Cartagena-Union. Mining activity was abandoned several decades ago.

Those silt ponds, due to their composition and location, may create important environmental risks of geochemical pollution, negatively affecting soil, water, plant, animal, and human populations, as well as infrastructure.

The Ministry of Economy, through the "Dirección General de Política Energética y Minas" has compiled an inventory of these abandoned silt ponds in 2003.

The major purpose of this inventory was to establish a classification of the existing silt ponds in the Province, according to their potential risk for the environment, human population, and infrastructure. The inventory offers an evaluation describing the potential affected receptors. Based on these evaluations, an action plan can be established.

To deepen in the knowledge of the current state of silt ponds with the most potential risk, detailed studies were conducted, following the recommendations of the inventory. These studies were carried out with the application of geophysical and geochemical techniques, which allowed the establishment of an analysis and quantitative evaluation of the contamination risks. This work shows the results of the studies corresponding to the silt pond called "El Lirio"

MATERIAL AND METHODS

Study area

The "El Lirio" silt pond is located in the area called Coto Ponce, Southeast of the mine of the same name, Southeast LLano del Beal. This mine from which this silt pond originated was built from 1940 to 1952, and "El Lirio", as a sedimentary structure, was finally consolidated in 1956, property of the "Mining company Celdrán S.A" together with the "Spanish company of Zinc S.A." that exploited this until its closing.

Until 1981, the exploitation and mineral treatment is characterized as stable and productive. Nevertheless, in this year, the Mining company Celdrán S.A. and "Spanish company of Zinc S.A." closed, and therefore the pouring of residual materials into the pond ended (Bautista y Egea, 1991).

Geochemical technique

For the geochemical characterization of the silt pond, a poll, located in a representative area, was carried out (Figure 1), which was driven down into the substrate (14.8 meters depth). Samples were taken every meter from 0 to 14 m, while 3 punctual samples (14.4; 14.6 and 14.8 meters) were taken in the substrate.

Samples were air dried, passed through a 2 mm sieve, and ground. For soil moisture determination, the samples were weighed and oven dried at 105 °C for 24 h. Soil pH was measured with glass electrode in a 1:1 soil/water suspension using the method of Peech (1965) referred to water and 1M KCl (pH-meter Basic 20 CRISON). Soil electrical conductivity was measured in a 1:5 soil/water suspension (Andrades, 1996). The soluble amount of metals was determined by ratio 1:5 soil:water suspension and measuring with atomic absorption spectrophotometer (UNICAM 969).

Geophysical technique

The geophysical equipment used was a Syscal R1 Bonus resistivimeter (IRIS Instruments), which had a cable multinodo with 72 connections and it allows measurements on each of the electrodes, simultaneously. Nine profiles of electric tomography with 72 electrodes were taken; eight of them were prepared lengthwise in the pond, and one traversing the pond. Coordinates are shown in Table 1.

Profile	West			East		
	X	Y	Z	X	Y	Z
1	692570.51	4165107.99	180	692730.00	4165180.48	183
2	692721.37	4165198.75	-	692562.12	4165126.20	179
3	692635.00	4164967.07	196	692867.00	4165080.00	179
4	692613.16	4165012.06	196	692846.07	4165122.43	183
5	692601.00	4165068.00	175	692760.00	4165138.00	191
6	692718.72	4164903.75	162.89	692885.72	4165008.75	166
7	692759.00	4164849.00	171	692900.00	4164946.00	162
8	692872.97	4164819.03	136	692908.94	4164872.94	132
	North			**South**		
	X	Y	Z	X	Y	Z
9	692678.00	4165157.00	180	692786.83	4165017.21	-

Table 1.- Coordinates of the geolectrical profiles

The electrodes were then located on the map using GPS coordinates (Figure 1), and the measures pre-handing is carried out, using the software Prosys. The software Res2dinv was used for the final data handling, which consisted of statistical algorithms (Edwards, 1977; Loke and Barker, 1996).

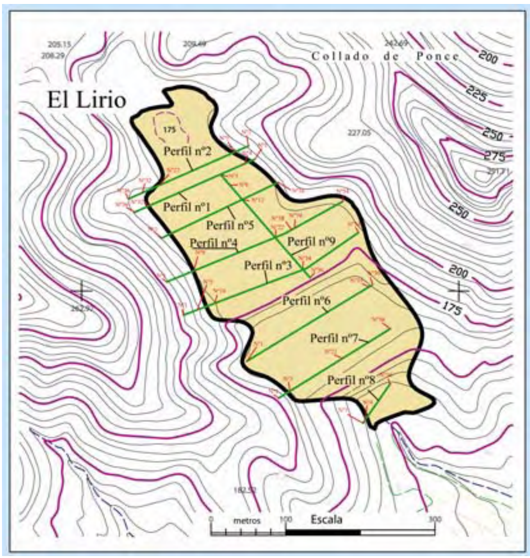

Figure 1.- Location of the electric tomography profiles and the geochemical poll at the "El Lirio" silt pond.

Comes of pre-handling and handling phases c the interpretation phase where the obtained results are analyzed; everything supported by the geologic information of the area, and the analytical data from mechanical poll samples.

RESULTS AND DISCUSSION

Geochemistry

pH values measured in H_2O and KCl are quite homogeneous (Table 2) in the different sampling layers. The range of pH_{water} values range from 6.36 to 7.89, this last value at 14.60 m depht. The highest pH values correspond to the last three samples of the poll, which represents the substrate. In the layers of the mining silt pond, pH range is lightly smaller (6.36 to 7.51); nevertheless, most of the samples present a pH from 6.6 and 7.3, considered as neutral silts, with the exception of some layers with basic pHs.

In the pH_{KCl} a slight decrease is observed in all the layers, respect to the pH_{water} values.

Depth (meters)	pH water	pH KCl	E.C. (ds/m)	% Clay	% fine silt	% coarse silt	% Sand
0-1	7.47	7.03	4.27	3.8	17.1	20.4	58.6
1-2	6.70	6.24	4.90	3.4	19.9	23.7	53.0
2-3	7.24	6.97	3.76	3.6	24.2	31.4	40.7
3-4	7.27	7.00	3.26	6.1	24.8	31.1	37.9
4-5	7.36	7.27	3.61	8.4	22.2	23.6	45.8
5-6	7.28	7.20	3.39	5.0	8.0	10.4	76.6
6-7	7.51	7.06	3.66	6.6	15.0	21.7	56.6
7-8	6.92	6.70	5.99	3.3	25.4	41.4	29.9
8-9	7.18	6.44	4.21	4.1	17.2	18.8	59.9
9-10	6.88	6.21	4.04	4.1	7.8	10.1	77.9
10-11	6.36	6.25	6.02	2.8	37.1	38.4	21.7
11-12	6.41	6.27	5.69	3.3	40.4	30.5	25.8
12-13	6.60	6.41	4.76	4.0	74.8	19.2	2.0
13-14	7.13	7.02	5.45	15.8	30.7	15.6	37.9
14.4 (substrate)	7.78	7.67	3.38	19.5	40.0	20.7	19.8
14.6 (substrate)	7.89	7.64	3.91	19.9	42.3	22.0	15.8
14.8 (susbtrate)	7.71	7.46	4.63	22.9	35.1	24.0	18.0

Table 2. pH water and KCl solution; electrical conductivity and clay, fine silt, coarse silt and sand content in the samples of the poll.

The soluble salts content of the layers, whose compose the silt pond, is variable. Four intervals can be distinguished, the first one formed by the first two meters depth, with E.C. values from 4 to 5 dS/m, characterized for being moderately saline; the second interval reaches 7 m depth and its saline content is inferior to the previous one, being lightly saline and quite homogeneous. On the contrary, salts content in the third interval (7-14m) is variable, although all the sampling points are classified as moderately saline. Lastly, the fourth interval is formed by the substrate, taking place in it an important decrease of the saline content in relation to the immediately superior layer and later increasing the value of E.C. from slightly saline to moderately saline (3.38 to 4.63).

The textural classification of the poll (Table 2) shows that the predominant class is the loam silt. Clay content is low and constant down to 13 meters depth; the clay content increases in the substrate with values next to 20%. On the other hand, sand percentage is important, the highest values are presented in the residual layers located between 5-6 m and 9-10m depth, being around 77%. In the case of fine and coarse silts, so much homogeneity don't exist in the first 14 m of the poll, being these higher ones; however in the substrate layers the percentages are more similar, around 40% of fine silt and 22% of coarse silt.

With the objective of determining the potential mobility of the metals, the evolution of soluble fraction is presented on Table 3 it can be observed that percentages of soluble Zn, Pb and Cu don't surpass 0.6%, although cadmium reaches 43.6%.

Depth (meters)	Pb (mg/kg)	Pb (%)	Cu (mg/kg)	Cu (%)	Zn (mg/kg)	Zn (%)	Cd (mg/kg)	Cd (%)
0-1	0.789	0.02	0.062	0.066	5.080	0.060	0.457	1.57
1-2	1.486	0.03	0.085	0.107	17.544	0.218	1.019	5.67
2-3	6.588	0.18	0.000	0.000	5.101	0.069	0.410	2.54
3-4	0.706	0.02	0.000	0.000	4.193	0.057	0.363	2.89
4-5	0.504	0.01	0.075	0.138	2.208	0.040	0.199	2.12
5-6	2.069	0.04	0.000	0.000	1.443	0.023	0.323	0.68
6-7	1.534	0.03	0.000	0.000	1.783	0.036	0.351	1.94
7-8	3.460	0.04	0.000	0.000	21.336	0.260	1.553	7.00
8-9	1.452	0.02	0.000	0.000	7.541	0.047	0.455	1.19
9-10	1.897	0.05	0.000	0.000	8.505	0.077	0.550	1.69

10-11	4.980	0.06	0.000	0.000	23.396	0.292	1.280	5.20
11-12	4.504	0.05	0.000	0.000	23.908	0.281	1.426	5.71
12-13	1.297	0.02	0.000	0.000	19.947	0.213	0.643	2.10
13-14	0.505	0.01	0.000	0.000	2.525	0.062	0.313	2.69
14.4 (substrate)	0.288	0.50	0.081	0.357	0.000	0.000	0.153	13.38
14.6 (substrate)	0.304	0.52	0.000	0.000	0.000	0.000	0.287	43.60
14.8 (susbtrate)	0.374	0.22	0.000	0.000	0.000	0.000	0.272	38.46

Table 3. Soluble heavy metals percentage of the total and concentration in the samples of the poll.

Regarding to lead, the maximum percentages in the soluble fraction appear in the three substrate samples (0.50, 0.52, 0.22%) and in the interval of the poll between 2 and 3 m deep (0.18%). The rest of the values, although are not null, they are not higher than 0.06%, so it shows that the mobility of this metal is not very important in the layers of the pond, being retained in each layer in a non mobile form. On the contrary, the mobility of the metal increases in the substrate because this has been able to suffer an incorporation of lead from the upper layers that have been accumulated in the soluble form of this metal; nevertheless, the concentration of lead in soluble form is very low in relation to the one in the layers of the pond.

In most of the samples taken in the poll, Cu does not appear in its soluble fraction. Only those silt layers located from the surface of the pond down to 2 m, from 4 to 5 m and in the limit with the substrate (14.4 m) show appreciable values whose maximum value is 0.36%, since it is a Pb-Zn mine, the fact that copper is in trace levels can be easily explicated.

In the case of Zn, the highest values are observed at 1-2 m, 7-8 m and 10-13 m depths, being around 0.2%. Most of the rest of the samples approaches the value of 0.05%, with the exception of the substrate samples that present a null value. The percentage of this metal in relation to the total is similar to lead, being its concentration higher in this case in most of the samples.

Contrary to the previous metals, cadmium presents the highest percentages in its soluble fraction. Of the registered values, the soluble fraction of this metal in the substrate samples is very high, reaching at the depth of 14.6 m a percentage of 43.6%. In the rest of the samples some fluctuations are appreciated ranging from 0.68 to 7%. This generates a contamination risk of lower material and aquifers.

Geophysics

Figure 2 represents the geoelectrical pseudosection of profile 1. Due to the nature of the mining residues, the resistivity in the first meters of the pond is very low, with values lower than 30 Ohm·m, even with values of 2-4 Ohm·m. The substrate of the pond is formed by natural land, and appears with resistivity values higher than 66 Ohm·m being located to depths from 5 m (external area) to 18 meters (central area). This "geometry" reflect the original undisturbed physiographical position.

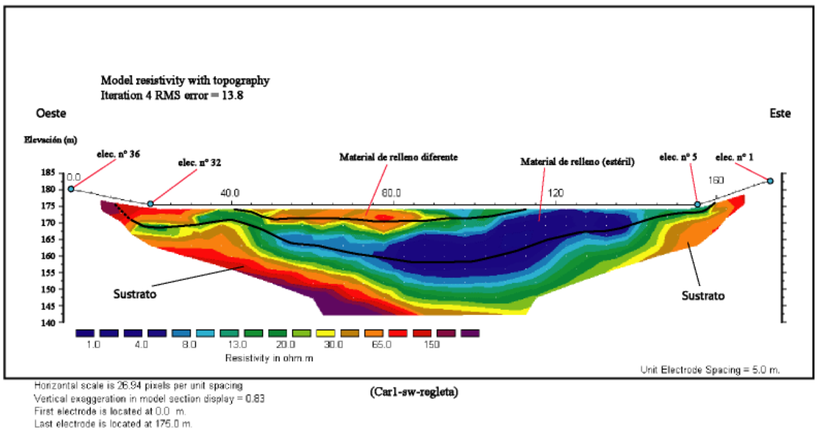

Figure 2.- Electrical Pseudosection of profile 1

Differences the resistivity between the right part (<10 Ohm·m) and left one (>20 Ohm·m) can be due materials of different origin, particle size or densities during the poured.

In the Figure 3 the electrical pseudosection of the profile 2 is shown, where materials of very low resistivity appear in the central area of the section, lower to 8 Ohm·m, clearly representative of a material coming from sulphur mines, and, on the other hand, a different material in the most superficial layer of the pond with values higher than 10 Ohm·m and reaching to 70 Ohm·m in some areas. The substrate is represented by more resistivity values and appears at 16 meters deep, in the centre area of the deposit. In the left part of the profile areas of high resistivity corresponds to fine materials.

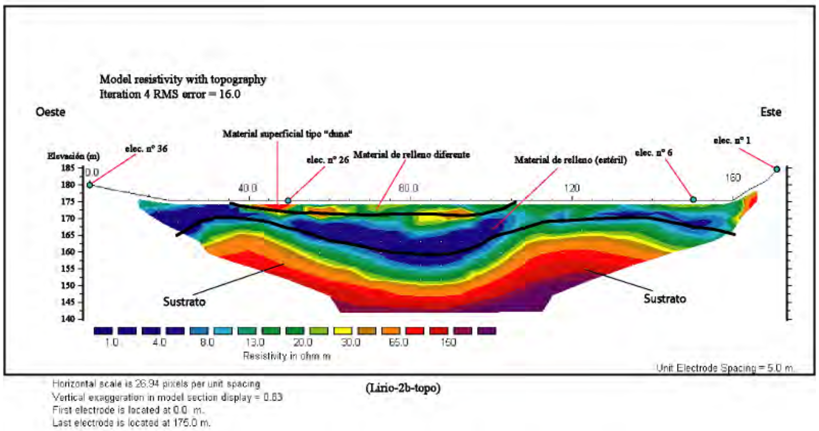

Figure 3.- Electrical Pseudosection of profile 2.

Figure 4 shows resistivity values very similar to those obtained in the previous profiles. In the right area of the section materials appear with values of very low resistivity (<8 Ohm·m) that contrast with the more superficial materials with resistivilities >10 Ohm·m. The substrate is identified by resistivity values >65 Ohm·m, which is located at 35-40 m depth in the central part; depth that decreases toward both the extremes of the profile.

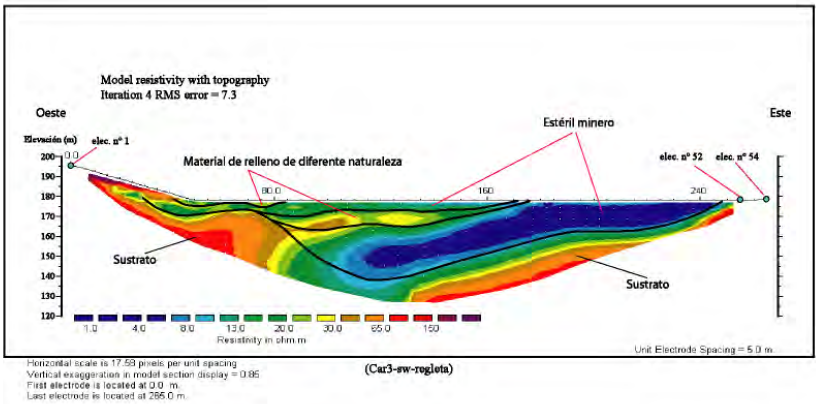

Figure 4.- Electrical Pseudosection of profile 3

Figure 5 shows the electric pseudosection of profile 4. In this figure three clearly differentiated areas can be distinguished. On one hand, an area with inferior values to 6 Ohm·m that identifies a silt that would reach depths between 35 and 40 meters in the central area. On the other hand, superficial material with resistivility values clearly different (>10 Ohm·m) that is presented in the first meters and in the left superior area of the profile. Lastly, the substrate has values higher than 30 Ohm·m. In fact, in this profile it has been carried out the mechanical poll whose location is indicated on Figure 5. In this point, the substrate starts at 13 meters, depth that corroborates the one obtained with this technique.

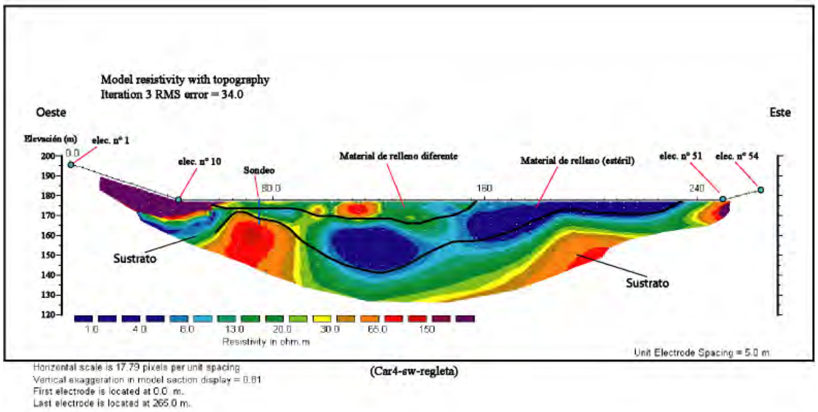

Figure 5.- Electrical Pseudosection of profile 4

The pseudoseccion of profile 5 appears on the Figure 6, where two differentiated areas are clearly observed, one with very low resistivity values (inferior to 6 Ohm·m) that prevails in the right part of the section, and another area with values higher than 10 Ohm·m that is distinguished on the left part of the pseudoseccion and reflects the presence of poured material of different nature. The substrate is characterized by resistivity values higher than 30 Ohm·m..

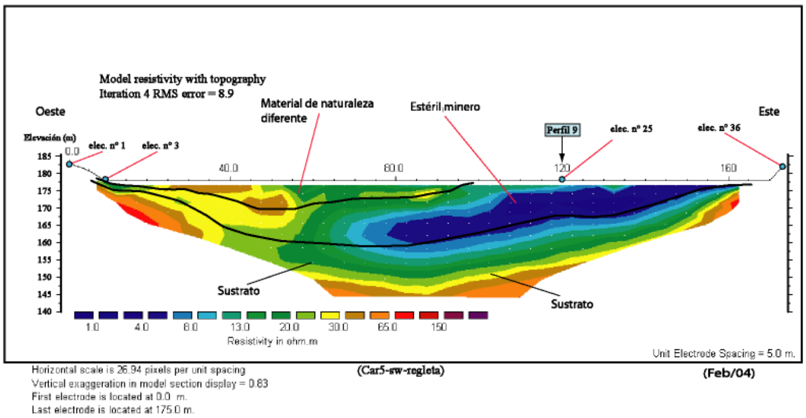

Figure 6.- Electrical Pseudosection of profile 5

The electrical pseudosection show on Figure 7 point out the presence of a deposition of conductive material on the right part of the profile with very low resistivity values (inferior to 6 Ohm·m), and, it also corroborates the superficial presence of the existent humidity in this part of the deposit. Silt pond's left area is characterized by resistivity values higher than 10 Ohm·m that show mining material without significant humidity. The resistivity values higher than 30 Ohm·m characterize the presence of the rocky material of the substrate.

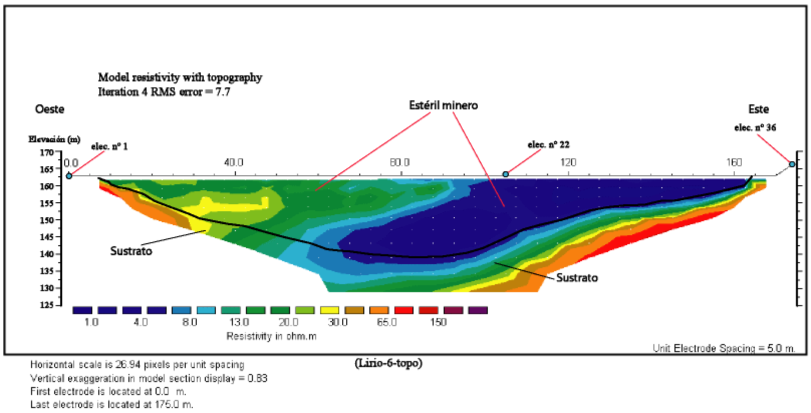

Figure 7.- Electrical Pseudosection of profile 6

Profile 7 is presented on Figure 8, showing a deposit of very conductive sterile materials in the right part, with material thickness of 15 meters, and of 20 meters in the central part. Inside the area classified as mining steriles, two areas of different resistivity are distinguished, on one hand the right area with the lowest resistivity values showing the presence of humidity and on the other hand the left area with values higher than 8 Ohm·m that show a material of different characteristics.

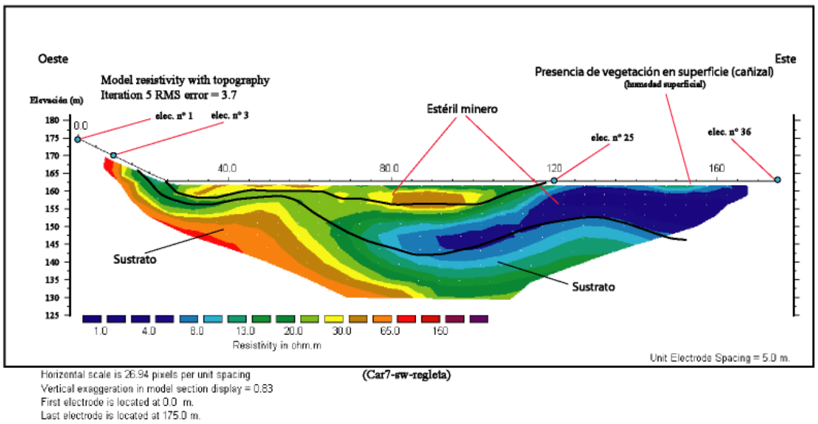

Figure 8.- Electrical Pseudosection of profile 7

Figure 9 presents the pseudosection of profile 8. This pseudosection indicates a similar tendency to the observed in the geoelectrical profiles 6 and 7; although, due to the heigh of the land on what it has been carried out, the thickness around of the deposited materials is inferior, estimating a thickness of poured material 1-1.5 m in the left part of the profile, which goes increasing toward the right part reaching a thickness of 1.5-2 m. The substrate is identified by high resistivity values.

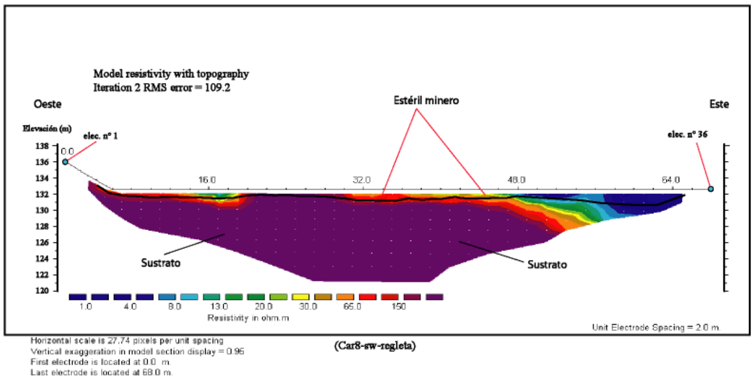

Figure 9.- Electrical Pseudosection of profile 8

Figure 10 shows the interpretation of profile 9 identifying the covered area by the mining steriles, characterized by resistivity values to 8 Ohm·m. On the surface of the pseudosection it have been pointed out that the electrodes of the profile 9 have coincided with the location of the traverse profiles (profile 5 and 4 mainly). The resistivity values range between 8 Ohm·m and 25 Ohm·m in the right superior. What represent mining steriles of different characteristics.

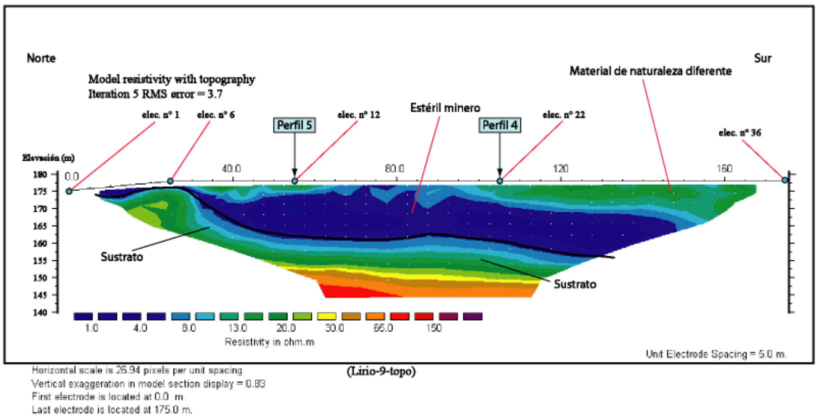

Figure 10.- Electrical Pseudosection of profile 9

The information obtained from the profiles has been imported to the program Surfer, in order to obtain the 3D pattern of the contact between the natural substrate of the land and poured mining silt material. The 3D model presented on the Figure 11, provides the depths of the contact silt/soil.

In the 3D pattern is checked that the higher volume of deposits is located under the location of the profiles 3, 4 and 6, concretely in their central part, coinciding with the original water-course of the land, where thickness is located at 35 and 40 meters depth

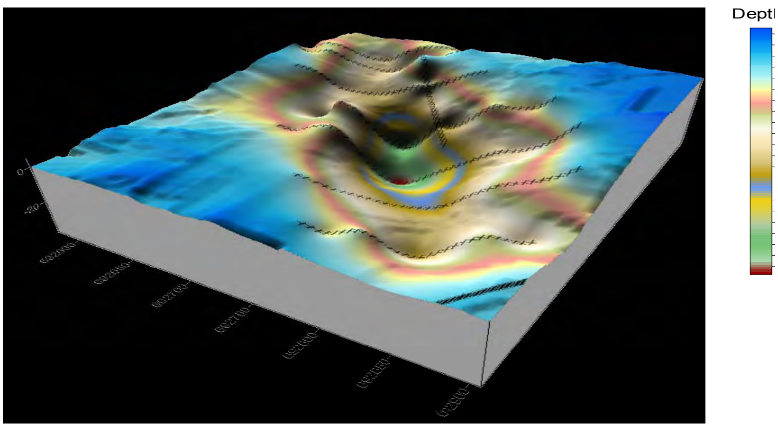

Figure 11.- 3D model

The determination of the amount of poured material in the silt pond has been carried out with the help of the information contributed by the profiles. Using the method of the geoelectrical profiles (Orche, 1999) a volume of 740325.13 m^3 has been obtained. The total amount of material assigned to this same pond by the National Inventory of the CARM (I.G.M.E, 1999) is 750000 m3.

CONCLUSIONS

In the silt pond "The Lirio", most of the residual layers present a neuter pH, except for slight exceptions where it reaches medium alkalinity, being observed the highest values in the substrate. The salts content of the layers that compose the silt pond is variable. On the other hand, the textural class is loam silt in the majority of the samples taken in the poll. The minority particle size in these residual layers is the clay.

The soluble fractions of Zn, Pb and Cu present lower content than 0.6%, on the contrary Cd reaches the highest value of 43.6% exactly in the contact area with the substrate that even is affected by this soluble metal, due to the high solubility of this metal and but also the saturation of the clay by lead and zinc inhibits any possible retention by the absortion complex.

In a general way, the electrical tomography shows that the sterile material located in the part east of the deposit presents higher conductivity and that the conductivity decreases progressing toward the west of the deposit. A surface area of the deposit abnormally resistive is also observed, mainly in the first profiles (profile 1, profile 2, profile 3 and profile 4) whose origin can be motivated by materials of different nature and particle size as it has been verified through mechanical data poll. The highest thickness of sterile is located under the profiles 3, 4, and 5, located approximately in the heigh 175 m, and under the profiles 6 and 7, located on the heigh 150 m. The 3D representation presents a good correlation with the natural basin, obtained with the geophysical investigation. Besides, It is also necessary to highlight the estimated volume by means of the geophysical information that is adjusted to the data contributed by the previous inventory.

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