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Environmental impact and retrival of coal dumps from the western side of Petroşani Basin (Aninoasa-Câmpu lui Neag)

Ph.D. Thesis

Summary

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<u>Key words</u>: ”Petroşani Basin”, ”coal dumps”, ”pit coal”, ”entiantrosoil”, ”ecological rehabilitation”.

INTRODUCTION

Ground coal or black diamond ”is nothing else than carbon under crystallized form; pit coal is the same thing, only it is black, while diamond is transparent. And even so, the diamond is demon, and the coal is angel”, said Mor, because together with its exploitation, the coal became the most valuable raw material of the nineteenth century. It led to the progress of the industrial revolution, provided jobs indirectly, became useful in metallurgy and energy industry, powered means of transport, lighted cities at night, heated homes and palaces, warmed the men souls in cold winter days.

”The coal is the petrified flora of the lost world” that the Earth sheltered together with ”the worlds gone herbarium”, as Mor wrote in ”*The black diamonds”*. Between the coal layers formed by ferns forests, huge gymnosperms and angiosperms are interspersed sedimentary rocks that preserve calcified shells and skeletons from the lost animals.

The coal abundance shows that it has been formed from a several hundred times richer vegetation than exists today on Earth.

With the coal discovery, it was classified according to composition, calorific value and forming method. Thus, the pit coal exploit in Petroşani Basin belong to upper Oligocene. The tectonic pressure and temperature were generated by the crystalline massifs that bordered the basin, had favored the carbonization till the pit coal stage. These aspects were presented by Petrescu et al. (1987) in their researches.

The pit coal exploit since the mid-nineteenth century in Petroşani Basin was very useful for industry but waste rock brought out together with useful rock formed ”dummy mountains” which inside mining perimeters already closed were rehabilitated. In the active mining areas continuously is observed the dump stability.

Most dumps have been rehabilitated with sea buckthorn, pine, acacia, hair grass, trefoil, orchard grass, because these species are not demanding to the substrate on which are planted and live in symbiosis with certain bacteria which facilitates the microelements accumulation in entiantrosoil (Blaga et al., 2005).

In this thesis we presented data about some dumps stability from the western side of Petroşani Basin and we investigated the entiantrosoil evolution using X-ray diffraction, optical microscopy and X-ray fluorescence spectrometry to identify quantitative and qualitative minerals composition and the chemical elements from the future soil. In the same time we collected sea buckthorn, brier and hawthorn fruits from the dump to track the amount of calcium and magnesium and the presence of ascorbic acid, flavonoids and polyphenols. The results were compared with those in the literature and we can say that the fruit can be used in food and pharmaceutical industry.

Based on these results we proposed an algorithm for the dumps rehabilitation and a recycling model for the iron microparticles presented in coal ash dump. The coal ash stocked in the dump comes from the coal burning in Paroșeni power plant.

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I would like to thank also to Prof. Ing. Dr. George Arghir and Ing. Dr. Ioan Petean from the Technical University Cluj-Napoca for their help in analyzing the sterile samples by X-ray diffraction and optical microscopy.

I thank to my colleagues Vasilica Mândroc and Ramona Câmpean for helping me to determine the quantity and quality minerals and essential organic compounds from the fruit of sea buckthorn, brier and hawthorn. Some of these determinations were made with the collaboration of Scientific Researchers Dr. Neli Olah.

To determine the chemical elements from the sterile sample and provide other useful information about dumps I wish to thank to Scientific Researchers Dr. Daniela Onofre from the Environmental Office of CNH Petroşani.

I am thankful to my colleague Prof. Călin Filip (Turda) and my friend Ing. Andrei Burtescu for their help in improving the English version in my articles.

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HISTORY

Petroşani Basin is located in the south-western side of Romania and it started to be known as a coalfield around 1780. The oldest geological information regarding the existence of plants in the Jiu Valley, which has been found, is attributed to Bielz (1858) and then resumed by Quaglio (1861).

The first geological reference about the coal from the second horizon and sterile between the coal layers are given by Stur (1863), which describes five species of plants and five animal fossils found on the left bank of the Hungarian Jiu at Petrosani. Some of them were later cited by Heer (*Cinnamomum lanceolatum* and *Daphnogene ungeri*), then the investigations were resumed by Hauer and Stache (1864).

Hofmann (1870) is the first author who made a successful organization of the deposits in the basin due his biofaciale and litofaciale investigations. After more research he named the first horizon like ”lower horizon”, the second horizon as ”productive horizon” and the third horizon as ”upper horizon”. He didn't describe the horizons from Sălatruc area.

The first paper about the Jiu Valley was written by Staub, *”Die Flora des aquitanische Zsilthales”* (1887), which was resumed by Givulescu. He describes the flora from a modern point of view in the *”Revision einiger Originale aus M.Staub”* (1983) or *”Étude sur la flore et végétation de la Vallée du Jiu”* (1986).

Petroşani Basin came to the attention of Mrazec in 1897. Further research was conducted by Blanckenhorn (1900), Murgoci (1905), Pax (1907), Lingelsheim (1908), Macovei (1908), Filipescu (1927), Popescu- Voiteşti (1932, 1936), Manolescu (1937), Ilie, Codarcea, Murgoci (1941), Ghica- Budeşti (1942), Voicu (1950-1954), Popescu (1976), Mateescu (1951), Pavelescu et Maria Pavelescu (1953-1966), Răileanu (1955).

Givulescu (1964 - 1983) expressed his views about the formation of coal in the basin. He write *“Die fossile Flora der Valea Jiului”* (1964), *“Some observations about the formation of the Jiu Valley coal”* (1974), *“Upper Oligocene Flora from Petroşani Basin”* (1996), etc.

Moisescu (1975-1985) deals with the geological problems in Dâlja-Lonea area. Later then (1978) summarize the explanatory sketches about fossil places with the fauna from the second horizon. It shows the species found in each place. In collaboration with Maria Chivu (1979) describes the mollusk fauna from the horizons 2 and 3 of the basin and achieve a distribution on this flora for each mining field.

With the exploitation of coal in Petroşani Basin were brought to the surface large amounts of sterile. They were placed in dumps and were chosen uneven places. Over time were made inquiries regarding their stability and their ecological rehabilitation attempts, so to be framed in the floor legally mountain and landscape. This step has been extensively studied and many studies (1960-2005) have been made by: Fodor, Baican, Lazăr, Dumitrescu, Georgescu, Rotunjeanu, Voin, Rebrişoreanu, Traistă, Ionică, Matei, Temelie, Onica, Pătraşcu, Biro, Dunca, Boyte.

1. Petroşani Basin- general presentation

Petroşani is located in the south-west of Romania, between 45°17`- 45°22` northern latitudes and 20°13`- 20°33 eastern longitude. It is surrounded by Retezat, Parâng, Şureanu and Vâlcan mountains. It is drain by the two major tributaries of Jiu: Western Jiu and Eastern Jiu. Triangular contour surface is oriented NNE-SSW, with a length of 45 km and a width of 2 km in west and 9 km in the east. The landscape consists of numerous high hills (700-950 m), separated by deep valleys, tributary of the two Jiu rivers and several terraces (levels 1-5), followed by common alluvial plains (the stretching variables), spread along the major rivers. (Fig. 1) (Badea et al., 1987; Pop, 1993).

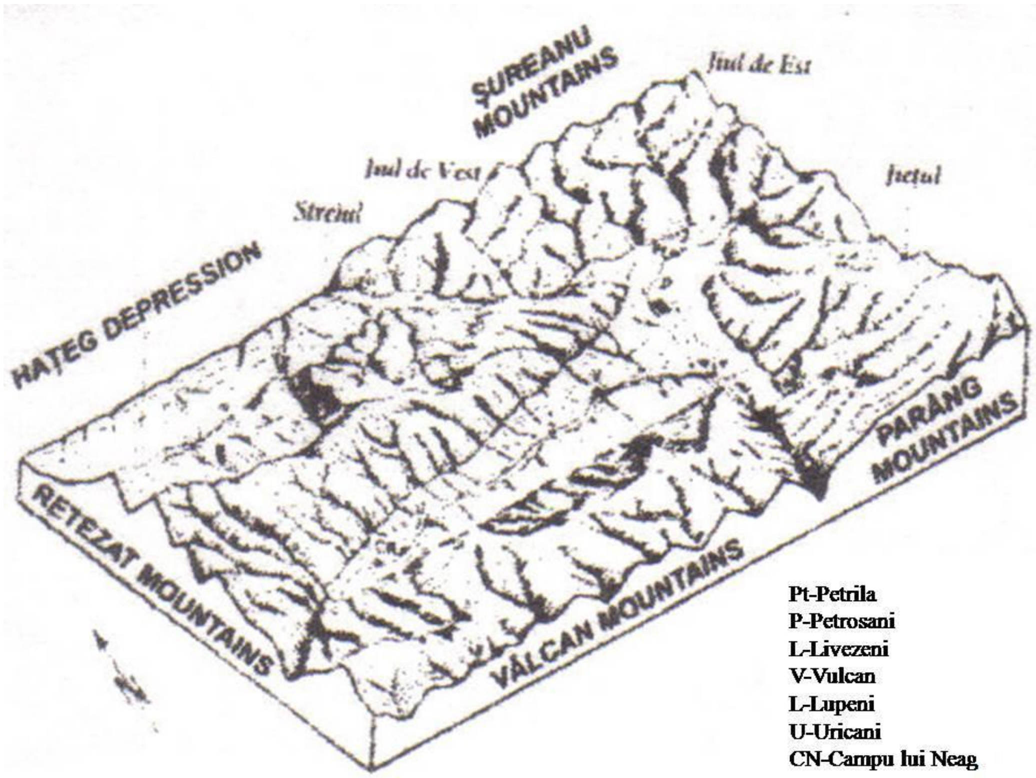


Fig. 1. Block diagram of Petroşani Basin (according Pop, 1993)

Petroşani Basin climate is characterized primarily by high relative humidity, the prevailing calm during the year (64%), and by frequent temperature inversions. From a climate perspective here are four levels:

- pre-mountain climate level between 500 and 800 m;
- lower mountain climate level between 800 and 1450 m;
- upper mountain climate level between 1450-1750 m;
- subalpine climate level between 1750-1900 m (Lupu, 1970; Preda et Pasere, 1985; Ardeiu, 2004).

Petroşani Basin began to be known as a coalfield around 1780. The deposits discovery is attributed to the shepherds and hunters whom have observed that this ”product” of soil burns if it is set on fire. In 1782 the mineralogist Janos Benko explains that he saw the ”coal combustion and the coal burned a long time”. Over time, ascertaining the presence of numerous coal dawn, in 1840 begins the first works in ”drift”. Around 1835 in Petroşani Basin starts the first exploration works and more detailed exploitation for knowledge the coal reserves (Fodor, 2005).

Since 1858 this coal field tickled up the geologists interest and they have begun to investigate the basin borders and its foundation. All geological research about the basin has resulted in petrographic, tectonic, paleontological, palynological and paleogeographical descriptions. Between 1858 and 1868 miners came from different regions of the country and abroad that has started to open mines and thus began the exploitation of pit coal in the basin.

After 1870 was built the railway between Simeria and Petroşani, so the basin quickly developed. Consequently were opened new mines in Lonea, Petroşani Vest, Dâlja, Aninoasa, Vulcan and Lupeni. This event led to increase the investment and production activity in the central and western side of the basin (Velica, 2004; Velica et Titel, 2005).

In Petroşani Basin the coal production was growing and required as like the other mines from Europa, coal after-treatment stations. First coal after-treatment station was open in Lupeni (1920-1930), then in Coroieşti (1961-1965) and the last at Uricani (1989-1990). Currently only the after-treatment station from Coroiești is still functioning (Munteanu et Ioniţă, 1971).

The first mining activities of research and power engineering started in 1949 in the former Institute of Industrial Engineering of Bucharest and in 1974 it established the Research and Design Institute of Mining in Petroșani. Scientific research in the field of mining gave important regional, national and international results (Fodor, 2005; Fodor et Baican, 2001).

In the mining industry an important role held the car industry that was responsible for building the mine locomotives, simple hydraulic pillars, wheel loaders with silo, rotor excavators, mechanized combine complex for slaughter and forward (Fodor, 2005).

Currently, due to very large debts that CNH Petroșani has to the state, a large number of mines were closed.

In conclusion, the pit coal from Petroșani Basin should not be completely abandoned, because in the future it could be a reliable alternative source of energy and at least 2-3 more profitable mines could be maintained in operation (Davidescu, 2006).

2. The geology description of Petroşani Basin

The Petroşani Basin is part of the post-laramic generation of sedimentary basin in South Carpathians. It started to outline in the Early Cenozoic. The basin involves a metamorphic basement and the molass filling, recurrent both în Paleogene and Neogene.

The basement refers to rocks on various degrees of metamorphism, belonging to the Danubian Units (Marginal dacides) and Getic Nappe (Median dacides) (Săndulescu, 1984). The median dacides are exposed in the north-east and partly in the south side of the basin. These take part from the Sebeş-Lotru Unit. The marginal dacides are exposed in the south and partly în the north side of the basin. These are represented by the Lainici-Păiuşi and Vâlcan Units (Stan, 1977; Balica et al., 2007, 2009).

The Cenozoic molass is exposed as narrow strips, parallel with the basin borders. It started to accumulate in Oligocene. Moisescu (1980) outlined the following lithostratigraphic units:

I-Cimpa-Răscoala (Rupelian- Early Chattian), known as ”1st horizon”;

II-Dâlja-Uricani (Early Eggerian) ”2nd horizon” also called ”lower productive”;

III- Lonea (Upper Chattian) ”3th horizon” or ”middle horizon”;

IV- Sălătruc (Aquitanian- Eggenburgian/Burdigalian), ”4th horizon” or ”upper productive”;

V- ”Formaţiunea cu pietrişuri” (? Langhian), ”5th horizon”or ”upper horizon”.

Petroşani Basin geological evolution started before the Getic thrust. The first sedimentary deposits date from the Upper Cretaceous (Maastrichtian).

The main resource of the Petroșani Basin is represented by the pit coal, known as energy and coking coal. Geological survey, exploration and exploitation of the pit coal revealed the existence of 20-22 layers of coal, numbered from 0 to 21, located in the second horizon, lower productive.

According to Givulescu (1996) the massive accumulations of coal, meters range, is due to large-scale swamp forests, respectively to the possibility of accumulation by a large quantities of carbo-generator material during a phase of slower subsidence, which can be roughly calculated. According to Schwarzbach (1949) 100 m of brown coal was formed in 250 000-500 000 year. There is the possibility that the lenticular layers of coal came from eutrophic swamps (Givulescu, 1974, 1997).

The pit coal from Petroşani Basin was formed after a strong metamorphism, which is due to tectonic pressure and temperature generated by the crystalline massifs bordering the basin.

Coking coal are in Lupeni, Uricani and Bărbăteni area.

The pit coal from Petroşani Basin is used for energy at Paroşeni and Mintia power stations. 10% of coal is delivered for home use.

In present, pit coal is exploited to Uricani, Lupeni, Paroşeni Vulcan, Aninoasa, Livezeni, Petrila mines (Davidescu, 2006).

3. Coal dumps stability in the west side of Petroşani Basin and the environmental impact

The coal dumps are engineering constructions in which are stock sterile rocks exploited together with the pit coal. The coal dumps are located near the mining areas. For the coal dumps location are chosen lands so the dumps causes minimal impact on the environment and requires the least expenditure of stockpiles. There are currently 43 coal dumps, 25 in operation and 18 in conservation (Biro, 2005).

Coal dumps evolution was marked by a long-term development strategy for the dump location, integration into the landscape, reducing the environmental impact, rehabilitation and vegetation cover. Coal dump shape may be modified from taper with steep slopes (first generation), to the terraces (second generation),being more stable and then to landscaping coal dumps (third generation), integrated in the environment, with new secondary biotopes, wet or dry, which help to the life environment insurance and the protection of many plants and animals species (Fig. 2).

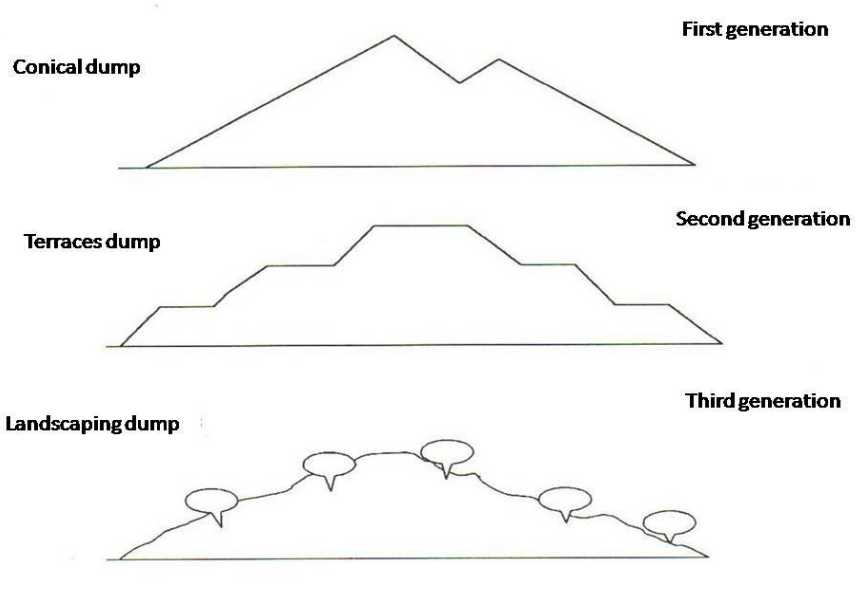


Fig. 2. Coal dumps evolution (Schultz, 1996)

The dumps from the western side of Petroşani Basin are shown in the following two tables.

Table 1. Technical condition of dumps from mines in the western side of Petroşani Basin (Environmental Office of CNH Petroşani)

No.	Economic unit	Coal dumps name	Active/inactive
1	Aninoasa	Tricoane Pisu	Inactive
2		Funicular Sud	Inactive
3		Puţ 7 Vest (halda veche)	Inactive
4	Vulcan	Puţ 7 Vest (tricoane)	Inactive

5		Valea Arsului	Active
6	Paroşeni	Halda funicular	Inactive
7		Valea Lupului	Inactive
8		Tericon cota 630	Inactive
9	Lupeni	Halda ramură I	Inactive
10		Halda ramură II	Inactive
11		Halda ramură III	Active
12		Halda veche Ileana	Inactive
13		Halda nouă Ileana	Inactive
14		Halda nouă Victoria	Inactive
15	Bărbăteni	Mierlaşu	Inactive
16		Galeria de Coastă	Inactive
17	Uricani	Funicular vechi	Inactive
18		Funicular nou	Active
19	Valea de Brazi	Funicular	Inactive
20		Puţ nr 8	Inactive
21	Câmpu lui Neag		Inactive

Table 2. Dumps classification in the western side of Petroşani Basin (Environmental Office of CNH Petroşani)

No.	Economic unit	Coal dumps surface (ha)	Coal dumps volume (mii m3)
Steril dumps			
1	E.M.Aninoasa	5,23	1619
2	E.M.Vulcan	34,25	3782
3	E.M.Paroşeni	5,34	773
4	E.M.Lupeni	28,04	10001
5	E.M.Bărbăteni	4,9	223
6	E.M.Uricani	18,3	1516
7	E.M.Valea de Brazi	28,3	4161
8	E.M.Câmpu lui Neag	207,84	31470
Steril dumps from coal aftertreatment station			
9	I.P.C.V.J.Uricani	0,10	100
10	I.P.C.V.J.Lupeni	22,10	3700
11	I.P.C.V.J.Coroeşti	16,50	3300
Ash coal dump from power plant			
12	C.T.E.Paroşeni	20	1450

The major damages caused by coal dumps to the environment are: unpleasant visual impact (Fig. 3.a and b); destruction of land covered with topsoil and vegetation (Fig. 4.a and b); pollution of the surface and underground waters with chemicals or suspended solid particles entrained from the dumps by rainwater or infiltration; air pollution with dust after sterile discharge into the dump (Fig. 5.a and b) and gas from mine; material damage and human lives, if the dumps lose their stability.

a

b

Fig. 3. Unpleasant visual impact: a) Green lake formed between the coal dumps at Lupeni, b) Bărbăteni coal dump

a

b

Fig. 4. Destruction of the vegetation and vegetal soil near the coal dumps from: a) Vulcan, b) Lupeni

a

b

Fig. 5.a şi b. Dust results after sterile discharge in coal dump from cable way (Lupeni)

Geo-mining negative phenomena which may affect the stability of waste dumps are:

- Compactions: Normal stabilization; Abnormal (excessive); Land base; After contractions
- Repressions: Embankment; Land base
- Slumps: Superficial; Depth; Plastic; On land base; In land base
- Erosions: Ravine; Themselves; Depth or suffusions
- Mine subsidence

Measures to reduce or eliminate negative geo-mining phenomena:

- proper drainage of dump hearth and aquifer ;
- rock compaction into the dump;
- runoff of precipitation;
- eliminate stagnant water;
- improve the granulometry of discharged rocks;
- machinery conveying as far as possible from the border of the step dump;
- proper sizing of the dump forward step and the tailing pond;
- avoid the accumulation of surface water by building drains;
- decreasing slope angle;
- removal the water from upstream and from the dump;
- the dump construction in a long time as to allow drainage of the land base layers;
- basic land improvement (Biro, 2005).

Analysis methods for slope stability and dumps foundation are: Jambu, Fellenius and Bishop. You can also use specialized software in geotechnical, GeoTecB, analyzing the stability of natural and artificial slopes with any geometry, both under static conditions, as well as seismic and the presence of water in the pores of the stockpile material or on the dump slope (Rotunjanu, 2005; Rotunjanu et al., 2001, 2005).

For the stability calculation it must be determined:

- mechanical values;
- values determined in the laboratory;
- calculated values.

Stability study was achieved based on 12 slopes belonging to 4 active dumps. The stability was investigated for the cylindrical-circular slip surfaces and polygonal slip surfaces at normal humidity and saturation humidity.

Stability coefficient can record the following values:

- F<1 ➞ the slope loses the stability;
- 1<F<1.3 ➞ the slope is relatively stable, should be monitored;
- F>1.3 ➞ the slope is stable.

Stability analysis results for cylindrical-circular slump surfaces are shown in Fig. 6 and can be observed that 16.66% of the slopes are unstable and 83.4% are stable at natural humidity, while at saturation humidity 50% of the slopes are unstable and should be monitored, 16.66% are partially stable and only 34.4% are stable.

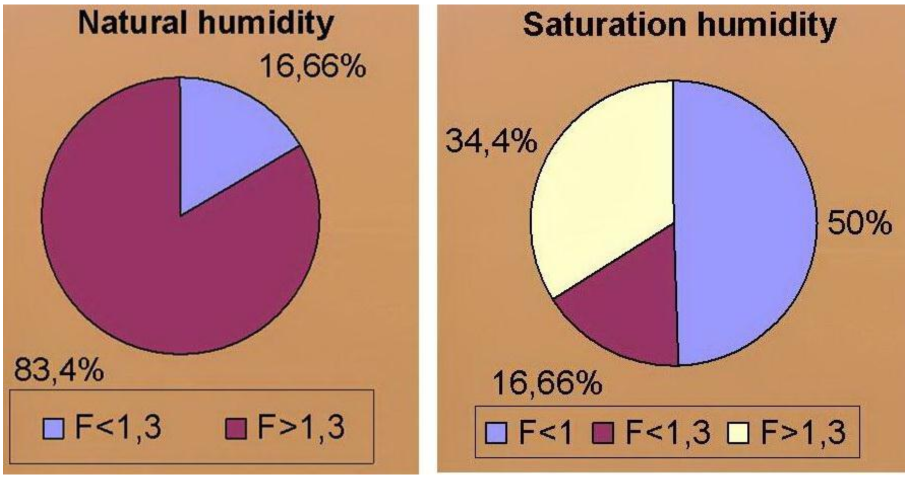


Fig. 6. Stability analysis results for the cylindrical-circular slump surfaces

Stability analysis results for polygonal slump surfaces at normal humidity are shown in Fig. 7 and for saturation humidity in Fig. 8.

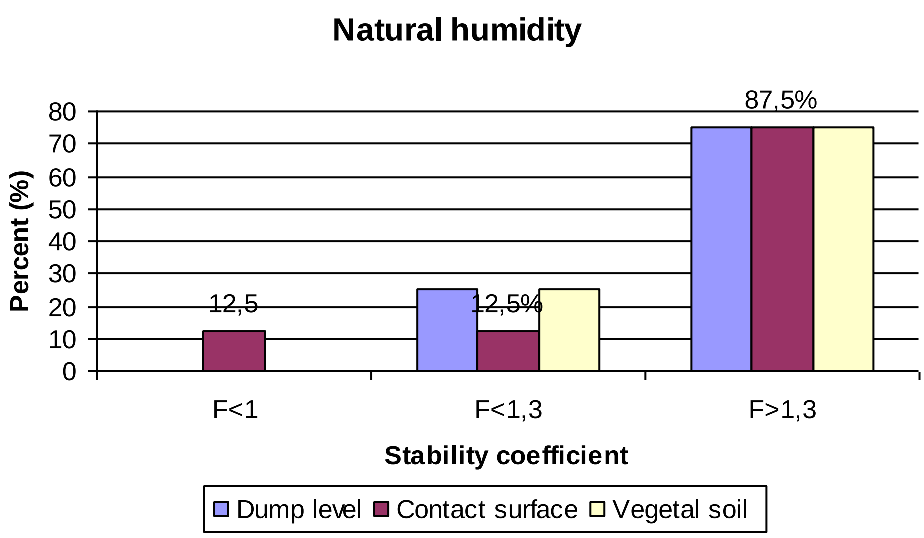


Fig. 8. Stability analysis results for the polygonal slump area to natural humidity

In fig.8 we can see that 87.5% of the slopes are stable at the dump, the contact surface and the topsoil, while 12.5% of the slopes are relatively stable in all three points of research.

In Fig.9 we can notice that 12.5% of the slopes are unstable at the surface, 25% are partially stable and 75% are stable in all three points of research.

Data on which have been made the histograms are shown in detail in the tables in chapter 3 of this thesis.

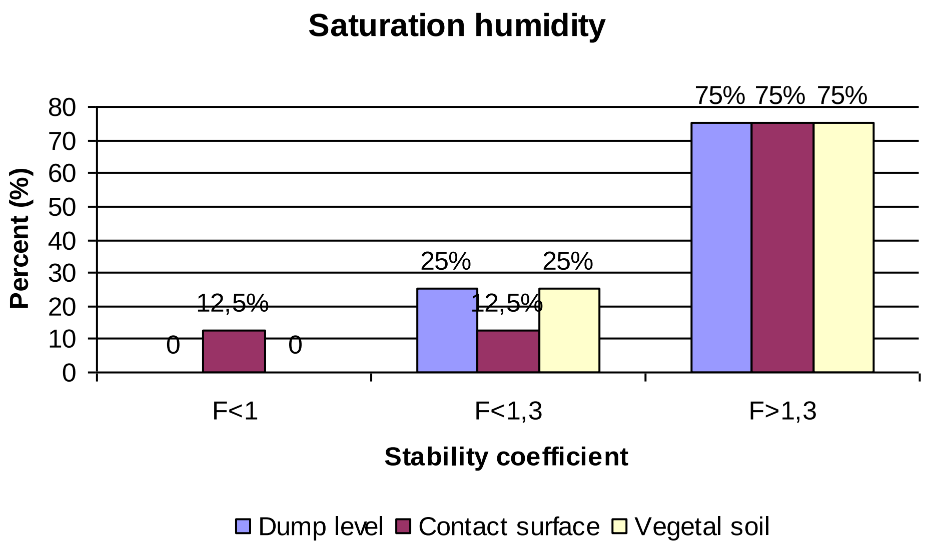


Fig. 9. Stability analysis results for the polygonal slump area to saturation humidity

4. Coal dumps inventory in the west side of Petroşani Basin

The mineralogical investigation of sterile samples collected from de coal dumps were made by X-ray diffraction method (XRD) using a DRON 3 diffractometer equipped with Bragg-Brentano acquisition module and Matmec VI.0 soft. The X-ray patterns were obtained with a Co Kα monochrome radiation. The samples were displayed in a thin film of neutral grease on a surface. The resulted X-ray diffraction peaks were identified by comparison with standard database Match 1.0 from Crystal Impact Corporation.

The minerals investigation by X-ray diffraction can detect traces of crystalline phases up to 1% by mass.

The mineralogical investigation of sterile samples by X-ray diffraction method (XRD) demonstrated that the sterile contains 50% quartz, and the other half is represented by potassium feldspar, biotite and calcite. The results are presented in fig. 10, 11, 12, 13, 14.

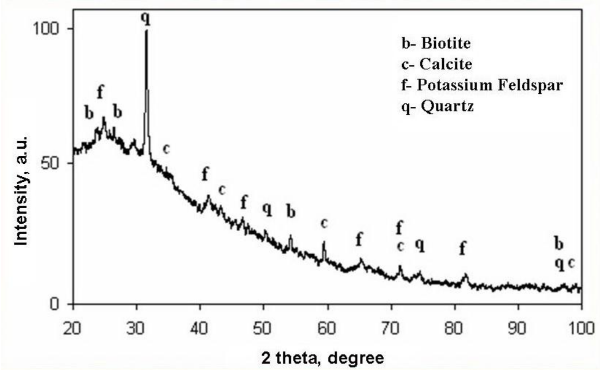


Fig. 10. X-ray diffraction pattern from west area by Vulcan sterile sample

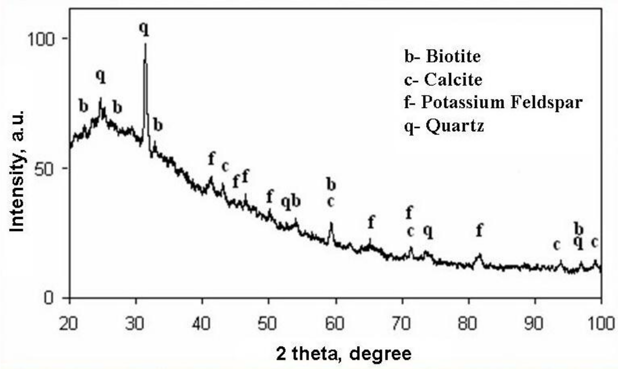


Fig. 11. X-ray diffraction pattern from Ileana Veche dump by Lupeni sterile sample

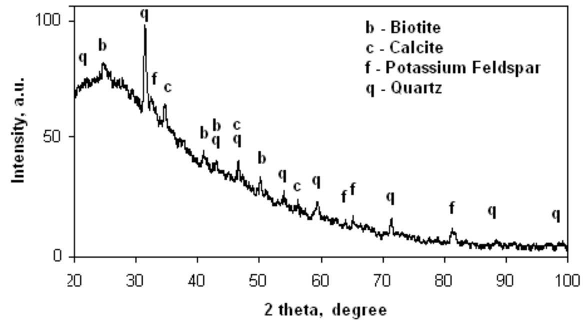


Fig. 12. X-ray diffraction pattern from Câmpu lui Neag sterile sample

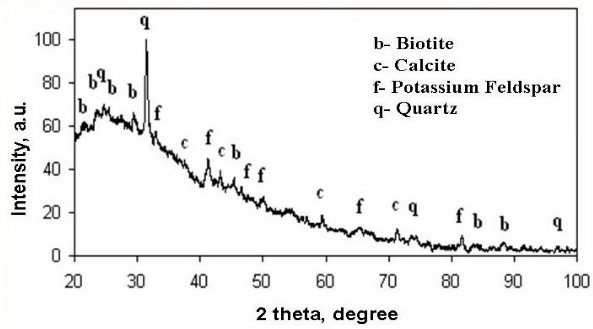


Fig. 13. X-ray diffraction pattern from Coroieşti sterile sample

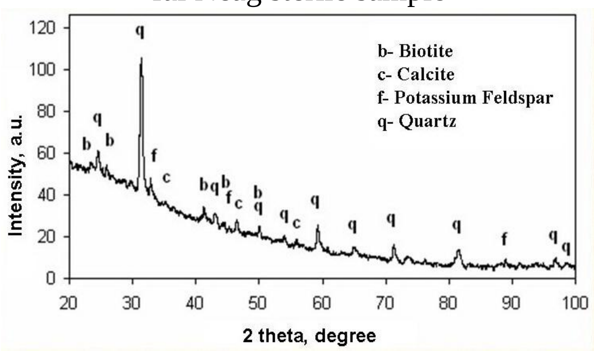


Fig. 14. X-ray diffraction pattern from Uricani sterile sample

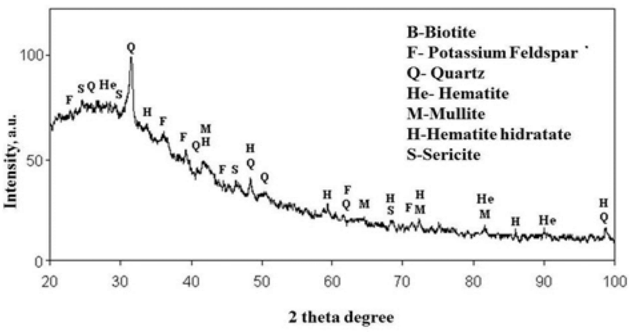


Fig. 15. X-ray diffraction pattern from Paroşeni sterile sample

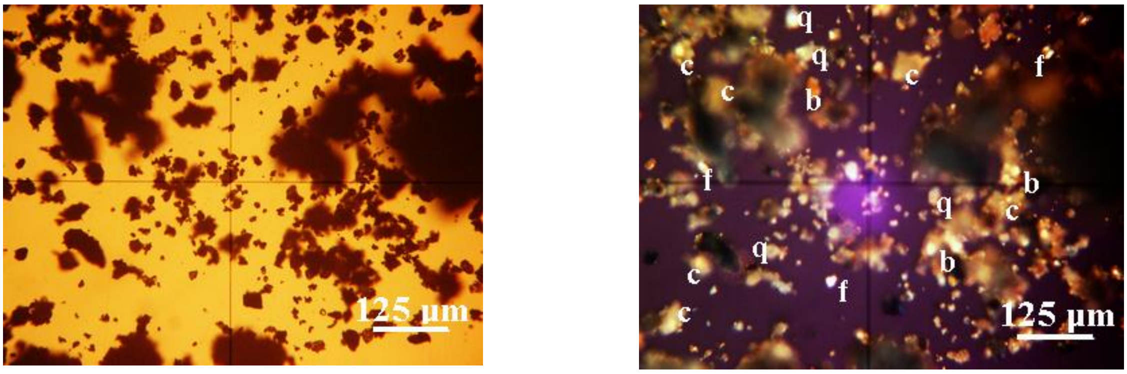
In Fig. 15 can be seen that the coal ash from Paroşeni also contains hematite, sericite, mullite and hydrated hematite.

The mineralogical investigation of sterile samples has been achieved by transmitted light and dark field optical microscopy.

The microscopic investigations in transmitted light and cross polarized light were made with an optical mineralogical microscope Laboval 2 produced by Carl Zeiss Jena equipped with a Samsung 8 MPx digital capture.

The dark filed microscopic investigation were made using an optical metalografic microscope IOR 8, with the same digital capture.

The optical microscopy results show that minerals are identical to those obtained by X-ray diffraction method. The results are presented in fig. 16, 17, 18, 19, 20, 21



a b

Fig. 16. Optical microphotographs from Vulcan sterile samples:
a) transmitted light; b) cross polarized light

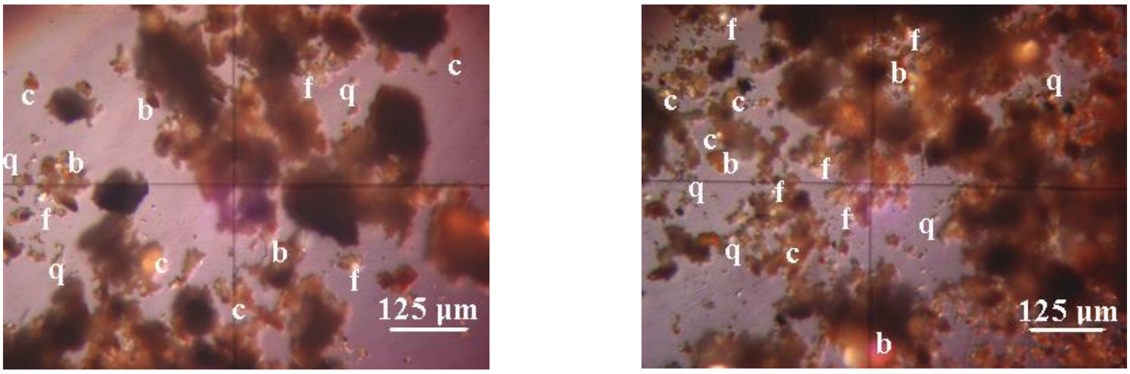
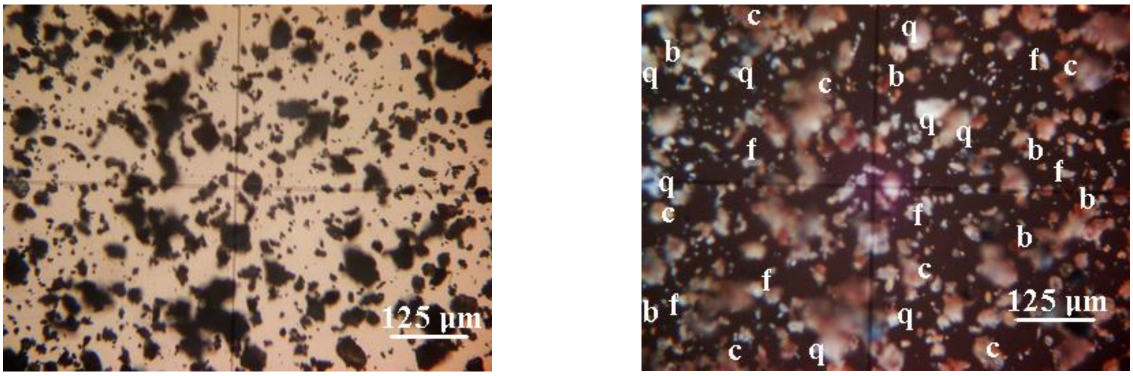


Fig. 17. Optical microphotographs in cross polarized light from Lupeni sterile samples



a b

Fig. 18. Optical microphotographs from Câmpu lui Neag sterile samples:
a) transmitted light; b) cross polarized light

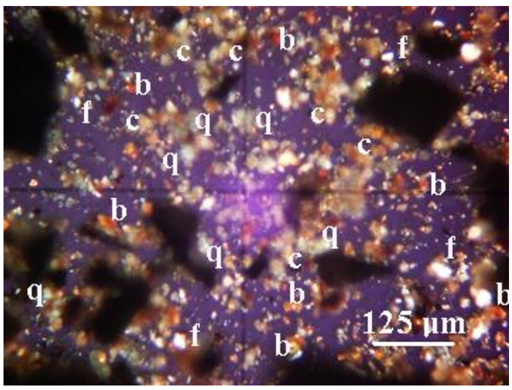
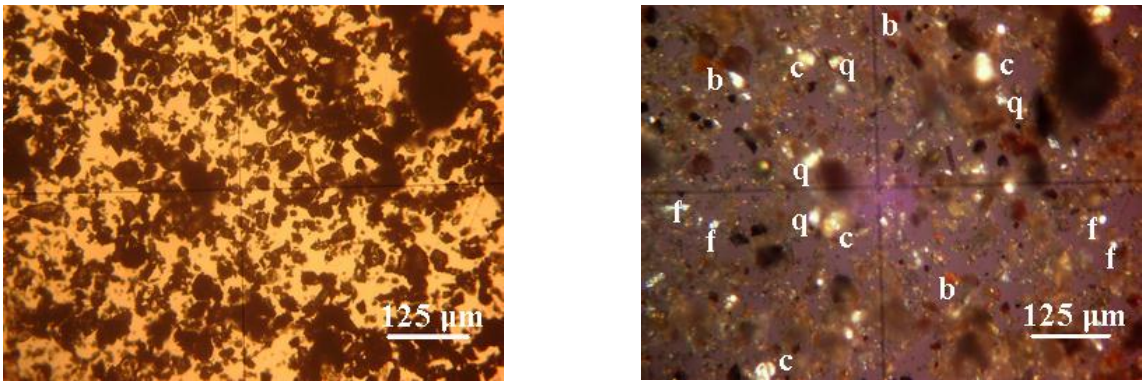
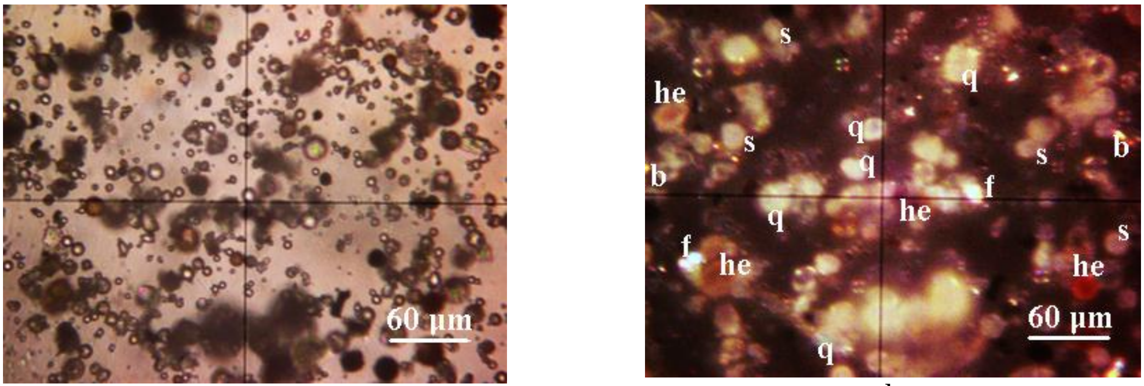


Fig. 19. Optical microphotographs in cross polarized light from Coroieşti sterile samples



a b

Fig. 20. Optical microphotographys from Uricani sterile samples:
a) transmitted light; b) cross polarized light



a b

Fig. 21. Optical microphotographs from Paroşeni ash sterile samples:
a) transmitted light; b) cross polarized light

Chemical investigation of sterile samples collected from the coal dumps were made by X-ray fluorescence spectrometry method (XRF), using a S4 Pioneer spectrometer produced by Bruker AXS. There was used a WDXRF wavelength detector for a wide range of atomic species from beryllium to uranium having a resolution of ppb range for various sample type such: soils samples or solution. The determinations are processed automatically by Spectra Plus soft using an integrated international Dyna Match database. The results are presented in fig. 22.

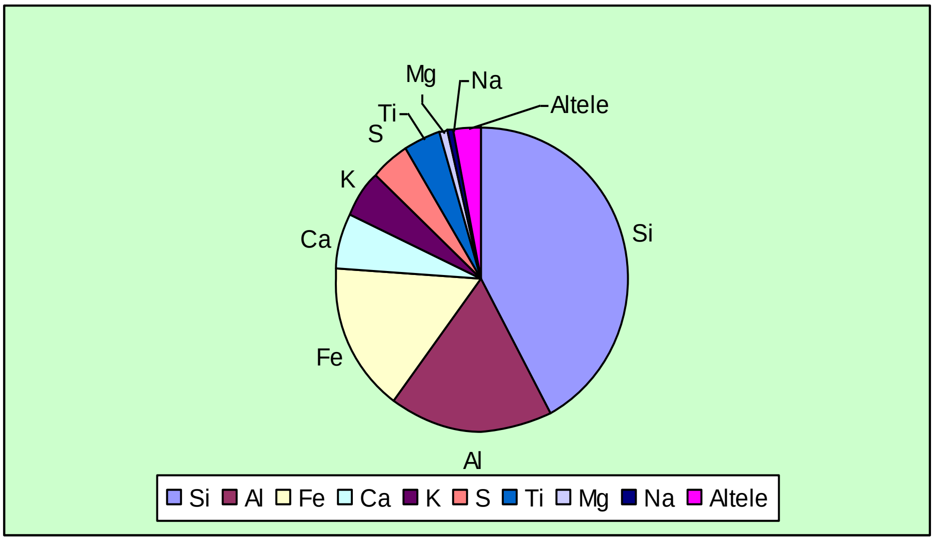


Fig. 22. Chemical elements in sterile samples investigated with the XRF

Chemical investigations have shown the presence of elements that appear in the minerals identified by optical microscopy and X-ray diffraction. The samples indicates the abundance of silicon, followed by aluminum, iron, and then in smaller quantities by calcium, potassium, titanium, magnesium, sodium. The elements present in concentrations less than 1%, cannot be detected by X-ray diffraction, for which are accepted as such in material.

5. Coal dumps rehabilitation in the west side of Petroşani Basin

Rehabilitation models of wasted mining areas are found in the works of: Marshall (1982), Chaudhury (1992), Hester et Harrison (1994), Norman et al. (1997), Georgescu (1989), Fodor (1995, 1996), Dumitru et al. (1999), Rotunjanu (2005), Biro (2005), Anghel (2009) etc.

The ecological rehabilitation of the dumps is done after ecological investigations (ecosystem type corresponding to bioclimatic zone), soil investigations (genetic type, texture and structure, cohesion, permeability, humus content, the nature of humus, litter, edaphic volume, degree of base saturation, C/N (carbon /nitrogen); pH; water holding capacity, the presence, the nature and the abundance of soluble salts, micro and soil macro-fauna; global trophicity.

The plants used for dump rehabilitation in Petroşani Basin are: sea buckthorn (*Hippöphae rhamnoides*), acacia (*Robinia pseudacacia*), pine (*Pinus silvestris*), hair grass (*Festuca pratensis*), trefoil (*Trifolium pratensis*), orchard grass (*Dadylis glomerata*). Spontaneously appeared briar (*Rosa canina*) and hawthorn bushes (*Crategus monogyna*), blackberry (*Rubus fruticosus*) and wild strawberry (*Fragaria vesca*).

To determine if the fruits of the plants that grow on the dumps can be used in food and pharmaceutical industries we have made some investigations of calcium and magnesium for the sea buckthorn, briar and hawthorn fruits. The results are presented in histograms in Fig. 23, 24 and 25. All these results were compared with those in the literature and can be observed that the investigated mineral content is within normal limits, the calcium content in fruits being higher. Only the sea buckthorn fruits have a slightly lower level of magnesium. The calcium and magnesium content was determined by atomic absorption spectrometry (AAS), using an AA 6300 Shimadzu AAS spectrometer. The results interpretation is presented in detail in the thesis in chapter 5.

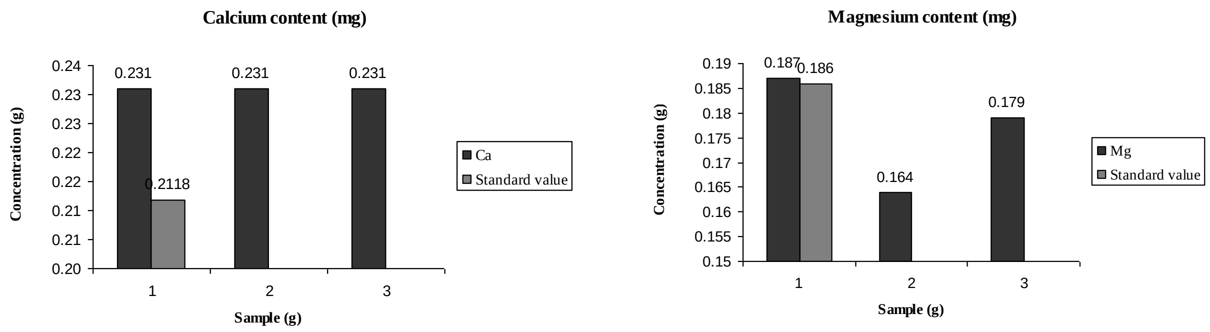


Fig. 23. a) Calcium and b) Magnesium content in sea buckthorn fruits

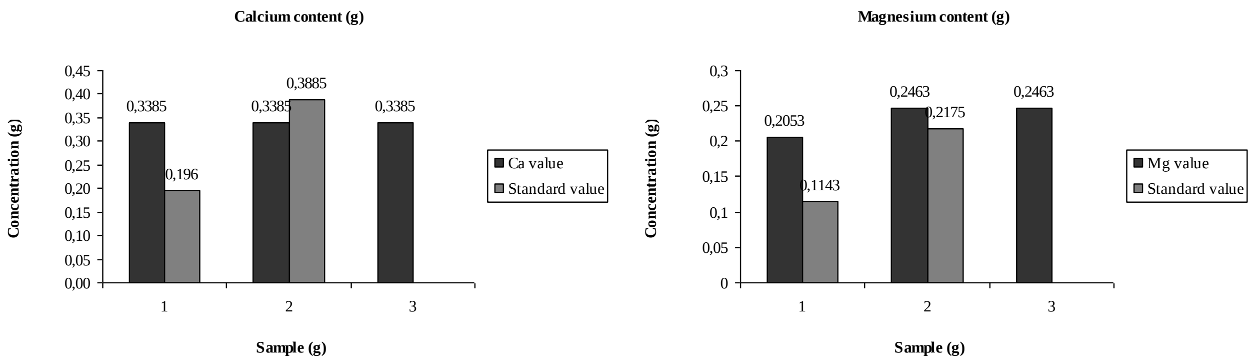


Fig. 24. a) Calcium and b) Magnesium content in brier fruits

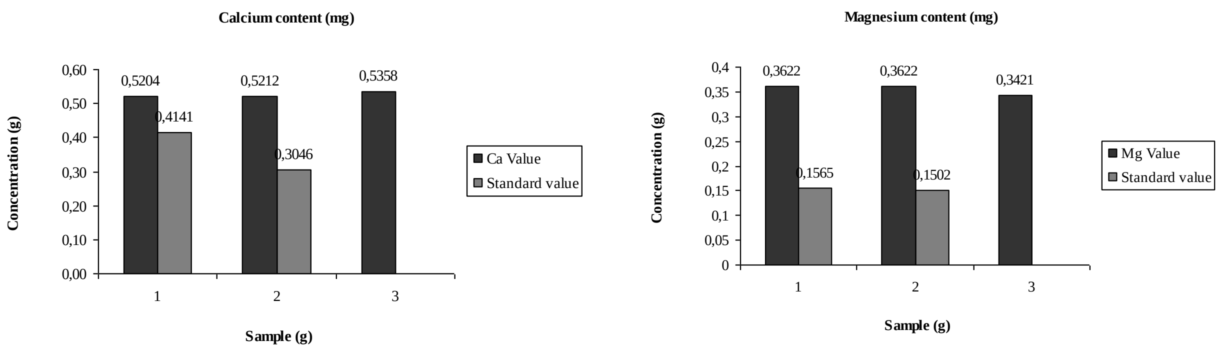


Fig. 25. a) Calcium and b) Magnesium content in hawthorm fruits

The determination of ascorbic acid in sea buckthorn fruits was done by thin layer chromatography (TLC) (fig. 26) using a silica chromatographic plate with fluorescence indicator at 254 nm. The ascorbic acid, presents a grey-yellow spot in the inferior third for ascorbic acid, in perfect resemblance with the standard sample. The sample's chromatogram reveals 1-2 grey-yellow strips after start, under ascorbic acid 2 yellow-grey strips, at level with ascorbic acid a grey-yellow strip, in superior third o yellow strip, one or more violet strips.

Hence results that fruits contain sufficient ascorbic acid pointed out by the spots but less than in cultivated plants. The sea buckthorn fruits can be used in food and pharmaceutical industry.

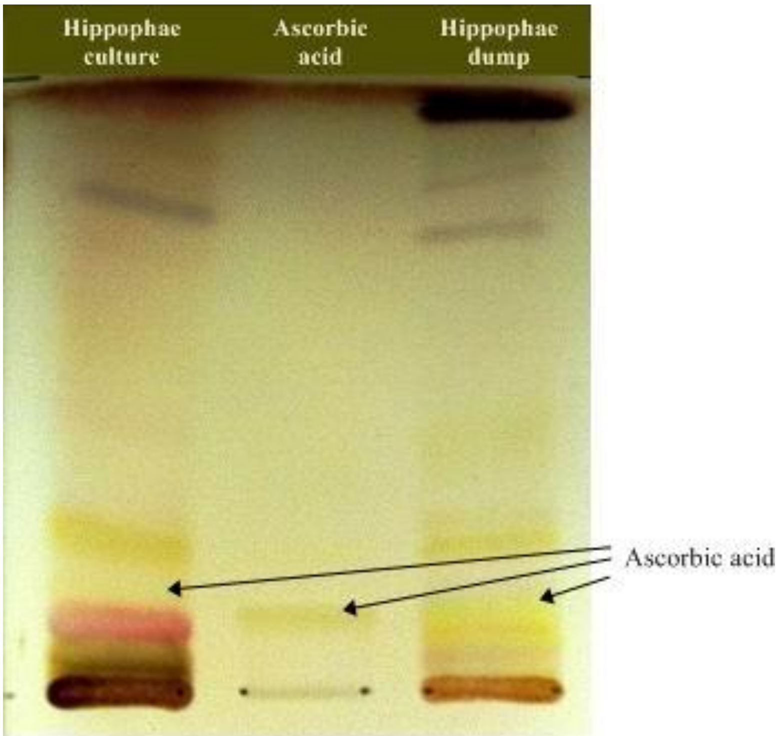


Fig. 26. Ascorbic acid determination in the sea buckthorn fruits (*H. rhamnoides*) through the CCS

The hawthorn fruit flavonoids determination was made also by thin layer chromatography (TLC) using a silica chromatographic plate with fluorescence indicator at 254 nm. The chromatogram is shown in Fig. 27.

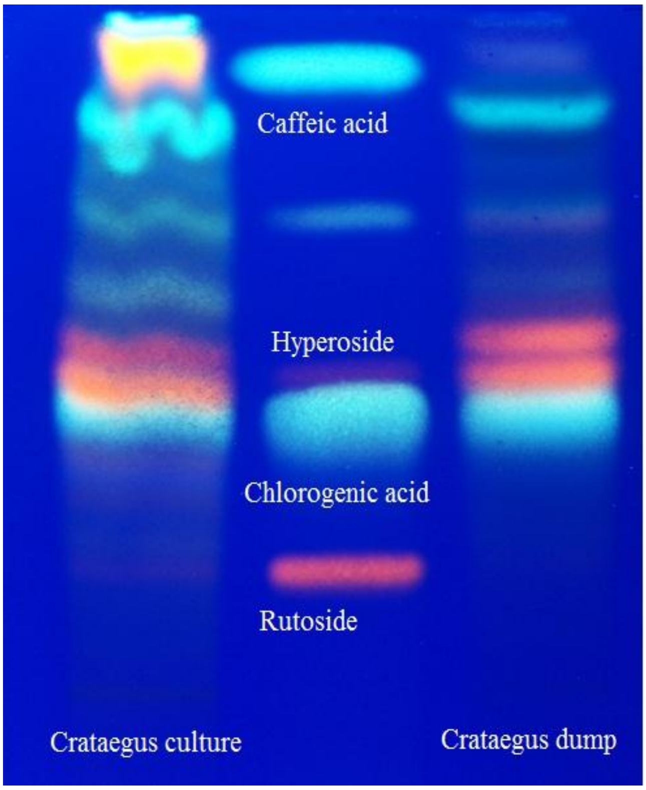


Fig. 27. Flavonoides determination in the hawthorn fruits (*C. monogyna*) through the CCS

The standards chromatogram shows: in the lower third an orange belt for rutoside, at the bottom of the middle third a blue belt for chlorogenic acid; for hyperoside an orange belt above and the upper third a green- blue belt for caffeic acid.

The sample chromatogram shows: just above the rutoside is a yellow belt, the right chlorogenic acid a blue-green belt, between chlorogenic acid and hyperoside is a blue-green belt, the right hyperoside is a orange belt, just above the hyperoside is a orange belt until the blue-green belt, and on top a blue-green belt, under the caffeic acid may be a blue poor belt, and above a blue-green belt and above caffeic acid can be: a orange belt and a blue- green belt.

Quantitative determination of procyanidine is determined by calculating the content of procyanidine expressed in cyanidine chloride and must be at least 1% according to european pharmacopoea edition (2012) and after laboratory investigations we obtained a content of procyanidine of 0.98%. Procyanidine quantity is exactly the limit, even less than 1%.

The flavonoids determination (hyperoside) from hawthorn fruits was achieved by high performance liquid chromatography (HPLC) using a Varian Star HPLC system. The chromatograms are shown in Fig. 28 and 29.

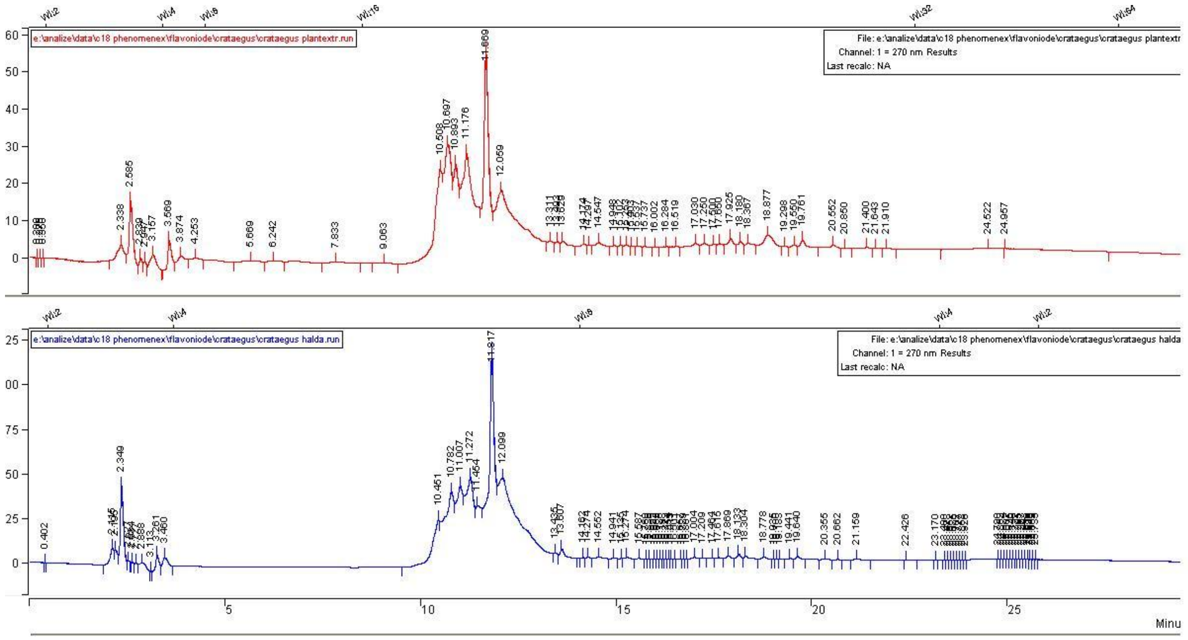


Fig. 28. HPLC chromatogram of flavonoids in hawthorn sample fruits collected from the dump and culture

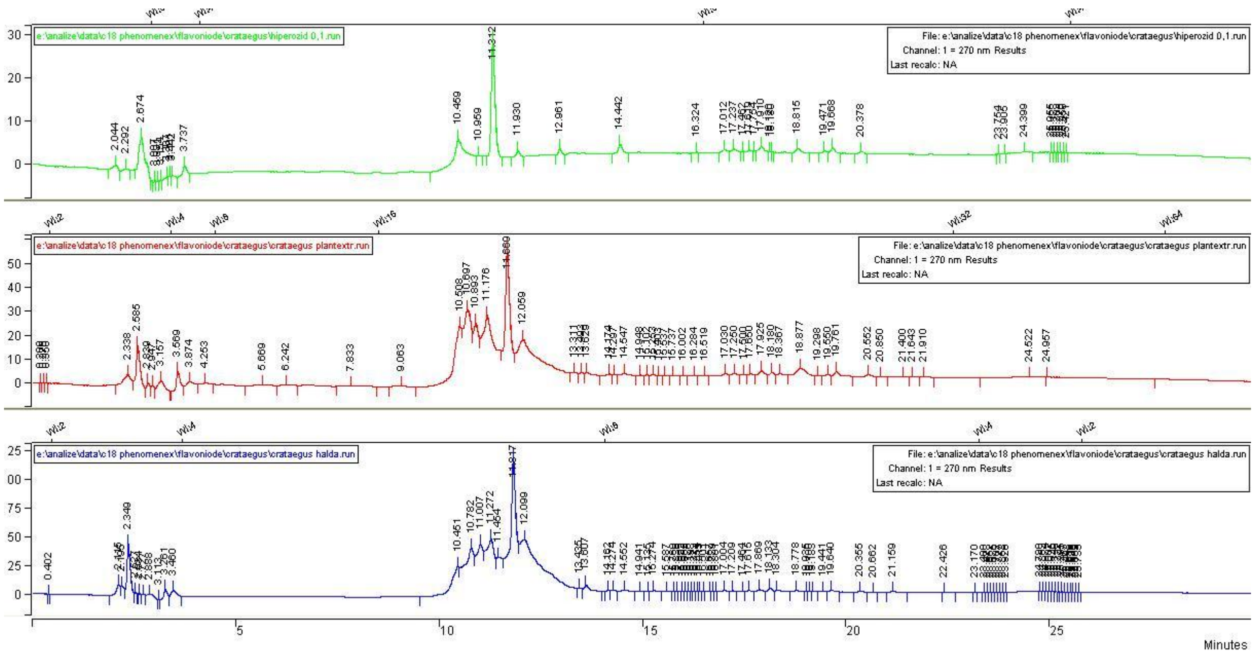


Fig. 29. HPLC chromatogram of hyperoside in standard sample hawthorn fruits, from culture and from coal dump sample

From HPLC spectrum obtained in Fig. 30, 31 and 32 we can identify the hyperoside who has the same maximum in all three figures. Small differences occur due to different concentrations of standard sample and investigated samples.

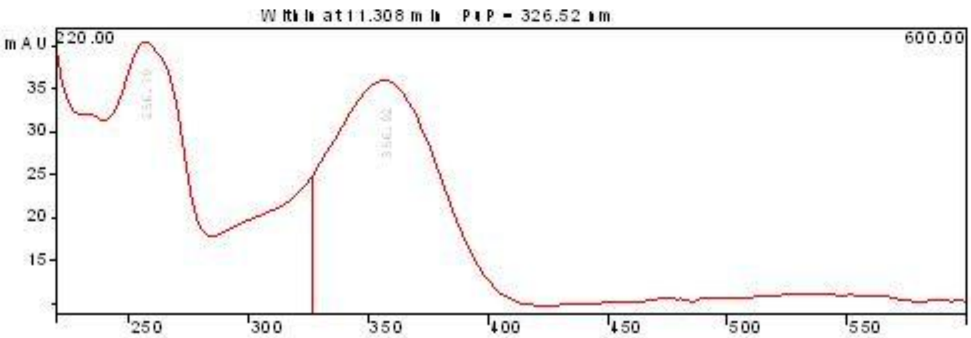


Fig. 30. Hyperozide spectrum in standard sample

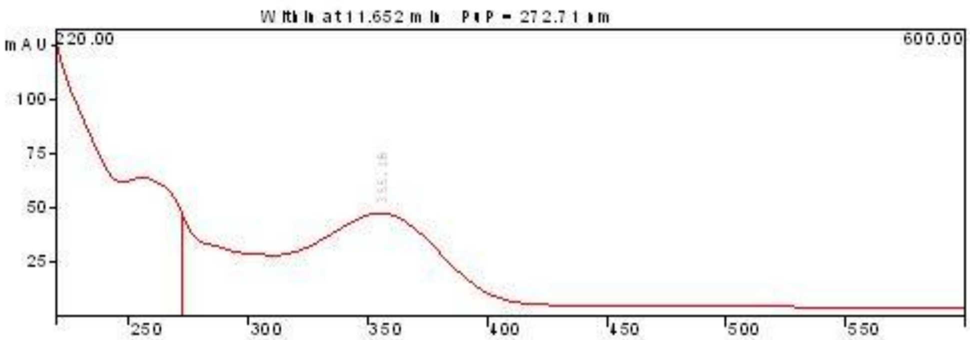


Fig. 31. Hyperozide spectrum in culture sample

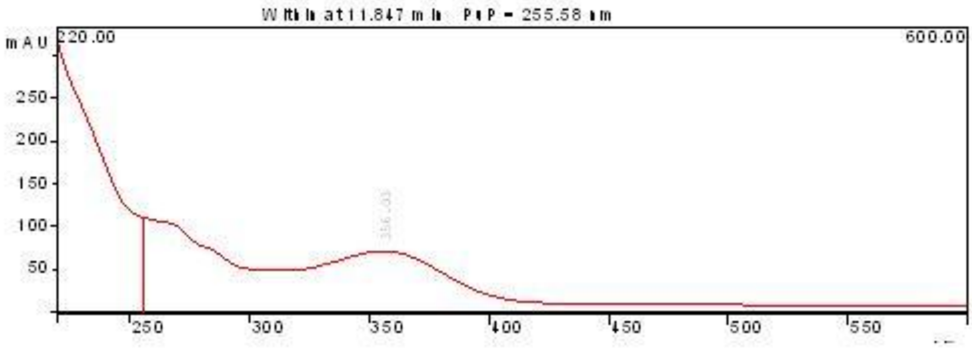


Fig. 32. Hyperozide spectrum in hawthorn fruits from the dump

Based on the results of all investigations we have proposed an algorithm to the dump rehabilitation (Fig. 33). This algorithm is presented in detail in the thesis in chapter 5.

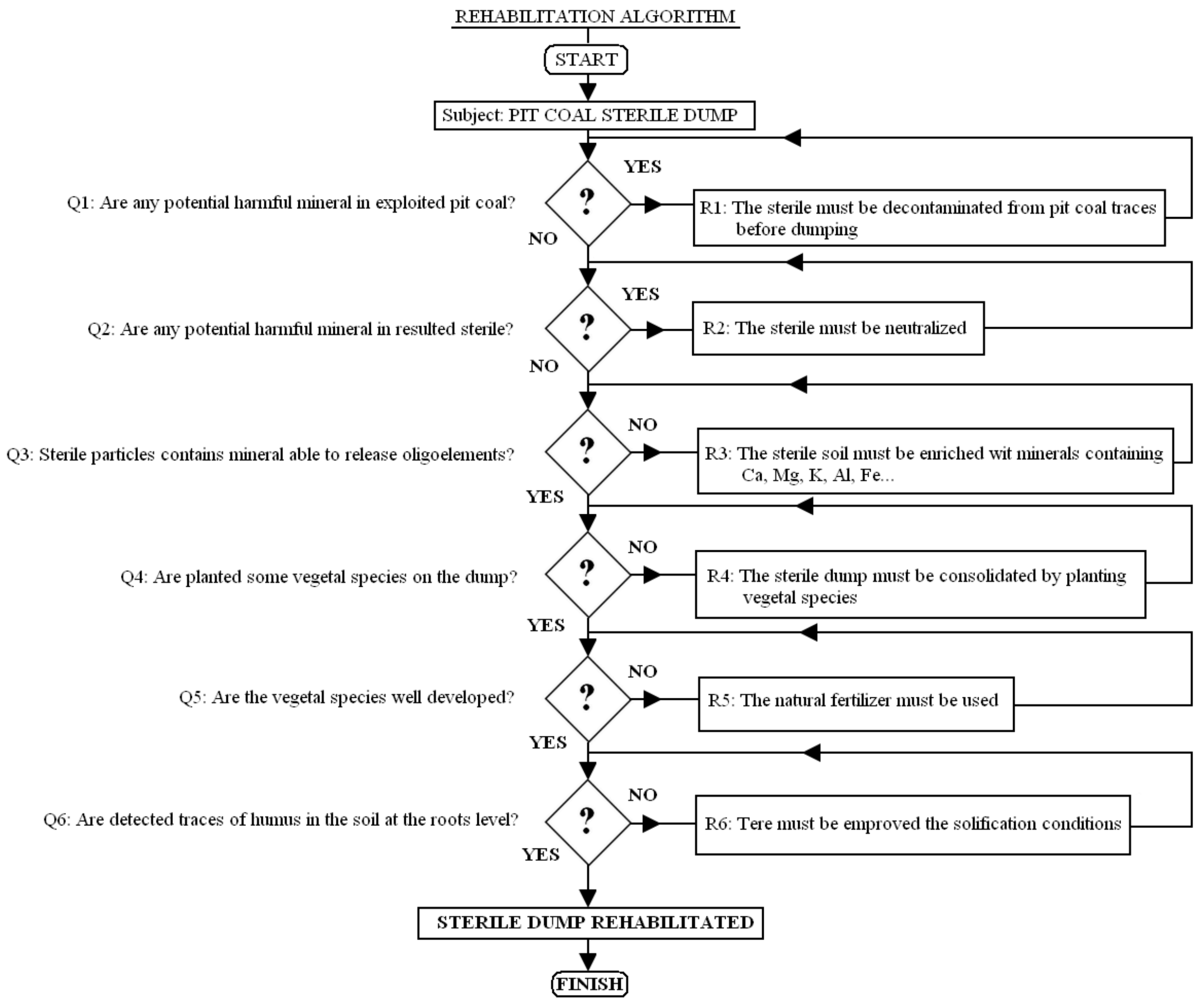


Fig. 33. The sterile dump rehabilitation algorithm

6. Coal ash recycling from Paroşeni power station by magnetic separation

Producing electricity by coal burning proves to be harmful for environment, due to the NO_2 and SO_2 emissions and resulted ashes. Some mineral intrusion in coal samples such: quartz, biotite, feldspar, hematite and sericite were found. Burning the coal, those intrusions become ash which is stored to dump via wet convey. Investigating the dumped ash we found: quartz, feldspar, hematite hydrate, sericite, and mullite. Mullite originated from biotite clay particles as a consequence of high temperature during coal burning. By same reason we assumed that the hematite particles are reduced to microscopic spheres of melt iron due to surface activity. We found some sphere in the coal ash revealed by optical microscopy, proved to be hematite hydrate by the X- ray diffraction investigation. By magnetic sorting results an amount of 10% particles, of hematite hydrate spheres evidenced by X-ray diffraction and optical microscopy. The explanation is given by formation of melted iron spheres during coal burning which are transformed further to hematite hydrate due to the re-oxidation process involved at dump by condition of wet transport and weathering. The observed hematite hydrate micro-spheres prove to be a raw material for powder metallurgy. We propose a technological flux for spherical elemental iron powder production (fig. 34). The hematite content of 10 % in some thousand tons of coal ash is a favorable indicator for industrial implementation of proposed technological flux on a recycling plant.

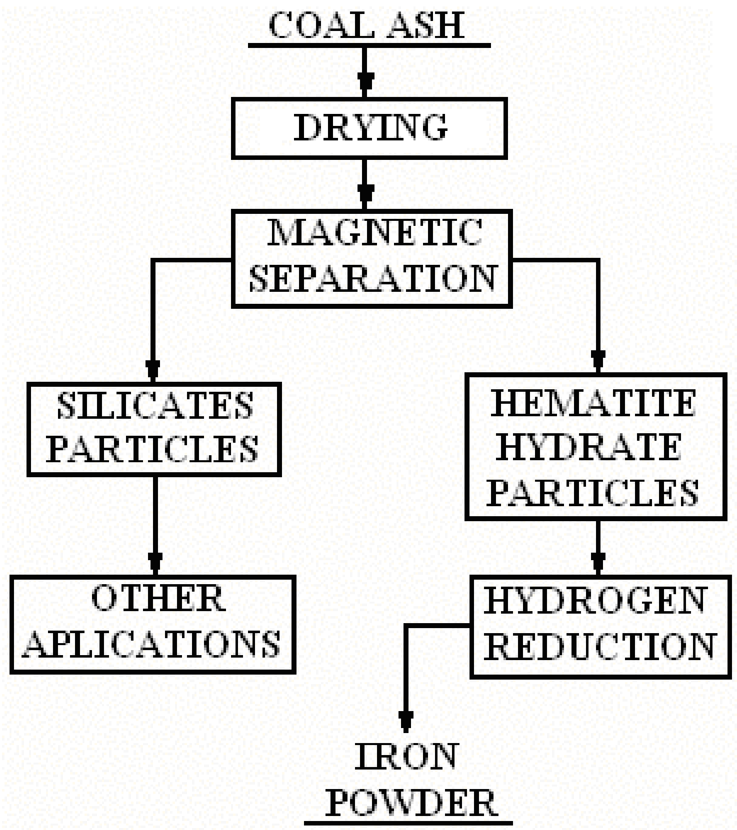


Fig. 34. The hydrated hematite recycling technological flux

Conclusions

1. Petroşani Basin is a post-laramic inter-mountain tectonic depression, characterized by intense subsidence suggested by the thick stack of sediments and the large number of coal layers.

2. The sterile stock in the active dumps is composed by a heterogeneous mixture that contains clays, sandstone, marl, shale, from petrographic point of view, and the particles grit correspond to sand, gravel and boulders. From the mineralogical point of view the sterile consists of quartz, potassium feldspar, biotite and calcite.

3. Dumps stability or resilience is expressed numerically by the safety factor which can be calculated with the Jambu, Fellenius and Bishop method or with a specialized software in geotechnical, GeoTecB.

4. In the power plant ash dump were found three different minerals missing in the sterile dumps: mullite, sericite and hematite. The hematite particles have to be reduced to microscopic spheres of melt iron due to surface activity. We found some spheres in the coal ash revealed by optical microscopy investigation, which proved to be hydrated hematite after analyzing by X-ray diffraction. After magnetic sorting results an amount of 10 % particles, which prove to be hydrated hematite by X-ray diffraction and optical microscopy. The explanation is given by the formation of melted iron spheres during coal burning, which are transformed further to hematite hydrate due to the re-oxidation process involved at dump by condition of wet transport and weathering. The hematite hydrate micro-spheres prove to be a raw material for powder metallurgy.

5. Investigations carried out by optical microscopy showed the particle size ranging from 5-10 μm to 150-300 μm and confirmed the mineralogical composition of the sterile which was investigated by X-ray diffraction.

6. For ecological rehabilitation of the dumps in Petroşani Basin were used plant species which were planted directly on sterile. These plant are represented by: acacia (*Robinia pseudacacia*), pine (*Pinus silvestris*) and sea buckthorn (*Hipppöhae rhamnoides*).

7. Landscape rehabilitation of dumps can be made using vigorous-growing plant species, strong rooting and well-developed crowns with rich foliage, to be reintegrated into ecological circulation. Temperature, light and rainfall are key factors for plant multiplication and their spread on the dumps.

8. Following quantitative determinations of calcium and magnesium in the laboratory of sea buckthorn, brier and hawthorn fruits collected from the dumps, we noticed high calcium content for all three fruit and lower magnesium content only for sea buckthorn fruit. In these circumstances, these fruits can be used in food and pharmaceutical industry.

9. Qualitative determination of ascorbic acid in sea buckthorn fruits was made in the laboratory by thin layer chromatography. The results were compared with a sea buckthorn culture sample. The sea buckthorn chromatogram shows that this fruit content ascorbic acid, so that can be used in food and pharmaceutical industries.

10. Flavonoids determination for the hawthorn fruits was done in the laboratory by thin layer chromatography, too. The results were compared with a hawthorn culture sample. The results showed the presence of rutoside, chlorogenic acid, caffeic acid and hyperozide.

11. Quantitative determination of procyanidine is determined by calculating the content of procyanidine expressed in cyanidine chloride and must be at least 1% according to European Pharmacopoea Edition and after laboratory investigations we obtained a content of procyanidine of 0.98%. Procyanidine quantity is exactly the limit, even less than 1%.

12. Flavonoids determination for hawthorn fruits was also carried out by high liquid performance chromatography (HPLC). Results show the hyperozide in dumps and culture sample having the same maximums and the same aspect. The small differences regarding the aspect are due to the different concentrations from the standard and the samples.

13. Dumps rehabilitation can be achieved based on calculus algorithms. We can design a suitable algorithm for any pit coal sterile dump rehabilitation considering the critical questions and presented cycling instruction. The logical scheme is suitable for any programming medium such Fortran, C++, Turbo Pascal.

14. The designed algorithm could be developed in a proper programming medium with additional data base regarding standard parameters and could be programmed into an interactive manner to evaluate the rehabilitation state of similar sterile dumps as well as to predict the necessary steps to achieve a good level of rehabilitation.

15. According to this proposed computational model, the humus presence and the adsorption of mobile phosphorous and nitrogen at the soil level confirms that the *P. sylvestris* population induce the transition from the entiantrosoil category to fertile one.

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