U.P.B. Sci. Bull., Series B, Vol. 77, Iss. 4, 2015 ISSN 1454-2331

AN INSIGHT INTO ROMANIAN SCHISTS AND THEIR USE

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By schist (shale) we mean a mixture of organic mass and various rocks existing in the environment, in which the inorganic mass is predominant. Usually, schists occur when magmatic rocks come in contact with the sedimentary ones. Classical analyses give erroneous results due to thermal changes suffered by the accompanying rocks. This paper presents new methods that can differentiate humic shale from bituminous *shale by extraction with solvents and by differential thermal analysis (DTA). The paper tries to demonstrate that exploitation of such schists directly into the reservoir (underground gasification and other new methods) may lead to environmental pollution. In this context, we suggest that the schist exploitation should take place by utilizing it where both the organic and inorganic mass are simultaneously exploited.*

Keywords: schist, humic schist, bituminous schist, blackstone

1. Introduction

Commonly schist deposits occurrences that are associated with organic carbonaceous and graphitic material have been reported from Paleozoic, Mesozoic and Tertiary periods [1-5]. Schist deposits (i.e. mixtures of inorganic rock and organic sediments of humic or sapropelic nature), usually occur at the contact between magmatic rocks and sedimentary deposits. They can, over time, get enriched with organic mass, and can turn into what we know as deposits of coal or crude oil. Such material exists in many European countries [6-8].

Polyphase mineral aggregates (PMAs) composed of clinozoisite kyanite, quartz, chlorite, paragonite, phengite have been found within garnet and in the matrix of talc-garnet-chloritoid schists from the Makbal ultrahigh-pressure complex in the northern Kyrgyz Tian-Shan. These mineral textures are interpreted as pseudo morphs after lawsonite, and the authors reconstructed the compositions of PMAs of clinozoisite, kyanite and quartz consistent with lawsonite. Trace element characteristics of the clinozoisite grains in the PMAs (former lawsonite) show a flat rare earth element (REE) chondrite-normalized pattern, comparable

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with the typical reported REE pattern of lawsonite, although the abundance of REE varied from sample to sample. Thus, the REE content of clinozoisite in the PMAs included in garnet was likely inherited from the former lawsonite as the decomposition reaction took place isolated from the matrix. Discrete clinozoisite grains in the matrix have high light REE enrichment over heavy REE in the chondrite-normalized pattern, consistent with the typical epidote pattern. Our results indicate that the talc-garnet-chloritoid schists in the Makbal complex were buried to great depth (> 100 km) with a low geothermal gradient (< 6 °C/km) during the Early Paleozoic (480–509 Ma). Lawsonite decomposition and clinozoisite-forming reactions accompany fluid release during the isothermal decompression stage, shows that the fluids can be generated not only during subduction, but also during exhumation of ultrahigh-pressure rocks in cold subduction settings [9].

Numerous mineralogical, micro morphological and geochemical studies have suggested that even the smectite present in the majority of Mesozoic sediments are mainly of continental origin. Furthermore, it is seen that the smectite present in many soils is usually a product of tri octhaedric smectite alteration inherited from the alteration of basaltic nature rocks. All this basic information can come in handy when working in the forensic archaeological field. Indeed, traces of soil adhere to various substrates (boots, shoes, fabrics , garments and parts of vehicles) most often differ significantly from the plot of origin for the particle size distribution and the finer fraction appears to be the best representative of the sediment of origin. The identification of the origin and / or the compatibility of mud, soil or other geomaterials traces found on objects can make a significant contribution at all stages of an investigation. In particular, the stages, clay have been shown to have a good discriminating power and identification of specific formations [10].

A few 5 or 6 decades ago there were attempts to exploit such schists by underground gasification or other local exploitations, but testing proved unsuccessful due to excessive pollution of the environment coming out as a result.

The methods of analysis used for coal and crude oil do not correspond to the case of schists, therefore, in this paper, we try to characterize the schist obtained by extraction [11].

Schist - sedimentary rock created by the simultaneous deposition of fine inorganic mass about 70% and more, and the remaining until 100%, organic mass. If organic mass is bituminous (oily material with different viscosities) this rock presents economic uses (shale in Estonia, USA, etc.). If organic mass is humic - carbonaceous type, the use in combustion is uneconomical. It consumes more heat in order to compensate endothermic effects of inorganic mass.

In the period 1980 - 1985 during researches for new energy sources for power Anina plant were exploited Anina and Doman schists by quarrying. Schists quality due to use without research for this type of fuels, lead to inoperative power plant and damages of about $ 1 billion. Research done by ICEMENERG (Ionescu Ionel and Barca Fr.) made in order to justify the failure, located at the level of preliminary investigations denied the bituminous structure of these materials.

In conclusion, there is no research results able to justify a comparative analysis with the results obtained in this paper.

This paper is a first study regarding the quality of Romanian schists, which reveals the humic, coal structure and their effective use possibilities.

IR spectra were done and presented in order to prove that their whole structure is humic and not bituminous. It is not normal to discuss maximum related to organic substance contaminated with more than70% inorganic substance.

In Lowry H.H. Chemestry of coal UTILISATION New York in 1964 and I. Blum, Boat FR., Musca G., Bidulescu A. Article published in FREIBERGER FORSCHUNGSHEFTE - Heft A 473 Romanian coal containing 80% organic mass spectra are presented. Given spectra show schists appearance without possibility to discuss maximum because are altered by inorganic mass.

The work represents a beginning for valorification of Romanian humic schists easily exploitable in career.

2. Materials

Samples were collected from surface schist in the Banat (Anina and Doman), area. Samples were lyophilised, ground and conserved in glass recipients out of light exposure before their analysis.

Reagents

All the reagents used were analytically grade and purchased from Sigma-Aldrich. For solutions preparation distilled water has been used. All the experiments were carried out in duplicate sets. All measurements were performed in parallels in each set.

Apparatus

Soxhlet and thermostatic bath (C Digibath-2) from Trade Raypa were used. Termogravimetric balance LABSYS evo and spectrographic equipment in infrared (ABB MB3000**)** was then used.

For the analysis, 0.5 g of lyophilised grass sample were spiked with 1 mL of a standard solution containing the organic solvent studied in a concentration of 0.1 mg/L, sonicated for 5 min and let to stay 20 min before extraction procedure usage.

The sample was introduced into a glass fibre filter and extracted in a Soxhlet equipment with 100 mL of organic solvent (1:1, v/v) during 20 h. After cooling, the extract was concentrated to 1 mL using a rotary evaporator. The extraction process was followed by a clean-up step using solid-phase extraction with florisil and alumine as adsorbents. Alumine was pretreated before its use. Soxhlet extraction of alumine was performed with Benzene, Benzene-alcohol, Methyl-Ethyl-Ketone, Pyridin, Quinoline, Diesel fuel, Tetralin (2:1, v/v) during 12 h and then another 12 h with Benzene, Benzene-alcohol, Methyl-Ethyl-Ketone, Pyridin, Quinoline, Diesel fuel, Tetralin (30:70, v/v). Once dried, alumine was activated at 350 ^{o}C for 12 h and further deactivated with Milli-Q water (10%). Then 2 g alumine was added to a Florisil Sep-Pak cartridge (5 g) connected to a Visiprep vacuum distribution many fold. Previously to its use, the cartridge was washed with the elution solvent and air dried during 30 min. Finally, the eluate was characterized. Organic mass thermogravimetric and spectrographic equipment in infrared was then used.

3. Results and discussion

The solvent selected for the extraction was composed of: Benzene, Benzene-alcohol, Methyl-Ethyl-Ketone, Pyridin, Quinoline, Diesel fuel, Tetralin (1:1, v/v) due to the fact that this mixture is one of the most adequate for the organic mass extraction due to good recoveries obtained and lower time consumed with evaporation compared to other solvents [12].

In order to know the capacity of processing the schist obtained by extraction and its behavior when burnt, we studied the interaction between specific and non-specific solvents on samples, one composed of schist with macroscopic earthy structure (aspect), called humic schist, and the other formed of schist with tar-like structure, called bituminous schist.

The organic mass of these samples was characterized by the extraction with specific and non-specific solvents. The results are listed in Table 1.

Table 1

Study of the possibility of extraction of different schist types, in Romania

Solvent	Ammounts %			
	Earthy schist		Tar-like schist	
	Extract	Residue	Extract	Residue
Benzene	thin traces	100	very thin traces	≈100
Benzene-alcohol	traces	100	thin traces	≈100
Methyl-Ethyl-Ketone	traces	100	thin traces	≈100
Pyridin	5	95	3	≈97
Quinoline	10	90	5	≈95
Diesel fuel	4	96	2	≈98
Tetralin	14	86	8	≈92

According to data presented in table 1, results that Romanian schists are characterized by a low content of organic mass, which can be extracted with a solvent specific to coal and not with solvents specific to sapropelic masses. It is expected that the nature of such material be clearly different from the one presented in most treatises in the field: they might be humic, not bituminous schists [13].

The influence of specific and nonspecific solvents on tar-like schist is much lower than the influence of the same solvents on earthy schist.

To throw light on certain aspects related to the chemical composition of organic mass within the schist, elementary analyses were performed on pyridine, quinoline, and Diesel fuel extracts. The results obtained are shown in Table 2.

Table 2

Elementary analysis of extracts and of extraction residues resulting from schist

Specification	Reported to the base of analysis %				Reported to the combustible mass %	
	Humidity W^a	Ash A^a	Carbon C^a	Hydrogen H^a	Carbon C^{mc}	Hydrogen H^{mc}
Extract with pyridin	1.13	27.02	60.83	7.02	84.32	9.77
Extract with quinoline	1.35	2.56	75.58	2.10	87.85	2.43
Pyridinic residue	1.16	5.54	11.76	2.17	50.47	9.31
Quinolinic residue	1.73	4.42	74.48	4.45	78.85	4.71
Diesel fuel residue	0.87	74.13	13.82	2.31	55.28	9.24

Analyzing the data in Table 2, results that humic material occurs in both schist samples, with a high percentage of carbon, i.e. with high carbonization level.

For tar-like schist samples were used both thermo-gravimetric [14] and thermo-differential analysis. The results are shown in Figs. 1 and 2. The assays were carried out in an oxidizing environment (air) at a heating rate of 10 °C/min.

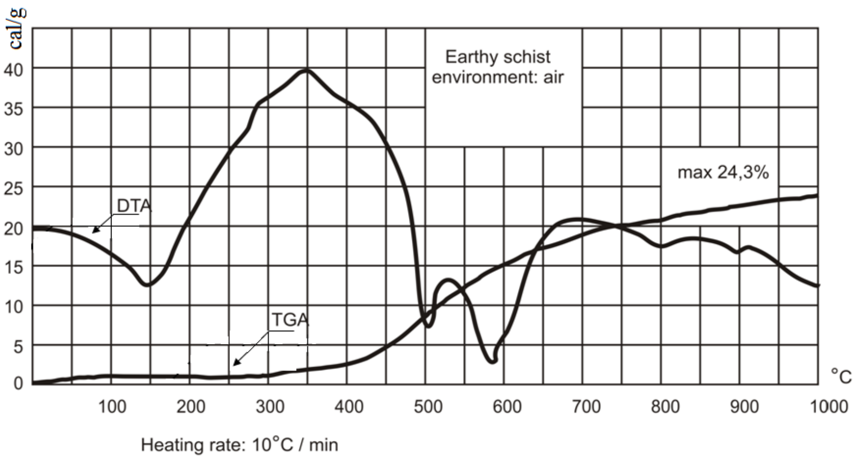

Fig.1. Thermogram of earthy schist

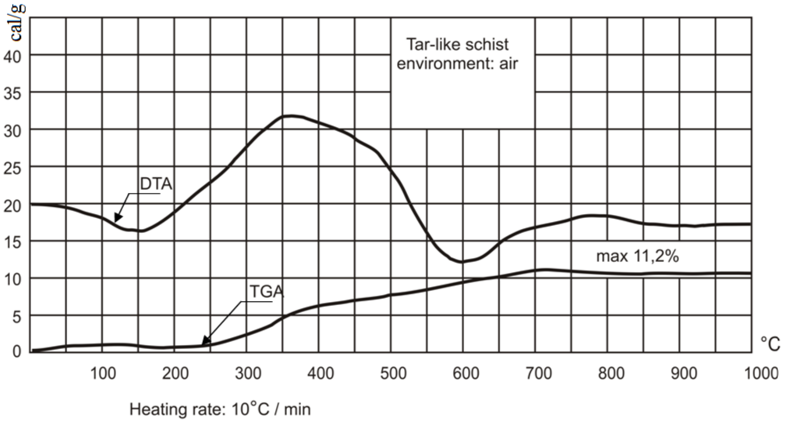

Fig. 2. Thermogram of tar-like schist

The analysis of the two thermograms showed that the combustion intervals are similar for the two materials, at the same temperature, i.e. between 250 and 480 °C; their maximum heating points could be interpreted as auto-ignitions, around 350 °C. The maximum mass losses reach 24.30%, for earthy schist, and 11.2%, for tar-like schist, thus highlighting the much lower content of organic mass in it.

For the earthy schist, three endothermic peaks were recorded at 150 °C, 500°C and 580°C; these maximum peaks could be attributed to some loss of water (150°C) or tailings isomorphic transformations (500-580 °C).

In the tar-like schist there are only two weak endothermic peak at 150°C and 580 °C. In order to be sure that these maximum peaks are due to tailings or organic mass, a sample of ash was prepared, at 300 °C using ICPET method [13], while its thermogram was made. The results are shown in diagram 3.

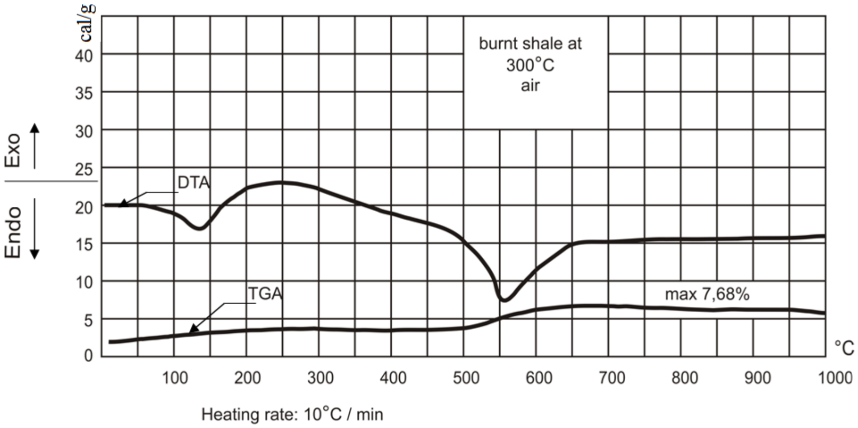

Fig. 3. Thermogram of ash resulting from the combustion of earthy schist at 300°C

The observation of thermogram presented in Fig. 3, confirms the presence of reversible endothermic conversion at 150 °C (probably water elimination) and also of endothermic transformations, which proved to be stronger at 580°C.

Both transformations are accompanied by mass loss. However, endothermic transformation, at a temperature of about 500°C does not occur any longer [13, 14].

In order to observe whether the substances are distillable or not, the thermograms were studied in an inert environment of hydrogen and respectively nitrogen. The thermograms are shown in Figs. 4 and 5.

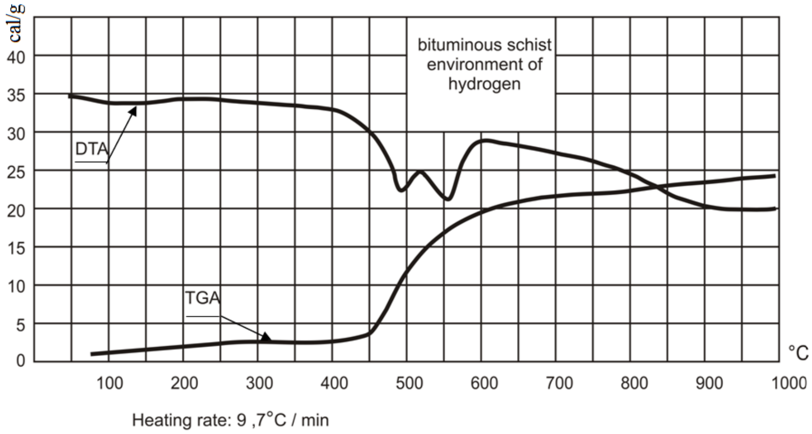

Fig. 4. Thermogram of bituminous schist in a reducing environment

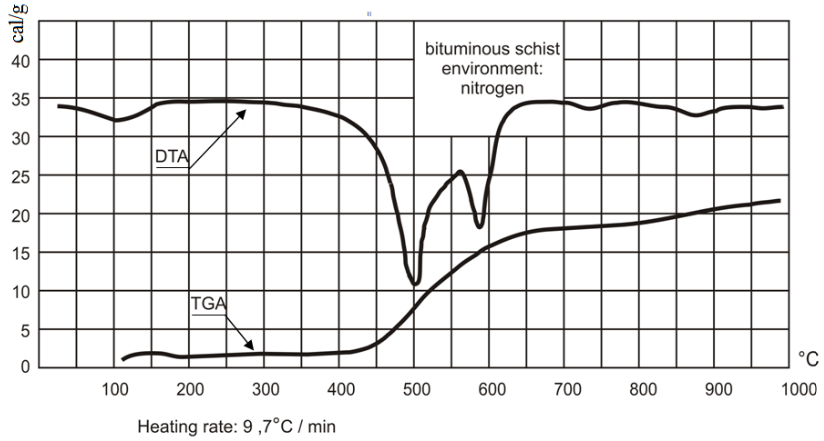

Fig. 5. Thermogram of bituminous schist in an inert environment

From the above thermograms, results that, between 400 and 500 °C, weight losses of about 15-18% occur, but were not entirely due to the products of decomposition of the organic mass; about a half of them might be due to dehydration of the kaolinite existing in the schist, whose maximum endothermic points occur in this area.

In order to monitor the schist quality, and to demonstrate that such losses, in the thermal process are due mostly to the organic mass, we designed diagram 6.

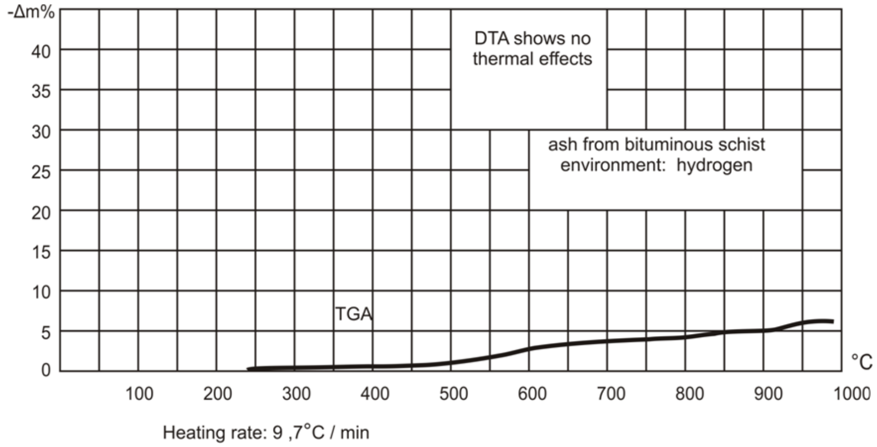

Fig. 6. Thermogram of schist ash in reducing environment

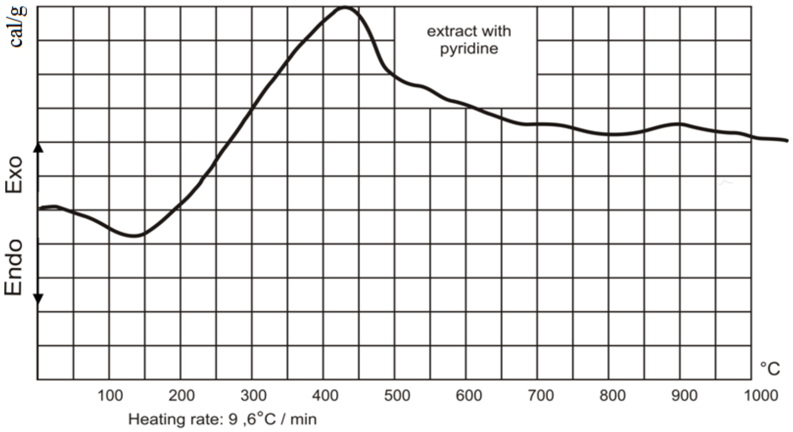

Fig. **7**. Thermogram of the extract with pyridine

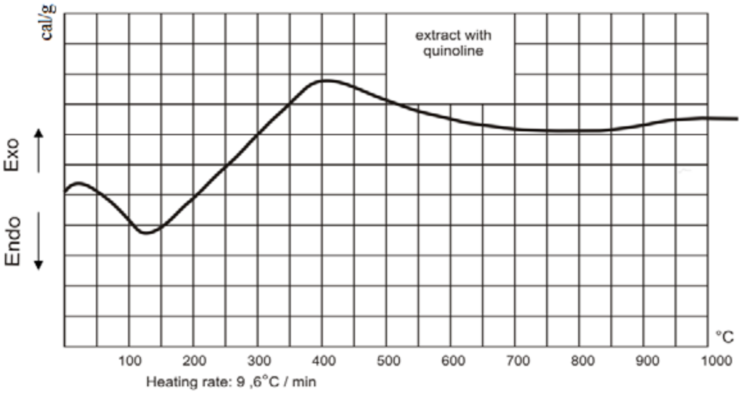

Fig. 8. Thermogram of the extract using quinoline

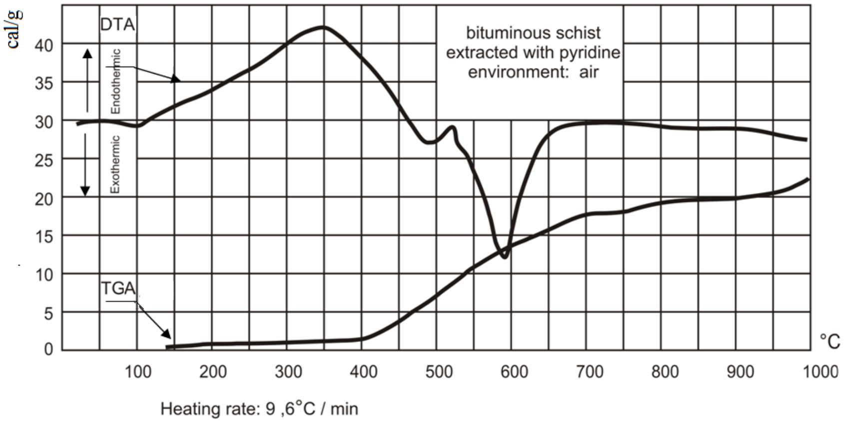

Fig. 9. Thermogram of the extraction residue using pyridine

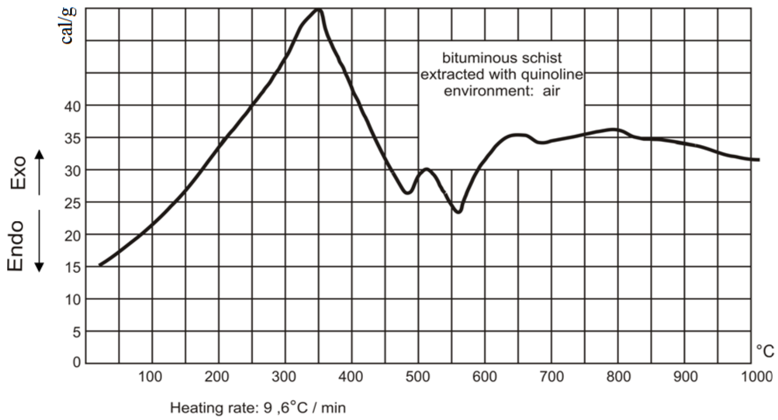

Fig. 10. Thermogram of the extraction residue using quinoline

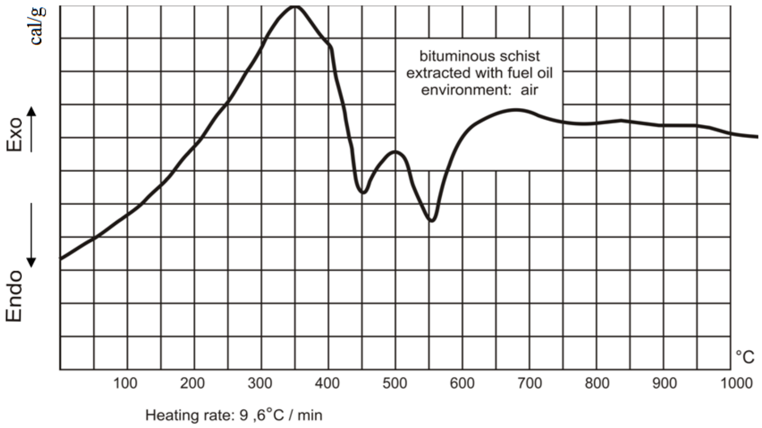

Fig. 11. Thermogram of the extraction residue using fuel oil/residue oil

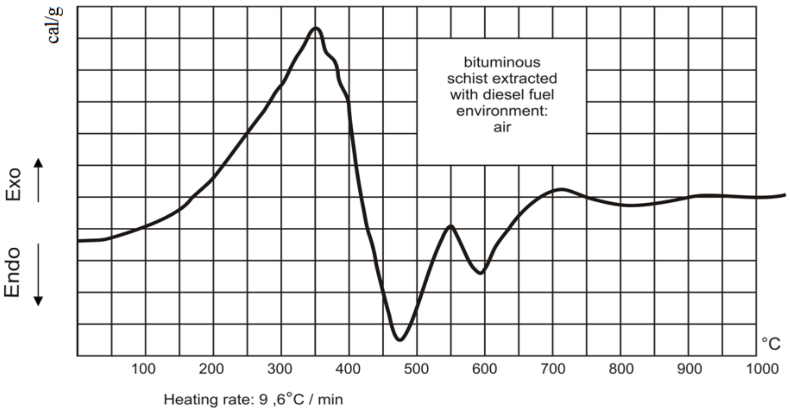

Fig. 12. Thermogram of the extraction residue using diesel fuel

If we analyze the data in the diagrams 7-12, we see that the losses caused by the thermal process, between 10 and 12%, mostly are due to the water eliminated by the inorganic mass; therefore, the schist samples are not capable of giving good results when they are distilled. Another conclusion can be that the schist may be of humic nature; in both cases the products resulted from thermal decomposition are, in a lower degree, volatile; it is much coke that results in the end.

The thermal effects of ashes after schist burning are shown in Fig. 11, which also shows that the material passed through the furnace has no thermal effects. Once more, this fact demonstrates that the schist has a humic structure, and its thermogram in air environment of pyridine extracted from schist, is shown in Fig. 12.

The thermogram shows, once more, that the endo effects within the range temperature of 400-600 °C are due to tailings and to the fact that the material extracted has a structure similar with the coal, with a flash point of about 400 °C.

For the confirmation of these structural elements characteristic to our schists, infrared spectra were carried out, with a Leiz type spectrophotometer, on schists, on the extract pyridine and quinoline; these spectra are shown in Fig. 13: a, b, c.

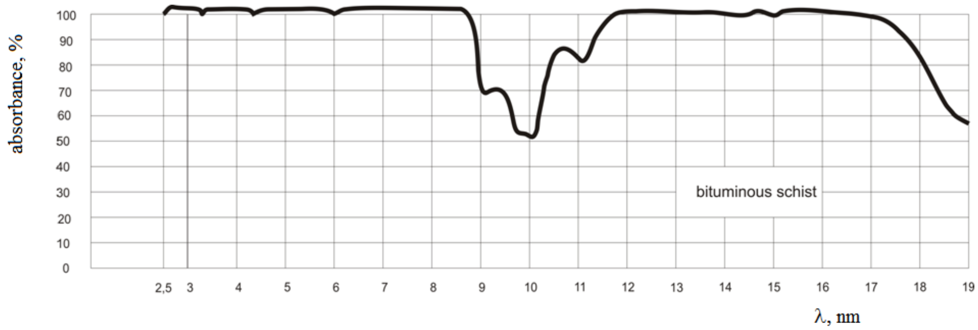

Fig. 13a. The infra red spectrum of bituminous schist

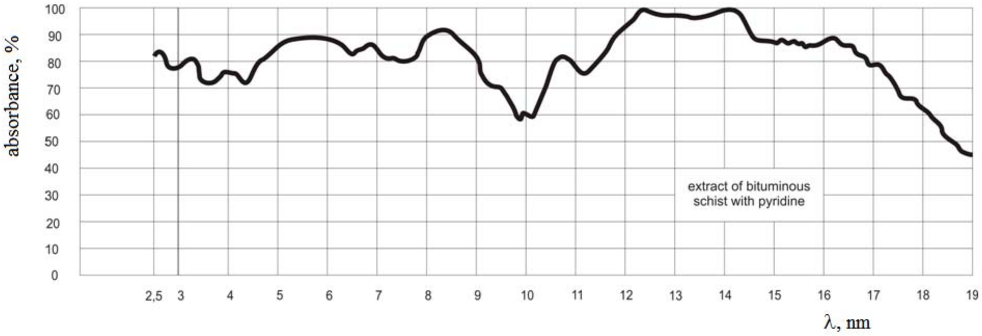

Fig. 13b. The infra red spectrum of the extract of bituminous schist with pyridine

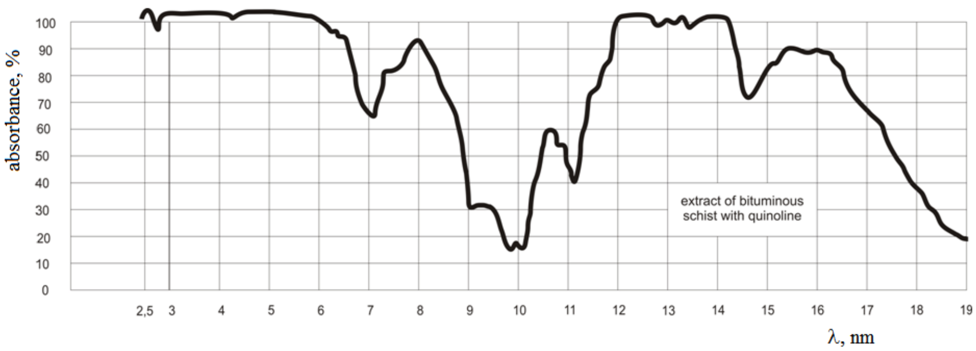

Fig. 13c. The infra red spectrum of the extract of bituminous schist with quinoline

The figures show that both schist and extracts are similar to coal, meaning that they have a humic structure; they are not similar to sapropel or mud. The schist humic mass contributes to spectrum formation in the same extent as in the case of the bituminous coal.

One can observe the frequencies of formation due to the inorganic mass contained in the respective extracts; the frequency is higher in the extract with quinoline, as compared to the extract with pyridine.

The frequencies specific to the bituminous mass cannot be limited, because many specific groups to sapropel existing in this material are found in the humic mass.

An elementary analysis of the characteristic structural elements resulted from infrared spectrographic studies show the humic-sapropel nature of the respective material, with a degree of carbonization characteristic to young pitcoal.

From material research results:

- the extraction method is able to show the nature of our schists, bringing arguments for their humic structure, whose processing and exploitation are clearly different, if we take into account the bituminous, sapropelic structure shown in the existing treatises on the subject.
- the research shows that the maximum endothermic peak around 350 °C appearing in all thermograms, of both the extracts and materials, and of residues respectively, can be attributed exclusively to the burning of the organic mass. To strengthen this idea we have to mention that the intensity of this maximum decreases in the extract residue.

The high enough auto-ignition temperature also indicates a well-advanced degree of carbonization of the organic mass.

Around 450-550 °C there is an endothermic maximum associated with a mass loss, existing in the thermograms of the schists and extraction residue. It does not appear in the thermograms of extract. This endothermic maximum in the schist is due to the inorganic material, and not to the organic mass. It has an interesting effect linked to the actual calorific power of the schist (it reduces its calorific power).

- research on extraction shows that Romanian schists cannot be processed by extraction.

- Romanian schists cannot be processed by distillation and their efficiency is related to some macroscopic experiments, not accompanied by thermal effects and distorted to a great exitent by the amount of water released in the dehydration of the inorganic mass, which takes placed in the temperature range of 450-600 °C (elimination of water from kaolinite and other similar materials, irreversible processes dependent on the surrounding environment).

The peaks due to these transformations of the tailings remain both in an oxidizing environment, and in an inert and reducing environment.

4. Conclusions

The study of the interaction between Romanian schists and organic solvents showed that the schists have mainly humic structure, and therefore, results the impossibility of their processing by extraction or distillation. The endothermic effects caused by the changes of tailings existing in schists were highlighted. The participation of inorganic rocks has effects on the characteristics of the schists. The existence of schists deposits, at a distance, over wide areas, with low organic mass shows that attempts to exploit the deposit affects the environment, creating seroius problems to the engineers.

It is recommended that the exploitation to be done through mining methods; also, by exploitation in such fields where both organic mass and inorganic mass are needed. Romanian schists produce small amounts of extract, which justifies their humic structure. Bituminous schists of other countries, processed by disruption and extraction, are not specific to our country.

Acknowledgements

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398 and POSDRU/159/1.5/S/132395.

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