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FACULTY OF ENVIRONMENT SCIENCE AND ENGINEERING**

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**PH.D THESIS**

**ABSTRACT**

**THE IMPACT OF NATURAL RAW MATERIALS  
ON THE KILN STACK EMISSIONS IN THE  
CEMENT MANUFACTURING PROCESS**

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**Key words:** *natural raw materials, facies, deposit architecture, chemical compounds, geostatistic, spatial distribution, selective mining, kiln stack emissions*

## Introduction

The sustainable development represent the total of the social-economical development methods whose base is characterized by ensuring the equilibrium between the social, economical systems and the elements of the natural capital. Durability starts from the idea that human activities depend on the environment and natural resources. We can admit and promote the idea that the economical development cannot be stopped, but we must acknowledge that the strategies must be changed so that they match the ecological limits offered by the planets resources. This concept was understood at industrial level and, as a consequence, the approaches appeared quite quickly. Such an industry with a responsibility assumed towards the concept of durable development is the cement industry.

Cement is a widely used material in the field of constructions and it is produced in great amounts in the entire world. However, the high request for cement is conditioned by the more and more serious constraints related to the natural resources, resources expressed as energy availability or raw materials availability. These raw materials originated from natural deposits contain various concentrations of chemical elements with impact on the environment, which are then released as emissions in the atmosphere.

At the same time, considering the limited resources of raw material and traditional fuels, the cement industry promotes as a sustainable solution the usage of certain wastes as alternative raw materials or alternative fuels. Still, we must underline the fact that all these alternative materials used in the cement production process can contain and hence, can generate the release of pollutants in the atmosphere. This, it becomes obvious that, in order to control and to maintain a total emission level within the standard limits, the knowledge and the control of the emissions generated by the natural raw materials is the starting point and the key control of the further use of wastes as solution for the sustainable development concept.

Starting from this idea, the present thesis studies **the impact of natural raw materials on the kiln stack emissions in the cement manufacturing production**. Such a research applied in practice gives the knowledge of the emissions level generated by the natural raw materials, a level considered the emissions reference level in case of each deposit, so than the extra amounts of emissions from the usage of alternative raw materials or traditional and alternative fuels can be correctly estimated. At the same time, this method contributes to the optimization of exploitation of natural resources, respectively the increase of their life time. The study is based on geological, geochemical and environmental data originated in the evaluation of the deposits exploited by Holcim (Romania) S.A. The deposits studied are essential for the core activity of this company having a significant influence in the production cost, the product quality and respectively their impact on the environment. Considering that the deposits are not renewable and they must be favourable to the environment and quality conditions, they must be rationally planned and exploited.

Chapter 1 introduces a series of general information on the cement industry and its impact on the environment, the current tendencies and development of the global, regional and national cement production, thus highlighting the usefulness of the theme of the current study.

Chapter 2 describes the materials and work methods used along this research. At the beginning, I described the methods used in the geological investigation phase, both on the field and in the laboratory, after which I presented the specific laboratory methods for the determination of the chemical and environmental elements (major and minor oxide chemical elements and significant trace elements). In the closing of the chapter, I listed the statistical analysis methods used for understanding the spatial distributions of these chemicals and

environmental elements as well as the software application used in the management of the block model of the deposits.

Chapter 3 describes the sedimentation processes which are genetically responsible for the accumulation and formation of the chemical elements present in the natural raw materials used in the cement production process and which later have an impact on the environment. These processes define the continuous or discontinuous spatial concentrations (stratiform, nodular, impregnate, irregular etc.) of the chemical compounds, thus ensuring the support of the modelling and then the statistical interpretation in the subsequent chapters.

Chapter 4 shows the geological characteristics of the studied deposits which are exploited as natural raw material sources, highlighting their geographical localization, the framing in the regional and local geological context, the architecture and respectively the facies and microfacies on the identified deposit environments.

Chapter 5 contains the theoretical standard information regarding the quantitative and qualitative evaluation criteria of the chemical composition of the natural raw material which are used in the production process as well as their impact in the composition of the clinker and then in the cement. These data come from the company internal procedures used currently by the laboratories of the cement cements.

Chapter 6 describes the process elements which interfere and influence the formation and concentration of the volatile compounds in the clinker production process. Later on, these compounds are transformed in emissions concentrations generated at the kiln stack. All the information regarding the processes and installations described in this chapter come from internal documentations of the company, technical specialized documentations presented and used currently within Holcim Group.

In Chapter 7 I presented my personal results of the geostatistical analysis performed on the lab determinations of the chemical compositions of the samples collected from the four studied deposits. This analysis method identified the laws and parameters of spatial distributions (linear, sinusoidal, Gaussian etc) of the chemical compounds and environment for these deposits. These results represented the base for the modelling parameters necessary and used in the generation of the block model of each deposit.

Chapter 8 describes two methods for control the generated emissions in the cement production process and the discussions regarding the results obtained by using these two methods. The first method is represented by the lab simulation of the real behaviour of the volatile compounds in the production process and the estimation of the concentration of emissions resulted stack through experimental tests. These tests have been performed entirely within the specialized labs of the Holcim Group and interpreted within this thesis. The second method presents the results of the implementation and use of a specialized software (QSO)<sup>1</sup> for the simultaneous exploitation of the limestone and clay deposits. By applying this expert product, the deposits can be exploited distinctively and through the mix of the materials they contain, a final product is obtained respecting the quality and environment production constraints imposed by the legislation.

From the scientific point of view, this work method used the real architecture of the deposit (geologic model) as support for the allocation of the chemical and environmental information, respecting the rules imposed by the sediment processes. The spatial distribution of these elements is statistically modelled calculating material volumes with homogenous compositions (block models). The advantage of such an approach is the fact these blocks can be found in practice, during exploitation, as a solution for the planning and selective exploitation of the deposits with the purpose to respect the quality and environment requirements.

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<sup>1</sup> QSO – Quarry System Optimization (internal expert product of the Holcim Group)

## **Chapter 1**

### **Introductory information related to the investigated subject**

“The cement is a non organic, non metallic powder, finely ground which forms together with water a paste which stabilises and hardens”<sup>2</sup>. Currently there are 27 types of cement which are grouped in 5 general categories and 3 resistance classes, respectively: normal, high and very high resistance cements. The clinker is an intermediary product in the process of the cement production, resulted through the sintering of raw materials and which presents in the shape of nodular structures.

The production in the cement industry is generally linked to the activity registered in the construction fields, this is why it is tightly connected to the global economic situation. The biggest cement producers at the global level are Lafarge Group (France), Holcim (Switzerland), Cemex (Mexico), HeidelbergCement (Germany) and Italcementi (Italy).

According to the data supplied by the CEMBUREAU<sup>3</sup>, between 2006 and 2008 the last inventory of the cement production installations was performed. This study indicates the fact that in 2008 there were 268 technological lines in the European Union and 377 clinker production kilns, although not all of them were functioning. There were also 90 grinding installation (cement mill without clinker kilns).

Currently, the typical capacity of a production kiln is approximately 3000 tons of clinker/day. The burning of the clinker is performed in the rotary kiln which can be integrated in several types of systems: long wet kilns, long semi-wet kilns or semi-dry kiln (Lepol), dry kilns with preheater in suspension and kiln with preheater in suspension and precalciner. According to the existing data in the cement industry, the most efficient system is considered the dry kiln with preheater in suspension on several steps and precalciner.

“In the year 2007, approximately 90% from the European cement plants have already dry kiln, 7,5% of it is still on semi-dry and semi-wet method and 2,5% is still on wet method”<sup>2</sup>. Because of the regulatory requirements development in the field of environment, more and more severe requirements are anticipated, which impose for Europe the transformation of all wet kilns in dry kilns.

The cement production process (Fig. 1.1) starts with the extraction of natural raw material from the quarries, mainly limestone and clay or marl, which are crushed in one or two successive phases. Then, if necessary, correction materials are added (quartz sand, diatomite, bauxite, kaolin, pyrite ash etc.) in order to obtain the recipe with the preferred chemical composition. This primary mixture is ground very finely in the raw mill and is homogenized in the silo. The product obtained is known as “raw mix”.

In order to obtain the clinker, the raw mix is introduced through the tower of the preheater in the clinker kiln where it is progressively decarbonized and synthesised at temperatures ranging from 1400 and 1500 °C using traditional fuels (coal, heavy oil, gas) and alternative fuels (various wastes in liquid or solid form).

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<sup>2</sup> European Commission, Reference document on Best Available Techniques in the Cement, Lime and Magnesium Oxide Manufacturing Industries, 2012

<sup>3</sup> European Association of Cement Industry Producers

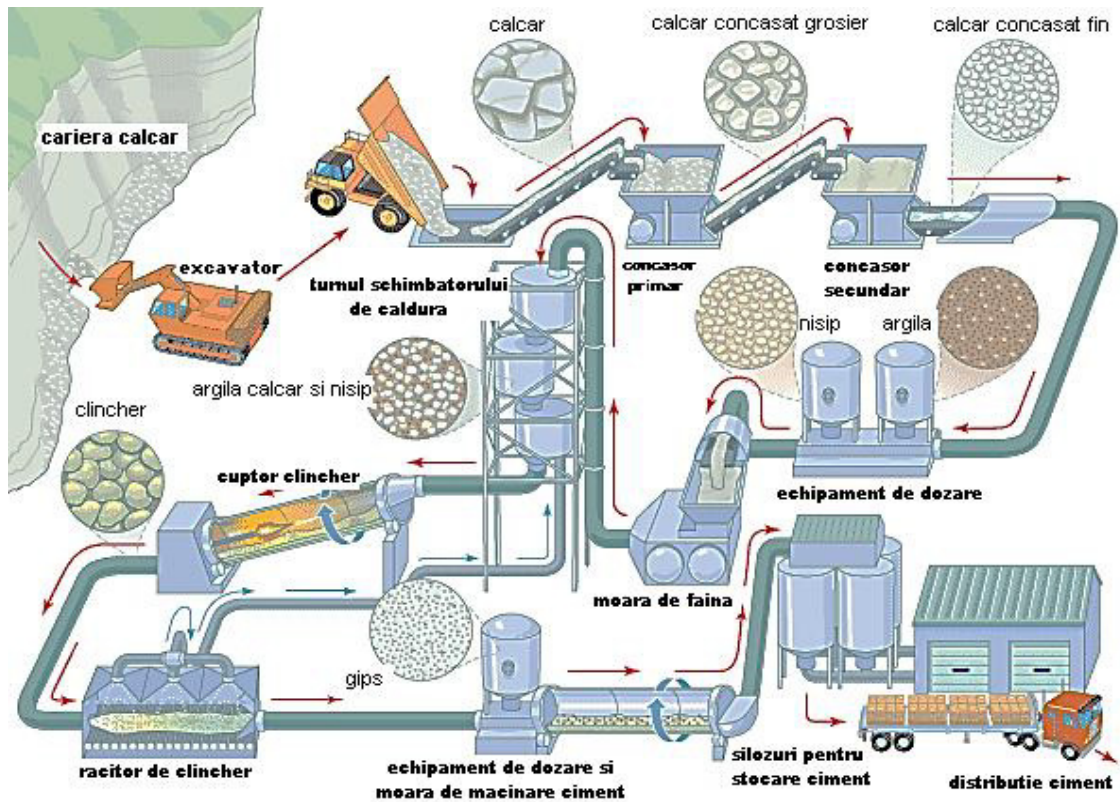


Figure 1.1 Presentation scheme of the cement production process (according to Encyclopaedia Britannica with modifications, 2007)

“For the production of one ton of clinker, the average consumption of natural raw materials in the European Union is 1,57 tons. The highest loss from the process is due to the calcinations reaction ( $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ ) through the emission of carbon dioxide in the air”<sup>2</sup>.

The burning of the clinker is the most important part of the cement production process in regards with the environment because of the energy used and the emissions released in the air. The most representative emissions for the cement production process are the nitrogen oxides (NO<sub>x</sub>), sulphur dioxide (SO<sub>2</sub>) and dust emissions. In all burning systems, the solid material circulates against the current with hot burning gas. This flow against the current affects the emission of the pollutant factors since it acts as an incorporated fluidized layer. A lot of the components which result from burning of the fuel or the transformation of the raw materials in clinker remain in the gas phase only until they are absorbed or condensed on the raw mix which circulates against the flow in the tower of the heat exchanger. The absorption capacity of the material is determined by its physical and chemical state. On its turn it depends on the position within the kiln’s system. For example, the material which leaves the calcinations phase of the process has a high content of calcium oxide and this is why it has a high absorption capacity for the acid elements such as the hydrochloric acid (HCl), hydrofluoric acid (HF), ammonia (NH<sub>3</sub>), volatile organic compounds (VOC) and sulphur dioxide (SO<sub>2</sub>).

The fabrication receipts of the various types of cement depend on its applications. As a consequence for the production of cement, various proportions of clinker, gypsum and mineral components (power plant ashes, slags, pozzolanic materials, microcrystalline silica etc.) are used and they are grind together in the cement mill to various levels of fineness. At

the exit of the cement mill, the final product is transported in silos from where it can be distributed in bulk or in bags to the end users.

## **Chapter 2**

### **Materials and work methods**

For the research of the chemistry and the understanding of the spatial distribution of the chemistry in the raw materials deposits, it was necessary to investigate them using direct access methods, respectively the investigation through drillings. In order to ensure the desired level of information, but also for the optimization of the research costs, two methods of drilling and core-drilling were used: core drilling with the collection of undisturbed rock core and respectively the destructive drilling with the collection through reverse recirculation of the detritus in the drill-hole bottom.

#### **Samples collection**

The systematic vertical sampling represents the most frequent sampling method of the drillings placed in a geological research network on the field. For such an approach, the research network has to be oriented randomly in space, which was achieved in our case by the positioning of the network according to the access restriction of the equipments in the field, respectively by following the major geological structural elements of the area.

The investigation of sedimentary successions with drills had thicknesses ranging from 50 to 200 m. From these drillings various types of samples which offer specific information and which sustain the following lab analyses have been collected: samples for geochemical analysis, samples for the analysis of the environment elements and samples for microfacies analyses.

The material samples used for elementary geochemical analysis were collected using a cutting machine, by splitting longitudinally the cores or by collecting the chips & debris from a destructive drill-hole. The length of the samples was limited to 2 and 2,5 m. The amount of sample ranged between 25 – 3 kg per each sample. The material collected from composite samples was used in the analysis of the chemical compounds relevant for the environment (pyrite sulphur, ammonia and organic carbon). These samples represent 10 m of investigated sequence and were recomposed from 4 or 5 elementary samples, according to their length, re-crushed, ground, homogenised and reduced from the 3 kg to 200 g. The samples used for the microfacies analysis have been collected by splitting longitudinally the cores or from relevant sequences observed in the natural outcrops or in the quarries in which each deposit is exploited. They had dimensions which allow the preparation of ground slides and the sections for the microscopic study.

#### **The primary preparation of the samples for the chemical analyses**

The material collected from half of the cores after the longitudinal cut or from the drilling returns collected at the exit from the outlet of the sample collection cyclone was prepared for future lab analyses as follows: controlled drying until the temperature of a maximum of 45 °C (for avoiding the volatilization of Hg), crushing and grinding under 2 mm, and preparation of the tables for the lab analyser.

#### **The method of analysis used for investigation of the carbonate microfacies**

This method implies a microscopic description on a thin section of the ensemble of composition elements of carbonate rock such as the primary figurate elements (paleontological, siliciclastic etc), the diagenetic processes and products and respectively the structural-textural elements of the rock. The thin section is obtained through cutting a fraction of the material from a sample oriented which is glued on a glass blade with the help of a balm or polymer and then progressively polished to a thickness of approximately 25-30 $\mu$ . The thin section is studied under the petrographic microscope in transmitted or polarized light. The

analyses of the carbonatic microfacies from the investigated deposits were performed entirely in the laboratory of the Geology Department within the Cluj Babeş-Bolyai University.

#### **Analytic methods for the analysis of the oxide compounds and for the determination of the environment relevant chemical compounds**

The main elements ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ), minor elements ( $\text{MgO}$ ,  $\text{SO}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ) and the trace elements ( $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Cl}$ ,  $\text{F}$ ) were determined with the XRF PAN analytical AXIOS 4400 device. The chemical compounds in the natural raw materials which are relevant in the formation of the emissions at the clinker kiln stack are: total organic carbon (TOC), pyritic sulphur and total sulphur, ammonia ( $\text{NH}_3$ ) and heavy metals. The samples prepared for the analysis of these compounds were achieved by mixing 4 – 5 elementary samples, thus resulting relevant composite samples for a geological sequence of 10 m.

The analyses for the total organic carbon (TOC) and pyritic sulphur ( $\text{SO}_3$ ) were achieved by using a Leco equipment SC – 144 DR on the sample residue after the treat with hydrochloric acid (HCl). The treating of the sample with HCl is performed in order to develop the carbonate and respectively the sulphur compounds. Subsequently, the sample levigate is burned in oxygen atmosphere and the gas compounds  $\text{SO}_2$  and  $\text{CO}_2$  are identified with infrared detectors. Total sulphur was determined with the same Leco equipment SC – 144 DR, but without to treat the samples with HCl. The sample was burned until the decomposing of all the sulphur compounds present in the sample in oxygenated atmosphere at  $1350\text{ }^\circ\text{C}$  and gas compounds  $\text{SO}_2$  and  $\text{CO}_2$  were identified with infrared detectors. Ammonia ( $\text{NH}_3$ ) was determined with an Ion chromatograph Dionex DX 500 equipment through the decomposing of the sample with hydrochloric acid (HCl) and boric acid ( $\text{H}_3\text{BO}_3$ ) respectively distillation in vapour atmosphere.

Non volatile heavy metals (V, CR, Mn, Co, Ni, Cu, As, Sb, Pb) were determined semi-quantitatively by using the standard program pro Trace of the XRF PANalytical AXIOS 4400 spectrometer. Mercury (Hg) was determined with a Leco AMA - 254 analyser. Mercury is released by heating and the gases as detected by atomic absorption spectroscopy at 254 nm. Cadmium and Thallium (Cd and Tl) were analysed through atomic absorption spectroscopy after the dissolution in nitric acid ( $\text{HNO}_3$ ) and hydrofluoric acid (HF).

These chemical lab analyses were performed partially within the local laboratories of the two cement plants participating to this case study – Aleşd and Câmpulung. But most of these determinations have been performed in the Regional quality control lab for Eastern Europe, a lab which is located in Slovakia and within the specialized lab of the Holcim Group in Switzerland.

#### **The lab method used for the simulation of the release in the atmosphere of the chemical elements with environment impact**

Natural raw materials used in the clinker production process contains variable concentrations of organic compounds, some of them being packed in pretty complicate structures of these materials. If they are heated in the clinker kiln, then the organic compounds separate (crack) at a temperature range between  $200 - 700\text{ }^\circ\text{C}$  and thus they are released in the atmosphere through the main clinker kiln stack. Starting from the experience of the practical results from the operation of the kiln and respectively the theoretical studies, a lab test was developed, test called test of release of the chemical compounds in the atmosphere, which stimulates the behaviour of the raw materials when they are heated in a clinker kiln.

Such a test used ground samples of raw mix from the feeding of the kiln, in normal production conditions or ground raw materials, for example a mixture of limestone and clay. The steps of an expulsion test are: the measurement of the temperature profiles of the most important components, the calculation of the expelled volumes from the temperature profiles (mg/kg) and the estimation of the emission generated by the kiln starting from the results of this test.



These simulation tests of the release of chemical compounds in the atmosphere were performed entirely in Switzerland, within the specialized labs of the Holcim Group.

### **Chapter 3**

#### **Sedimentation processes responsible for the formation and concentration of the chemical compounds present in the natural raw materials and their impact on the environment**

The limestone and clay exploited as raw materials for the cement industry may sometimes contain critical amounts of organic compounds, sulphur and respectively ammonia, elements which are part of the production process and which might generate emissions with impact on the environment. In their wide majority, these elements are related to the chemical compositions of the initial sediment and the presence of the organic substance in it and respectively the diagenetic processes of transformation of the corresponding rocks and sediments.

The organic compounds are represented by various types of kerogen and bitumen subordinate, with marine or continental origin, representing organic matter rests accumulated in the sedimentation basin. The evaluation of the organic matter content present in the rock and respectively the potential of generating some emission of volatile organic compounds is obtained through the measurement of the total organic carbon (TOC).

Sulphur can be present both in an inorganic form, pyrite, greigit, marcasite, native sulphur or sulphate and in organic form. The proportion between inorganic pyrite and organic one depends on the type and source of kerogene preserved in the rock. The sulphur origin is mainly related to the microbacterial processes which can put at disposal the sulphur both from the sea water, where it is present as sulphate ion ( $\text{SO}_4^{2-}$ ) and from the organic substance during its bacterial degradation. In the production process, the sulphur emissions in the raw materials are controlled by the sulphur compounds present in reduced form, both from the sulphide and from organic substances. As a consequence, the evaluation of the unstable sulphur content and respectively the monitoring of the sulphur emission generation is achieved by measuring the pyritic sulphur (sulphur from sulphides).

Ammonia also represents a degradation product of the organic substances present in the rocks. The extraction and release of nitrogen from organic compounds takes place as a consequence of the intervention of the bacterial transformation processes, of which the most important one is the ammonia process. In the clinkering process, the ammonia is released from raw materials in the atmosphere as gas emissions. As a consequence, the evaluation of its presence is achieved by the quantification of the  $\text{NH}_3$  content.

### **Chapter 4**

#### **Geological features of the studied deposits and exploited as natural raw material sources in the cement fabrication process**

Considering the limestone participation (75-78%) in the mixture of raw materials used by a cement plant and respectively the big volumes which must be mined in the quarries and transported in the cement plants, the industrial sites studied were correctly placed right near relevant limestone sources. Beside the carbonate deposits, with a genetic connection with or not, marl and clay deposits have also been investigated and developed.

## 4.1 Limestone and clay deposits mined in Câmpulung area

### 4.1.1 Limestone deposit from Hulei – Mateiaș

The limestone deposit mined by Câmpulung Cement plant is located in the NE part of the city Câmpulung Muscel, nearby the village of Valea Mare Pravăț and Nămăiești, Argeș county. From the geographical point of view, the studied area is representing the limit between the Southern Carpathians and the structures of Getic Subcarpathians.

From the geological point of view, the carbonatic formation of Mateiaș limestone belongs to Upper Jurassic, Kimmeridgian - Tithonian and represents the East termination of the Getic Nappe (Patrulius, 1969). In the studied area, this formation is outcropping starting from Măgura—Mateiaș – Hulei area in the North, and Piatra – Stoenеști area in the south, being opened and exploited in the Hulei quarry.

During the period 2007-2009, the geological studies of the limestone deposit, using drillings and respectively field observations, inside of Hulei quarry and the outcrops around, highlighted the presence of the following major lithological units (Fig. 4.1):

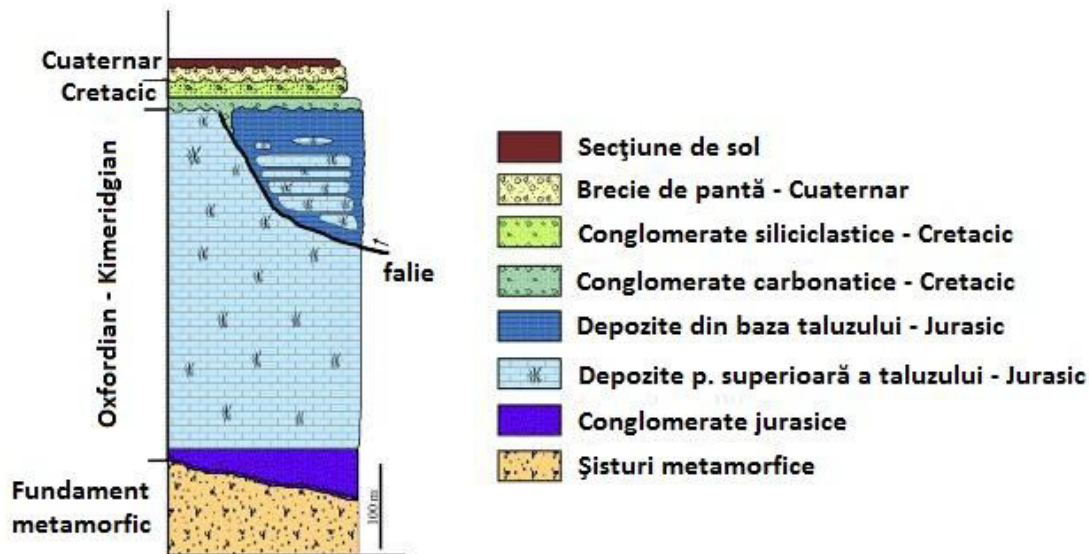
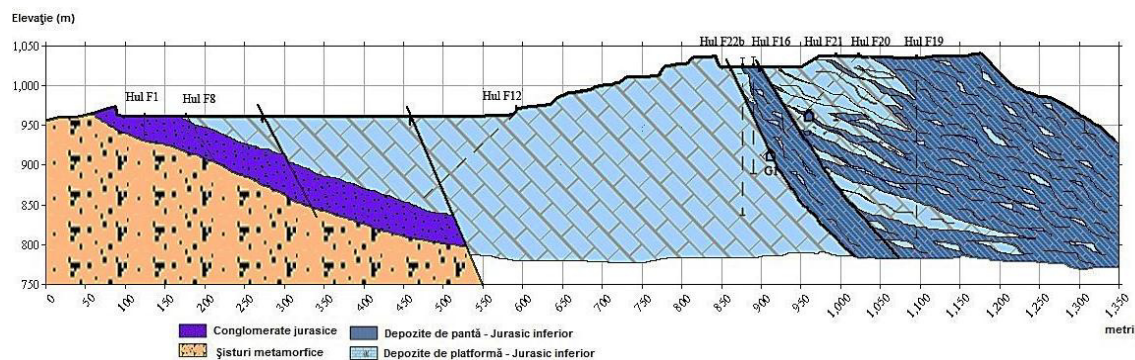


Figure 4.1. Synthetic litho-stratigraphic column of the carbonate deposit in the Hulei-Mateiaș area

The description of these lithostratigraphic units was performed for the first time internally, Holcim reports (2009), and later on in Bucur et al. 2010. **The metamorphic basement** consists dominantly of grey-green chlorite schists, outcropping in the North-Easter part and the South-Western part of the studied area. **The massive reefal limestone** represents the dominant lithological feature in the area of Hulei – Mateiaș, signifying the reef bone structure, including breccia formed in front of the reef (fore-reef). In the South-Western areas, both in Hulei and in Mateiaș oliostrome type structures are present, with blocks of reefal limestone of variable dimensions, from  $m^3$  to hundreds of  $m^3$ , embedded into the finely stratified limestone. **The fine stratified limestone** (deposits of turbidites and hemipelagites with silica nodules) are present both in the Hulei and in the Mateiaș area, being represented by centimetre to decimetre layers, often containing carbonate turbidites with frequent silica nodules. In comparison with the massive reefal facies, the turbidite sequence represents the only sequence of the limestone deposit with visible structural elements, offering consistent

geological information concerning the stratification and hence elements of space positioning (Fig.4.2).



**Figure 4.2. Geological cross-section in Hulei quarry, showing the spatial relationship between the major facies units**

**Carbonate conglomerates and Cretacic siliclastic units** were identified inside of several small basins, developed in the area between Mateiaș and Măgura. On the outcropping areas, these *in situ* deposits appear most of the time as isolated blocks. **Quaternary deposits** are represented by paleosoils, karst infillings and carbonatic breccia, accumulated at the base of the slopes. The geological observations confirm the model according to which the limestone is contaminated at all levels and the contamination does not restrict to a surface effect. Consequently, the in-depth exploitation will not improve or modify this situation (Beleş & Hosu, 2012).

The microfacies study of the limestone in the Hulei-Mateiaș was performed on cores collected from the drills-holes performed and it highlighted the presence of five microfacies types with genetic significance (Bucur et al., 2010): bioclastic-intraclastic rudstone, finely granulated grainstone-packstone, boundstone coral-microbialitic, the breccia and the microbreccia, bioclastic grainstone.

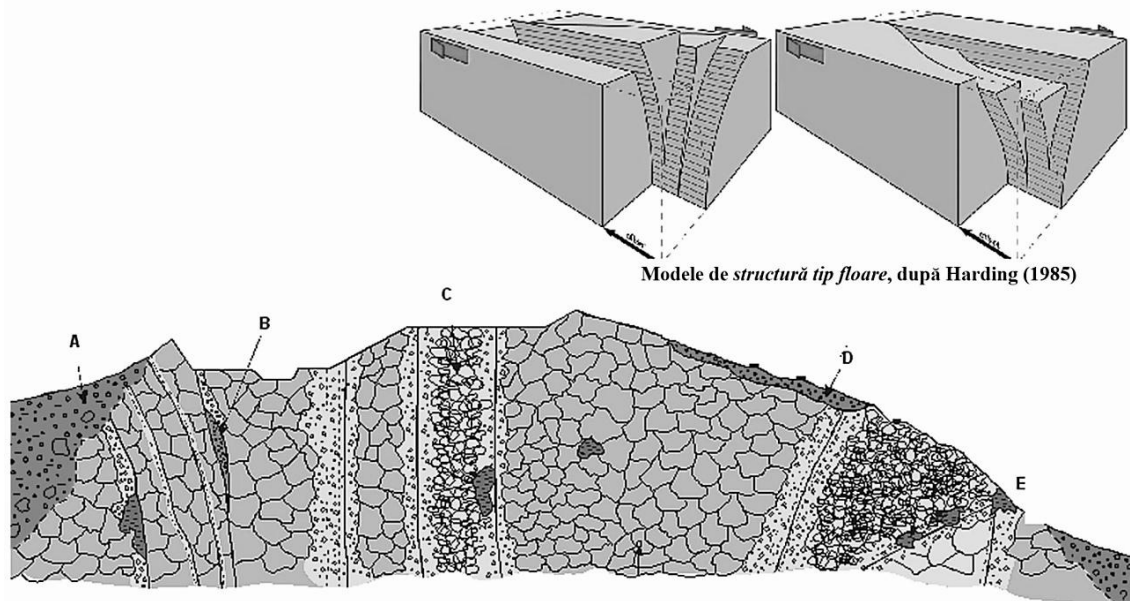
**The carbonate depositional environments identified in the Mateiaș limestone**

The mentioned facies associations, both at the outcrop scale and the microfacies one, allowed a series of evaluations in terms of depositional environments.

The dominance of the facies with reef limestone (reef's bone structure) indicate the presence of the depositional environment of carbonate platform edge. It is obvious that the facies of the internal platform, as well as the granular one are missing; as consequence, the carbonatic platform is present in this area through his external edge. The scarce presence of the allodapic limestone deposits, as well as the distal equivalent facies, allowed the identification of the external ramp / embankment of the platform. Next to the sedimentary structure, the deposit arguments include the presence of sponges, mainly the spongier spicules, which actually contribute to the secondary diagenetic concentrations of amorphous or microcrystalline silica as nodular cherts

**Tectonic processes: strike-slip, oblique-slip and flower type structures**

The strike-slip deformations represents the frequently found model for the tectonic deformations present in the Hulei-Mateiaș and develop at various levels. The transtensive strike-slip duplex feature is outlined by the presence of following elements: fan architecture, strongly inclined faults which converge in depth in a single sub-vertical fault, normal and reverse offsets along a single fault plan, sometimes resulting in the inversion of a relative moment on the fault. This upwards flared shape of the subsidiary faults is called flower structure.



**Figure 4.3. Flower-type tectonic structure developed in the Hulei quarry, underlining the distribution and the types of tectonic/ karst sediments which contaminate the limestone deposit: A – embankment detritus, B – sandstone lenses and clay tectonically injected, C – strongly fractured limestone impregnated with clay and sand, D – superficial pockets with detritus, E – karstic cavity filled with sandstone, conglomerates and clays (Beleş & Hosu, 2012)**

#### 4.1.2. Stoenеști clay deposit

The Stoenеști – Plaiul Cheii is situated next to the Stoenеști village, being limited in the West by the Valea Miriuța, on the south by the Valea Cheii and the East the Valea Goii and it opens and exploits the clay and sands deposit, Upper Albian (Vraconian) – Cenomanian-turonian of the Dumbrăvioara Formation.

The decision to open this new clay deposit was determined by the requirement to replace the old deposit (Argeșel quarry, with Oligocene deposits in the disodilic facies), which due to the high content of organic and pyrite substance was generating a high atmosphere emission during the process of clinker production (Beleş & Codrea, 2011).

The geological formations which form the clay and sands deposits from Stoenеști belong to the upper Cretacic from Valea Dâmboviței, having a representative development especially in the Stoenеști area, in North and respectively in South, in the area Cetățeni-Lăicăi. These deposits belong to the Western extremity of the Ceahlău nape, respectively the External Dacide (Săndulescu et al., 1984).

In the Stoenеști area, over the massive Albian sandstones, appears the Dumbrăvioara Formation (Albian terminal – Vraconian – Turonian) which on its turn is covered by the Plaiu Formation (Upper Santonian – Upper Campanian).

##### **The siliciclastic facies in the Stoenеști deposit**

In Valea Dâmboviței, Dumbrăvioara Formation consists of a sequence of silica-rich marl, accumulated in the terminal Albian (Vraconian), followed by green marls and green-greyish marl inter-stratified with thin levels of sandstones (under 30 cm), accumulated during the Cenomanian time.

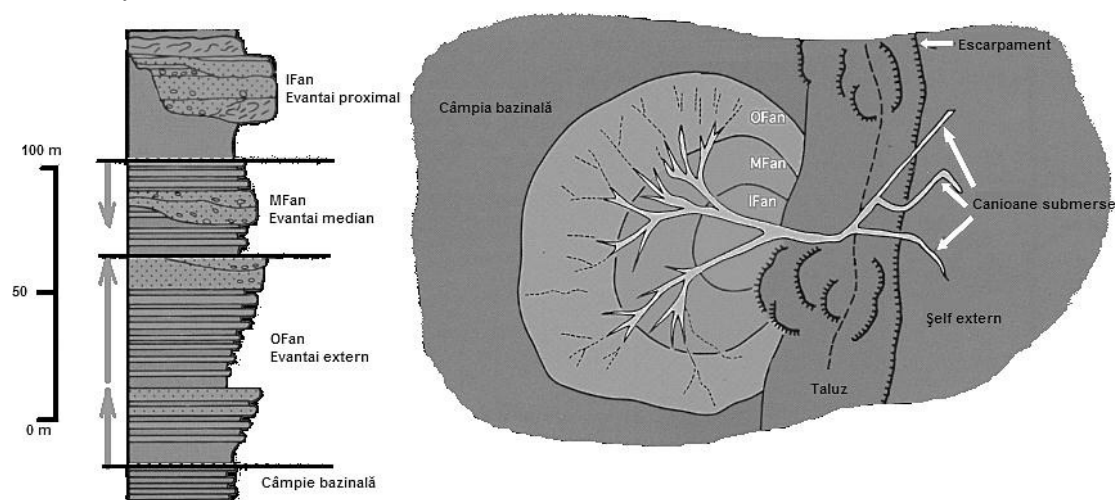
The geological research performed in Stoenеști perimeter in the period 2005 - 2006 by Holcim (România) SA highlights the presence of a complete sequence from the Upper Albian to Lower Turonian, starting with sandstones and siltites in the lower part, followed by clay siltites characteristic to the Cenomanian from the Dumbrăvioara Formation. The Cenomanian-

Turonian transition is made by black schist clays, while the lower part of the Turonian is represented by alternations of red and grey clays.

**Massive or graded fine sandstones** with clay matrix are gray blackish coloured and forms sequences with meter thicknesses. They usually have complex architectures in which there are amalgamated canalized complexes with weak tendencies of internal grading (Ta facies), separated by levels of clay siltites with centimetre thickness (Te facies). The stratigraphic sequence represented by **clay and sandstones alternations** is a few meters thick. The layers tend to look flat, without indications of erosion / canalization. The sandstones levels have flat bases and the tendency to gradually pass to fines sands, siltites and clays. In the coarse sandstones levels there are combinations of convoluted parallel lamina. **Grey-bluish – black schist clays** form tenths of meters thick sequences. The sedimentation is seldom interrupted by centimetre levels of fine sandstones and siltites with fine parallel lamination.

Siliciclastic Depositional environments identified in Stoenesti deposit

The detailed observations of the facies identified in drill-holes, the outcrops and quarry benches, allowed an identification and interpretation of the main facies of a turf system in the terms of the Bouma sequence (Fig.4.4.); massive fine or grades sandstones (Ta), centimetre alternations of sandstones and clays (Ta, Tb, Te) and respectively grey-blue-black schist clays (Te).



**Figure 4.4** The spatial position of the deposit environment of a submerged fan system: Ofan (outer fan) – External fan; Mfan (medium fan) – Median Fan; Ifan (inner fan) – Turf proximal fan (in Mutty & Ricci Luchi, 1972)

In the investigated sequences, there were no identified complete sequences in which all the terms of this Bouma sequence are present. Their association and dominance tendencies, offered the possibility of the interpretation of the facies in the terms of the depositional model. The facies identified have been assigned as follows: massive sandstones (proximal section of fans, clay and sandstones alternations (distal section of the fans) and massive clays (the distal section of the basin).

#### 4.2. The limestone and marl deposits exploited in the Aleşd area

The limestone and marl deposits exploited in Subpiatră and Hotar perimeters, in the Bihor county belong to the sequences of Cretacic formations, developed in the Northern part of the Pădurea Craiului massif. This unit of the Northern Apuseni mountain is situated in the



NV part of the Apuseni mountains, being delimited by the Valea Crişului Repede (in North) and Valea Crişului Negru (in South), respectively between the Borod Depression (in North) and the Beiuş Depression (in South). Based on the geological survey performed in Subpiatră – Hotar area, a new stratigraphic model for this area have been promoted by Bucur et al. (2008 – 2009), especially tacking into consideration micropaleontological and faciesal arguments, interpreted in a different manner compared to the Patrulius model (in Ianovici et al., 1976). Hence the authors assign: a. the carbonate deposits in the Supiatră quarry – Vârciorog formation, Upper Aptian – Albian age (Cociuba, 1999, 2000), which is the equivalent of the “formation with the glauconitic sandstones and the Upper limestone with pachiodont” (Patrulius in Ianovici et al., 1976); b. siltic marls in alternation with allodapic limestone, belong to the same Vârciorog formation.

#### 4.2.1. The Subpiatră limestone deposit

The deposit is localized on the Southern edge of the Borod basin, nearby the Southern part of Subpiatră village. The geological formations exploited in Subpiatră quarry belong to the pre-Gosau Cretaceous formation on the Bihor Unit, respectively the Lower Aptian – Neocomian – Albian, represented by the pachiodont limestone (Patruilis, in Ianovici et al., 1976) in the old stratigraphic model, respectively the Vârciorog formation (Upper Aptian – Albian) after the redefinition of the sequence by Cociuba (1999, 2000).

##### Major lithostratigraphic units and macrofacies

The detailed study of Subpiatră limestone deposit was performed in the period 2008-2009 using a set of specific geological investigation methods, both at outcrop and exploitation benches level, respectively the microfacies studied on outcrops or core samples level.

The quarry sequence is dominated, macroscopically, by three major facies: rudist biostrome, *Bacinella* nodular limestone and respectively coralgal bioconstructions and their associate sediments (Bucur et.al., 2010) (Fig 4.5). In all these macrofacies, should be mentioned the presence of interbedded granular limestone, often rich in orbitolinids. The sequence often develops cyclically subtidal cycles. In the lower part, the rudists are more abundant and the facies shift laterally into granular facies, often significantly coarse. In the upper part, the sequence finishes with finer to muddy facies (shallow subtidal). In the upper part of the sequence should be mentioned many coralgal bioconstructions and coarse bioclast blocks (rudstone). The coral colonies occupy an important place here, being sometimes colonized by rudists. In the middle part of the sequence the *Bacinella* nodules are dominant. Above the nodule facies (oncoidal) there are either granular facies or muddy facies.

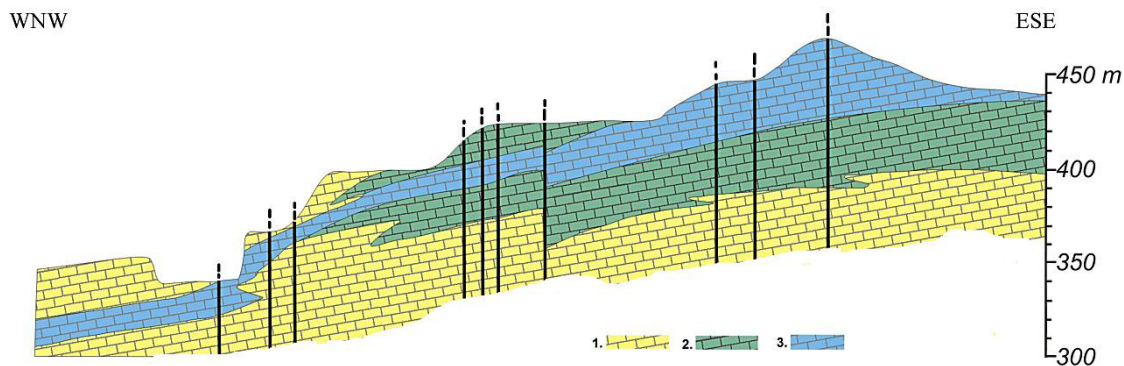


Figure 4.5. Geological section through the Subpiatră limestone quarry illustrating the spatial distribution of the main lithofacies types: 1 – rudists biostrome, 2 – oncoid limestone with *Bacinella*, 3 – coral bioconstructions and their derivatives (after Bucur et al., 2010)

The microscopic study of the samples collected from cores and outcrops highlighted a variety of microfacies, specific to the various areas of the carbonate platforms. Among them, the most representative microfacies are connected to the main hydrodynamic environments, conditioned by the functioning of the carbonate platform, that is: bioclastic wackestone – packestone with *Baciness* oncoides, wackestone-packstone or bioclastic packestone-grainstone, coarse bioclastic Grainstone (rudstone), bioclastic packestone with rudists or wackestone-packstone intercalated with rudists, wackestone-packstone with foraminifers, coral-generated boundstone and peloidal wackestone containing scarce orbitolinides (Bucur et al., 2010)

### Depositional environments of limestone from Subpiatră deposit

Taking into account the facies associations identified in the outcrops and drillings, the dominant depositional environment in Subpiatră deposit is the peritidal one in which three sub-environments have been separated: the shallow subtidal zone, the intertidal zone and the supratidal zone (Bucur et al., 2010), according to the model illustrated by Read (1985) (Fig. 4.6.).

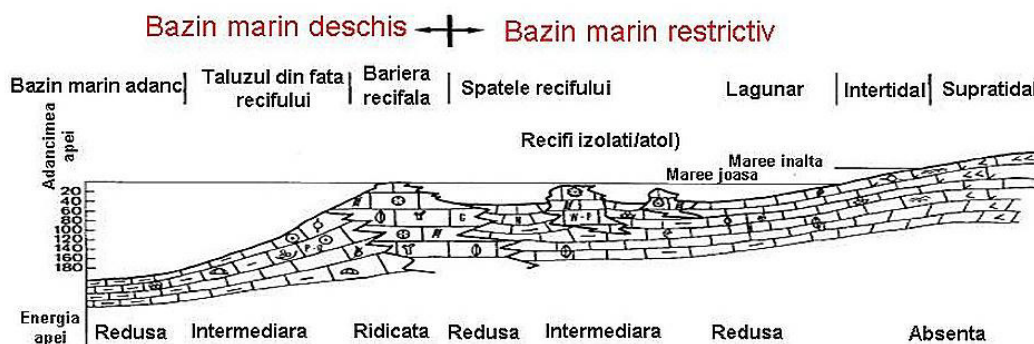


Figure 4.6. Deposit model of a carbonate platform (in Read, 1985 with modifications)

The identified shallow **subtidal deposits** were formed both in high and in low hydrodynamics conditions. The limestone formed in conditions of low hydrodynamics has centimetre or decimetric thicknesses and are represented predominantly by “muddy” facies type wackestone-mudstone. **Intertidal deposits** can be easily mistaken for subtidal limestone formed in conditions of high hydrodynamics because from the point of view of the composition they can be identical. The fenestra-type structures are characteristic for these deposits (fenestra with flat to irregular shapes, placed parallel with the lamination), but in equal measure are found in the discontinuous surfaces (hard ground) at millimetre scale and horizontal laminations. **Supratidal deposits** have generally small thicknesses, millimetre to centimetre and are represented by sediments of supratidal fields and through supratidal lakes. The most characteristic diagnostic features of this environment are the “muds” with traces of dehydration cracks, laminated micrites with ostracodes and algal-microbial “layers”.

#### 4.2.2. Hotar marl deposit

The Hotar marl deposit is located on the Southern edge of the Borod basin, near the Southern part of the Hotar village. The geological formations mined in Hotar quarry belong to the group of Cretaceous pre-Gosau formations from the Bihor Autochthon, respectively Lower Aptian – Neocomian – Albian interval, more precisely Vârciorog Formations (Upper Aptian – Albian) (Cociuba 1999, 2000).

### Sedimentary facies from Hotar deposit

From litological point of view, the investigated sequence, both in Hotar quarry and in the lateral extension areas, Eastward in Subpiatră quarry and in South in Fâșca-Vârgiorog localities is formed mainly from fine siliciclastic-marl deposits and subordinated through interbedded limestone, in the marl group.

The litofacies and micropaleontologic – biostratigraphic analysis of the cores collected from the drill-holes from the East, highlighted the fact that the Mesozoic sequence of the “Ecleja marls” is represented by two main categories of facies: hemipelagites siliciclastic-carbonatic and granular intraclastic-bioclastic flows.

The siliciclastic-carbonatic hemipelagite facies (wackestone, wackestone-mudstone and wackestone-packstone), respectively clayish limestone and hemipelagic marl-clays are very rich in spicules and contain a rich association of small bentic foraminifers. Granular intraclastic-bioclastic (grainstone and grainstone-packstone) flows (allodapic limestone), include bivalve fragments (rudists), echinoderms fragments, calcareous algae and frequent bentic foraminifers coming from the edge of the carbonatic platform. Frequent allodapite units are interbedded in the lower and median part of the hemipelagic sequence.

### Siliciclastic depositional environments in Hotar deposit

Between the levels intercepted by the drill-holes performed in the Eastern part of the Hotar deposit and the ones in the Hotar quarry, there is a significant difference: the first ones are generally more coarse, with a more pronounced carbonate character and with more frequent allodapic intercalations. Considering the fact that these drill-holes are located approximately in the area between the limestone of Subpiatră deposit and respectively the marls from Hotar deposit, and taking into consideration that the age of all these deposits is Upper Aptian – Albian (in both areas the Texan Mesorbitolina texana has been identified, Bucur et al., 2010), one can state that these deposits and the ones in the fields represent the ramp, respectively the area at the base of the ramp of a basin situated near a continental area which supplied an important amount of terrigenous material (Fig. 4.7). It is noteworthy the content as well, which is after high in glauconite, identified in some levels of the sequence, next to the presence of the terrigenous quartz of siltic or fine arenitic dimensions.

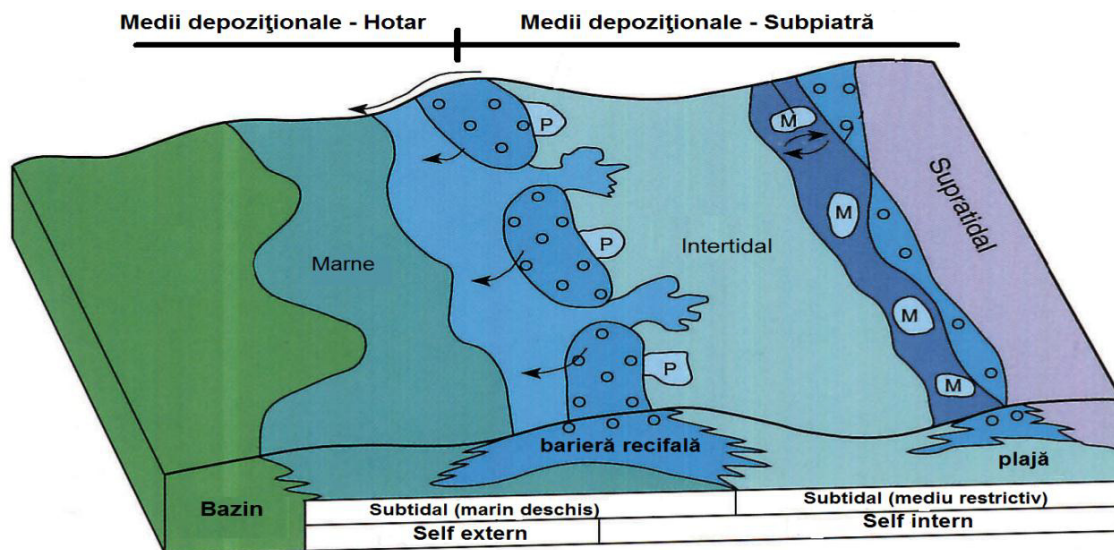


Figure 4.7 Diagram block showing the transition from deposit environment of carbonatic platform on the embankment / siliciclastic basin (in Rekmann and Friedmann, 1982 with modifications)



As a consequence, we can appreciate the fact that in the marginal area of the basin an important carbonate platform (limestone from Subpiatră deposit), on whose edge they have been removed, at certain intervals, bioclastic sediment towards the ramp area of the basin (allodapic interpositions). The situation in the closest area to the platform of the intercepted deposits of drill-holes in the Eastern part explains their much more carbonatic feature than the deposits in the Hotar deposit and respectively the Western area, which were deposited in a distal area of the basin and which probably benefited of a more important fine terrigenous intake (clay), from adjacent continental sources of the carbonatic platform.

## **Chapter 5**

### **The quantitative and qualitative evaluation of the raw materials which are used in the cement production process**

This chapter contains theoretical information regarding the qualitative and quantitative evaluation of the chemical composition of the natural raw materials which are used in the production process as well as their impact in the composition of the clinker and then the cement. These information comes entirely from the company internal norms and procedures which are used currently by the laboratories of the cement plants.

## **Chapter 6**

### **The formation and circulation of the volatile elements in the clinker production process**

This chapter describes the process elements which interfere and influence the formation and concentration of the volatile compounds in the clinkering process, compounds which later are transformed emissions in concentrations generated in the clinker kiln stack. All the information regarding the processes and installations described in this chapter come from the internal documents of the company, specialized technical documents currently presented and used within the Holcim Group.

## **Chapter 7**

### **Discussions and interpretations about the spatial distributions of the chemical elements of the studied deposits**

#### **7.1. The geochemistry of the deposits illustrated by elements of descriptive statistics**

The geochemical analysis of the lime deposits and clay / marl studied was performed on the basis of the results obtained after the lab determinations of the samples collected from drilling works of outcrops. This analysis methods identified the laws and the spatial distribution parameters (linear, sinusoidal, gaussian etc.) of the chemical and environment compounds in these deposits.

## 7.2. The spatial distribution of the chemical elements in the studied deposits

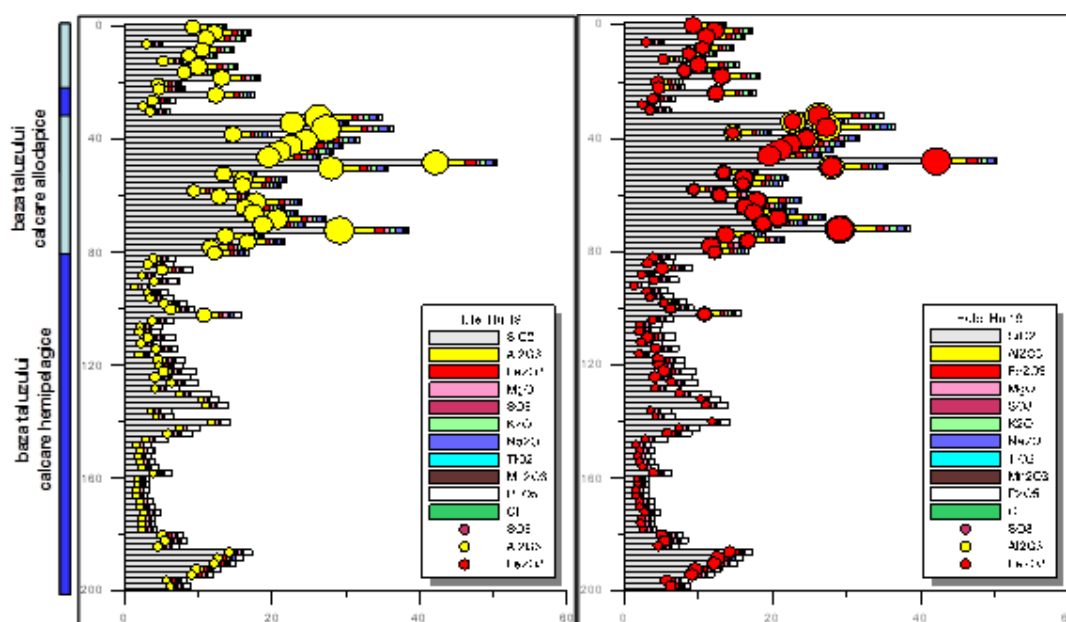
The geological investigations made on the studied formations, formations which represent the main sources of raw materials were performed through continuous coring (CC) or reverse circulation (RC), destructive.

### The spatial distribution of the chemical elements in the lime deposits through the analysis of the litofacies columns

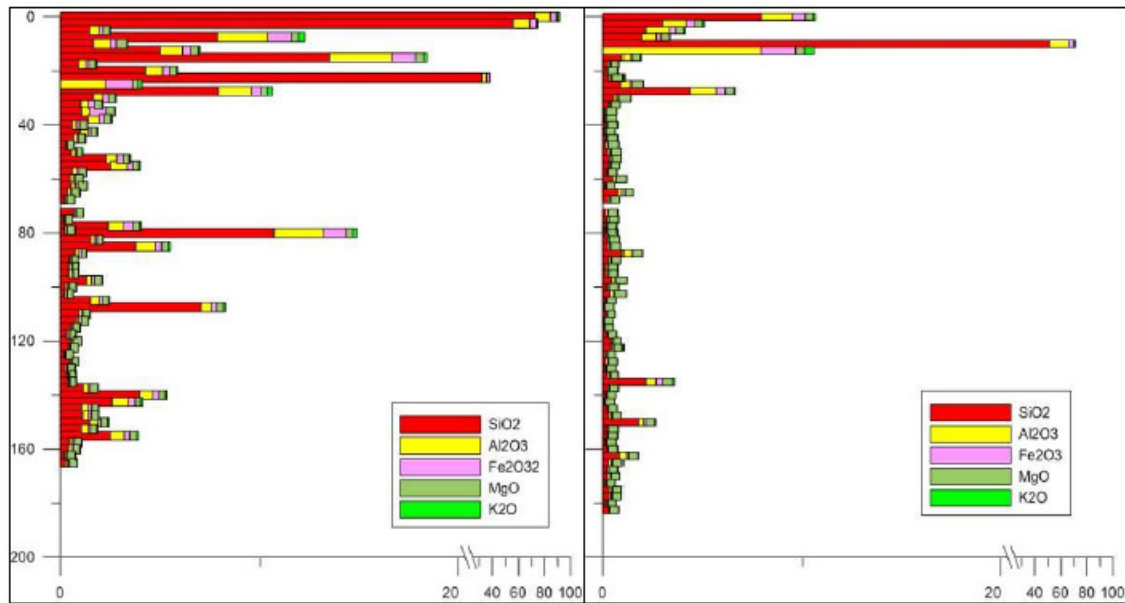
The previously considered carbonatic platform formations, with a relatively homogenous chemical composition, both the limestone in Hulei-Materias and the ones in Subpiatră have been analysed in detail and were proven to show variations both at the level of the main chemical elements and at the level of the minor ones, and trace, respectively.

Considering CaO as an implicit parameter of a limestone deposit, the analysis of the spatial distribution of the chemical elements was concentrated mainly on the contaminated chemical elements SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O etc as well as the ones resulted by diagenetic processes SiO<sub>2</sub>, MgO or SO<sub>3</sub>. In order to exemplify the spatial non-homogeneity of the carbonatic groups, this paper presented the analyses of a few drills relevant for these deposits.

In the case of the Hulei-Mateiaş lime, we must underline the fact that, in the normal sequence of reef carbonatic platforms the tectonically interposes deeper carbonatic ramp sequences, rich in concentration of secondary diagenetic silica. This means that, except for the terrigenous clastic-original silica (clays and sands) which contaminate the carbonatic platform facies, we also have a diagenetic silica, concentrated in deep sequences. It is noteworthy that the two drillings exemplified here (Hul11 and Hul22b) cross both carbonatic sequences, with a normal degree of contamination with siliciclastic material, as well as pelagic lime sequences with significant enrichments with silica oxide (diagenetic concentration on behalf of the silica tests, mainly radiolarian and spongers) and at the same time in clay material (Fig. 7.1.). In the case of the lime deposit in Subpiatră we exemplified the vertical variability in two drillings, Sub03 and Sub16. If in the Sub03 drilling we see a fragmented distribution of the non-carbonic elements, distributed in sequences with differentiated siliciclastic, in case of the Sub16 drilling the sequence crossed by the drilling is much more homogenous (Fig. 7.2.). In both cases it is considered that SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O are genetically connected to the siliciclastic intake, the spatial correlation being extremely tight.



**Figure 7.1 The vertical distribution of the chemical elements related to the non carbonatic components in the Hul11 and Hul22B in the Hulei-Mateiaş limestone deposit**



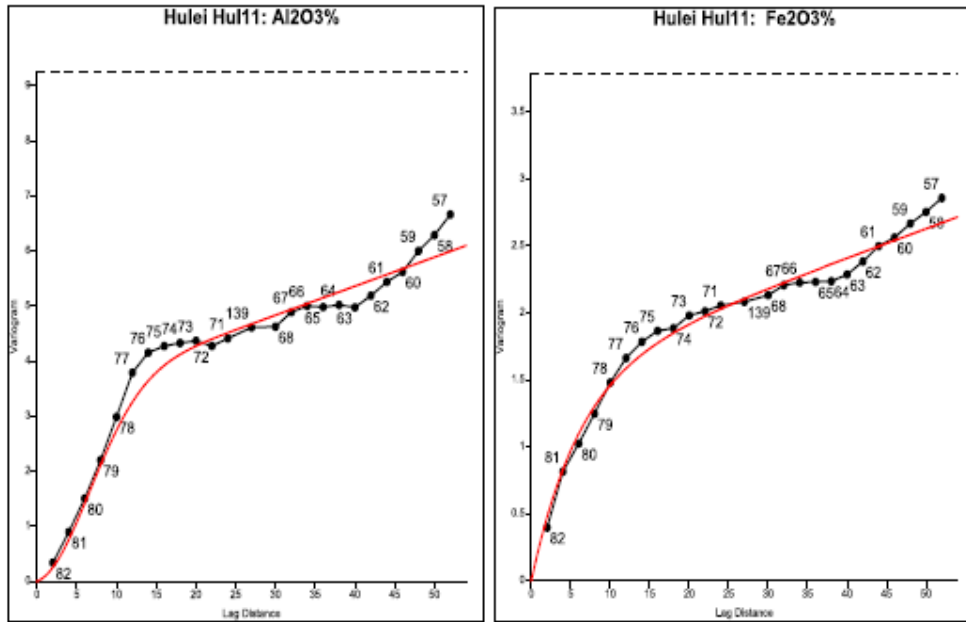
**Figure 7.2. The vertical distribution of the chemical elements related to the non carbonatic components in the Sub03 drillings and Sub16 in the Subpiatră limestone deposit**

**The spatial distribution of the chemical elements in the limestone deposits using the variogram models**

In order to evaluate the variation tendencies and laws of the spatial distribution of the chemical compounds we used the statistical study through the calculation of the chemical elements variograms for the major, minor and trace compounds. In order to evaluate the dynamics of the evolution in a 3D space, the calculation of the variograms had an omnidirectional character, which means that it has been performed taking into account the vertical evolution of the chemical variables in the drilling data, from the surface towards the depth.

**The similarity of the spatial distribution of the chemical elements and its genetic significance**

In the case of Hul11 drilling it is easy to observe the relationship between the presence and participation of iron in relationship with the participation of the clastic clay material. This way, we can underline and sustain the genetic relation between the siliciclastic intake in the sedimentation area and respectively the iron oxi-hydroxides (Fig. 7.3.).



**Figure 7.3. The variograms of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  underlying the genetic relationship of iron with clay minerals in the Hul11 drilling from the Hulei-Mateiaș limestone deposit using an ascending linear model combined with a gaussian one**

### **The control of the marine eustatic cycles on the vertical distribution of the researched chemical elements**

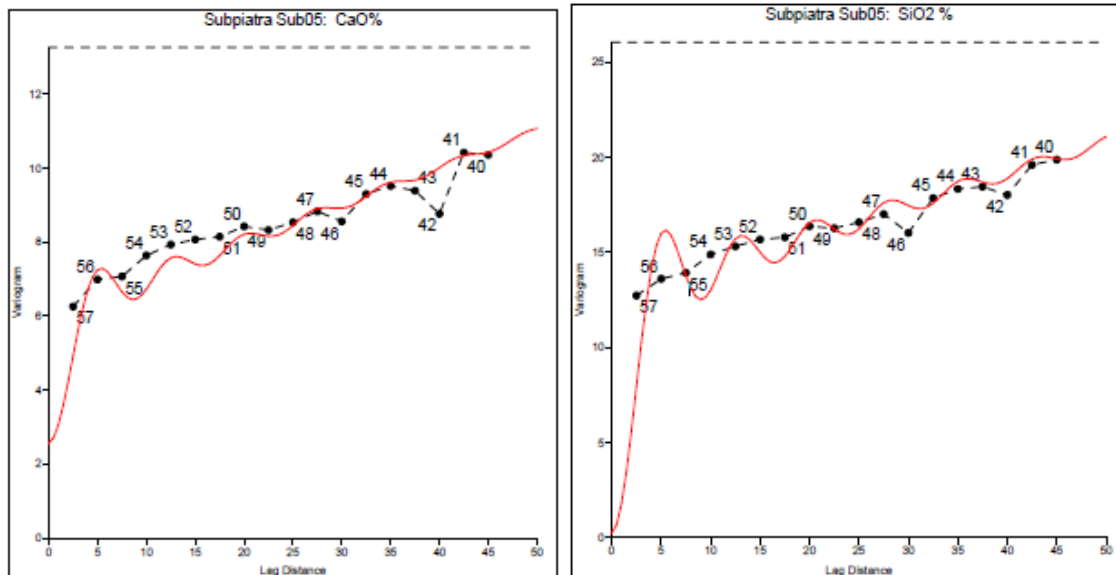
Each directional sequence is the recording of a relative marine level. As a consequence the depositional sequences have a predictable internal structure compared to the surfaces and stand systems they are made of.

There are a few models of the stand systems inside the deposit sequences, the most famous and applicable one in the field of the carbonatic series has the following sequences: the low system of the marine level (LST – Low Stand System Tract), transgressive system (TST – Transgressive System Tract) and the high system of the marine level (HST-High System Tract). From this point of view, a sequence starts with a slow growth, followed by a lowering of the sea level, which continues with the second level drop. These stand systems are limited by important limit surfaces. The lowered and transgressive stand systems are separated by a transgression surface (TS – Transgressive Surface). The transgressive tract systems and high stand are separated by a maximal flooding surface (MFS – Maximum Flooding Surface).

In the case of the research drillings of the carbonatic sequence from the Subpiatră drilling, the study of the variograms showed frequently a repetitive vacillating evolution of the experimental pattern.

The modelling of this process could not be performed by using two types of models, a linear one with an ascending ramp, on which a sinusoidal pattern was overlapped.

A representative example is the case of the Sub05 drilling from the Subpiatră limestone deposit, drilling which crosses a continuous stratigraphic sequence and in which the modelling parameters are identical, both in the case of autogenic products, represented by the calcium oxide (CaO) and in the case of the allogenic ones (siliciclastic) transported on the carbonatic platform from the edge of the basin and represented by the clayish material ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  etc) (Fig. 7.4).



**Figure 7.4. Modelling of the cyclicality of the experimental model of the CaO and SiO<sub>2</sub> variograms using a linear model combined with a sinusoidal pattern in the Sub05 drill from the Subpiatră limestone deposit**

The sincronism of the behaviour of the carbonatic autogenic compounds with the one of the clay siliciclastic compounds and respectively with the one of iron prove the simultaneous transport of the allogenic compounds in the sedimentation basin and respectively a sediment distribution, controlled by the same type of basin process (Fig 7.5).

Such a process can be assigned to a global control factor in the sedimentation basin of the type of the relative sea level fluctuations (Houlding, 2000). Considering the scale of the cycles at which these develop in the range 15-25 m, these basin variations could influence and hence control the development of the carbonatic platform, as a consequence these variations can be considered eustatic.

Accepting an eustatic influence on the studied sedimentary influence, the increasing tendency of the variogram's model seems to indicate to the same extent an increase of depth of the sedimentation basin. One must observe here the higher amplitude of the cycles in the upper part of the sequence, cycles which dim towards the basal part. This hypothesis is sustained by the microfacies study of the limestone sequence ion the investigated perimeter, which in depth highlights carbonic platform facies with rudists, while in the upper part it identified loferitic facies with frequent intertidal cycles, in which the eustatic cycles mark is well preserved.

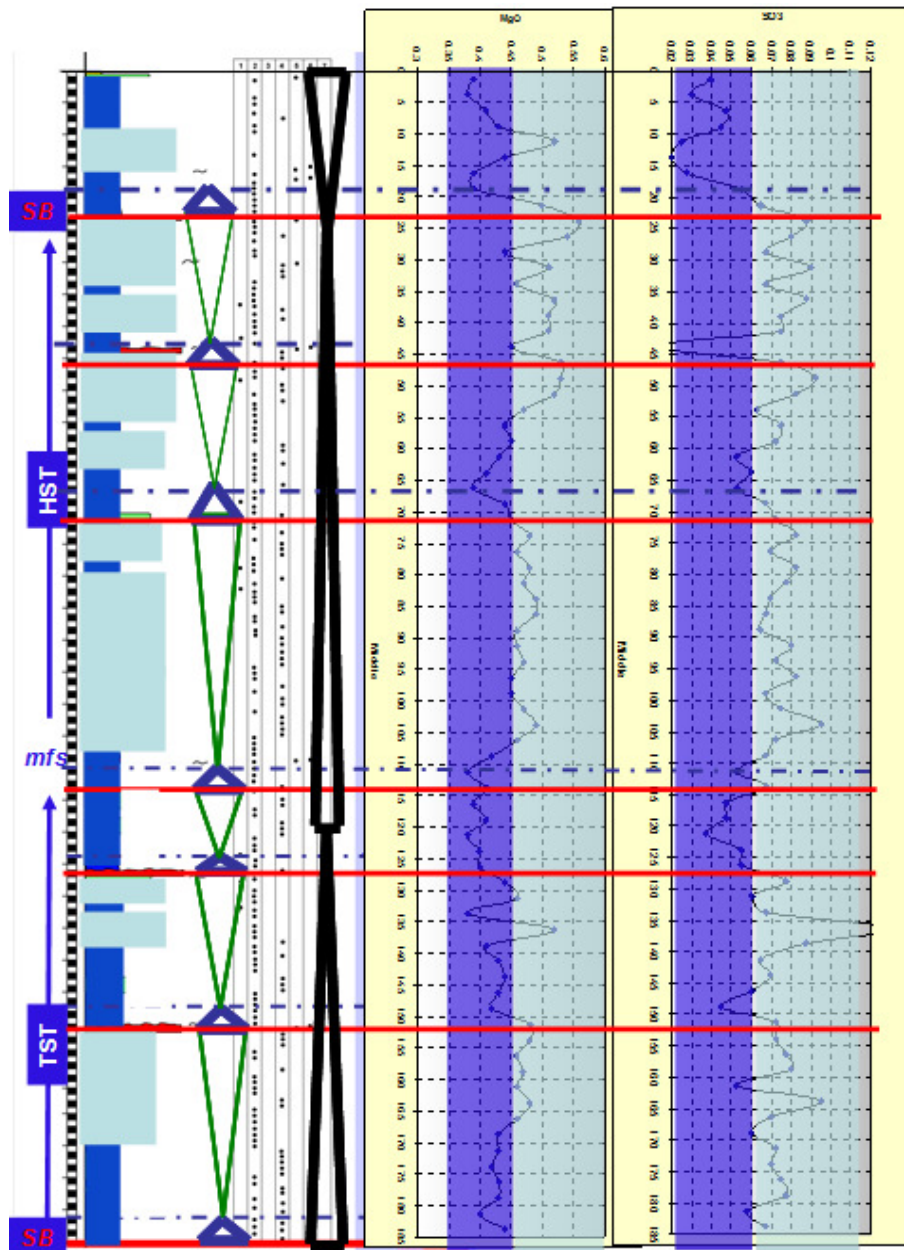


Figure 7.5 The use of the variations of MgO and SO<sub>3</sub> from the Sub16 from the Subpiatră deposit in the definition of the sedimentation sequences. SB – limit sequence, TST – transgresive stand, mfs – maximal flooding surface, HST 0 high stand

In the case of investigation of discontinuous stratigraphic sequences, interrupted by sudden lithological exchanges (the intercepting of faults or karstic filling), the experimental model registered distinct jumps (Fig. 7.6).

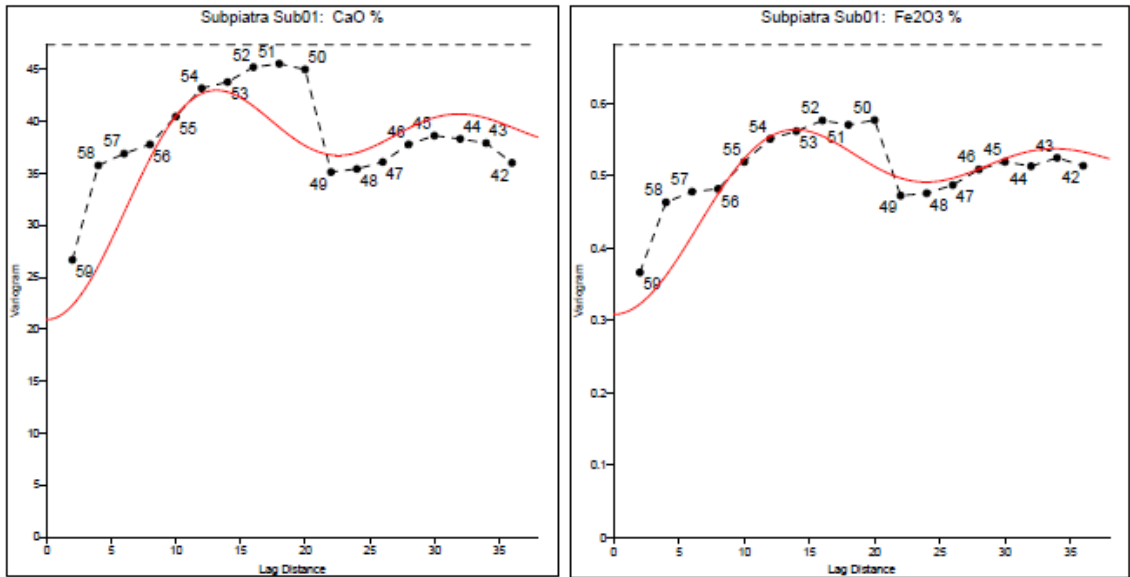


Figure 7.6. Major lithological exchanges in the experimental pattern of the variograms through the crossing of a fault in the Sub01 fault from the Subpiatră deposit

### The control of the diagenetic processes in the vertical distribution laws of the researched chemical elements

For the analysis of the vertical distribution of some compounds which have a mark of the diagenetic processes, such as SO<sub>3</sub> and MgO, the continuous series of the drilling data was divided into classes for a histogram analysis. They were compared with an optimal curve of normal distribution (Fig 7.7.). In both cases one can observe a distribution of the two compounds which, except for mild asymmetries, are close to a normal distribution law.

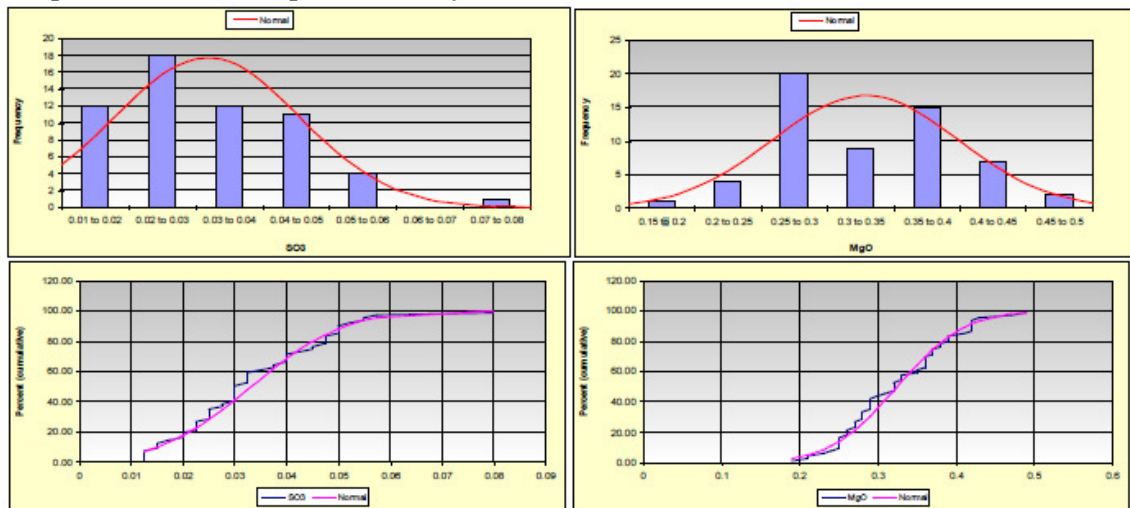


Figure 7.7 Normality tests in the statistic distribution of SO<sub>3</sub> and MgO in the Sub05 drilling from the Subpiatră deposit

Such an analysis can identify a possible distribution law, but it does not offer the image of the spatial variability of the two variables, as it can be determined through the analysis of the variograms. In both cases, the experimental model of the variogram could be modelled using a model with Gaussian distribution parameters.

In the experimental model of the variogram, one must observe the presence of a series of periodical cyclicity, especially in the upper part of the sequence, which suggests the



influence of fluctuation generated by a eustatic control. Although these fluctuations could not be modelled with a vacillating model, they do not exclude the possibility that these chemical products bear the mark of a control at the marine level in the sedimentation basin (Fig 7.8.).

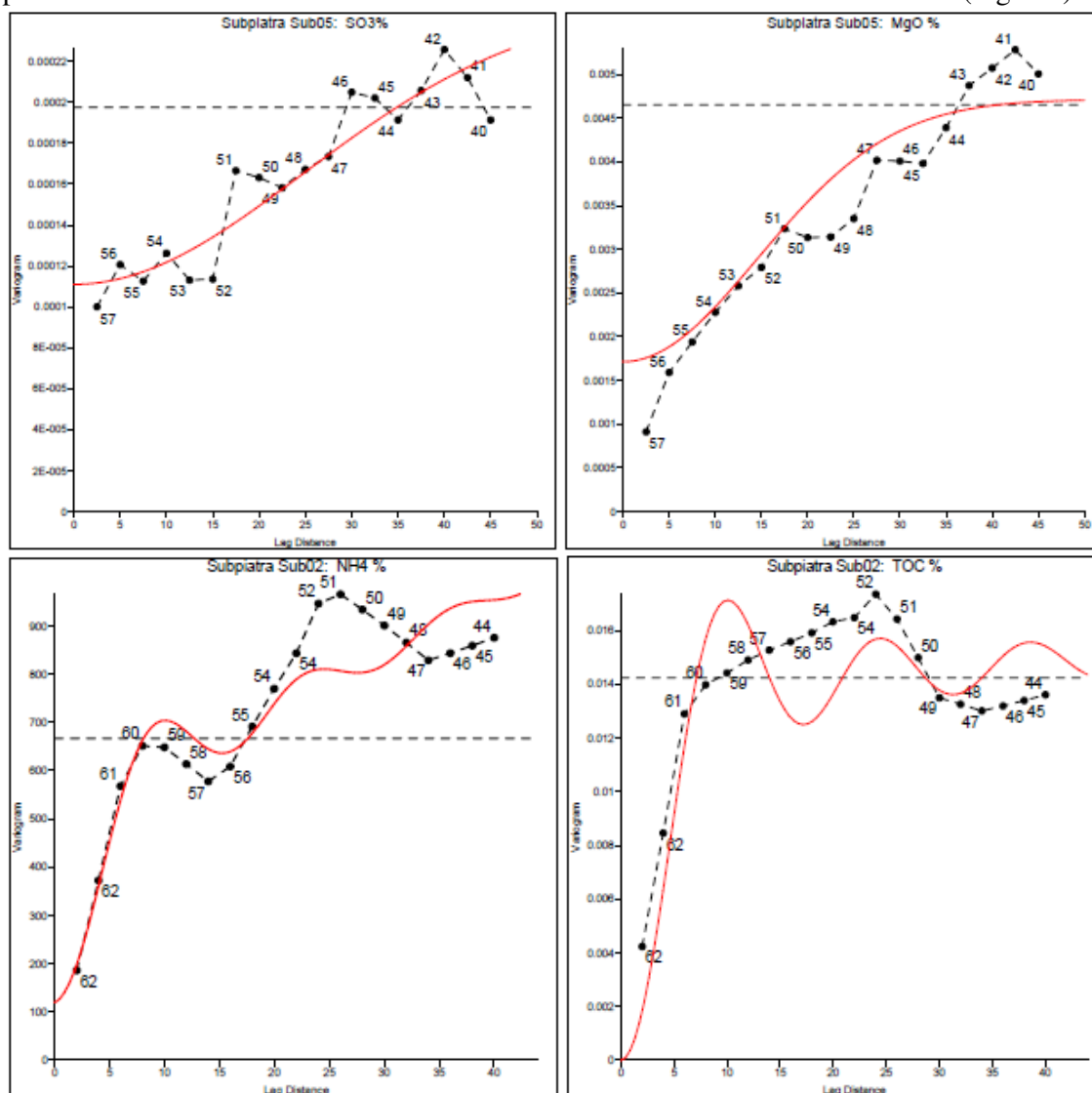


Figure 7.8. The experimental models and the gaus distribution law of SO3 and MgO in the Sub05 drilling, respectively NH4 and TOC in the Sub02 drilling, both drillings in the Subpiatră limestone deposit

In conclusion, the calculation of the variograms managed to highlight and the differentiate each time the distribution model of the autogenic compounds in comparison with the allogenic siliciclastic ones and also the random pattern of the diagenetic compounds.

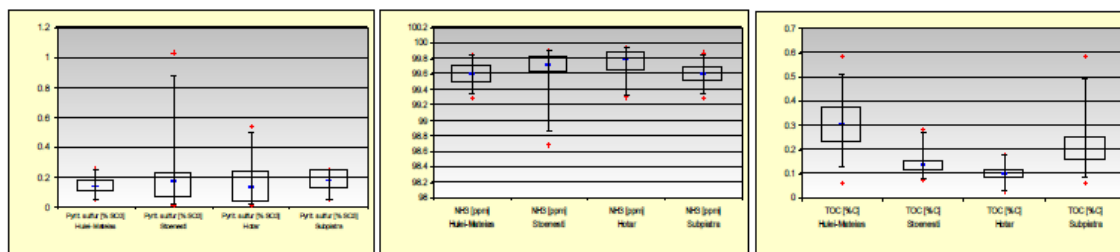
### 7.3. The analysis of the chemical elements with environment impact: TOC, NH3, SO3, pyrite and heavy metals

The study of these chemical elements from natural raw material which have an environment impact relevant in the production process was focused mainly on the following components: total organic carbon (TOC), ammonia (NH<sub>3</sub>) pyritic sulphur (pyrite SO<sub>3</sub>) and heavy metals.



The lab investigations were performed on composite samples of core material or drilling detritus. One composite sample is representative for 10 m of cored geological sequence and it is made of five 2 m long elementary samples. For each type of deposit, 23 to 46 composite samples have been analysed.

The behaviour differences of the three environment elements studied are highlighted in figure 7.9 and it can be seen in the case of each type of deposit through the calculation of the distribution of the major statistical elements with the help of Box & Whisker diagrams.



**Figure 7.9 Box & Whisker Diagram for pyrite SO<sub>3</sub>, NH<sub>3</sub>, TOC for the four deposits studied**

According to the diagrams, the average contents of pyrite SO<sub>3</sub> are found in the same order range but it is noteworthy the wider variation of the values in the case of the Hotar marl and the Stoenesti clay, in comparison with the values registered in the limes. At the same time, the maximum of pyrite SO<sub>3</sub> content are higher in the clay and marl sequences, in comparison with the carbonatic sequences.

NH<sub>3</sub> has a behaviour similar to pyrite SO<sub>3</sub>, with a wider variation spectrum in the case of clay deposits and at comparable average contents.

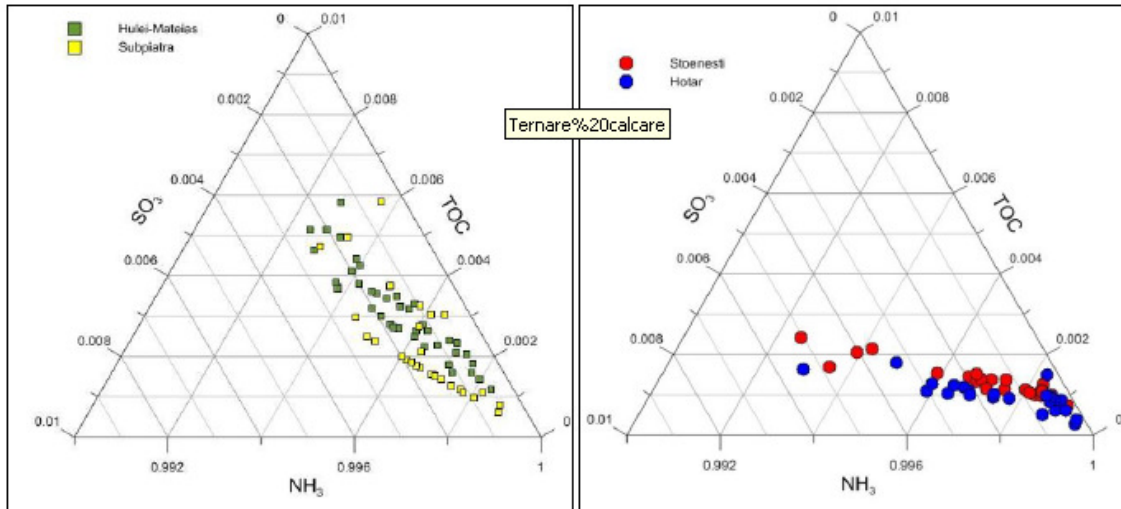
The mean values of TOC are higher in carbonatic deposits (organogenic deposits) and lower in the clay ones. At the same time, the variability of the TOC is higher in limestone, which have a wider distribution spectrum.

In addition to the previous calculations, further on I tried to present the relative process of these elements in three components system with the help of ternary diagrams. Such an approach is pretty frequently used in the environment chemistry and engineering in order to show the distribution schemes of the chemical composition in the case of rocks.

For such a ternary representation, the three studied components were normalized.

The analysis of the two diagrams underlines two distinct behaviour tendencies:

- in the case on limestone, for a relatively limited TOC variation field, pyrite SO<sub>3</sub> and respectively NH<sub>3</sub> varied in quite wide limits (Fig.7.10 left);
- in the case of clays, at narrower variation values of NH<sub>3</sub>, TOC and pyrite SO<sub>3</sub> are developed in wider limits (Fig. 7.10 right).



**Figure 7.10 Ternary diagrams showing the distribution of the chemical elements with environment impact for the four studied deposits**

In order to detail the behaviour tendencies of the three components, I also used an analysis with Scatterplot and Class Scatterplot system correlation diagrams. In the case of these diagrams, the elements of the two given variables are projected case after case, one according to the other. Moreover, these cases can be grouped according to the additional values of a third variable, considered grouping variable. If we project the values of pyrite  $\text{SO}_3$  and respectively TOC on a diagram according to the  $\text{NH}_3$  content in the samples, in all four deposits there can be easily seen a negative correlation on variable groups: a strongly negative correlation between  $\text{NH}_3$  and TOC and a negative correlation between  $\text{NH}_3$  and pyrite  $\text{SO}_3$ . If we project the values of pyrite  $\text{SO}_3$  according to TOC on a Scatterplot diagram and we use  $\text{NH}_3$  as a grouping variable, we can observe again the existence of some correlation tendencies, but this time a positive correlation: TOC is positively correlated with pyrite  $\text{SO}_3$  are influenced by the content of the grouping variable, respectively  $\text{NH}_3$  (Fig 7.11).

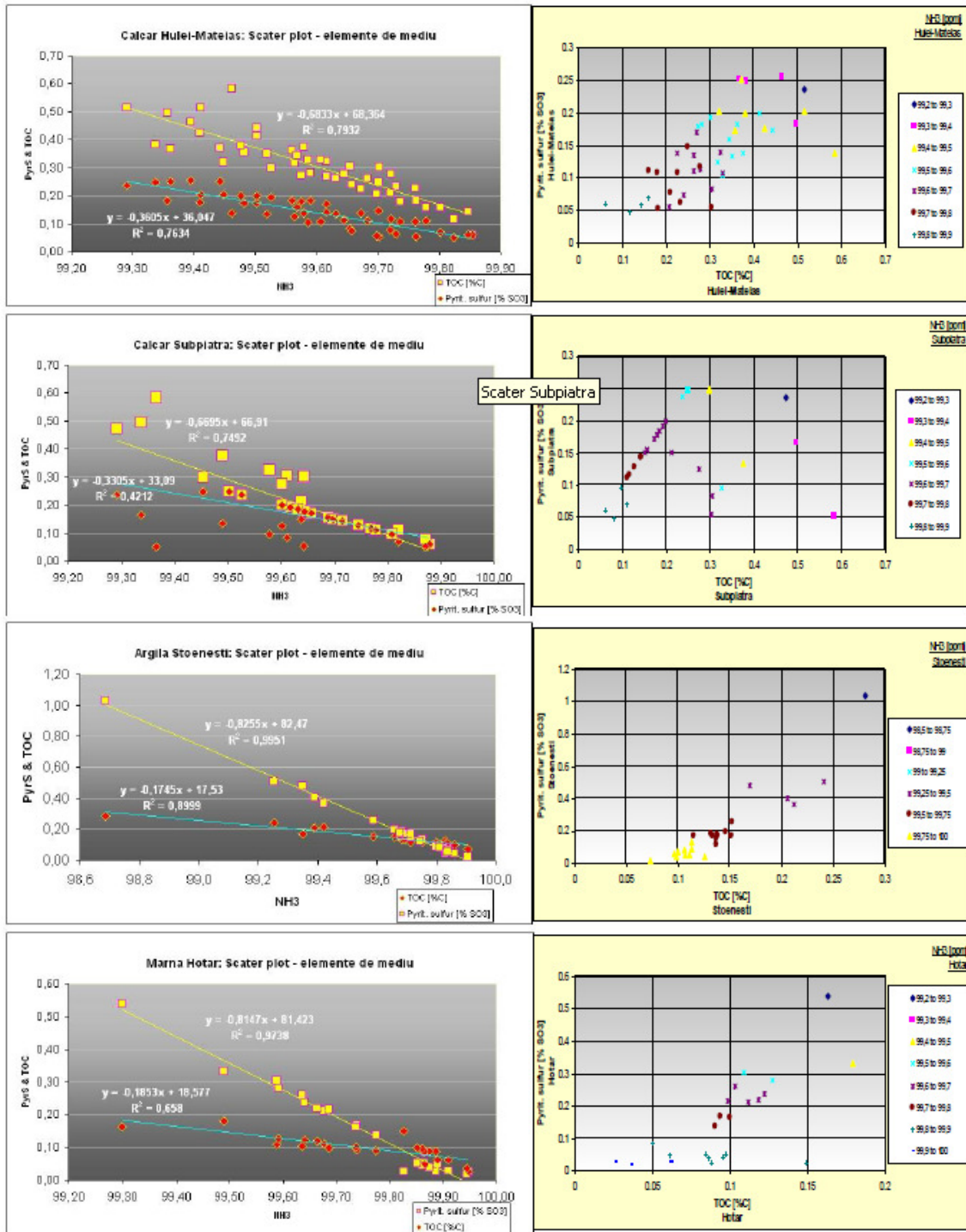


Figure 7.11 ScaterPlot and ClassScaterPlot Diagrams for NH<sub>3</sub> vs. TOC and pyritic SO<sub>3</sub> showing the correlation of the environment elements for the four studied deposits

In order to understand how the way the three chemicals interact affects the environment, we also used a Pearson type diagram. The Pearson correlation coefficient represents a measure of the linear dependence between the analysed variables, considering a

certain measurement interval. The matrix of the Pearson correlation coefficients is presented in Table 7.1 and it confirms the previously stated work environments.

**Table 7.1. The Pearson correlation diagram for the four studied deposits: the yellow cells represent the negative correlation coefficients between the pyritic SO<sub>3</sub>, TOC and NH<sub>3</sub> and the blue and grey cells represent positive correlation coefficients between pyrite SO<sub>3</sub> and TOC**

Pearson correlation	NH <sub>3</sub> [ppm] Hulei-Mateias	NH <sub>3</sub> [ppm] Stoenesti	NH <sub>3</sub> [ppm] Hotar	NH <sub>3</sub> [ppm] Subpiatra	TOC [%C] Hulei-Mateias	TOC [%C] Stoenesti	TOC [%C] Hotar	TOC [%C] Subpiatra	Pyrit. sulfur [% SO <sub>3</sub> ] Hulei-Mateias	Pyrit. sulfur [% SO <sub>3</sub> ] Stoenesti	Pyrit. sulfur [% SO <sub>3</sub> ] Hotar	Pyrit. sulfur [% SO <sub>3</sub> ] Subpiatra
	NH <sub>3</sub> HM					-0.89				-0.87		
NH <sub>3</sub> Sto						-0.95				-1.00		
NH <sub>3</sub> Hot							-0.81				-0.99	
NH <sub>3</sub> Sub								-0.87				-0.65
TOC HM	-0.89								0.70			
TOC Sto		-0.95								0.92		
TOC Hot			-0.81								0.71	
TOC Sub				-0.87								0.18
Pyrit. sulfur HM	-0.87				0.70							
Pyrit. sulfur Sto		1.00				0.92						
Pyrit. sulfur Hot			-0.99				0.71					
Pyrit. sulfur Sub				-0.65				0.18				

The analysis of the heavy metals was realized on composite samples from cores, 5 to 14 samples for each type of deposit, representing generally the product of 8-10 elementary samples (16 to 20 m length of the ample core). As a consequence, the information at the level of the heavy metals is rather a characterization of the deposit in its entirety and less specific to its internal architecture. The contents of heavy metals influence both the quality elements of the end product and the concentration of the emissions in the chimney of the clinker kiln. As a consequence, these elements are monitored both at quarry level (in natural raw material) and in conventional and alternative fuels, in order to obtain an estimative final level of the kiln emission within the maximum allowed levels (Tab. 7.2).

**Table 7.2 The values of the heavy metal concentration in the four investigated deposits**

	Subpiatra (calcar)	Hulei-Mateias (calcar)	Hotar (marna)	Stoenesti (marna)
Hg (ppm)	0.01	0.01	0.05	0.03
Σ(Cd,Tl) (ppm)	1.01	1.02	1.09	1.05
Σ (Sb, As, Pb, Cr, Cu, Mn, Ni, V) (ppm)	133.40	112.24	578.36	687.47

## Chapter 8

### Discussions and interpretations of the control methods of the emissions generated in the clinker manufacturing process

#### 8.1. The quality control of the emissions coming from the natural raw material using lab tests

8.1.1. The results of the lab tests for the limestone deposit in Subpiatră and marl deposit in Hotar, Aleșd

##### The results of the simulation of atmospheric release of the volatile organic compounds (VOC)

The first steps of such a test is the analysis of the behaviour of the natural raw material samples in the lab. In this phase, for the Subpiatră limestone and Aleșd marl samples the main volatile components (CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> etc) are released in the atmosphere in a normal temperature range, an interval specific to the components of the raw materials used in the clinker product, respectively in the interval between 200 – 600 °C. CH<sub>4</sub>, as the most abundant organic species

is released at a slightly higher temperature (approximately 700°C), which is also considered a normal level for this relatively stable compound.

According to the lab tests, it is estimated that the raw material used in the Aleşd will develop low VOC emission in a 4 level preheater kiln, considering that they will be used 100% (marl or lime) (Tab. 8.1).

**Table 8.1 The prediction of the VOC emission at the clinker kiln considering the participation of 100% of each material, reported to normal values (normal conditions, dry, 10% O<sub>2</sub>)**

Organic compound	Measurement unit	Limestone composite sample	Marl composite sample
VOC <sup>1)</sup>	mhC/mc <sup>3)</sup>	10	16
VOC nm <sup>2)</sup>	mhC/mc <sup>3)</sup>	5,8	11
C <sub>6</sub> H <sub>6</sub>	Mh/mc <sup>4)</sup>	0,7	1,8

- 1) volatile organic compounds (including methane)
- 2) non methanic VOC (organic compounds without methane)
- 3) mgCarbon / cube metre of gases
- 4) mgSubstance / cube metre of gases

#### **The results of the simulation of sulphur dioxide (SO<sub>2</sub>) release in the atmosphere**

During the investigation it has been observed that the lime sample does not contain detectable amounts of pyrite SO<sub>3</sub>. The marl sample contains small amounts of pyrite SO<sub>3</sub> and which after heating released a part of it as SO<sub>2</sub> in a temperature range of 250 – 400 °C. The amounts of SO<sub>2</sub> released from the sample are very small.

The expression of the SO<sub>2</sub> emission through the test of atmosphere release in the case of the two composite lime and marl samples indicate very low values, in the limit of 0-10 mg/Nmc (Tab. 8.2).

**Table 8.2 The prediction of the SO<sub>2</sub> emission at the clinker kiln considering the participation of 100% of each material, reported to normal values (normal conditions, dry, 10% O<sub>2</sub>)**

Type of material	Masses of S <sub>2</sub> released (mg SO <sub>2</sub> / kg)
Lime composite sample	<5
Marl composite sample	10

#### **The results of the simulation of ammonia (NH<sub>3</sub>) release in the atmosphere**

The investigations on the release of NH<sub>3</sub> from natural samples were executed in a pure nitrogen atmosphere (N<sub>2</sub>). During the test it has been noticed that, upon heating, ammonia is expelled in a relatively large temperature interval, included between 200 – 500°C. Within bigger temperature intervals, between 400-500°C, the release of the nitrogen from the sample was dominated by the oxidised form (NO).

As a rule observed both during the laboratory tests and in real production conditions, approximately one quarter of the ammonia content is released in the kiln stack. (Tab. 8.3).

**Table 8.3 The prediction of the NH<sub>3</sub> emission at the clinker kiln considering the participation of 100% of each material, reported to normal values (normal conditions, dry, 10% O<sub>2</sub>)**

Type of material	Masses of NH <sub>3</sub> released (mg NH <sub>3</sub> / kg)
Limestone composite sample	<5
Marl composite sample	10

### 8.1.2 The results of the lab tests for the Hulei-Mateiaş limestone deposits and the Stoienişti, Câmpulung clay deposits

This time, two formations of the same deposit, Hulei and Mateiaş have been analysed in order to identify if there are differences between the relevant parameters in the estimation of the emissions. The clay material comes from the Stoienişti clay quarry and it is investigated separately in the three distinct lithological existing units in this deposit: silts, silt and clay alternations and the sand unit, respectively.

#### **The results of the simulation of volatile organic compounds (VOC) release in the atmosphere**

The material collected in the Hulei-Mateiaş leads to a low release of the organic compounds in the atmosphere. The main volatile compounds (CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> etc) are released at a temperature level which is normal for the components of the raw materials used in production, which means a temperature level between 200 and 600 °C. The methane is released at a temperature of up to 700°C, normal temperature for this relatively stable component and which represents approximately a third of the total of VOC emission.

The material sample from the Mateiaş deposit released a slightly lower level of VOC than in the sample in the Hulei deposit. The samples coming from the lime material pertaining to the Hulei deposit release a relatively low level of VOC. In the hypothesis we had as a raw material for the kiln a material made 100% of this mixture, the VOC estimated emission would be around 12-18 mg/Nmc (tab. 8.4).

**Table 8.4 The prediction of the VOC emission at the clinker kiln considering the participation of 100% of each limestone material, reported to normal values (normal conditions, dry, 10% O<sub>2</sub>)**

Organic compound	Measurement unit	Composite sample of Hulei limestone	Composite sample of Mateiaş limestone	Composite sample of Hulei limestone
VOC <sup>1)</sup>	mgC/mg <sup>3)</sup>	15±4	18±4	12±4
VOC nm <sup>2)</sup>	mgC/mg <sup>3)</sup>	10±4	12±4	8±4
C <sub>6</sub> H <sub>6</sub>	mg/mc <sup>4)</sup>	1,3±0,4	1,0±0,3	0,8±0,2

In what regards the clay sample, the methane is the predominant element of the VOC emissions, with a contribution of approximately 40-60% from the organic carbon release. The samples of sandy material released significantly more VOC than the ones collected from silts or alterations of silts with clays. The estimation of the emissions registered is the typical VOC emissions scale for a limestone and, respectively, clay deposit. As expected, the samples from the clay material release in the atmosphere a higher content of VOC. The collected samples from the silt formations and respectively clay-silts alteration indicate the fact that the deposit has a very good quality in what regards the content of organic material and, if used 100% as raw material at the kiln entrance, the VOC estimated emission would be around 18-23 mg/Nmc. In what regards the collected samples from the sandy material formation, one can state that it has a lower quality as organic material content and if it were used 100% as silicon-aluminium component at the kiln entry, then the VOC estimated emission would be around 50 mg/Nmc (Tab. 8.5).

These emission amounts estimated for each type of material used in the raw material mixture must be cumulated and the result is considered the total estimated emission of VOC, emission coming from the natural raw material for the production of clinker in the case of these two deposits.

**Table 8.5 The prediction of the VOC emission at the clinker kiln considering the participation of 100% of each clay material, reported to normal values (normal conditions, dry, 10% O<sub>2</sub>)**

Organic compound	Measurement unit	Composite sample of Hulei silt clay	Composite sample of Stoenești alternation of silt and clay	Composite sample of Stoenești sandy material
VOC <sup>1)</sup>	mgC/mg <sup>3)</sup>	18±4	23±5	48±10
VOC nm <sup>2)</sup>	mgC/mg <sup>3)</sup>	9,7±4	13±4	37±7
C <sub>6</sub> H <sub>6</sub>	mg/mc <sup>4)</sup>	1,0±0,4	1,3±0,5	2,0±0,6

- 1) volatile organic compounds (including methane)
- 2) non methanic VOC (organic compounds without methane)
- 3) mgCarbon / cube metre of gases
- 4) mgSubstance / cube metre of gases

**The results of the simulation of sulphur dioxides (SO<sub>2</sub>) release in the atmosphere**

Unlike the release of VOC, in the case of SO<sub>2</sub> the release test must be achieved only on the mixture of raw material and not on each component separately because the clay component releases high amounts of SO<sub>2</sub>, but a big part of this amount will be reabsorbed and stabilized by the carbonatic component from the raw material mixture (for example as sulphate).

In the case of the carbonatic material there was no release of SO<sub>2</sub> emissions while the clay material and the mixture one released SO<sub>2</sub> at the temperature ranging between 300 – 450°C.

The estimation of the SO<sub>2</sub> emission concentrations coming from the natural raw material in the case of the deposits belonging to the Câmpulung cement plant are written in the Table 8.6.

**Table 8.6 The prediction of the SO<sub>2</sub> emission at the clinker kiln considering the participation of 100% of each material, reported to normal values (normal conditions, dry, 10% O<sub>2</sub>)**

The type of mixture used	The emission of SO <sub>2</sub> estimated in the direct operating mode of the kiln (with the raw mill stopped) mg SO <sub>2</sub> /Nmc	The SO <sub>2</sub> emission estimated in the composed operating mode of the kiln (with the raw mill functioning) mg SO <sub>2</sub> /Nmc
Silt mixture	2 (0-50)	1 (0-50)
Silt alternation mixture	7 (0-60)	3 (0-50)
Sandy material mixture	140±50	50 (0-100)

**The results of the simulation of ammonia (NH<sub>3</sub>) release in the atmosphere**

During the lab test, the NH<sub>3</sub> amount released from a limestone sample took place at a temperature ranging between 200-400°C and the NH<sub>3</sub> amount from a clay sample at a temperature ranging between 400-600°C.

The estimation of the NH<sub>3</sub> emission coming from the natural raw material in the case of the deposits pertaining to the Câmpulung cement plant are written in Table 8.7:

**Table 8.3 The prediction of the NH<sub>3</sub> emission at the clinker kiln considering the participation of 100% of each material, reported to normal values (normal conditions, dry, 10% O<sub>2</sub>)**

Type of material	Emission of NH <sub>3</sub> estimated in a direct or composed operating mode of the kiln (mg/Nmc, dry, 10% O <sub>2</sub> )
Hulei 1 limestone	23/1
Mateiaş 1 limestone	21/1
Hulei 1 limestone	18/1
Silt clay	41/3
Alternation of silt and clay	49/3
Sandy material	35/2

A natural raw material mixture made of 75% limestone and 25% clay can be calculated from the percentages of raw material mass and the individual emission for each type of material could be estimated. For example, in our case, if we considered the most unfavourable scenario and we formed a mixture of raw material from 75% limestone and 25% clay of the poorest quality (only sandy material), the total emission of HN<sub>3</sub> estimated in this case would be 28 mg/Nmc in direct operating mode, respectively 1,5 mg/Nmc in the case of the composed operating mode.

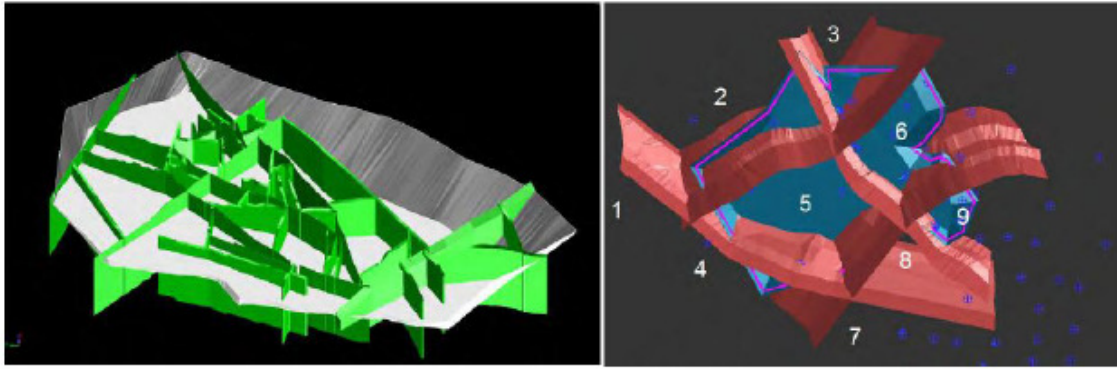
## **8.2. The quantitative control of the emissions coming from the natural raw material through the use of block models**

Natural raw material represents an essential factor in the basic activities in the cement industry. Although, normally they have a reduced participation in the total production cost of the cement, they can still have a significant influence through the quality of the end product. The block model represents such a work tool, a tool used for describing the spatial distribution of the chemical elements, the inventory and the assessment of the deposit, respectively. This model represents the support of some strategic decisions regarding the way of using the raw materials and the exploitation strategy and the development of quarries. The objective of the calculation of a block model is to obtain a sound and reproducible description of the deposit, as such a block models represents three-dimensional description of the deposit.

For the calculation of a block model, the deposit is divided in a big number of small blocks, each block representing a homogenous unit and respectively a convenient one as dimension in the exploitation planning process. The dimensions of the blocks and the orientation of the block models depend on the orientation of the geological structures, the chemical variability and the constraint elements in the future development of the quarry exploitation.

In the first step, each block is assigned a numeric code representing the geological unit it belongs to, a unit defined according to the deposit's geologic model. Then, each such elementary block is assigned the chemical information gathered from the drillings. These data specific to each block are the result of the statistic analysis processes (variograms) and the processes of spatial interpolation, respectively (Fig. 8.1).





**Figure 8.1. Example of 3D geological model for the Subpiatră limestone deposit and in Hotar marl deposit**

The next phase of the data evaluation is the statistical analysis of the data collected from the geological exploitation phase. This implies the calculation of the elementary parameters of descriptive statistics, the calculation and the visual evaluation of the histograms, the calculation and evaluation of the correlation matrix and the analysis of the correlation graphs.

Starting from the quality parameters of the variograms and respectively the vertical logs of the drills, the lateral and vertical extrapolation limits of the chemical and environment elements were defined, respectively the maximum dimension of the elementary blocks from the block model:

- Subpiatră deposit: 25m x 25m x 15 m
- Hotar deposit: 25 m x 25 m x 5 m
- Hulei-Mateaş deposit: 25 m x 25 m x 12 m
- Stoenеşti deposit: 25 m x 25 m x 4 m

The chemical and environmental variables analyzed / interpolated, respecting the spatial distribution laws have been statistically identified and were memorized in the block model. Additionally, a series of data types have been added in the model with the purpose to allow the visualizing of the deposit, for example the geological unit and the detailed evaluation of the resources and reserves, as well as the programming, considering the various types of materials and the prediction confidence level.

For the exploitation of the information in the block model there are various specialized computer programs of which some are widely available, while others are custom made and developed only by certain companies. In the current paper, the block model is operated with the QSO Expert software. The program has been created within the Holcim Group and it allows various operations with the block model, among which: the visualization of the spatial distribution of the various variables in this model (for example the environment elements), the inventory of the blocks or volumes with a certain quality and content, the simulation of exploitation of the deposit taking into account a set of constraints such as the environment or quality ones in the current case.

For the purpose of the analysis of the spatial distribution of the environment elements in the investigated deposits, the block model allows a quick visualization of these variables. In these cases, the environment elements which could be modelled through their amount and spatial variability are chlorine (Cl) and sulphur (expressed as SO<sub>3</sub>). In the case of ammonia, the third environmental element investigated within the geostatistical chapter, its amount and variability were less relevant for it to be accurately calculated and introduced as a variable in the block model afferent to these deposits. The spatial distribution of chlorine and sulphur indicates the type of the genetic, tectonic, lithological and diagenetic subordinate control, phenomena which are easily visible in the siliciclastic sequences and to the same extent in the carbonatic ones. In the case of clay and marl deposits, both the distribution of chlorine (Fig.

8.2.) and the one of sulphur (Fig. 8.3.) are highlighted by the stratification elements which underline relevant lithological and facies differentiations, such as the clay / sand ones.

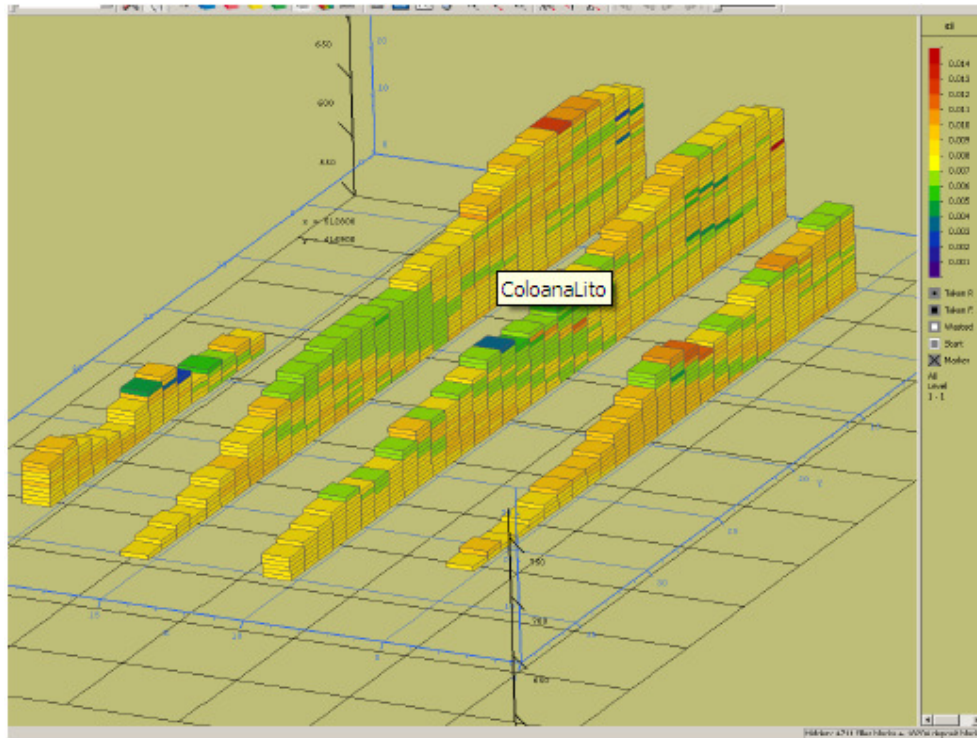


Figure 8.2 The block model which shows the chlorine distribution in the Stoenești, Câmpulung clay deposit

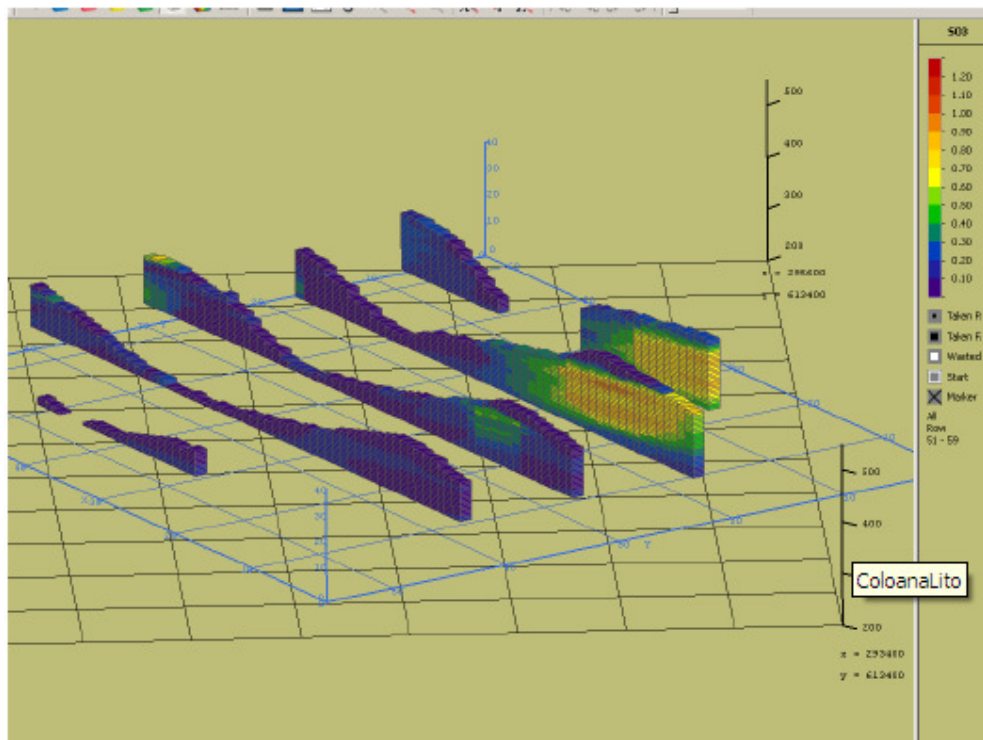


Figure 8.3 The block model which illustrates the SO<sub>3</sub> distribution in the Hotar, Aleșd marl deposit

In the case of limestone deposits, the clay contamination areas such as the fractures in the case of the Aleşd limestone or tectonic contamination facies or distal embankment in the Câmpulung are the ones showing obvious accumulations of chlorine and sulphur, in comparison with the general mass of the deposit.

Once these block models have been calculated, with the use of the QSO Expert, the variations of the environment elements in the deposit can be controlled and stabilized through the solutions offered by the selective exploitation and mixing of the material of various blocks. Such a method allows the entire use of the deposit, including the material with apparently toxic contents, increasing the entire life duration of the deposit and the possibility to supply a material with the requested solicitations in the production process, that is a natural raw material with constant composition and without impact risk on the clinker kiln emissions.

## Conclusions

This paper is entitled **The impact of the natural raw materials on the kiln stack emissions in the cement manufacturing process** and addresses an issue placed on the edge between geology respectively environmental engineering, identifying an immediate practical applicability in the cement industry. The study is based on geological, geochemical and environmental data, which come from the evaluation of the deposits exploited by Holcim (Romania) SA in the cement plants from Aleşd, Bihor county and Câmpulung, Argeş county. The investigated deposits are essential to the core business of this company, having a direct influence on the production cost, product quality and their impact on the environmental protection. At the same time, we considered that the deposits of natural raw materials are not renewable resources and in order to be favorable not just for the environmental requirements but equally to the quality standards they must be planned and exploited rationally.

Such research provides a controlling method on the level of chemical compounds that generates a contribution of emissions from the raw materials used in the actual process of cement production. Among these compounds are also those studied by this paper, namely SO<sub>2</sub>, VOC and NH<sub>3</sub>. Emissions levels generated only by the natural raw materials, considered the **baseline emissions** should be well defined and known in order that subsequently to be able to estimate the amount of additional emissions from the use of alternative raw materials and traditional and alternative fuels. Therefore, the method proposed in this paper contributes on one hand to the optimization of exploitation of natural resources, respectively increasing their lifespan, and on the other hand provides a control tool in the formation and release of the final amount of emissions generated in the atmosphere.

Natural raw materials used in the cement industry are represented by sedimentary rocks, limestone, clay, sand and transition rocks of these. Analysis of the impact of environmental elements intake was made using specific methods of sedimentary rocks geology study (petrogeny / sedimentary processuality, facies analysis, analysis of sedimentary depositional environments etc.) and respectively geochemical and descriptive geostatistical methods and spatial distribution modeling. All measurements, modeling and interpretations have had as final goal deciphering depositional and post-depositional processuality (diagenetic), which helps at quantifying the spatial distribution laws of environmental reservoir elements and building model of blocks of the deposit.

**Organic compounds** are represented by various types of kerogen and bitumen subordinate with marine or continental origin, representing fragments of the organic material accumulated in the sedimentation basin. Evaluation of organic material content in the rock

and the potential to generate emissions of organic compounds is achieved by quantifying the **total organic carbon** content (TOC).

**Sulfur** may be present both in inorganic form, pyrite, greigit, marcasite, native sulfur or sulfate as well as in organic form. The proportion of inorganic and organic respondent depends on the source and type of kerogen preserved in the rock. The origin of sulfur is primarily related to micro-bacterial processuality that can dismiss sulfur, both from seawater where it is present as sulfate ( $\text{SO}_4^{2-}$ ) as well as from organic material during its bacterial degradation process. In the production process, the raw material sulfur emissions level is controlled by sulfur compounds present in the reduced form, both of sulfur and of organic substances. Consequently, the evaluation of unstable sulfur content respectively the measurement of potential sulfur emissions generation is achieved by quantification of the pyrite sulfur content.

**Ammonia** also represents a breakdown product of the organic material present in the rocks. Extraction and release of nitrogen from the organic compounds occurs due to bacterial transformation processes intervention of which the most important is the process of ammonification. In the production process, ammonia is released from the raw material into the atmosphere as gaseous emissions. Therefore its evaluation is done by quantifying the presence of  $\text{NH}_3$  content.

For understanding the genetic conditions, the geological deposits were investigated with a large number of diggings, described, sampled and analyzed with facies and geochemical methods. Facies and microfacies data analysis allowed the identification and the description of environments and specific depositional processes of each deposit.

**The limestone** which is constituting the **Subpiatră deposits** was formed under shallow carbonate platform, isolated from the mainland and thus with reduced siliciclastic input, but sensitive to small amplitude variations of the sea level. Carbonate sequence is represented by a set of subtidal sequences of 20-25m thickness, with developments from normal marine to restricted and supratidal marine. The potential for accumulation and preservation of organic substances (expressed as TOC) and formation of pyrite (expressed as  $\text{SO}_3$  pyrite) was reduced. In the karst fillings materials (over thrust zones, shearing, fracturing and exo and endokarst) minimal concentration of pyrite of diagenetic nature can exist.

**Limestone deposit from Hulei - Mateias** was formed under a distal carbonate platform and respectively on its slope. Carbonate succession records high dynamic facies, karst and bioclastic dunes but also breccia facies of slope and distal allodapite. The potential for accumulation and preservation of organic material (TOC) and formation of pyrite ( $\text{SO}_3$  pyrite) and ammonia was negligible. In carbonatic slope facies zones, minimal concentration of pen contemporaneous pyrite could have existed.

**Marl** from the **Hotar deposit** was formed under distal shelf conditions, where it gained a relatively homogeneous series of marls with thin layers of glauconite. The potential accumulation of organic materials was relevant, but apparently, diagenetic transformations did not allow preservation (low TOC). Instead, the potential of pyrite formation was relevant, explaining the presence of an average  $\text{SO}_3$  pyrite content.

**Stoenești clay deposit** was formed in an environment with dynamic continental slope with high sedimentary dynamic and highlighted by high frequency siliciclastic fans. The potential accumulation of organic material was low (low TOC and ammonia) and the potential of pyrite formation was negligible (low  $\text{SO}_3$  pyrite content).

The analysis of the genetic potential regarding the formation of some compounds with environmental impact, performed on metric scale level and using the standard methods of facies analysis, expressed in terms of depositional environments, was required by an immediate practical purpose, but at the same time the result has a relevant scientific significance, regarding the geological knowledge level from the areas studied. Taking into

consideration the given information currently available, it is for the first time in Romania when such an applicative geological research was developed.

Geochemical analysis of these deposits were performed based on the laboratory results on elementary geochemical samples (cores with lengths of between 2.0 and 2.5m), taking into account the large groups of oxidizing compounds and the major elements (CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>), minor elements (MgO, SO<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O) and trace elements (TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, Cl). For the analysis of environmental elements, such as TOC, SO<sub>3</sub> pyrite, NH<sub>3</sub> and heavy metals, an additional set of laboratory tests was considered, this time on composite samples (composite sample with a length of 10m, representing a mixture of 5 elemental samples of 2m).

Considering CaO as default parameter for a limestone deposit, the spatial distribution chemistry analysis focused mainly on the chemical contaminants, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, etc and those resulting from SiO<sub>2</sub>, MgO, and SO<sub>3</sub> diagenetic processes.

On the scale of the investigated deposits, the concentrations of the environmental elements are variable, being controlled mainly by major lithofacies units, but developed in the normal range for raw materials used in the cement industry. Spatial distribution of TOC, SO<sub>3</sub> pyrite and NH<sub>3</sub> was influenced by the syngenetic evolution processes and the diagenese of the organic material. Cycle conservation or degradation of organic substance highlighted by TOC and NH<sub>3</sub> controlled the potential of pyrite formation and consequently the SO<sub>3</sub> pyrite concentration.

Geochemical analysis was used to identify depositional environments control over the vertical and lateral variation of the limestone and clay composition in the investigated deposits. Thus, with **descriptive statistics and/or graphics method** the following processes could have been identified:

- Diagenetic concentration of nodular silica in facies ramp, hemipelagic / deep;
- Carbonated granular flow that transported, besides figurative elements of carbonate and figurative elements of siliciclastic terrigenous material, quartz and clay minerals (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, etc.) and thus contrasts with distal hemipelagic sedimentation characterized by low sedimentation rate of the terrigen material;
- Pelagic sedimentation sequences developed in the bottom of the carbonate ramp, highlighted by significant accumulations of organic materials associated by diagenetic concentration of organic phosphorus (P<sub>2</sub>O<sub>5</sub>);
- Rich organic levels with desulphurization processes from the organic material, respectively the microbial degradation of sulfur compounds from the organic material with hydrogen sulphide availability and enriched pyrite (SO<sub>3</sub>);
- Differentiated Siliciclastic input sequences, which causes a difficult spatial correlation.

Sedimentary or more complex tectonic processes could be highlighted using also the variogram analysis. Such were highlighted:

- Facies fragmentation due to vertical overlapping of different depositional environments and the amplitude of this process in vertical profiles of the drillings;
- Discontinuous stratigraphic succession, interrupted by sudden lithological changes caused by the interception of faults or of karst fillings;
- High correlation between the content of iron and clay allogenic compounds (Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> variograms), underlining their close genetic relationship;
- Eustatism mark on carbonate platform sedimentation conditions, highlighted by repetitive oscillatory evolution of the experimental variogram model; modeling this process could be carried out using two types of models, one linear with a slope upward, over which a sinusoidal pattern was superimposed. This phenomenon was observed both for authigenic products (CaO) and in the case of siliciclastic allogens (SiO<sub>2</sub>,

Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Na<sub>2</sub>O) represented by clayey material and transported on a carbonate platform from the edge of the basin;

- Cyclical variations of MgO and SO<sub>3</sub> that through the variation, frequency and amplitude domain variations define the depositional overlapping model, respectively the lateral correlation limits on distances of sedimentary sequences.

In conclusion, the variograms calculation managed to highlight and to differentiate every time the distribution model of the comparative authigenic components from the siliciclastic allogens and also penecontemporaneous random or cyclical pattern of diagenetic compounds distribution. Using statistical geochemistry methods in describing and modeling of sedimentary depositional or diagenetic processes with metric resolution is again an additional relevant contribution to the geological knowledge of the formations studied.

Chemical study elements in natural raw materials with relevant environmental impact in the production process focused on components: total organic carbon (TOC), ammonia (NH<sub>3</sub>), pyrites sulfur (pyrites SO<sub>3</sub>) and heavy metals. In the case of **pyrite sulfur** (SO<sub>3</sub> pyrite) average contents are in the same order of magnitude, but it is worth mentioning the larger variation values when compared with limestone. Also maximum contents are higher of clay and marl sequences compared with carbonate successions. **Ammonia** (NH<sub>3</sub>) has a similar behavior with SO<sub>3</sub> pyrite, with a wider range of variation for clay deposits, and that the average comparable contents. As expected, the average values of **total organic carbon** (TOC) are higher in the carbonate deposits (deposits with origins of organogenetic excellence) and are lower in the clay deposits. At the same time, the variability of TOC is higher in limestone, which in this way has a wider distribution range.

Analysis of **normalized values on ternary diagrams** highlights two distinct behavioral tendencies. In the case of limestone, for a range of variation of TOC's relatively limited, sulfur pyrite and ammonia varies among relatively large limits. In case of clays, at small values of ammonia variation, TOC and pyrite sulfur develops in wider limits. Data analysis on **Scatterplot diagrams and Scaterplot Class** of SO<sub>3</sub>, pyrite and TOC values according to the ammonia contents from the samples demonstrates that in all four deposits is relatively easy to recognize a negative correlation on groups of variables: strong negative correlation between NH<sub>3</sub> and TOC negative correlation between NH<sub>3</sub> and SO<sub>3</sub> pyrite. If on a Class Scatterplot diagram we project the SO<sub>3</sub> pyrite values according to TOC and we use NH<sub>3</sub> as grouping variable, we can notice again the existence of correlation trends, but this time a positive correlation: the TOC is positively correlated with pyrite SO<sub>3</sub> for all studied deposits and correlation coefficients between TOC and pyrite SO<sub>3</sub> contents are influenced by the grouping variable content, respectively NH<sub>3</sub>.

Heavy metals, especially cadmium, thallium and mercury have lower concentrations, with average subunit values and a clustered distribution of samples, highlighted by different small standard deviations ranging from 0.01 to 0.1 ppm. Other elements as, vanadium, chromium, manganese, copper, arsenic, antimony and lead show relatively higher concentration compared to the firsts and a slight increase in distribution and variability, highlighted by larger standard deviations ranging from 2 to 40 ppm, but none of the heavy metals concentrations are relatively critical with respect to legal emission limits.

To confirm whether environmental compounds content of natural raw materials, has an impact on total emissions from clinker stack, was virtually simulated in labs the volume and quality of volatile compounds that can be released into the atmosphere in the actual process conditions. **Quantitative estimation of emissions of organic compounds by laboratory tests** was performed for the three compounds that may have relevant impact on emissions and on every deposit from Aleşd and respectively Câmpulung. Values of volatile organic compounds (VOC), of sulfur dioxide (SO<sub>2</sub>) and of ammonia (NH<sub>3</sub>) have low concentrations at both Aleşd and Câmpulung as well, significantly lower values than the legal

limit and respectively lower than the average emissions of organic compounds in the Holcim cement plants.

In addition to the quantitative estimation of the emissions of organic compounds by laboratory tests, the second quantity control of emission measures the amount of emissions from natural raw materials is the **model blocks**. Applied to each deposit, this method enables selective exploitation to its sustainable use, while respecting quality and environmental constraints. In other words, taking into consideration the constraints of the mixture of chemical raw materials that need to be introduced in the production process and the maximum limits of the compounds with an impact on emissions from raw material can be selected each time the blocks with proper chemical composition. From scientific point of view, this working method uses real architecture deposit (geological model) as support for the allocation of chemical and environmental information, respecting the rules imposed by sedimentary processuality. The advantage of such a scientific approach is that these blocks can be found in practice during exploitation as the solution for the selective planning and exploitation of deposits by respecting the quality and environmental requirements.

Spatial distribution of chlorine and sulfur indicates the type of genetic, tectonic, lithologic and subordinate diagenetic control, phenomena that are easily visible in siliciclastic succession and equally in the carbonate succession. In the case of marl and clay deposits, the distribution of chlorine and the sulfur is highlighted by elements of stratification, elements that underline the lithological differences and relevant facies, such as those for clay / sand. In case of limestone deposits, clay contamination areas such as fractures in the case of Aleșd or limestone facies of tectonic contamination or distal slope in the case of limestone from Câmpulung are showing obvious rich content of chlorine and sulfur compared to the overall mass the deposit. Once these patterns of blocks are calculated by using the average QSO Expert variations of the environmental elements from the deposit, these can be controlled and stabilized through the solutions offered by selective exploitation and respectively of mixing material from different blocks. Such a method allows the use of the entire deposit, including materials with apparently harmful content, increasing the lifespan of the deposit and can provide material specifications required by the production process, i.e. a natural material with constant composition without risk of impact on emissions from clincher oven's chimney.

The theme approached in this work was determined by the real needs of Holcim (Romania) SA, a cement producing company, and the results are immediately applicable. Model blocks are already operational for each deposit. These models have a direct impact on operating costs, product quality, especially on the control of emissions from clinker stack.

Such research on natural raw materials combining specific methods of investigation and interpretation of the geology, geochemistry and environmental engineering, applied in practice provide baseline knowledge for emissions generated by natural raw materials. Knowing this benchmark subsequently can be further investigated and correctly estimated the additional quantities of emissions that can be derived from the use of alternative raw materials or the use of traditional or alternative fuels until the permissible limits set by environmental legislation in force. Additionally, this method contributes to the optimization of the natural resources exploitation and to increase their lifetime, respectively.

Following the line of scholars from this paper also the possibility of further research is open, researches detailing the additional emissions generated by alternative raw materials, and those generated by the combustion of various natural or alternative fuels.

Summarizing the obtained results, this paper demonstrates that in order to control and to maintain a total emission level within the regulated limits, knowledge and control of emissions from natural raw materials is possible and it represents the starting point and key to control the subsequent use of alternative raw materials, fuels as solution for the concept of sustainable development.



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