BABEŞ-BOLYAI UNIVERSITY OF CLUJ-NAPOCA
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING
DEPARTMENT OF CHEMICAL ENGINEERING

PhD. THESIS ABSTRACT

THE ORGANIZATION OF MICRO AND NANO PARTICLES IN COMPLEX STRUCTURES WITH IMPLICATIONS IN ENVIRONMENTAL CHEMISTRY

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THESIS SUMMARY

THEORETICAL PART

EXPERIMENTAL PART – PERSONAL CONTRIBUTIONS

IMPORTANCE OF RESEARCH THEME (INTRODUCTION)

The Ph.D. Thesis entitled "The Organization of Micro and Nanoparticles in Complex Structures with Applications in Environmental Chemistry" approaches a wide study concerning particulate matters. The study is focused on the potential damages caused by these particulate matters on air pollution mitigation strategies. Air pollution with solid particulate matters (PM) presents main concerns due to the complex substances involved which affect the living environment in an obvious manner. PM become a global problem which leads to intensive researches in order to improve the atmospheric pollution legislation and to develop mitigation strategies.

Key words: particulate matters, pollution, atmosphere, AFM, XRD, SEM.

1. ENVIRONMENTAL MICRO AND NANO PARTICLES
1.1 STREET DUST

Environment manifestation leads to the formation of new phases and phenomena investigated by scientists in order to understand them and discover new data of interest [5]. Street dust is a complex, formed by particulate matter due to the constructive or destructive phenomena happened in the nature. Street dust presents environmental concern due to its high content of impurities and possible polluting factors. Figure 1.1 presents the **main street dust sources**.

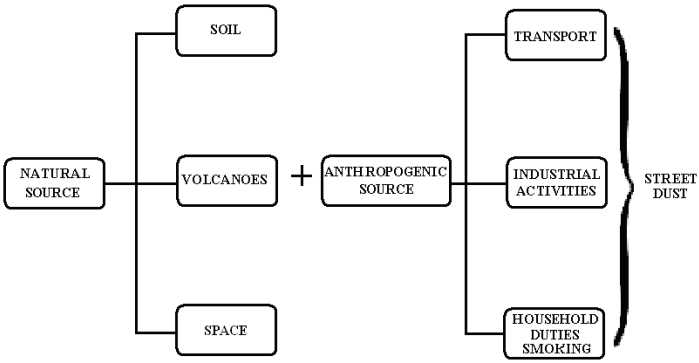

Figure1.1. Street dust classification scheme [6, 7].

Natural sources ranges form soil decay, volcanoes and even outer space sources. Anthropogenic sources summarize transport, industrial, and household activities. These sources are able to modify the atmosphere quality [8, 9]. Several known pollutants are generated from these sources like PM10, PM2.5, and PM1 [10, 11].

According to their composition street atmospheric pollutants can be classified as: **allergen** such pollen, spores and fungi originated in the vegetal reign; **bacterial** summarizing bacteria originated in the nose secretions and other animal emissions, **residual** emissions originated into the industrial wastes, irritant emissions are mainly gaseous nature originated into the industrial and combustion chemical processes; and particulate matters which are close related to street dusts.

ATMOSPHERIC SUSPENSIONS

They represent solid and liquid particles suspended in the atmosphere. Form environmental point of view it is a matter of size and chemical composition [6, 28]. Some of them could be observed by the human eye like sand and dust whirlpools formed by strong air currents, but can contain also ashes, soot which consist in fine particles unable to be seen by the human eye. There also could be fractions of bacteria, viruses and other pathogens which are able to increase the environmental danger. Such fines particles could be observed only by physical-chemical methods such microscopy and spectrometry. Further we describe the main class of atmospheric suspensions.

1.2.1 PM10

PM10 are the particles suspended into the atmosphere having the aerodynamic diameter $\leq 10\mu m$ [29, 30, 31]. Their sources are very similar with the street dust ones being natural and anthropogenic, see figure 1.2.
According to US and UE Environment Protection Agency the maximum accepted level of PM10 is 50 $\mu g/m^3$, the limit excesses should not happened more than 35 times per year, and from 1 January 2010 the excesses number are restricted to only 7 times per year [42, 47].

Thus, starting with 1 January 2015 the number of limit excesses per year is 35 like before 2005. Although, in UE the PM10 limits are strongly prescribed and respected. There are no limitations for the dust present in the street, which is a major cause of PM10 [48].

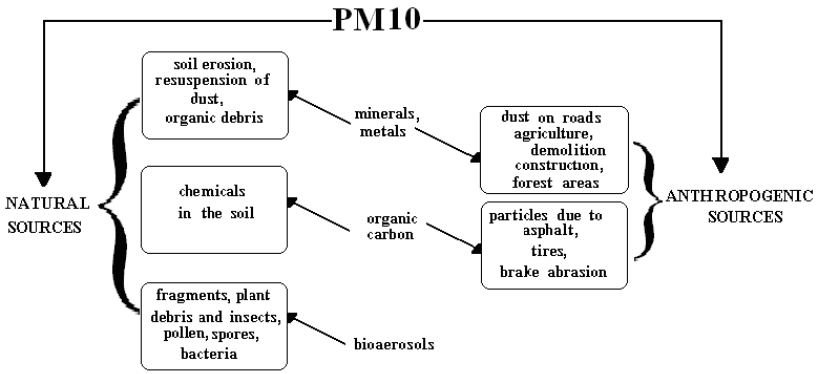

Figure 1.3. PM10 sources [32-35].

1.2.2 PM2.5

The aerodynamic diameter of PM2.5 is situated „d_{ae}" ≤ 2.5 μm [49, 50]. This small fraction could last long time suspended in the atmosphere due to their floatability. It could be transported for long distances on the air currents, sometimes several kilometers far away [51].

The sources of PM2.5 could be primary and secondary, Figure 1.4. The primary sources directly emit particles into the atmosphere and secondary sources release particles via chemical or physical processes. Both sources could have natural and anthropogenic components. The literature mention several components like: minerals, metal fractions, carbon, organic matter, biologic particles, etc.

The maximum accepted limit is slightly lower in US than in UE, perhaps due their more enhanced monitoring features displayed in the field. The UE target for PM2.5 of 20 $\mu g/m^3$ should be achieved until 2020 [58-60].

1.2.3 PM1

Laboratory analysis of PM10 and PM2.5 often evidenced submicron particles which are susceptible to form a new category of particulate matter suspended into the atmosphere called PM1. Their aerodynamic diameter is situated at 1μm and below [62-65]. Such particles often belong to the secondary sources like biomass burning, fuel burning, industrial emission [66-68]. Primary sources are also able to from PM1 by submicron and nano-particles present in the street dust like quartz, kaolinite and muscovite.

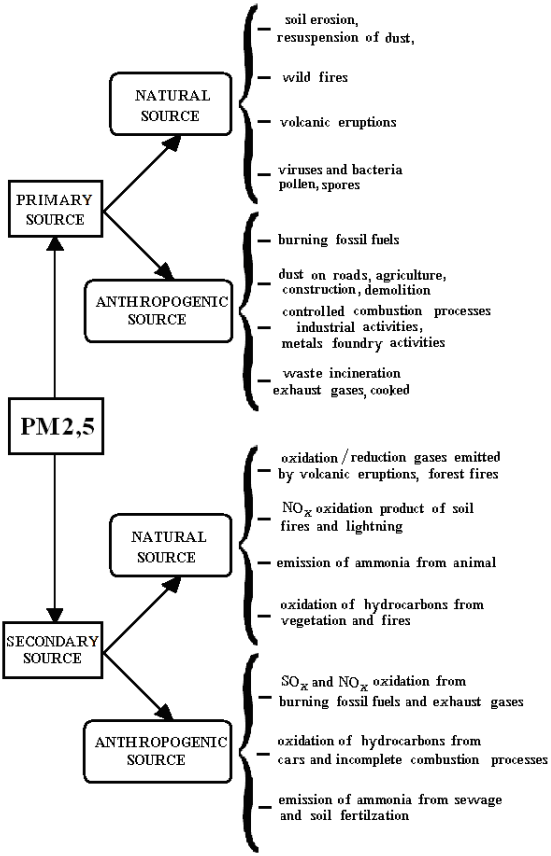

Figure 1.4. PM2.5 sources [32-34, 53].

1.2.4 PM transport into the respiratory system

Particulate matter present in the atmosphere could be easily inhaled, mainly if they are in the micron range. See a windy weather you can feel, the dust trespassing into the mouth. PM range from 10 to 1 is even worse because they cannot be felted as dust like. They simply are gone with each breath inside of the body. The nose mucosa catches a lot of them mainly PM10 and fractions of PM2.5 but small particles, especially submicron and nano particles are able to get into the lungs and penetrate the membranes of pulmonary alveoli [77, 79, 80].

1.2.5 Methods for PM pollution mitigation

The mitigation of PM pollution actions consist mainly in: enhancement of roads cleaning associated with a proper disposal of collected dust. Rehabilitation of pathways and damaged streets and roads is a powerful method for dust mitigation. The rehabilitation process includes the automotive tracks of the road as well as sidewalks. The maintenance of adjacent green areas is another mitigation method very useful in urban areas.

The PM mitigation process needs to be sustained by proper laws packages which implements proper activities rules. These rules act by distinct protocols at each environment protection unit in the territory.

1.3 PARTICULATE MATTERS ANALYSIS METHODS

The investigation of environmental particulate matter is very important for a proper management. The best physical and chemical characterization of such samples is given by several methods like:

- Atomic Force Microscopy (AFM);
- X-Ray Diffraction (XRD);
- Mineralogical microscopy;
- Scanning Electron microscopy (SEM);
- SEM elemental analysis EDX;
- Transmission electron Microscopy (TEM);
- Fourier Transformed Infrared Spectroscopy (FTIR).

All these physical and chemical characterization methods were employed to investigate the samples which belong to present PhD Thesis.

2. INVESTIGATION OF PARTICULATE MATTERS MAJOR SOURCES

2.1 Clay soils

The clay soil is a ground containing small and very small particles belonging to the clay mineral class. They are silicates having lamellar structure (phylosilicate mineral class). Muscovite and kaolinite are the most often found clays in Cluj-Napoca on large areas. We could mention few representative sites like: Taietura Turcului Hill, Cetatuia Hill, and Sf.

Gheorghe Hill. A sample of such soil was investigated from diverse point of view, the most representative is the XRD pattern presented in Figure 2.1.

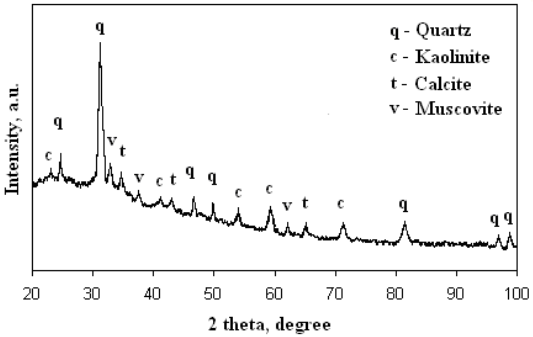

Figure 2.1. XRD pattern for clay ground sample.

The peaks belonging to muscovite and kaolinite are well developed and intense proving that a great amount of clay is present. They are accompanied by quartz and calcite from sedimentary sources.

2.2 Sand

Sands are formed by rocks disintegration resulting particles with a wide range of dimensions and shapes. The most common one is quartz. Sands have a wide spread of the earth's surface. The XRD pattern of a quartz sand sample collected from the Somes River in Cluj-Napoca is presented in Figure 2.2.

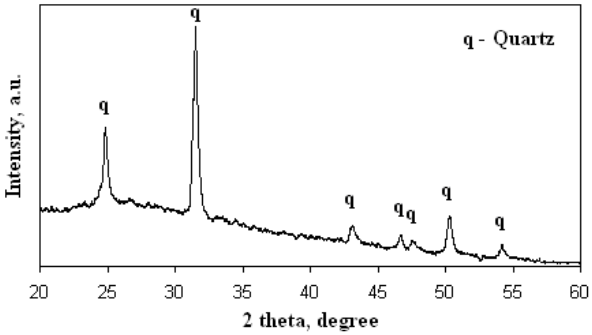

Figure 2.3. XRD for quartz sand sample.

Another sand category is the mixed clay sands where the mineral composition is almost similar with the clay soils, in this case each particle is independent from another. Thus clay peaks are quite intense in the XRD pattern, Figure 2.5. .

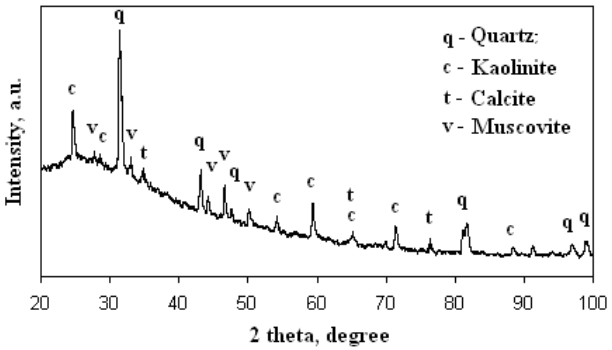

Figure 2.5. XRD pattern for clay sand sample.

All sand particles are susceptible to be lifted into the atmosphere in proper environmental condition, that is why sands represent a major source for street dust, and a major environmental risk.

2.3 Marble erosion under acid rain

Marble, one of the most precious construction materials [106, 107], is often used for building decorations and statues. Acid rain falls caused by industrial pollution may harm marble ornaments in a very destructive manner. By X-ray diffraction and optical mineralogical microscopy, calcium sulphate and calcium nitrate are found to be the most important reaction products. Atomic force microscopy [117] approach was used to reveal the erosion structure of the marble samples exposed to a moderate acid rain of pH 4 for about several weeks. Initial polished marble surface is observed in Figure 2.13. Two stages of nano erosion are evidenced [113]. The first stage affects the inside structure of calcite grain, inducing a nano erosion promotion at an exposure from 0 to 6 days. The transition to the second stage is substantially related to the propagation of nano erosion to the grain borders, which is very pronounced on day 6. At this stage the marble ornaments are seriously damaged. The second stage corresponds to the massive erosion of the surface at day 24, with irremediable damage to the marble ornaments. The surface roughness was found to progressively increase during the 24 days of exposure to acid rain.

The erosion reactions are:

$$CaCO_{3(s)} + H_2SO_{4(aq)} = CaSO_{4(aq)} + CO_{2(g)} + H_2O_{(l)} \quad (2.1)$$

$$CaCO_{3(s)} + 2HNO_{3(aq)} = Ca(NO_3)_{2(aq)} + CO_{2(g)} + H_2O_{(l)} \quad (2.2)$$

Initial marble sample is formed by pure calcite as observe in the XRD spectrum, Figure 2.8a. The reaction result contains calcium nitrate and calcium sulfate after erosion under acid rain condition as observed in Figure 2.8b.

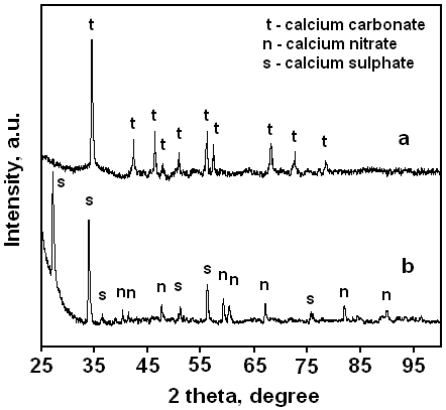

Figure 2.8. XRD patterns for: a) marble sample and b) reaction product.

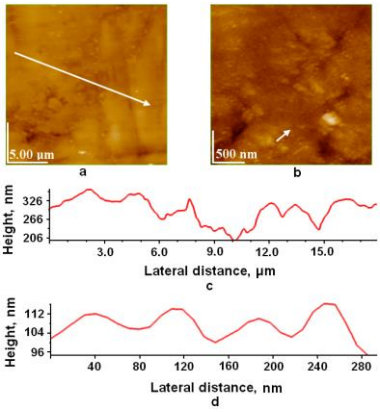

Figure 2.13. AFM images for mirror polished marble: a) topography 20 µm x 20 µm, b) topography 2.5 µm x 2.5 µm, and c) cross section on image a, d) cross section on image b. Area RMS 42 ± 2 nm.

Finally, at 24 days of exposure we observe a totally ruined marble surface, figure 2.18. The entire scanned area roughness increases at 292 nm, as observed in figure 2.18a. The local height in the scanned area has over 3000 nm turning on the surface nanostructure into an eroded fine microstructure. This situation is similar to a mechanical abrasion. The cross section reveals larger erosion clusters having around 2 μm diameter, with a damaged aspect. The nano-structural detail in figure 2.18b shows the deep erosion of calcite grains and the enhanced erosion of grain borders.

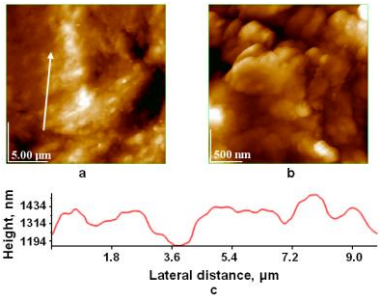

Figure 2.18. AFM images for sample exposed 24 days: a) topography 20 μm x 20 μm, b) topography 2.5 μm x 2.5 μm, and c) cross section on image a. Area RMS 292 ± 5 nm.

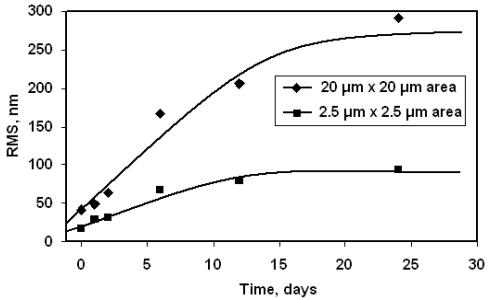

Figure 2.19. RMS surface dependence on time for two distinct scanned areas: 20 μm x 20 μm and 2.5 μm x 2.5 μm.

The most representative surface parameter is the surface roughness. We collected all roughness features resulted from the scanned area (20 μm x 20 μm and 2.5 μm x 2.5 μm) and plotted them versus exposure time, figure 2.19.

Both variations present the same allure, revealing the chemical erosion tendency. The roughness values resulted for 2.5 μm x 2.5 μm are situated beneath 100 nm because of the close relation with the observed nanostructure. The roughness values for 20 μm x 20 μm scanned area overtake 100 nm after 6 days of exposure. It reveals two ranges of values: low roughness from 0 to 6 days of exposure and high roughness after 6 days.

In conclusion:

The performed investigations prove that the calcite marble is strongly affected by acid rain. Exposing the marble samples to a moderate value of pH of acid rain (e.g., pH 4) we observe two stages of erosion. The first stage affects the inside structure of calcite grain inducing a promotion of nano erosion during this stage that took place from 0 to 2 days of exposure. The transition to the second stage is a propagation of nano erosion to the grain borders having a very pronounced character after 6 day of exposure. In this stage the surface of marble artifacts is seriously damaged. The second stage corresponds to the massive erosion of the surface, with irremediable damage to the quality of marble art objects and ornaments. The roughness of marble nanostructure increases with 250 nm after 24 days of exposure. The damages caused by long term exposure to acid rain solution are better observed by comparing this value with the initial one (of 42 nm).

2.4 PM formation from marble and limestone erosion crusts

Further, the question is how the marble and limestone acid erosion is able to form solid particles. The liquid reaction product formed by acid erosion of the marble was vaporized until the solid phase crystallized. The powder resulted was washed from residues and filtered and completely dried in desiccators.

It was observed in mineralogical microscopy, Figure 2.20. It appear prismatic particles of gypsum (calcium sulfate) having around 200 μm length and 20 μm width, and lamellar crystals of calcium nitrate having an average diameter of 50 μm. Their aspect is bright white in cross polarized light proving the high cristallinity, fact in good agreement with XRD spectra in Figure 2.8b.

Limestone are not pure calcite as marble, they often contains significant of quartz sand which is embedded in calcite mass. Quartz particles become free after calcite erosion due to acid rain and become part

of street dust via secondary sources combining a natural occurrence with an anthropogenic source of pollution.

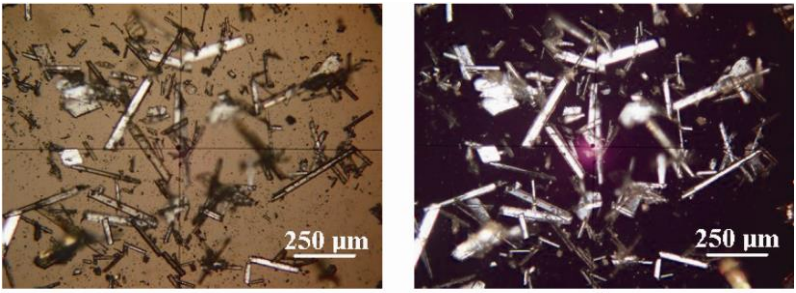

Figure 2.20. Optical microphotographs for calcite erosion product: a) Transmitted light and b) cross polarized light.

Thus, we elaborate a scheme which depicts the mechanism of particulate mater formation via calcite material erosion, Figure 2.21.

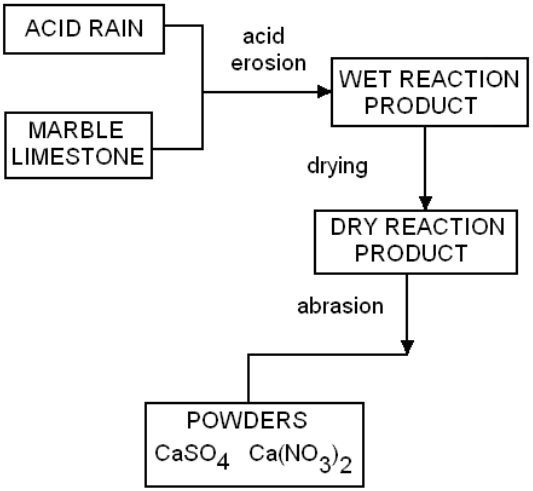

Figure 2.21. Formation of particulate matter scheme via acidic erosion.

The mechanism in Figure 2.21 is conducted by two phenomena subjected to the reaction product. Drying effect conducts to the particle formation and abrasion effect allows particles to be free and incorporable into the street dust.

2.5 Silicates fragmentation

Air pollution represents one of the most important issues concerning the urban environment. Street dust samples collected in Cluj-Napoca, Romania contain silicates particles. XRD analysis evidenced mainly quartz, kaolinite, and muscovite (e.g. clay), which belong to silicates. SEM-EDX analysis confirms the XRD results, establishing connections between particles shape and their composition. The identified quartz nano particles have 90 nm diameters and are surrounded by small clay nano particles which have the diameter between 40 and 60 nm. The Si-O bonding is very strong, while the Si-O-Al bonds are weaker allowing a pronounced cleavage in the clay particle, Figure 2.23. Thus, quartz particles are tougher due to Si-O bonds in the hexagonal lattice, meanwhile clay features layers of SiO_4 tetrahedrons stacked into a fold by Si-O-Al bonds which are less strong than Si-O bonds. These arrangements of silicate particles explain how the dynamics in the urban environment causes an intensive dust fragmentation, which is developed on the weaker crystallographic planes. The fact is sustained by the crystallographic calculation performed on the XRD patterns, where the cleavage planes are observed (e.g. (002) planes). Furthermore, silicate nano-particles were clearly evidenced by AFM and TEM images on the street dust samples made by adsorption from the dust aqueous dispersion. The floating particles collected form the atmosphere contain the same particles observed in the street dust mainly the quartz and clay nano particles.

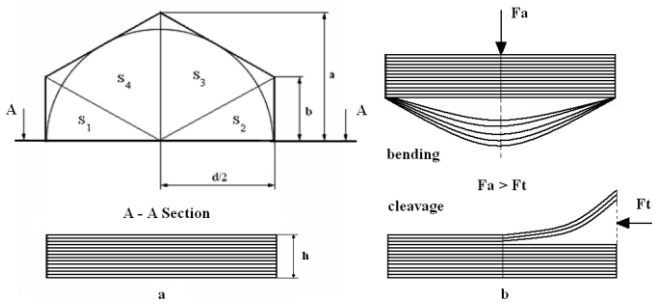

Figure 2.23. Clay particle model: a) geometrical shape and b) external forces acting on the clay particle.

The fragmentation mechanism described for quartz and clay particles is proved by microscopic investigation of SD sample dispersion in deionized water. TEM images are presented in Figure 2.24. PM1 is a critical

step among PM emissions representing particulate matter with maximum diameter of 1μm [10-12]. Several PM1 particles were observed in SD aqueous dispersion, Figure 2.24a; in the left side of TEM image is a quarter of a pseudo-hexagonal clay particle having a planar dimension of 700 nm. This particle thickness is very low (around 100 nm), since it appears semi-transparent in the TEM beam. In the right side of TEM image, Figure 2.24a, a quartz PM1 particle is observed. It appears opaque in TEM beam proving its spherical shape. The diameter is situated around 800 nm.

Beneath these two PM1 particles appear more fragmented ones with diameters ranging from 40 nm to 200 nm. It is a wide domain of submicron dimensions. It is very interesting that well individualized nanoparticles were identified in SD sample. Such particles are observed better at high magnification in Figure 2.24b. A well nano-structured film is formed: quartz nano-particles have around 90 nm and feature a dark aspect due to their spherical shape. Clay particles are smaller around 40 nm and exhibit a light aspect due to their low thickness, and surround quartz particles. The SD nano-particles deposition film is better observed in AFM microscopy.

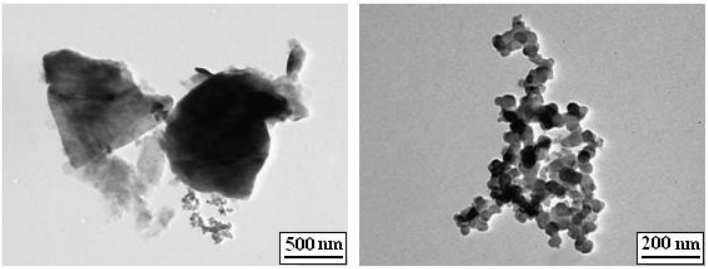

Figure 2.24. TEM images proving street dust particles fragmentation until nanostructural level: a) Clay and quartz submicron particle and b) clay nanoparticles.

The increasing of PM2.5 and PM10 in the cold seasons is strongly related to the efficacy of silicates fragmentation favored by presence of antiskid material which acts like milling bodies. The intensive fragmentation at low particle size correlated with intense traffic registered in some days (one day per month) leads to values of PM2.5 which exceed the limit. It could be an environmental concern because the appearance of a potential health risk. This potential risk could be diminished by a better street dust management.

3. ORGANIZATION OF MICRO AND NANOPARICLES FROM STREET DUST

Particulate matters found in the street dust are very dangerous from the environmental point of view as was observed in previous chapter. The most affected are walking people being in direct contact with such powder emissions. Thus, intensive physical and chemical analysis of street dusts is required.

3.1 Street dust from Piaţa Gării

The urban environment contains several sources of particulate matters (PM). The street dust (SD) summarizes particles from all PM sources in urban area. Our present research is focused on the street dust collected from Piata Garii of Cluj-Napoca in autumn. The particle distribution analysis shows that 60.84 % of the collected SD is gross (over 200 μm diameter), only a small fraction of 0.83 % is situated below 64 μm diameter. Even a small rate of this could be harmful considering the street dust amount reported for all square surfaces. The mineral components were identified by X-ray diffraction: quartz, muscovite, calcite, kaolinite and lepidocrocite. Finest particles were trapped on the solid substrate (e.g. glass) by adsorption from SD aqueous dispersion. The obtained PM film was investigated both by AFM microscopy and X-ray diffraction. Our findings suggest that a thin layer of nano – scaled PM containing finest quartz particles and finest clay fragments is adsorbed on the glass. The average diameter of nano – scaled PM is situated at 95 nm for quartz and around 45 nm for clay particles. As a final remark all these ultra fine PM are sensitive to humidity proving the cohesive tendency to form bigger particles. This could be a way to reduce their propagation in air.

At the beginning of the observation time we observed that infrastructure works were developed into the area few underground pipes being replaced. A mixture of clay and quartz sand was used to isolate the pipes inside the pit. Mineral particles were dispersed into the adjacent environment (e.g. muscovite, kaolinite, and quartz). This supplementary amount of clay issued was observed by corresponding intense XRD peaks, sample SD1 in Figure 3.1a.

During the observation time, the intensity of clay XRD peaks decreases slowly due to their propagation at far distance, attending finally the normal average content in clay typical for Cluj-Napoca street dust, sample SD 2 in Figure 3.1b. Finally ASD (average street dust sample) feature the same clay content like the one observed for SD2.

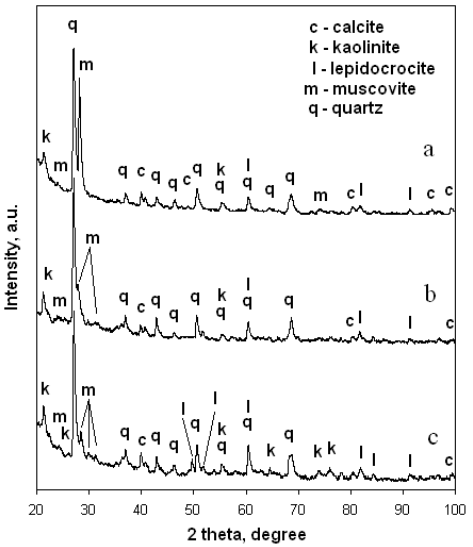

Figure 3.1. XRD patterns for dust samples from Piata Garii:
a) SD1, b) SD2, and c) ASD.

Quartz and lepidocrocite are natural components very often found in common soils [147], but in this case the presence of lepidocrocite in ASD is caused by anthropogenic sources like rust from unprotected metallic structures exposed to open environment, rust form car chassis [148].

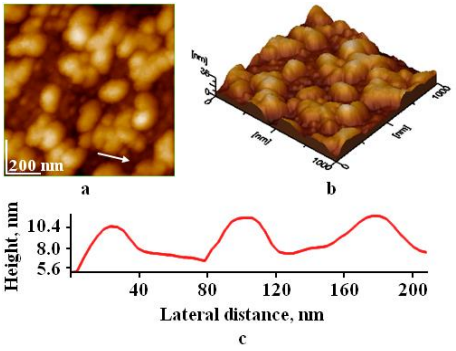

Figure 3.8. AFM images of the smallest particles in the PTL formed on the glass surface: a) topographical image, b) 3D view of topographical image, c) cross section on the white arrow in image (a).
Scanned area: 1 μm x 1 μm.

The topographical AFM image taken on the lower areas of the PTL sample is presented in Figure 3.8. A closer look to the street dust nano-particle layer makes us to believe that is not the end of the smaller particle quest. The small area investigation (e.g. 1 μm x 1 μm) reveal that the above mentioned particle layer is surrounded by small nanoparticles. These are revealed in the AFM topographic image presented in figure 3.8a and better viewed in the 3D image, Figure 3.8b.

Concluding: the street dust found in Railway Station Square Cluj-Napoca during 2010 autumn contains particles derived from natural and anthropogenic sources. The minerals found are quartz, muscovite, calcite, kaolinite, and lepidocrocite. This is a normal composition for an urban street dusts, minerals like quartz, muscovite, calcite, and kaolinite deriving from natural sources and lepidocrocite from anthropogenic sources. Minerals amount in the individual ASD sample vary according to the human activities developed in the area at the sampling period.

The particle distribution analysis reveals that 0.83 % of total amount of the street dust is able to form air sedimentary particle dispersion (ASP). Ultra fine particles were found among ASP and were evidenced by adsorption form aqueous dispersion on solid substrate (e.g. glass). The resulted particle thin film is formed by quartz particles having 95 nm diameter surrounded by clay particles having an average diameter around of 45 nm.

This behavior of street dust proves to be typical for autumn season. It is the starting point for an enlarged new study developed for six months beginning with October 2015.

3.2 Dust from Bariţiu Street

The sample collection time interval was 28 October 2010-25 November 2010. The weather was still gentile to assure green areas at the soil level containing mainly grass and several herbaceous plants. This fact assures a relatively good protection against erosion of the street adjacent soils. The same sample collection protocol was used similar to the one for the Piata Garii. Several street dust samples were collected weekly. The average dust sample was prepared by mixing equal quantities of dust from each collected sample.

The mineral composition was investigated by XRD, Figure 3.12. The XRD patterns feature well developed peaks corresponding to the high level of crystallinity of the dust samples. Quartz is the dominant mineral followed by clay minerals (e.g. muscovite and kaolinite), calcite and low

amounts of lepidocrocite and portlandite. Overall, the street dust has a similar composition with the one observed in Piata Garii, portlandite being a different mineral. It is related mainly to house facades erosion, portlandite being a major component in plasters.

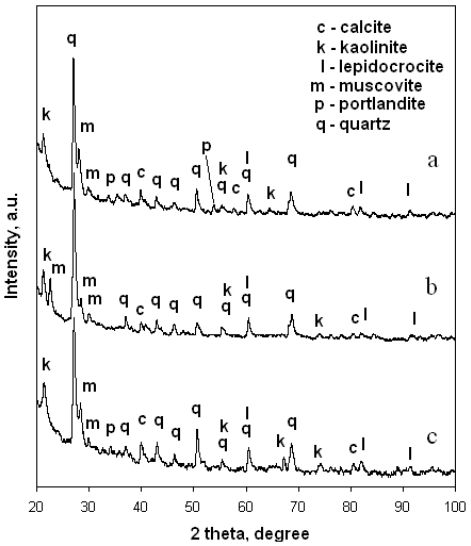

Figure 3.12. XRD patterns for dust samples collected from Bariţiu Street: a) sample from the first week of collection, b) sample from the third week of collection, and c) average representative sample.

The presence of ultra fine particles is obvious, and for a proper investigation they were dispersed in ultra pure water and transferred onto solid substrate via adsorption on glass slides. These samples were subjected to AFM, Figure 3.16.

The surface topography evidences a uniform thin film of particles with two kinds of areas: high areas around 22 nm and low areas of 10 nm height, Figure 3.16a. The higher areas are formed by the top of quartz nanoparticles having around 90 nm and the lower areas are formed by the clay particles with an average diameter of 40 nm.

The uniformity of the particle film and the lack of surface defects are revealed by the phase and amplitude images, Figure 3.16b and c. A better view of the deposition layer is observed in the 3D image presented in Figure 3.16d. Considering the close packaging of the nanoparticles in thin

layer we supposed that there are no free nanoparticles in Baritiu Street, they being attached to small micron ones.

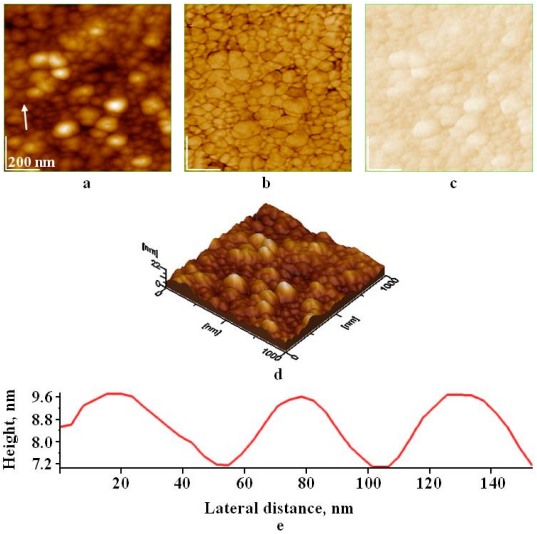

Figure 3.16. AFM images for average representative sample collected from Bariţiu Street, adsorption on glass: a) topographical image, b) phase image, c) amplitude image, d) 3D image of figure (a), and e) profile along the white arrow in figure (a). Scanned area: 1 μm x 1 μm.

3.3 Dust from Tăbăcarilor Street

Tăbăcarilor Street represents a combined area between residential area and industrial facilities field. There are situated some block of flats with two floors and some houses with gardens. There are also found some industrial plants like: SC. Unirea S.A., SC. Carbochim S.A., Clujana S.A., SC. Jolidon SRL, etc. So, we collected samples from Tabacarilor Street, which were treated according to the procedure described in previous chapter.

The XRD patterns obtained on the collected samples are presented in Figure 3.20. All spectra presents well developed peaks corresponding to the high cristalinity of the contained particles. The results are very similar with the one obtained for Piata Garii and Baritu Street. We found quartz as dominant mineral, followed by clay mixture of kaolinite and muscovite, followed by calcite and traces of iron hydroxide crystallized as lepidocrocite and traces of portlandite.

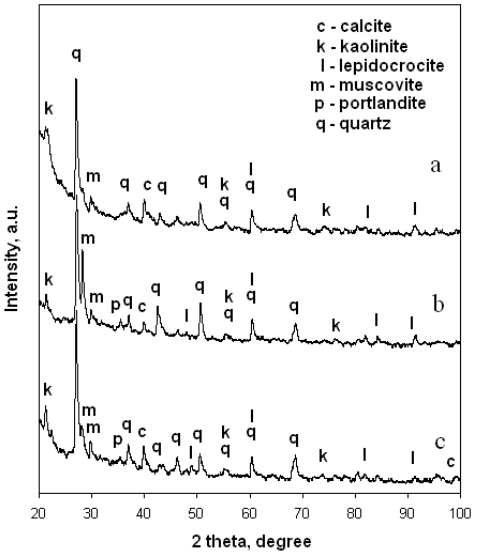

Figure 3.20. XRD patterns for dust samples collected from Tabacarilor Street: a) sample from the first week of collection, b) sample from the third week of collection and c) average representative sample.

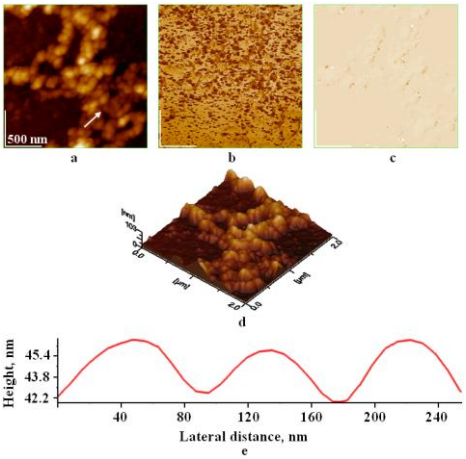

Figure 3.23. AFM images for average representative sample collected from Tabacarilor Street, adsorption on glass: a) topographical image, b) phase image, c) amplitude image, d) 3D image of figure (a), and e) profile along the white arrow in figure (a). Scanned area: 2 μm x 2 μm.

The AFM images resulted for dust collected from Tabacarilor Street are displayed in Figure 3.23. The thin film transferred onto solid surface (e.g. glass slide) feature a multi-layered structure. A thin layer of fine particles is situated in the background of Figure 3.20a having diameter situated around 40 nm. The heights of the image are formed due to the quartz particles having around 90 nm which are surrounded by a complex network of clay particles (having around 40 nm diameter) interconnected each other. Phase image, Figure 3.23b, evidence distinct the fine particle network appearing well contoured in dark brown color meanwhile the lower film appears in bright color. Thus, a relative independence of the quartz particles is evident compared to the finest particles which are well attached. Amplitude image, Figure 3.23c, proves that scan was performed in good parameters and evidences the good cohesion of the thin film. The 3D representation of the topographic image is presented in Figure 3.23d and allows a better view of the two layers adsorbed on the glass slide.

3.4 Dust from Dâmboviţei Street

Dâmboviţei Street is situated in Marasti Square neighborhood. This is an intermediary position between industrial field and workers block of flats. Several main industrial facilities are situated in the close proximity of this street: SC. Sanex S.A., Fortpress S.A., SC. Fortur S.A., and SC. Tehnomag S.A. Many of these companies have metallurgical profile, so there is a high possibility to release ferrous compounds into the atmosphere. The Eastern road access in Cluj City is situated in the proximity of Dambovitei Street and also a high traffic related particles could occur into the area.

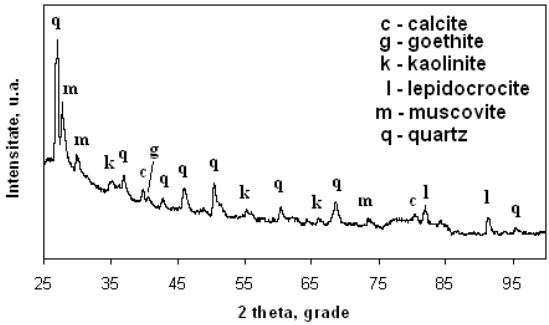

Figure 3.26. XRD pattern for street dust sample form Dâmboviţei Street.

The XRD spectrum in Figure 3.26 feature well developed peaks proving the high level of crystallinity of the sample. Quartz is the dominant mineral, considering the relative intensities of the diffraction peaks. It is followed by clay mixture of muscovite and kaolinite, calcium carbonate crystallized as calcite, and at last iron hydroxide. We notice a relatively high amount of it comparing to the other dust samples (e.g. Piata Garii or Baritiu Street). Both crystalline state of iron hydroxide were found: lepidocrocite and goethite.

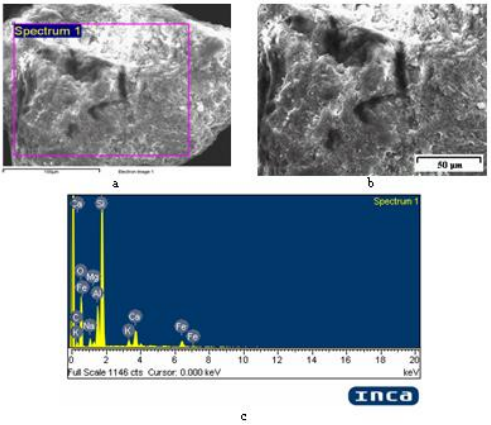

Figure 3.29 SEM images and EDX analysis of a quartz particle filled up on the surface with fine particles (Dambovitei Street dust).

Table 3.8. Elemental composition of dust from Dâmboviței Street

Element	Weight, %	Atomic, %
C	17.75	25.79
O	49.95	54.48
Na	2.61	1.98
Mg	0.75	0.54
Al	5.45	3.52
Si	19.43	12.07
K	0.65	0.29
Ca	2.13	0.93
Fe	1.28	0.40
Total	100.00	100.00

The micro structural detail in Figure 3.29b reveal the morphology of a quartz particle having small particles adsorbed on its surface. There are

some dark valleys, fact in close connection with the lack of cleavage of quartz crystal. Small particles having diameter between 1-10 μm are positioned inside on these valleys and on the particle surface. Such particles present environmental concern because of possibility to be included into PM10, PM2.5, and PM1 category. EDX analysis proves that these small particles belong to the clay category, fact in good agreement with XRD observations.

AFM images resulted for the small particles adsorption thin film is presented in Figure 3.32. Surface topography reveal two kinds of particles bigger ones inducing a height of 28 nm and smaller ones inducing a height of 13 nm. The same hierarchic structure is observed like for the dust samples collected in autumn of 2010.

The particles adsorbed layer is compact with a high degree of uniformity, fact sustained by phase image in Figure 3.32b, where particles limit appears with dark brown nuance. Amplitude image, Figure 3.32c, shows that the scanning process occurs in the best condition without artifacts. The height distribution in the film structure could be observed better in 3D view of topographic image, Figure 3.32c.

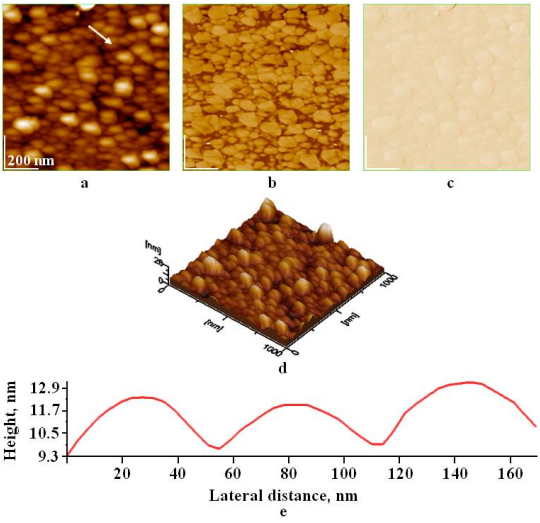

Figure 3.32. AFM images for average representative sample collected from Dâmboviţei Street, adsorption on glass: a) topographical image b) phase image, c) amplitude image, d) 3D image of figure (a), and e) profile along the white arrow in figure (a). Scanned area: 1 μm x 1 μm.

The average diameter of quartz particles is situated around 90 nm meanwhile clay particles feature a diameter of 40 nm as is observed in profile in Figure 3.32e. The measured values are in good agreement with the observations done on TEM images in Figure 3.33.

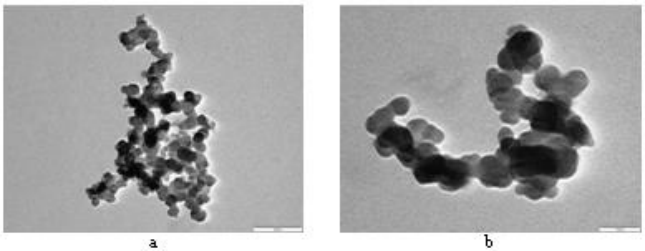

Figure 3.33. TEM images for average representative dust sample form Dâmboviţei Street, aqueous dispersion.

Some bigger particles having around 90 nm are observed in TEM images coresponding to the high particles observed at AFM investigation. These particles have a darken nuance at TEM due to their compact structure and rounded shape. The clay particles have around 40 nm similar to those observed by AFM, and exhibit a light gray nuance decause of their partial translucence to the electron beam.

3.4 Dust from Aurel Vlaicu Street

Aurel Vlaicu Street is the primary access line of the Est of Cluj-Napoca and represents a very intensive traffic, sometimes with 25 cars / minutes. An automatic station monitoring the quality of air is in the ARPM custody of Cluj-Napoca and was located in this street.

The identified minerals from Aurel Vlaicu Street sample can be observed in Figure 3.35. The dominant mineral is quartz showing very developed peaks throughout the sample followed by the second major component like clay minerals, a mixture of muscovite and kaolinite. Another component found in this sample is calcium carbonate crystallized as calcite form. All these minerals have natural sources (e.g. decomposition and erosion of soil). Also we found trace of lepidocrocite and goethite, both components crystallized as iron hydroxides.

A microscopic fine particles exposure from dust is presented in figure 3.38 where the fine fractions was visualized with SEM microscopy and also was performed the elemental analysis EDX.

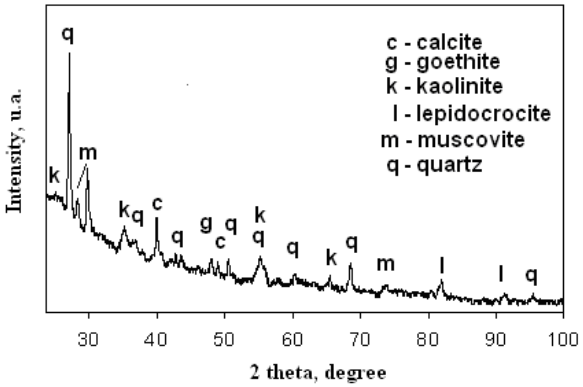

Figure 3.35. XRD spectra of representative dust sample from Aurel Vlaicu Street.

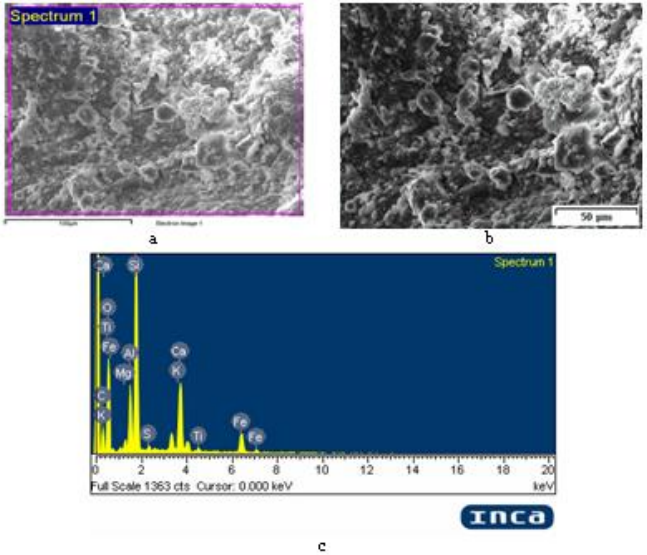

Figure 3.38. SEM analysis for agglomeration of microscopic fine particles: a) overview with EDX spectrum dial, b) SEM image detail, and c) EDX spectrum.

Table 3.11. Elemental composition for agglomeration of fine particles from Aurel Vlaicu Street.

Element	Weight, %	Atomic, %
C	19.14	27.39
O	53.48	57.44
Mg	1.10	0.78
Al	4.60	2.93
Si	13.31	8.15
S	0.33	0.18
K	1.01	0.44
Ca	4.36	1.87
Ti	0.21	0.08
Fe	2.44	0.75
Total	100.00	100.0

We observe a fine quartz particles mixture having from 5μm to 25μm diameter which include most of them in PM10 category although. They are surrounded by fine particles with typical aspect for clays. They have from 2.5 μm below included in PM2.5 and PM1 category risk. Elemental analysis evidence a typical composition for mixture of silicate particles, quartz and clay, Table 3.11. Figure 3.38b shows the way of assembly of this mixture dust in the street.

The dispersion of representative sample dusts from Aurel Vlaicu Street allows the realization of adsorption sample on the glass for AFM and given the necessary drop for TEM microscopy.

The topography surface shows in this case a hierarchical deposition film with some rare and high particles (the maxim high of the scanned area is 28 nm) which present an average diameter of 90 nm. They are surrounded by a less tall layer (approximate 10 nm) with fine particles having the diameter between 40 and 60 nm, as we see in cross section, figure 3.39c.

Conclusions:

From those studies done so far, we can say that street dust from main points in the Cluj-Napoca city present components which come mainly from natural sources, the anthropogenic one is low. This kind of dust is relatively easy to convert at fertile soil because factors are not significant polluters and for arrangement of green spaces can be a usable material base. For the other side the investigated dust samples revealed submicron and nano-structured particles which may be dangerous if they are involved in the atmosphere.

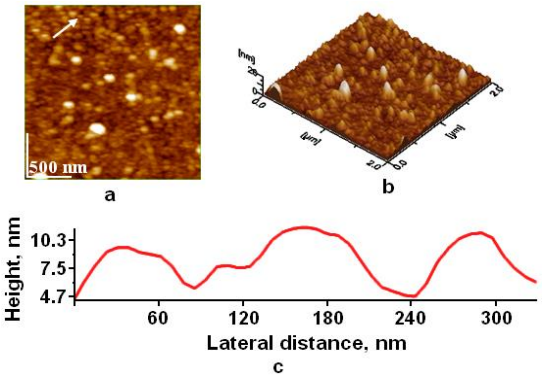

Figure 3.39 AFM images for average representative sample from Aurel Vlaicu Street, adsorption on glass: a) topographical image b) 3D image of figure (a), and c) cross section along the white arrow in the image (a). Scanned area: 2 μm x 2 μm.

4. ORGANIZATION OF MICRO AND NANOPARICLES FROM ATMOSPHERIC SUSPENSIONS

It depends on environmental conditions that some particles are entrained in the atmosphere, from the previously discussed. If we have intensive currents air (e.g. turbionar currents) it will be involved in air microscopic particles with rather large diameter. For this purpose, we meet a representative sample for this phenomena, namely sediment particles in the atmosphere that represent the totals particles who was involved in the air at a given time and then settles under the weight of their own when the buoyancy force is no longer acting.

4.3 Floating particles collected from atmosphere

Particulate mater from the air is an important object of study in terms of environmental protection because we show a direct correlation with the sources they have caused. In Cluj-Napoca city, the powdery emissions into the atmosphere are continuously monitored using a network of automatic stations monitoring air parameters in the Regional Agency of Environmental Protection custody, Cluj-Napoca.

The quartz mineral is dominant in PSA Dâmboviţei sample followed by the clay minerals (muscovite and kaolinite); calcite and feroxide minerals (goethite and lepidocrocite). Mineralogical composition is

similar to the dust from Dambovitei Street, fact that proves the origin of PSA in training dusty street in the atmosphere. Particulate matter sample collected from air using the automatic station from Aurel Vlaicu Street was investigated with X-ray diffraction. Resulted spectra are presented in Figure 4.5. That means the particulate matter sample have similar composition like street dust.

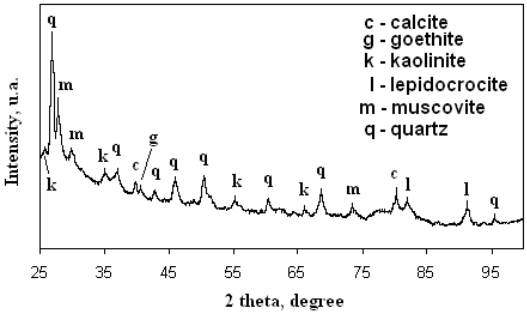

Figure 4.4. XRD pattern for particulate matter sample collected from air from Dambovitei Street.

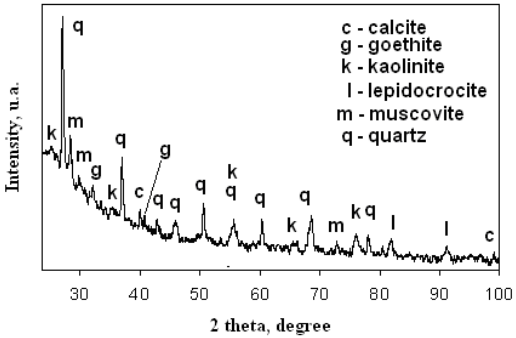

Figure 4.5. XRD pattern for particulate matter sample collected from air from Aurel Vlaicu Street.

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These minerals have been identified: quart, clays (muscovite and kaolinite), calcite, lepidocrocite, and goethite. The mineralogical composition is strong evidence that the floatability particles in the air have their origins in street dust.

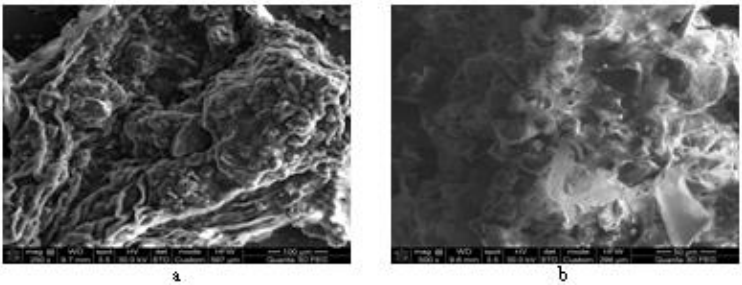


Figure 4.7. SEM images of PSA evidenced in the powder material collected from air: a) Dambovitei Street and b) Aurel Vlaicu Street.

The morphological and dimensional aspects highlighted by the optical microscopy techniques are sustained and confirmed by SEM imaging, the images corresponding to the two representative sample of particulate matter from air is shown in Figures 4.7a and b.

4.4 PM10 from different locations

PM10 morphological aspects are similar for the both samples as we observe in SEM images, figure 4.9. The samples characteristics show rounded-angular quartz particles in a dimensional range which belongs to the PM10 category, meaning 10 μm diameter. These particles observed at SEM investigation are surrounded by fine particles which vary from 1 to 2.5 μm, which are included the PM1 and PM2.5 fractions in the visual field of the images.

The most of fine particles characteristics present tabular-lamellar shape typical for the clays category. Quartz particles are significant smaller than those observed in street dust sample and the clay particles are finest showing a strong tendency to cohesion. Clay particles are sensitive to environmental factors due to their high cleavages ability under the influence of mechanical stress [157]. The binding effect of micro dimensional clay in the presence of humidity, have large industrial applications such as metal casting and alloys which was highlighted in other studies [168]. Such a binding effect is observed in figure 4.9b, for the clay components in FP which present a big cohesion for quartz particles.

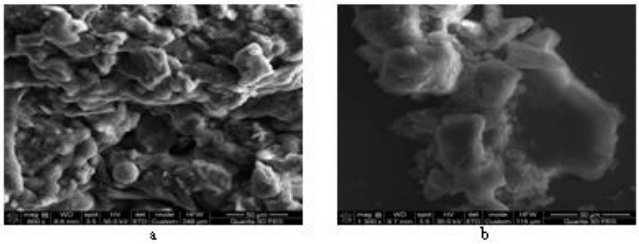


Figure 4.9. SEM images of PM10 evidenced in the particulate material collected from air: a) Dâmboviţei Street and b) Aurel Vlaicu Street.

The highlighted particles from PM10 samples are sensitive to physical-chemical factors of environment (e.g. wind, rainfall, climate). Urban environment around Dambovitei and Aurel Vlaicu Streets allow medium intensity of air currents formed by heavy traffic in sunny days and slight increase in days of storm. PM10 values for April 2013 are displayed on Figure 4.10 for Dambovitei and Aurel Vlaicu Streets.

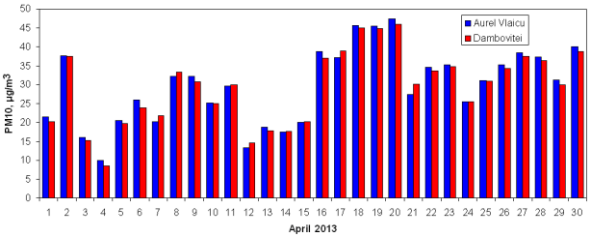


Figure 4.10. PM10 emissions level measured with monitoring stations of air quality from Dâmboviţei and Aurel Vlaicu Streets during April 2013.

Constant storms and air currents increase most of time the quantities of PM induced in the atmosphere [171]. Storms in Romania are usually related to significant precipitation depending on the continental temperature which leads to natural purifications of PM in the atmosphere. Street dust conversion to particulate matters entrained in the air is explained by interactions of automobile traffic and adjacent environment which is in good agreement with the models presents in the literature [35].

4.5 PM2.5 from different locations

As we observed in particulate matter samples collected from air we identified a lot of particles from PM2.5 class. These are mostly very fine

particles of fragmented clay mineral that may contain traces of iron hydroxides. In figure 4.12 are presented the fractions morphologies of PM2.5 for collected samples with monitoring stations of air from Dâmboviţei and Aurel Vlaicu Streets.

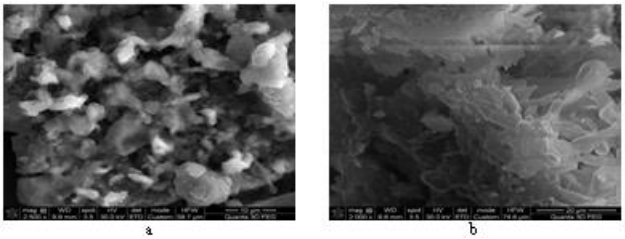


Figure 4.12. SEM images of PM2.5 highlighted in powder material collected from air: a) Dâmboviţei Street and b) Aurel Vlaicu Street.

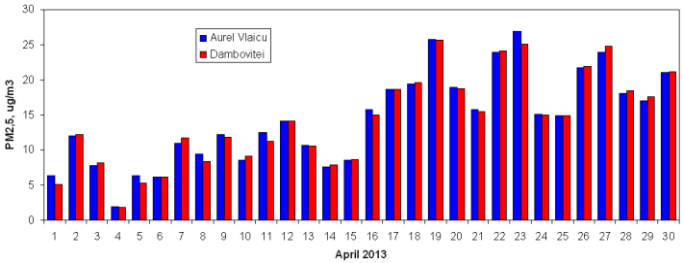


Figure 4.13. PM2.5 emissions level measured with monitoring stations of air quality from Dâmboviţei and Aurel Vlaicu Streets during April 2013.

Measurement results for PM2.5 are shown in the graph presented in figure 4.13. We notice very similar values between daily measured results of the two air monitoring stations. These indicate that both streets are affected by the same mechanisms as possible pollutant from a common street dust forming susceptible to be trained in the atmosphere.

4.6 PM1 from different locations

Recent investigation in the field of minerals found both natural and anthropogenic emissions from PM1 class [158, 159]. The tendency for PM1 emissinos classification is obvious because there is no evidence of sub-micron fractions observed in open atmosphere [167]. Such fine particles emissions are credited with combustion process (e.g. soot and acids aerosols).

AFM imaging help us to visualize and analyze particulate matter from PM1 category by scanning an area with such particles well spreader on solid support (e.g. glass) and working at a large areas scan (10 μm x10 μm, Figure 4.15). The surfaces topography highlighted a lot of rounded particles (with typical aspects for quartz) having diameter up to 1μm and they are surrounded by fine particles.

The deposition film is compact as observed in the phase image, Figure 4.15b, and in amplitude image in figure 4.15c. The deposition has a hierarchical manner of the particles arrangement. PM1 form a high film and submicron fractions making a below deposition film. This situation is similar to that observed in the TEM microscopy where beside PM1 particle we observe nano-particles.

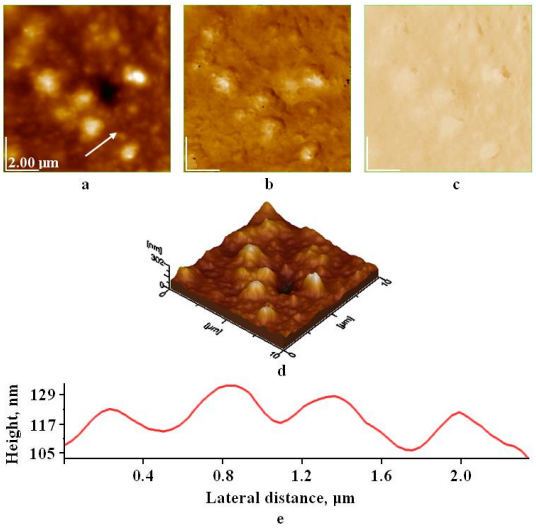


Figure 4.15. AFM images for PM1 sample from Dâmboviţei Street, aqueous dispersion followed by adsorption on glass: a) topographic image, b) phase image, c) amplitude image, d) 3D image of figure (a), and e) cross section along the white arrow in the image (a). Scanned area: 10 μm x 10 μm.

The profile, in Figure 4.15e, is traced from these fine particles by an average diameter of 300 nm, that means sub-micrometer particles but not nano. Considering the amount and the multitude of particles that appears in street dust and atmospheric suspensions to various Dambovitei and Aurel Vlaicu Streets we can foreshadow the emergence of a new class of particulate matter in the air that could be called PM0.5.

4.7 Discovery of PM0.5 fraction - new found component

To evidence the nano-particles, they were made aqueous dispersions of particulate matters collected in the air well stirred from which they were carried out by adsorption on glass lamella. These lamellas were used to X-ray diffractions (XRD) and liquid dispersions for TEM microscopy.

Two things were followed by XRD analysis: the establishing of minerals nano-particles nature in the deposition film and the determination of the average diameter using Scherer's relation. This relation is applicable in this case because the dust particles do not contain residual tension. Thus, it has registered some spectra at small angle to catch peaks well developed especially for clay minerals, Figure 4.16.

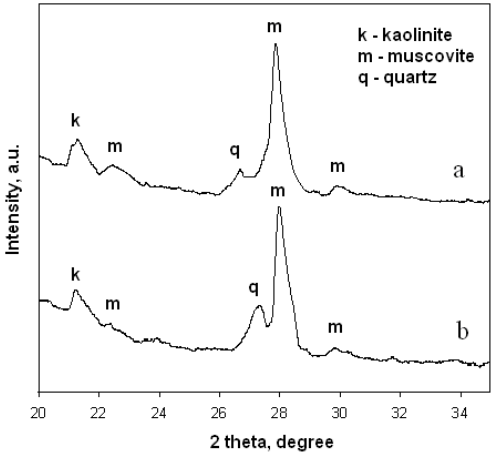


Figure 4.16. XRD spectra results for fine fractions particles collected from air (low angles domain 20-35 two theta degree) for a) Dâmboviţei Street and b) Aurel Vlaicu Street.

It proceeded to use a low speed mode (0.5 two theta degree / minute) to ensure the optimum development of diffraction peaks, Table 4.4.

Table 4.4. Nano-particles diameter resulting from XRD spectra.

Mineral	Particle diameter, nm		
	Dâmboviţei	Aurel Vlaicu	Rounded
Kaolinite	40.12	58.49	60
Muscovite	59.24	58.99	60
Quartz	90.12	92.37	90

The advanced in microscopy techniques is able to perform investigations at higher magnifications which are able to view molecular formations and/or grouping of several tens to several hundreds of atoms. The fact is possible due to AFM and TEM microscopy.

The deposition film of nano-particles collected in the air in Dambovitei Street is very uniform as we see in figure 4.17a. Topographic image reveals two ranges of particles having around 90 nm, in good agreement with the quartz nano-particles characteristics, otherwise we notice particles with typical morphology for clay having diameters between 40 and 60 nm. The amplitude image, figure 4.17b, highlights clearly the particular contour of each nano-particle from deposition film stressing the uniformity. The uniformity of film is apparent from 3D image in Figure 4.17c, were in addition to particles with diameter 40-60 nm, we observe some fine particles in second plan surrounded de big ones. To measure their dimensions we went through such three particles in figure 4.17d. So we obtain a diameter of 20 nm for these fine particles that is a sign of fragmentation clay material has progressed a lot and in the atmosphere were entrained nano-particles with dangerous potential due to their small diameter.

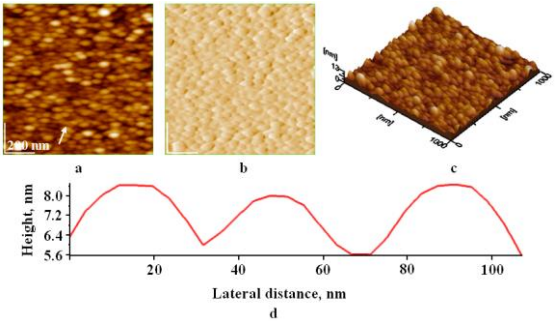


Figure 4.17. AFM images for submicron particles from Dâmboviţei Street, aqueous dispersion followed by adsorption on glass: a) topographical image b) amplitude image c) 3D image of figure (a), and d) profile along the white arrow in the image (a). Scanned area: 1000 nm x 1000 nm.

A similar correlation was observed for nano-particles collected from the air in the Aurel Vlaicu Street. The fine minerals nano-particles are examined by AFM, figure 4.18.

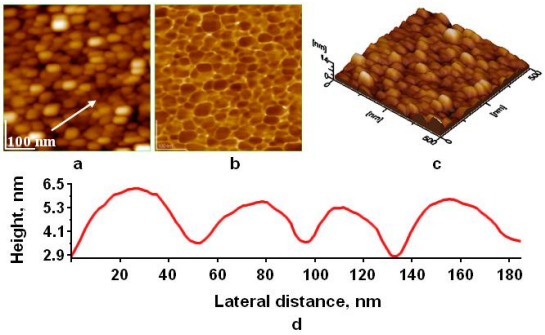


Figure 4.18. AFM images for submicron particles from Aurel Vlaicu Street, aqueous dispersion followed by adsorption on glass: a) topographical image b) phase image c) 3D image of figure (a), and d) profile along the white arrow in the image (a). Scanned area: 500 nm x 500 nm.

The nano-particles collected from atmosphere layer are uniform and allows viewing through AFM imaging in good conditions. Topographical image in Figure 4.18a highlights with high contrast the particles layer. Their shape is in good agreement with crystallographic model of clay. More equiaxed particles with larger diameter situated around of 90 nm, was identified, as mostly quartz particles. The edges of the mineral particles collected from the air are highlight with high resolution in phase image; Figure 4.18b, a network with bright-contrast that surrounding the particles. The FP layer homogeneity can be seen better in a 3D representation of the topographic image, Figure 4.18c.

Conclusions:

The samples analyses from this chapter show that street dust was able to induce atmospheric particulate matters having a chemical composition similar to the dust of origin. The fact is due to the decaying of adjacent spaces as well as intense auto traffic leading to the formation of suspended particles in the atmosphere.

A important fact appears from the detail analysis of particulate matter collected sort in the atmosphere with the two air monitoring stations Dâmboviţei and Aurel Vlaicu Streets and the mineral component derived from soil degradation actually overwhelms PM10, PM2.5, PM1 mass fractions and even PM0.5. The fact proves that repeated fragmentation hypothesis of silicates is available under environmental factors as the main force driving in forming very fine particulate matters.

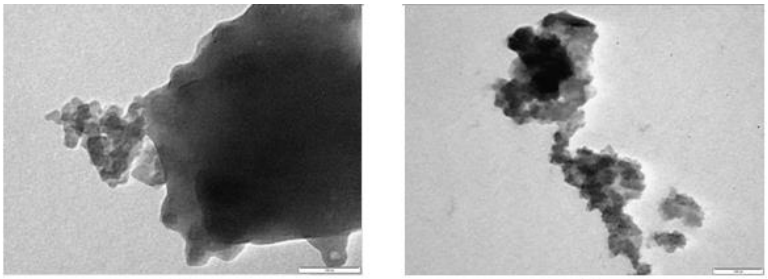
SEM, AFM, and TEM microscopy analysis shows the formation of a balance between particulate matters collected from the atmosphere. These are not totally independent but interrelate with one another high-lightening two directions: fragmentation that tends to progressive grinding particles; coalescence that tends to gather the very fine particles in the formation larger and more complexes. PM10 and PM2.5 emissions levels depends on meteorological factors such as intense air currents that favoring dissipations of fine particles in the atmosphere and maintain the fragmentation processes; one the other hand the humidity associated with precipitation are likely to "wash the air" act as a binder between finest particles to favor the coalescence.

5. POTENTIAL MEASURES FOR PARTICULATE MATTERS POLLUTION MITIGATION

In this thesis we have identify at least three main net nodes connected to the mechanism of formation, release and lifting into the atmosphere of powders related to the street dust. They are: the relationship and balance between street dust and multiply sources; relationship and balance between dust particles and lifting in the atmosphere process; interrelation between particles lifting into the atmosphere. Following sequencing of the fact and consequences, its turns possible actions to counteract the effect of formation and propagation of particulate matters in the atmosphere. If we monitor the sources of dust and minimize their effect → less dust, less likely particulate matter to be entrained in the atmosphere. If we have consistent dust still monitoring the sources, these can be collected with the street vacuum cleaner→ less dust, less likely particulate matter to be entrained in the atmosphere + dust to be collected: to be processed; stored and well neutralized. If we still have atmospheric suspensions due to street dust we most work of two operations mentioned before. A good environmental management will consider the environmental care in the streets proximity, so the dust formed is in small amounts and still the amounts formed to be collected and stored.

5.1 Nano-particles binding to larger fractions

Generally, smaller particles are attracted to larger ones in accordance with universal gravitation law, fact more pronounced when the particles exert attraction are 10 or even 100 times larger than the particles attracted.



a b

Figure 5.1. TEM images of nano-particles being binding on larger submicron particles: a) Dâmboviţei Street and b) Aurel Vlaicu Street.

In the Dâmboviţei Street, we meet two PM1 submicron particles category having diameters around 900 nm. The left have tabular-pseudo hexagonal aspect (about half of pseudo hexagonal specific clay minerals) so is a clay particle, we note the semi translucence fact that shows the beam of accelerated electrons were able to pass partially through particle. The right has rounded aspect and dark shade that shows the beam of accelerated electrons was not able to pass through particle due to its considerable thickness. All features highlighted so far shows that PM1 particle in right image, Figure 5.1a is quartz one. Around the both PM1 particles we have nano-particles with high tendency association larger particles.

Figure 5.1b present a submicron particle having a diameter around 250 nm surrounded by nano-particles, it can be seen in the top center of microphotography. Submicron particle have quartz aspect meanwhile nano-particles surrounding it have predominantly clay. In this formation the nano-particles binding starts a sequences of sub-micron particles with clay aspect which are continuous with an area of agglomeration. Coalescence of these particles also tends to form sub-micron structures.

Solid film deposition achieved by adsorption from aqueous dispersion of fine powders from dust collected in Dâmboviţei Street highlights some sub-micron clusters surrounded by compact nano-particles deposition, Figure 5.2. The binding effect of nano-particles on submicron formation resist on solid phase transition.

The topography of the sample in Figure 5.2a shows double string sub-micron diameter units with diameter around 250 nm. Nano-particles surround very closely these sub-micron formations highlighting a strong attraction. Phase image, figure 5.2b, and amplitude image, figure 5.2c, show the compactness film deposition which is free of structural defects.

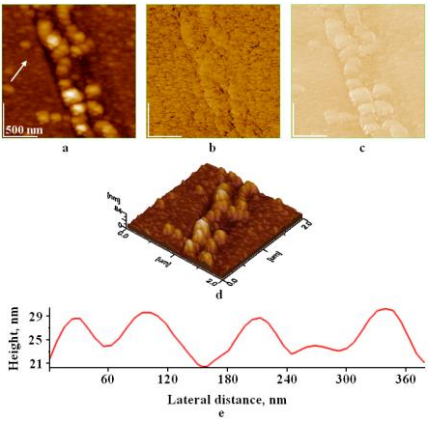


Figure 5.2. AFM images for sub-micron clusters with nano-particles binding on surface: a) topographical image b) phase image c) amplitude image d) 3D image of figure (a), and e) profile along the white arrow in the image (a). Scanned area: 2 μm x 2 μm.

The 3D representation of deposition film, figure 5.2d, shows better the structuring of deposited layer. Sub-micron particles are arranged in two series which has a local high of 84 nm while the nano-particles film is situated at an average high of 30 nm. Average diameter of nano-particles is around of 40 nm as we see in profile along the white arrow of topographical image, figure 5.2e.

We illustrate how the particles about 250 nm knowing to bind on their surface particles of 40 nm. Once formed this structural cluster, if meets favorable conditions increase continuously the uptake of new nano-particles. This phenomena is similar with the heterogeneous crystallization were the nano-particle plays the role of seed crystal. As we observe in this thesis, moist environment facilitates attraction and nano-particles bonding on sub-micron particles.

5.2 Finest particles coalescence

The particle coalescence depends on their mobility. It is very low in solid phase but dispersed into gaseous phase it increases very fast. The experience reveals that a proper coalescence between small particles is favored by wet environment. The dosage of appropriate amount of water is the success key for the small particles cluster formation. This way could be

useful to produce macroscopic aggregate of micro and nano particles to assure a better handling and neutralization. The reintegration into the fertile soil is preferred. Such soils could be used for the reconstruction of decayed green areas in the parks and streets adjacent areas.

5.3 Street dust agglomeration and binding into stabile soils and their recycling

The simplest method for street dust conversion to environmental soil is the assimilation of controlled dose of street dust in fertile soil. Figure 5.5 presents the technological scheme for the street dust recycling.

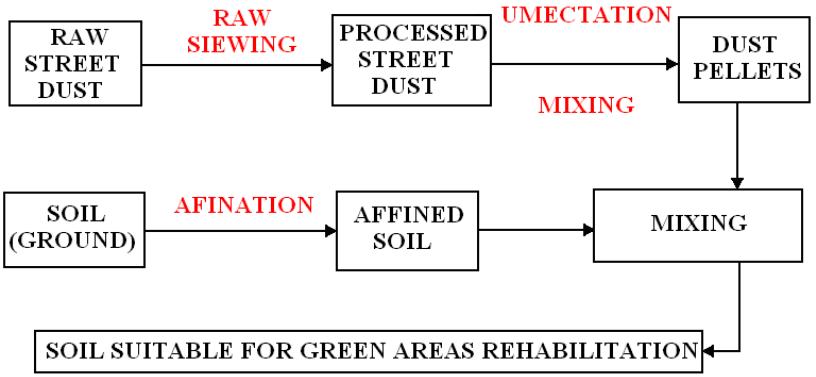


Figure 5.5. Technological scheme for the street dust recycling.

The street dust is subjected to a raw sieving to remove the trash and big particles. The processed street dust is umected to form pellets which are mixed together with affined soil into a mixing reactor. Finally, it results soil suitable for green areas rehabilitation.

We performed some soil treatment on controlled environment, using blended soils: first mixture was 75 % street dust mixed with fertile soil and the second have 20 % street dust mixed with fertile soil. We test the mixtures using Dahlia bulbs. In both cases the Dahlias rise up from the treated ground but the second mixture allows a proper growth meanwhile the first mixture presents a growth failure.

6. GENERAL CONCLUSIONS

Teoretical studies of thesis are concern on chapter 1. They were found the risks associated with PM10 and PM2.5 particulate matters and also the maximum admissible values associated with air quality index. Based on literature, PM1 fractions were dashed because they are limited finesse from the air that will be standardized in the near future and will be held environmental directives as well maximum admissible limits.

Experimental part begins with chapter 2 of thesis. They were investigated only original samples collected in this thesis and have been investigated with modern techniques of physic-chemical analysis. It went to study dust sources on the street, natural one that is uninfluenced by man, anthropogenic sources born from humans activities or environmental disintegration built it. Natural sources of street dust were been identified: clay soils, sands, marble, and limestone erosion of the masses under the acid rain action, silicates fragmentation.

Street dust investigation it is the third chapter of this thesis. The first aspect was considered the areas of samples collection. Looking at the map of Cluj-Napoca city was chosen the following areas of collecting samples:

- Piaţa Gării: is an area of intense activity for passenger travel and freight. Also the railway station is the focal point where passing thoroughfares into Baciu village and to industrial area on Muncii Avenue.

- Bariţiu Street: it is a specific residential area positioned in the center of Cluj-Napoca. Here we found different construction periods, parks (Central Park and I. L. Caragiale Park) and a principal road line that hosts the tram line from the train station to Manastur neighborhood.

- Tăbăcarilor Street: represent a specific area with industrial activities. Here we found industrial facilities such as SC. Unirea S.A., SC. Carbochim S.A., Clujana S.A., SC. Jolidon SRL., and also medical units like ,,Clujana" Hospital.

- Dâmboviţei Street: is a mixed complex combined residential and industrial area. The reason of choosing this street is that here is located one of the monitoring stations of air quality in custody of Regional Environmental Protection Agency Cluj-Napoca.

- Aurel Vlaicu Street: represent a modern residential area. Here is located the second monitoring station of air that have the role to measure the traffic activities.

Street dust composition of Cluj-Napoca was establishing by conducted analysis and the components are:

- **Quartz** mineral is the dominant in all investigated street dust samples with a wide variety of dimensional nano-particles having around 90 nm to microscopic particles having of 250-500 μm.
- Clay minerals (**muscovite and kaolinite**) having variable proportions. Clay particles are very fine since the nano-structural domain 40-60 nm and reaching the PM10 class.
- **Calcite** found in Cluj-Napoca soils is the third place. Calcite particles can easily be in a variety of size starting with PM1-PM10 and microscopic fractions having around 500 μm.
- **Iron hydroxides: lepidocrocite and goethite** appears in all street dust samples. It proves the propagation efficacy due to the car traffic (e.g. cars with rust under chassis) rather than the corrosion of metallic structures placed in the close proximity of the streets.
- **Portlandite**: it was randomly found in street dust samples in low amounts. It is often associated with building facades erosion and with building sites because of significant usage of cement and other Portland building materials.

Particle size range represents one of the most important parameters followed in this PhD thesis. All mineral species identified have gross fractions over 500 μm diameter, average fractions between 200-500 μm diameter, and fine fractions below 200 μm diameter. We found in the street dusts ample very small fractions which belong to PM10 and PM2.5 categories. The discovery of PM1 particles category in the street dust is one of the most important achievement of this thesis. This category includes fine particles with the diameter up to 1 μm. The performed analysis on various sample of dust and particles collected from atmosphere reveals nanoparticles clay like having 40-60 nm diameter and quartz like having 90 nm. There are also found submicron particles which almost are formed by nanoparticles coalescence and association. The nanoparticles identification in the street dust is a scientific premiere.

The presence of PM10; PM2.5 and PM1 fractions in the street dust lead us to the possibility of them to be lifted into the atmosphere. We collect particulate matter samples from atmosphere using the Automate Stations for Air Quality Monitoring from Dambovitei and Aurel Vlaicu streets. The performed on air collected sample analysis reveal the same composition with the street dust. Quartz amount was higher on PM10 samples meanwhile clays are predominant in PM2.5 and PM1 samples.

Nanoparticles and their submicron associations presence into the street dust as well as in to the atmosphere are the most important finding of present PhD thesis

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A) ISI Articles

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B) BDI Articles

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2) **A.-G. Hosu-Prack** and M. Tomoaia-Cotisel, "Particulate matters found in urban street dust of Cluj-Napoca", *published in Proceedings, Knowledge, Culture, Science, The Fundament of Quality of Life in Society*, Edited by: Ioana Ionel, Speranta Stanescu, Daniel Vizman, *Editura Politehnica*, Timisoara, 2011, 120 – 124, (2011). ISBN 978 – 606 – 554 – 314 – 0.

C) Conferences

1) G.-A. Hosu-Prack, G. Arghir, L.-D. Bobos, I. Petean, - "Identificarea fazelor cristaline constituente ale unei mostre de praf stradal", a IX-a Conferinta Multidisciplinara Nationala cu Participare Internationala, "Profesorul Dorin Pavel Fondatorul Hidroenergeticii Romanesti", organizator AGIR, Sebes, 2009, Stiinta si Inginerie, vol. XVI, Editura AGIR, 2009, Bucuresti, ISBN 978-973-720-246-8, p.251-258.

2) A.-G. Hosu – Prack a prezentat lucrarea: **A.-G. Hosu-Prack** and M. Tomoaia-Cotisel, "Particulate matters found in urban street dust of Cluj-Napoca", "*Humboldt-Kolleg: Knowledge, Culture, Science The Fundament Of Quality Of Life In Society"*, Timisoara, Nov. 23-28, (2010). (**Poster**).

3) A.-G. Hosu-Prack a prezentat lucrarea: "Evidentierea particulelor microscopic fine PM in praful stradal" in Proceedings of the 7th International Conference "Students for Students", Cluj-Napoca, Romania, 23-25 April 2010, p.50-51, ISBN 978-973-133-738-8. (**Poster**).

4) A.-G. Hosu-Prack a prezentat lucrarea: **A.-G. Hosu-Prack**, I. Petean, L.-D. Bobos and M. Tomoaia-Cotisel, "Physical and chemical characterization of the street dust in dispersed systems", The 10th International Conference on Colloid and Surface Chemistry (Cea de a 10-a Conferinta de Chimia Coloizilor si a Suprafetelor cu Participare Internationala, *Ediţie omagială dedicată Anului Internaţional al CHIMIEI – 2011*), "Dunarea de jos" University of Galati, Galati, June 9-11, 2011. (**Prezentare orala**).

5) Gh. Tomoaia, L.-B. Pop, G. Furtos, C. Prejmerean, I. Petean, R.-D. Pasca, **A.-G. Hosu-Prack**, A. Mocanu, M. Tomoaia-Cotisel, - "The effect of various calcium phosphate particles on collagen mineralization", *The 3rd Workshop and 4th Management meeting of the COST TD0903* Understanding and Manipulating Enzymatic and Proteomic Processes in Biomineralization, Cluj-Napoca, Romania, 11th-13th October, 2011.

6) A.-G. Caprar, I. Petean, G. Arghir, L.-D. Bobos, I. Iurcut, M. Tomoaia-Cotisel, - "Marble Nanoerosion Under Acid Rain Evidenced by Atomic Force Microscopy", *The XXXII-nd Romanian Chemistry Conference*, Caciulata, Romania, 3-5 October, 2012, Poster Presentation, Poster Session V., No. 17.

7) Gh. Tomoaia, **A.-G. Hosu-Prack**, I. Petean, A. Mocanu, M. Tomoaia-Cotisel, The Effect of Hydroxyapatite Nanoparticles on Collagen Mineralization, Cost Action TD0906, WG3 and WG4 Scientific Workshop Biological Adhesives: from Biology to Biomimetics, Cluj-Napoca, 9-11 April (2013), pag. 55.
8) A.-G. Caprar, I. Petean, G. Arghir, L.-D. Bobos, I. Iurcut, M. Tomoaia-Cotisel, - "Nano erosion of marble under acid rain. AFM investigation", *The 11 th Conference on Colloid and Surface Chemistry* ,Iasi, Romania May 9-11, (2013), Poster No. 15. **First prize for poster.**
9) A.-G. Hosu-Prack, I. Petean, G. Arghir, D. F. Muntean, M. Tomoaia-Cotisel, - "Air Induced Nano - Features due to the Urban Street Dust", *DUST2014 - 1st International Conference on Atmospheric Dust - Italy*, 1 - 6 June 2014, Abstract Book, p. 182, ISBN 978-88-7522-095-2.
10) . R.D. Paşca, Gh. Tomoaia, A. Mocanu, I. Petean, **A. G. Hosu-Prack** and M. Tomoaia-Cotişel, - "Fibrous Structures of Collagen Type I Investigated by Langmuir-Blodgett Technique and AFM", The 5th Conference on Advanced Spectroscopies on Biomedical and Nanostructured Systems (*BioNanoSpec 2014*), Cluj-Napoca, România, September 7-10, 2014.
11) R.D. Pasca, Gh. Tomoaia, A. Mocanu, I. Petean, C. Garbo, **A.G. Paltinean**, M. Tomoaia Cotisel, - "The interaction between collagen, hydroxyapatite and APTES. Langmuir-Blodgett and AFM study", The 11th International Conference on Physics of Advanced Materials, Cluj-Napoca, România, September 8-14, 2016, Poster Prezentation, Abstract book pp. 200.**First prize for poster.**

Summer School
1. Participation in the Summer School: 2nd EBSA BIOPHYSICS COURSE ON: Membrane Biophysics and Lipid-Protein Interaction, that took place in BORDEAUX-LACANAU from (24-29 June 2012).

Honors
1. Scientific Performance Scholarship awarded by Babes-Bolyai University in the year 2009-2010 as a student in the Faculty of Chemistry and Chemical Engineering according to the list approved in the Board Meeting dated November 23, 2009. This is confirmed by the Certificate no. 30746 dated may 03, 2012.