Universitatea „Alexandru Ioan Cuza” Iaşi
Facultatea de Geografie şi Geologie
Şcoala Doctorală de Chimie și Ştiinţe ale
Vieții și Pământului
Specializarea Știința Mediului

# NEW PHYSICAL- CHEMICAL SYSTEMS USED IN THE TREATMENT OF SURFACE AND GROUNDWATER FOR POTABILIZATION

## SUMMARY – DOCTOR’S DEGREE THESIS

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Universitatea “Al.I. Cuza” Iasi
Școala doctorală de Chimie și Științe ale Vieții și Pământului

Către,

……………………………………………………………………

Vă facem cunoscut că în ziua de 12.12.2014, ora 11:00, în SALA FERDINAND, va avea loc şedinţa publică de susţinere a tezei de doctorat intitulată:

*“NOI SISTEME FIZICO-CHIMICE UTILIZATE ÎN TRATAREA APELOR DE SUPRAFAȚĂ ȘI SUBTERANE ÎN VEDEREA POTABILIZĂRII”*

în domeniul Ştiinţa Mediului, elaborată de doamna MONICA-ANCA HUȚANU (CREȚU), în vederea obţinerii titlului ştiinţific de Doctor.

Comisia de doctorat are următoarea componenţă:

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Vă invităm să participați la ședința de susținere a tezei.

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(married CREȚU)

# C O N T E N T S

# I N T R O D U C T I O N

The doctor’s degree entitled „N***ew physical-chemical systems used in treating the surface and groundwaters for potabilization”***was elaborated based on the eprimental data and studies concerning the diversification of the techniques used for the improvement of the organoleptic, physical-chemical and icrobiological characteristics of the groundwaters and surface water, meant for human consumption.

The purpose of the research takes into account drawing up new materials and procedures for treating the groundwater and the surface water with minimum impact on the environment and having superior organoleptic characteristics. In order to accomplish this, we have taken into account on one hand the chemistry of the gound water from the Hidrographic Basins of Siret and Prut, analysing in real time the evolution of the chemical charges on one hand, and on the other hand the chemistry of the ceramic from burnt clay, also studying the corelation between the caustic mode and other chemical and phisico-structural characteristics with the capacity of ionic exchange for some toxic cationi, mainly those with retention in the purification equipment, that in the end we would elbaorate a new patentable technology by involving a filtration step based on ceramic materials that will offer to the drinking water obtained organoleptic characteristics of „fresh and cristal-like water”, resembling the spring water. Another aim of the research has been connected to the mathematic corelation of hidrodiynamics and scattering of fluor into the river Prut and the elaboration of two numeric models that imply the RMA4 programme.

The theme of the doctor’s degree thesis represents an important chapter from the science and technology of the environment, using knowledge from areas connected to chemistry, physics, hydrology, the materials engineering, etc., respectively: the obtaining, the physical-chemical characterization as well as the involvement of some ceramic materials in the treatment processes of ground and surface waters in order to make them drinking water. Thus, the thesis develops two important aspects: one of theceramic materials’ engineering, studying the chemical decontamination capacity through the optimization of the acid-basic and redox chemistry of internal granuites ( basic nanostructures) and of the marginal groups (that generate ionic, hidric exchange processes of zeolitic type, as well as the redox type) and the other of the environment science, that of obtaining the drinking water with physical-chemical and organoleptic characteristics superior to the national and european standards usind the existing treating stations, with accessible costs even for the local communities from the under-developed areas.

The choice of the theme is justified by the necessity of the elaboration of new technologies in treating surface and ground waters with the final end of making them ready for drinking obtaining some physical-chemical indicators within the limits imposed by the national and European standards, and from organoleptic point of view to offer "spring crystal-like water" characteristics.

The achievement of the doctor's degree thesis, we have observed ***two directions of research:***

***a.Theoretical objectives,*** connected to the documentary synthesis and the critical analysis of the actual stage of materials and procedures of treating the surface and groundwater that have aimed at the following aspects: the main types of domestic waters; methods and techniques of investigation of the physical-chemical, organoleptic and microbiologic characteristics of surface and groundwater, before and after the treatment; modern materials and innovative procedures for treating these waters with the final end of making them drinking water; methods and techniques of investigation of the physical-chemicak systems involved in the treating process.

***b. Practical objective***s, which subscribe to the following directions of research: establishing an experimental protocol regarding the selection of the geographical areas to study the ground and surface water and of some natural litic materials, industrial ceramic and traditionally processed ceramic, hydrodynamic, biological and technological (souce debits, limits of the physical, chemical and microbiological charge) and the monitoring of their evolution; the characterization and the testing of various new materials studied, used in the purification of the ground and surface waters, drawing up a mathematic model of hydrodynamic and the scattering of fluor into the river Prut and the elaboration of two numeric models involving the RMA4 programm; the morphological, chemical and pgysico-structural characterization of litic materials studied; the processing of the experimental data and writing paper that will be communicated to various national and international manifestations and also published in specialty magazines; presenting new patented procedures to various world inventions salons, in order to have their value classified and to realize the technological transfer.

Thus, the purpose of the thesis is that, based on the previous experiences obtained within our collective, a new approach especially of the aspects related to the ceramic materials used in water purification.

The paper has a length of 200 pages, being structured in two parts: *Theoretical part*, which gathers three chapters and the *Experimental Part* made from six chapters.

Chapter I presents an analysis of the actual research concerning the water sources used in alimentation, alimentary industry and agriculture, such as: aspects reagrding the actual problems of the water consumption; modern concepts regarding the natural waters used in purification of the water; the dynamics of drinking water demands; quality indicators of the water (organoleptical, oxigen consumption, buffer capacity and other physical- chemical and bacteriological indicators of water);

In Chapter II reference is made to the characterization of ground and surface water in vue of using them as drinking water sources (from the point of view of ecological and chemical state, respectively of active normatives and purity principles), a special attention being given to the monitoring activities of the physical-chemical, microbiological and organoleptic indicators. This chapter also presents, as well as in the following chapters, a set of conclusions which underline the novel elements developed or obtained.

Chapter III concentrates on the instrumental methods and techniques used in the analysis of the ground and surface waters, presenting detailed a series of aspects conncted to: the prelevation manner of the waters samples, the determination of the chemical indicators of water pollution; the determination of the organoleptic indicators; the determination of the toxic and undezirable substances. Starting with Chapter IV the original part of the thesis is being developed, part which we will present in summary.

## Cap. IV. THE CHEMISM OF GROUND AND SURFACE WATER FROM THE DRAINAGE BASINS OF SIRET AND PRUT

This chapter studies certain parameteres (salinity, pH) of the surface waters from the collecting drainage basin between Siret and Prut. We have analyzed the connection between the geologic substrate (ground and surface deposits) and the chemical composition of the surface waters. Moreover, we analyse the ways through which the salty waters (expecially the salty wells) have been exploited and used within the human communities, mainly rural and the way in which the sweet waters are contaminated.

It is well-known that, the cllecting basins of Siret and Prut contain the greatest density of population in Romania. Under these circumstances, the water ressources need to benefit from an efficient management, especially duet o the fact that the climatic condition does not allow a significant water debit [Romanescu și Lasserre, 2006].

The Administration authority of the Drainage Baisin Prut-Birlad and the Administration authority of the Drainage Baisin Siret analyse the annual assessment of the water resources and they carefully monitor their quality. Consequently, within the last twenty years (1990-2010) many campaigns have been carried on for the qualitative analysis of the most important hidrographic trunks. Unfortunately, most of the small rivers have been the subject of such studies, despite the very important role they play for the local communities [Date inedite, 2010a și b].

The most detailed analysis concentrate on the pollution degree of both stream waters, as well as of those still waters. Some chemical parameters (pH and salinity) are often neglected, because they do not represent important indicatators of pollution. Most of the springs are analysed from quantitative point of view, with direct reference for the debit and less for their organoleptic qualities. The only exception is that of mineral waters with therapeutic effect, but these are rarely found in the plateau of Moldova and more frequent in the mountain area.

The aim of the study was to draw up a detailed analysis of the most important hydrographic branches situated in an area that suffer from a grave water deficiency. Although the pH is not an indicator of water quality, it is related to some parameteres, such as salinity or the geological substrate of the area [Hanor, 1994; Tzortzakis, 2010; Valdez-Aquilar și colab., 2009; Williams si Buckney,1976].

Concerining the study made on the collecting basins of Siret and Prut, based on the analysis of some chemical parameters (salinity, pH) and a connection with the correlation between the nature of the geological substrate (ground and surface deposits) and the chemical composition of surface waters, the following can be mentioned: the two hidrographic arteries that go accross Moldavia from north to south – Siret and Prut- are the most important rivers in Romania; duet o the great density of rthe population, the water supplies here are limited, most of the rivers have small debits and dry aut during summer, part of these are most times salty, so that they cannot be used in economical activities; Siret and Prut are in the category of very big rivers ( that come from the mountain area) contain sweet water and have a series of affluents from the range of big and average rivers (Bistrița, Moldova, Suceava, Tazlău, Trotuș, Jijia, Bârladul etc.); the majority of the surface waters from the studied area are alcaline, their salinity determine an increase of the pH value, especially in the south-west part of the Siret basin ( within the Arch of the Carpathian Mountains and the Arch of the Lower Carpathians), as well as in the north-eastern part of the Moldova plateau (the hill area of the Moldavian Plane); the nature of the geological substrate from the drainage basins Siret și Prut has a specific influence on the salinity of surface and groundwater, correlated with the human activities related to the salt reserves exploitation; as sources of salty waters; the increased salinity is only specific to the springs, the small rivers with low debits being strongly influenced by salinity; because their debits are reduced during summer, the big stream waters contain sweet water duet o the great force of water dillution; the fresh water (especially the surface water) is being exploited using modern ways and it has a large scale usage in all economical areas; the population in the eastern part of Romania uses river water and, rarely ground water. Only the rural population uses the ground water on a large scale, water that is usually contaminated with nitrates and nitrites; more than 80% of the water in the Moldova wells is not adequate for the human consumption, the slatines need a specific etno-management for the salty rivers exploitation in the rural areas.

## Cap. V. THE WATER QUALITY EVOLUTION IN THE SUCEAVA RIVER WITHIN 2008-2010

### 5.1. General presentation of the Suceava hidrographic basin

The Suceava River springs from the mountains Obcinile Bucovinei (jud. Suceava) and flows into the Siret River near Liteni (jud. Suceava), it has a length of 173 km. the hydrographic drainage basin of the Suceava river has a surface (on Romanian territory ) of 2298 km2, and it is being administrated by the "National Administration of Romanian Waters", through the "Basin Administration Siret" and it belongs to the geographic systems from the eastern part of Romania, system which is characterized by constant debits, more accentuated in the spring due to the rainfall and snow melting.

Its main affluents are Putna, Pozen, Suceviţa, Somuz, Solca, Horaiţ, Soloneţ, Hătnuţa și Dragomirna. Its hydrographic basin drains through the aflluents aprox. 26,6% of the county surface, and the riverbed is located at the bottom on the right versant, except for the clough „Caraula" between Falcău and Straja, having the following characteristics: the accumulative relief is represented mainly of the bottom valley and versant terraces, on which the residential places of Falcău and Straja are located); the majority of affluents on the right side of the Suceava river have underdeveloped alluvial cones ; it has the superior flow almost totally in the area of the flysch, made of conglomerated, gritstone and clay; the friability of the rocks from the riverbed allow the infiltration of the trickling waters, but the rough relief from the superior flow of the Suceava river determined by the quite bold bents (10 – 18 ‰) have led to the organization of a well established hydrographic network; the litology of the hydrographic basin has a very large variety of Kliwa rough gritstones in the mountain area to the friable clays and sands down on the plateau. The study made during 2008-2010, the Suceava river was monitored on a monthly basis in the following control areas: the Brodina section (Coord. X = 709,813; Y = 531,613; Z = 585); the Mihoveni section (Coord. X = 687,222; Y = 590,375; Z = 265) șand the Tișăuți section (Coord. X = 683,204; Y = 597,946; Z = 250), havind the following conclusions: the values CBO5 on the three sections vary if we follow different laws: in Brodina section there is an increase in 2010, when in the Mihoveni section, the maximum is attained in 2009, and for the Tișăuți section the values increase gradually in 2009 and 2010; the values CCO-Cr on the three sections vary on the same laws in Mihoveni and Tișăuți and much more different in Brodina; The values for phosphor in total for the three sections vary after different laws, in the Brodina section there are approximately constant and reduced, in the Mihoveni section they decrease very little in 2009, registering an increase in 2009, and in Tisauti they increase very much with a maximum in 2009. The values for nitrites on the three sections decrease in the section Brodina and Mihoveni, but for Tișăuți they increase and they have a maximum in 2009; the values of the nutrients on the three sections vary following different laws for each nutrient, the greatest concentration being registered for the azote in the azotates, following the azotate from the ammoniac abd the azotate from the nitrites, the latter having the lowest concentrations. The values for the ammonium ion are very high in Tișăuți area, as it is downstream from the treating area and which presents a thick bedding of mud, with bacteria that generate ammonium. If the CBO5 values continue to increase, with a low decrease in 2009 for Mihoveni, the dissolved oxygen vary following different laws (Fig. 5.10), with a minimum in 2009,for all the sections, due to the great volume of rainfall in the year (flood); The graphic evolution of the ammonium azotate remains practically constant in the first sections, registering a great increase in the Tișăuți area, and in 2009 there is a maximum, which is explained by the flooding, which have refilled the basins and the septic tanks, but as well as the products resulted from the rotting of animal dead bodies. The values of the azotate increase in all the sections, with the remark that in the Tișăuți section it varies following the same law, they remain practically constant before and after the purification station; The Graphic evolution of the total phosphos on correlation with the concentration in phosphate anions in the three sections present the same evolution law, their concentration is minimum and practically constant in Brodina section, slow increase in Mihoveni section and very strong increase in Tișăuți section.

## Cap. VI. MONITORING THE GORUND WATER QUALITY IN THE VULNERABLE VILLAGES IN BOTOŞANI COUNTY

In this chapter we are going to present the results of the monitoring of the phreatic water within 2001-2008 in a number of 37 drillings placed in the vulnerable zreas (ZV) as well as in the areas diagnosed as not being vulnerable. The selected parameters for the survey of the quality of the phreatic water are the indicators of the nutrients frame: the concentration of the ions azotate, nitrite, phosphate, and ammonium.

Within 2001-2006 there have been 20 drillings monitored. The results of the monitoring are presented in table 6.1, in medium annual values of the concentrations mg/L .

**Table 6.1.** Ground water quality in the hydrogeological drillings

| Nr. crt. | Foraj | 2001 | | | | 2005 | | | | 2006 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $PO_4^{3-}$ | $NO_3^-$ | $NO_2^-$ | $NH_4^+$ | $PO_4^{3-}$ | $NO_3^-$ | $NO_2^-$ | $NH_4^+$ | $PO_4^{3-}$ | $NO_3^-$ | $NO_2^-$ | $NH_4^+$ |
| 1. | Baluseni F1 | 0,14 | 2,2 | 0,044 | 0,162 | 0,1 | 4,6 | 0,07 | 0,199 | 0,199 | 1 | 0 | 0,364 |
| 2. | Corlateni F1 | 2,76 | 4,4 | 0,264 | 1,49 | 2,18 | 4,06 | 0,044 | 2,77 | 0,261 | 2,86 | 0,059 | 0,157 |
| 3. | Corni F1 | – | – | – | – | – | – | – | – | 0,045 | 13,23 | 0,262 | 0,182 |
| 4. | Dangeni F1 | 2,12 | 3,9 | 0,06 | 0,19 | 4,19 | 2,19 | 0,039 | 0,115 | 4,58 | 3,16 | 0,011 | 0,298 |
| 5. | Dangeni F2 | 0,08 | 90 | 0,07 | 0,43 | 0,096 | 0,35 | 0,036 | 0,794 | 0,039 | 14,8 | 0,143 | 0,712 |
| 6. | Dracsani F1 | 0,02 | 7,8 | 0,43 | 1,09 | 0,013 | 0,3 | 0,044 | 4,55 | 0,199 | 3,7 | 0,021 | 0,455 |
| 7. | Mascateni F2 | 0,6 | 1,2 | 0,24 | 2,68 | 0,037 | 21,98 | 0,091 | 2,08 | 0,494 | 7,62 | 0,024 | 0,232 |
| 8. | Pasateni F1 | – | – | – | – | – | – | – | – | 0,074 | 21,46 | 0,062 | 0,19 |
| 9. | Prisecani F1 | – | – | – | – | – | – | – | – | 0,029 | 0,54 | 0,015 | 0,53 |
| 10. | Prisecani F2 | – | – | – | – | – | – | – | – | 0,789 | 0,624 | 0,029 | 0,952 |
| 11. | Prisecani F3 | – | – | – | – | – | – | – | – | 0,069 | 0,73 | 0,017 | 0,513 |
| 12. | Radauti- Prut F2 | 0,08 | 24,2 | 0,12 | 0,343 | 0,146 | 5,44 | 0,166 | 0,14 | 0,104 | 28,23 | 0,021 | 0 |
| 13. | Radauti - Prut F1 | 0,08 | 42 | 0,02 | 0,705 | 0,018 | 4,18 | 0,013 | 0,124 | 0,1 | 11,59 | 0,039 | 0 |
| 14. | Sadoveni F1 | 0,24 | 14,2 | 0,024 | 0,2 | 0,018 | 37,174 | 1,54 | 1,018 | 0,114 | 27,98 | 0,029 | 0,273 |
| 15. | Saveni F1 | | | | | 0 | 0,45 | 0,1 | 1,37 | 0,079 | 0,944 | 0,013 | 0,49 |
| 16. | Stefanesti F1 | 0,2 | 730 | 0,236 | 0,38 | 0,183 | 194,86 | 0,037 | 0 | 1,259 | 10,69 | 0,029 | 0,604 |
| 17. | Stefanesti F2 | 0,08 | 10 | 0,04 | 0,44 | 0,0 | 0,59 | 0,02 | 1,2 | 0,0 | 0,679 | 0,015 | 0,323 |
| 18. | Stefanesti F3 | 0,08 | 3,6 | 0,088 | 1,798 | 0,246 | 355,75 | 1,37 | 0,52 | 1,98 | 33,88 | 0,031 | 0,141 |
| 19. | Todireni F1 | 0,08 | 2,2 | 0,2 | 0,22 | 0,762 | 6,18 | 0,011 | 0,34 | 0,144 | 2,62 | 0,032 | 0,662 |
| 20. | Todireni F3 | 0,14 | 6,4 | 0,11 | 0,04 | 0,045 | 3,64 | 0,063 | 1,11 | 3,01 | 8,48 | 0,021 | 0,696 |

### 6.2.2. Variation of the concentrations of the water quality indicators from the observed drillings in the vulnerable areas in Botosani County in 2006-2008

The analyse of the qualitative parameters of the phreatic water sampled in 2008 from the drillings placed in the vulnerable areas in Corni and Pasateni, we found out that the water in these drillings is greatly surpassing the maximum limit admitted.

The same decrease tendancy of the nitrate and nitrites ions from the phreatic water in the drillings placed in the vulnerable areas ZV Corni, Pasateni and Ştefăneşti is to be found analyzing as a whole the values registeres in the time frame 2006-2008 (Fig. 6.7). In exchange, there is an increase tendancy of the concentrationof the nitrate indicator in the ground water in the Sadoveni F1 drilling, although this *village has not been diagnosed as vulnerable* area to the nitrate pollution from agriculture sources. (Fig. 6.8).

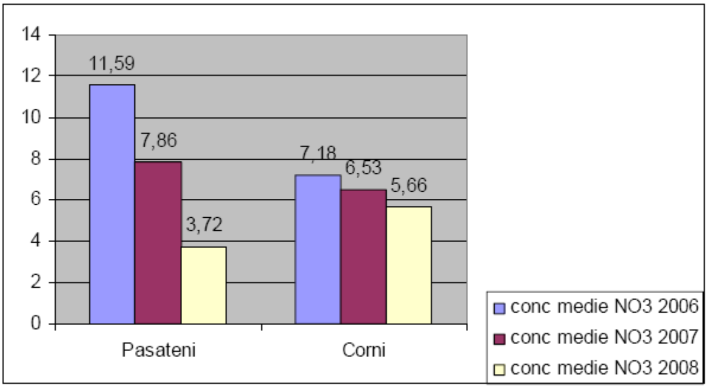


**Fig. 6.7.** The variation of the water quality indicators from the observed drillings in the vulnerable areas Corni and Pasateni in the time frame 2006-2008.

The analysis of the physical-chemical indicators of the phreatic water in the observed drillings from other villages than those declared as vulnerable areas show that in the time frame 2006-2008 a deterioration of its quality has been registered as far as the ammonium indicator is concerned, and in some villages the indicators of nitrate and nitrites as well. (Ex. Sadoveni).

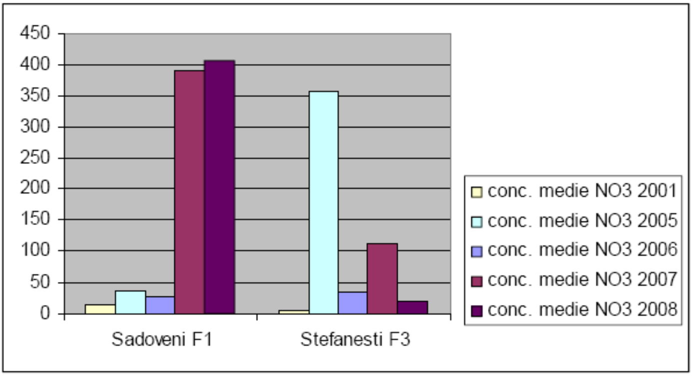


**Fig. 6.8.** The variation of the water quality indicators from the observed drillings in the vulnerable areas Sadoveni and Ştefăneşti in 2006-2008

This tendency of depreciation of the water quality is confirmed by the issue of the Order MMDD/MADR nr. 1552/743/2008 which, following the evaluation of the polluting risk with nitrates of the ground water, all the territory of Botosani area has been diagnosed as vulnerable to nitrates polluting (77 villages and towns).

## Cap. VII. THE STUDY OF DOMESTIC CERAMIC OF BURNT CLAY IN ORDER TO BE USED FOR PURIFICATION OF WATERS

Our group of work has experimented and patented lately two new systems based on industrial ceramic, normal or inflatable, with vitrified or non-vitrified structures, having properties of ionic exchange and retention through chemoabsorption or those of redox type through which, some of the toxic substances using disproportioning processes are transformed in inert products from the metabolic point of view [*Sandu și colab., 1999, 2010a*, *2014*].

The antimicrobian capacity is based on some metallic cationi with an inhibition activity of the micro-organisms metabolism. As an example, we have the case of the Ag(I), Zn(II), Cu(II) and even Fe(III), Mn(IV) or others cationic in superior states of [*Sandu și colab., 1999, 2009, 2010a, 2014*].

The capacity of ionic exchange is due to the hidroxidic marginal structures Al–OH and of the acid ones of type Si(Ti)–$O^-H^+$. These marginal groupings are put on the stoechiometric report (caustic mode). Si:Al, but also on the position of those two coordination centers of the tetrahedrons from the basic structure. It is well known that, the industrial ceramic have as basic unitstetrahedrons and octahedrons of silicat and aluminat ions and unified through piro connections in various structural forms bidimensional stratified or co-planning and tridimensional, which in the marginal structures present hidroxidical groupings (Al-OH), double bonded oxygen and acid structure by the type $Si(Ti)\text{-}O^{-}H^{+}$. Usually, due to the different minearological nature (the composition in different ores: caolinit, montmorillonit, clorit, halloysit, illit, verniculit, smectit, pirofilit etc.), respectively of the burning technology, but also of the fluxing, platifiers and other additives used in the production, the acid-base character, given by the marginal groupings vary in very large limits, from the acid (pH=4.5) up to alcalin (pH = 9,5) [*Klusch, 1981; Murray, 2007; Sandu și colab., 1999; 2009; 2010a și b; 2014; Niculica si colab., 2013, Vasilache și colab., 2013a și b*].

The number and the distribution of the marginal groupings capable of ionic exchange is given by the mineral composition of the raw material, of the composition before the plastic processing and calcinations, as well as by the calcinations conditions, vitrification, having as varable parameters: the heating speed, the burning speed, the burning system (closed, open or semi-open), in direct source or hidden source, oxidant or reductive, etc. [*Grim, 1968; Kenney, 1967 și 1977; Koster, 1989; Peterson, 2003; Sandu și colab., 2010a, 2014*].

The ionic exchange is explained by the acid marginal structures $Si\text{-}O^{-}H^{+}$, $Ti\text{-}O^{-}H^{+}$, as well as those of the type of $Fe(III)\text{-}O^{-}H^{+}$. So, the ceramic with higher concentrations in Al(III), Ca(II), Mg(II), K(I) and Na(I) have a character that varies from the amfoter towards base values to light medium, while those with Si(IV), Ti(IV) and Fe(III) have a character that varies from amfoter to acid values, the second type being very much speculated in the producing of the granules used in water treatment. [*Sandu și colab., 1999, 2010a, 2014; Teoreanu, 1995*].

In addition to the great capacity of absorption and ionic exchange, the burnt clay ceramic, with a certain caustic module, where the dominant is given by the poliedric micro-structures of Si(IV), Ti(IV) and Fe(III) have a redox behavior, which allow through some molecular structures the elimination of the harmfull effect of some molecular structures with retention following the purification processes, such as: molecular chlorine which is reduced to the chlorine ion and a series of catoni ($Hg^{2+}$, $Pb^{3+}$, $Pb^{4+}$, $As^{5+}$ etc.) which reduce themselves to the hard soluble structures (Hg(I), Pb(II), As(III) etc.) retained by ceramic.

The main advantage of the ceramic products used in treating and purification of the waters is explained by the mechanic resistanc, the acide-base and redox stability, of the termic and photo-chemical resistance, but also by a great series of very importance characteristics in these applications such as: the apparent density or the specific weight under $1500kg/m^3$ and the resistence at compression, which varies between 50 and $200daN/cm^2$; the maximum quantity of water absorbed which varies between 8 și 20%; the gelivity of the phenomenon of mechanical deterioration (breaking) of the products saturated with water as a consequence of frost and defrost, but also the their degradation through chemical and biochemical products due to the specific charges of waters that are subject to treating. Also, another advantage of the industrial ceramics or technical ceramics are represented by the minimum concentration in soluble components in watery systems. [*Sandu și colab., 2010a*, *2014*].

Due to this, the granules used in treating the waters are initially subject to some washing processes through their dispersion in de-ionized water containers- light acid, keeping them previously in this environment for a few minutes, afterwards the water is clarified, and the ceramic are dried off with warm air [*Sandu și colab., 1999, 2010a, 2014*].

In this chapter we have studied a great deal of technical ceramic, made by the Brikstone Society Iași and traditional ceramic (pottery fragments) produced by the potters from Stavnic Church, different as the custic mode Si(Ti)/Al and through composition in Ca, Mg și Fe, from the compositional and morphotalogical point of view. The chemical composition through the SEM-EDX method has been correlated with the acidity of ceramic and their capacity of retention of cations of Fe (III).

The purpose of this study has been to select the optimal ceramics for the chemoabsoption processes in the final stage of filtration from the surface and groundwater treatment with final result of purification for drinking water, respectively of obtaining a pure water with organoleptical special characteristics.

## 7.2. Experimental part

### 7.2.1. Ceramics taken for study

The research was based on two types of ceramic: CI, industrial or technic made by the Brikstone Society in Iași, presented as some granules obtained by breaking some freshly burnt bricks; CT, traditionally produced by some potters from the Stavnic church, presented as granules obtained by breaking the collar of the vitrified pots, freshly burnt.

From the two types of ceramic we have gathered samples, such as they were, or nicely broken down, then separated through the granulometric bolt with mesh of 1,5 - 2,5mm; 2,5 – 3,5mm și 3,5 – 6,5mm. The samples processed in this manner have been put in plastic containers with a bottle cap for screw thread, from where they were taken for the analysis.

### 7.2.2. The processing and the analysis of the samples

In order to determine the composition of each lot of the two types of ceramic, we have taken a small piece of chip of approx. 10-20 g, with two paralled surfaces that have been noted as samples through the following index: $CI_a$, acid industrial; ceramic; $CI_{sa}$, industrial ceramic light acid $CI_{am}$, industrial amfoter ceramic ; $CI_{saHCl}$, industrial ceramic light acid treated with HCl 3M; $CI_{amHCl}$, industrial ceramic amfoter treated with HCl 3M; $CT_a$, ceramici tradiționale acide; $CT_{sa}$, traditional ceramic light acid; $CT_{amsa}$, traditional ceramic amfoter towards light acid; $CT_{am}$, ceramici tradiționale amfotere; $CT_{amsb}$, traditional ceramic amfoter light base; $CT_{amHCl}$, traditional amfoter ceramic treated with HCl 3M; $CT_{amsbHCl}$, traditonal amfoter light acid treated with HCl 3M.

These samples have been analysed, from the point of view of the elementary chemical composition and of the internal micro-structure, through the technique of electronic microscopie of scanning, coupled with the microscopie of X (SEM-EDX). For all the samples taken we have determined the free acidity, respectively the pH of the solution resulted through the dispersion of 90 g from each sample smoothly smashed (fraction1,5-2,5 mm separated through the granulometric bolt.) at 100 mL bidistillated. The data obtained have been corelated with the elementary chemical concentration evaluated based on the EDX.

The free acidity has been determined at the pH value at the dispersion of the granules in bulk with a diameter 1,5-2,5 mm in bidistilated water, respectively, : $[H^+] = 10^{-pH}$, moli/L.

In order to evaluate the retaining capacity of the ion $Fe^{3+}$ the two groups of ceramic (industrial and traditional) have been separated in 3 groups of samples using a granulometric bolt. with 1,5 - 2,5mm; 2,5 – traditional have been grouped on a series of samples, indexed as follows: $CI_m$, industrial ceramic witness (not treated with watery solution of chlorine acid for the solubilization of the liquid components) with granulometer $CI_m$1,5 - 2,5; $CI_m$2,5-3,5; $CI_m$3,5 - 6,5; $CI_{HCl}$, industrial ceramic treated with watery solution for the solubilization of the components solubilization with the granulometers $CT_m$1,5 - 2,5; $CT_m$2,5-3,5; $CT_m$3,5 - 6,5; $CT_{HCl}$, traditional ceramic with watery solution treated with chlorine acid 5M for the siolubilization of the labile componments with granulometers $CTT_{HCl}$1,5 - 2,5; $CTT_{HCl}$2,5-3,5; $CTT_{HCl}$3,5 - 6,5.

The retaining capacity of the ion $Fe^{3+}$ from the watery solution 0.5M has been realized through the dispersion in 100 mL solution 90 g ceramic granules, under very light agitation at the room temperature, for 20 min. Before the dispersion, the ceramic granules have been washed with bidistalated water and then dried at 105°C for 4 hours. After the 20 min of dynamic dispersion the quantity of Fe residual has been decantated, through the atomic absorbtion spectroscopie.

The retaining capacity has been evaluated through the formule CR = $(C_r/C_i)$x100, where CR represents the retaining capacity (%),$C_r$ - the final or residual concentration (moli/L), and $C_i$- final concentration (moli/L).

## 7.3. Results and discussions

### 7.3.1. Determining the chemical nature and the physical microstructure of ceramic

The SEM analysis allow based on the photograms ( right up of the EDX spectres) the evaluation of the structure and morphology of the synterized granules of the ceramic material.

The industrial ceramics have the granulation blander and have a distribution in the volume phase uniform, while the traditional ceramics have a thick granulation and non-homogenous. In table 7.1. we present the chemical composition of the 12 ceramic studied.

**Tabelul 7.1.** Compoziția chimică elementală a ceramicelor luate în studiu

| **Proba** | **Compoziția elementală, procente gravimetrice (wt%)** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Si** | **Al** | **Fe** | **Ca** | **Mg** | **K** | **Na** | **Cl** | **Ti** | **O** |
| $\mathbf{CI_{a}}$ | **29.8319** | 7.7825 | **6.7811** | **6.3895** | **2.5286** | **3.5031** | 1.2765 | - | **1.2873** | 40.6195 |
| $\mathbf{CI_{sa}}$ | **21.9435** | 8.3038 | **7.2024** | **6.6367** | **1.6832** | **2.5392** | 0.6137 | - | 0.7843 | 50.2932 |
| $\mathbf{CI_{am}}$ | 19.9764 | **17.7569** | 2.5077 | 0.3323 | 0.5004 | 1.0144 | 0.2427 | - | **1.4641** | 56.2051 |
| $\mathbf{CI_{saHCl}}$ | **20.8800** | 7.5779 | **6.0392** | **3.4116** | **1.3091** | **2.3301** | 0.9003 | **0.2795** | 0.7694 | 56.9021 |
| $\mathbf{CI_{amHCl}}$ | **20.8231** | **14.5458** | 3.2689 | 0.2223 | 0.2986 | **1.6096** | 0.4703 | **0.1890** | 1.1665 | 57.4059 |
| $\mathbf{CT_{a}}$ | **20.9302** | 7.1707 | **5.0387** | **7.3636** | **1.4994** | **2.3099** | 0.5552 | - | 1.3011 | 53.8312 |
| $\mathbf{CT_{sa}}$ | 18.9996 | 6.6452 | **6.1149** | 7.4298 | **1.3951** | **2.3841** | 0.2899 | - | 1.3337 | 55.4077 |
| $\mathbf{CT_{amsa}}$ | **23.4618** | **13.8536** | **6.1805** | **1.0970** | 0.8441 | **1.4689** | 0.6655 | - | 1.143 | 51.2856 |
| $\mathbf{CT_{am}}$ | 12.4096 | 14.4304 | **5.9096** | 0.2568 | 0.0463 | 0.1654 | 0.0959 | - | 1.1226 | 64.5634 |
| $\mathbf{CT_{amsb}}$ | **25.8595** | **10.0714** | **5.4116** | **10.2199** | **1.8305** | **4.1472** | 0.5140 | - | 1.019 | 40.9269 |
| $\mathbf{CT_{amHCl}}$ | **23.7496** | **14.4702** | **6.1234** | - | 0.6628 | **1.4494** | 0.1042 | **0.3242** | 1.2254 | 51.8908 |
| $\mathbf{CT_{amsbHCl}}$ | **20.9927** | **17.8287** | 2.0833 | 0.3424 | 0.3404 | 0.9278 | 0.0760 | **0.3161** | 1.4154 | 55.6772 |

The elementary analysis data EDX confirm a very close composition between the samples, which is explained by the rigurously controlled dosage the components at obtaining the biscuit, in exchange, this vary in very large limits for the traditional ceramics which came from different lots from the same potter or from different potters, moreover these have been using different clays and compositions when producing the biscuit.

We have to remind that initially we have used more samples for these analysis, industrial ceramics (12), as well as traditional ones (23), from which we have selected the most representative through their chemical structures obtained following the SEM-EDX analysis.

Based on the elemental analysis EDX the 12 samples studied have been grouped based on the following characteristics compositional specific for the ceramic materials: $CI_a$, acid industrial ceramics, with the caustic mode Si/Al 3,05; Ti 1,29; Fe 6,78; Ca 6,39; $CI_{sa}$, industrial ceramic light acid, with the caustic mode Si/Al 2,64; Ti 0,78; Fe 7,20; Ca 6,64; $CI_{am}$, amfotere industrial ceramic, with the caustic mode Si/Al 1,13; Ti 1,46; Fe 2,51; Ca 0,33; $CI_{saHCl}$, industrial ceramic light acid treated with HCl 3M, with caustic mode Si/Al 2,8; Ti 0,77; Fe 6,04; Ca 3,41; $CI_{amHCl}$, amfoter caustic ceramic treated with HCl 3M, with caustic mode Si/Al 1,43; Ti 1,17; Fe 3,27; Ca 0,22; $CT_a$, acid traditional mode, with caustic mode Si/Al 2,9; Ti 1,3; Fe 5,04; Ca 7,36; $CT_{sa}$, traditional ceramic light acid, with caustic mode Si/Al 2,86; Ti 1,33; Fe 6,11; Ca 7,43; $CT_{amsa}$, traditional amfoter ceramic light acid, with the caustic mode Si/Al 1,69; Ti 1,14; Fe 6,18; Ca 1,10; $CT_{am}$, amfoter traditional ceramic, with caustic mode Si/Al 1,0, Ti 1,12; Fe 5,91; Ca 0,26; $CT_{amsb}$,traditional amfoter light base, with the caustic mode Si/Al 2,57; Ti 1,02; Fe 5,41; Ca 10,22; $CT_{amHCl}$,amfoter traditional ceramic with the caustic mode HCl 3M, cu modul caustic Si/Al 1,64; Ti 1,23; Fe 6,12; Ca 0,0, $CT_{amsbHCl}$, amfoter traditional ceramic liht acid with 3M, with caustic mode Si/Al 1,18; Ti 1,42; Fe 2,08; Ca 0,34.

Initially the samples have been indexed with $CI_{1-12}$ și $CT_{1-23}$, after this analysis they have been indexed by the explicitation of the acid-base character.

Based on the elementary chemical analysis EDX we can make corelations between the value of the normal caustic way and the sumativ one and the free acidity. To the free acidity a special contribution is brought by the $Cl^-$, native or induced in the treatments with HCl.

It is well known that, the module of the base structure of a ceramic that determine the acid-base behavior is given by the report Si(IV)/Al(III). In the discussion of the chemical function acid-base, an important role is played by the nature of the connections (covalent polarised or ionic) and their position in the tridimensional structure.

### 7.3.2. Free acidity of the ceramic studied and the retaining capacity of the Fe ion (III)

In table 7.2 we present the values of the normal caustic modules Si/Al and the summative Si(Ti/$Fe^{III}$+Cl)/Al(Ca/Mg+Na/K) of those 12 ceramic types, which are corelated with their free acidity.

**Tabelul 7.2.** free acidity of the ceramics expressed by the concentration [$H^+$] in mol/L in correlation with the caustic mode

| Proba | Modulul caustic normal Si/Al | Modulul sumativ Si(Ti/$Fe^{III}$+Cl)/ Al(Ca/Mg+Na/K) | pH | [$H^+$] ($x10^{-5}$ mol/L) |
|---|---|---|---|---|
| $CI_a$ | 3,0495 | 1,7644 | 5,0 | 1,000 |
| $CI_{sa}$ | 2,6426 | 1,5134 | 6,0 | 0,1000 |
| $CI_{am}$ | 1,1250 | 1,2107 | 7,0 | 0,0100 |
| $CI_{saHCl}$ | 2,7554 | 1,8010 | 4,7 | 1,9953 |
| $CI_{amHCl}$ | 1,4316 | 1,4841 | 5,8 | 0,1585 |
| $CT_a$ | 2,9189 | 1,4429 | 6,5 | 0,3162 |
| $CT_{sa}$ | 2,8591 | 1,4606 | 6,2 | 0,0631 |
| $CT_{amsa}$ | 1,6936 | 1,7171 | 5,2 | 0,3162 |
| $CT_{am}$ | 0,9983 | 1,2966 | 7,0 | 0,0100 |
| $CT_{amsb}$ | 2,5676 | 1,2056 | 7,1 | 0,0080 |
| $CT_{amHCl}$ | 1,6413 | 1,8831 | 4,5 | 3,1623 |
| $CT_{amsbHCl}$ | 1,1775 | 1,2712 | 7,5 | 0,0031 |

According to the data in this table, we have succeeded the grouping of the 12 ceramic types treated and non-treated in theorder of their free acidity decrease.From these ceramics we have chosen for the evaluation of the chemoabsoption capacity of the $Fe^{3+}$ ion the most acid samples , $CI_a$ și $CT_a$.

### 7.3.3. Retaining capacity of $Fe^{3+}$ și $Al^{3+}$

For the evaluation of the retaining capacity of the $Fe^{3+}$ ion the two types of granules, using only ceramics acid, $CI_a$ și $CT_a$, these after the bland breaking have been separated in 3 groups through the granulometric bolts with meshes: 1,5 - 2,5mm; 2,5 – 3,5mm și 3,5 – 6,5mm. Following this separation, the samples have been indexed, as follows: industrial ceramic witness, with granulometers $CI_m$1,5 - 2,5; $CI_m$2,5-3,5; $CI_m$3,5-6,5; *industrial ceramic treated* with solution HCl 5M, with granulometers $CI_{HCl}$1,5-2,5; $CI_{HCl}$2,5-3,5; $CI_{HCl}$3,5-6,5; : industrial ceramic witness, with granulometers $CT_m$1,5-2,5; $CT_m$2,5-3,5; $CT_m$3,5-6,5; *ceramic treated* with solution HCl 5M, with granulometers $CTT_{HCl}$1,5-2,5; $CTT_{HCl}$2,5-3,5; $CTT_{HCl}$3,5 - 6,5.

In table 7.13 we present the retaining capacity through the pourcentage of Fe exchanged through chemoabsoption on the analysed ceramic, function of three goups granulometrics for the industrial ceramics

(CI) and the traditional ceramics (CT), as such and treated with watery solution of HCl 3M.

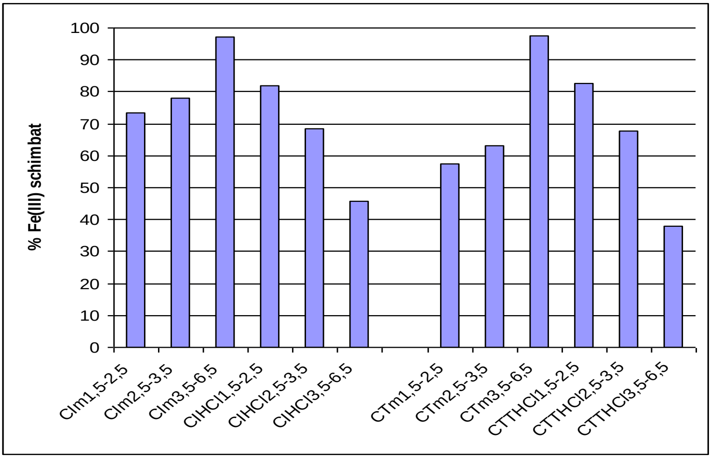


**Fig. 7.13.** Pourcentage of Fe exchanged through chemoabsorption on the industrial and traditional ceramic treated with HCL and untreated

According to the data in the fig. 7.13 we can state that the traditoonal ceramic trated with solution HCl 0,3M the iron pourcetage exchanged decreases as the granulometry increases, thus for the granulometry of 1,5-2,5, compared to the 3,5-6,5 the iron pourcetange decreases from 81,9% la 45,6%. The tendancy is inversed for the untreated traditional ceramic, where we observe that the iron pourcentage increases directly proportionally with the increase of the granulometry. Thus, for the granulometry 1,5-2,5mm, față de cea de 3,5-6,5mm, the iron exchanged pourcentage increases proportionally 73,5% .t 97,2%.

The same tendency is being noticed for the industrial ceramic. Thus, the industrial treated ceramic presented for the granulometry 1,5-3,6 compared to the 3,5-6,5 mm a decreasing iron pourcentage from 82,7% to 37,9%, and for the untreated one the effect was reverse, the value of the percent increased has risen from 57,5% la 97,5%.

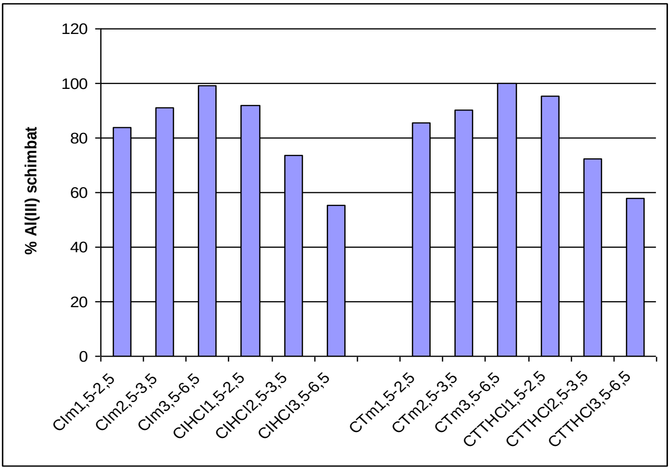


**Fig. 7.14.** Aluminium pourcentage exchanged through chemoabsorption on the industrial and traditionally treated ceramic treated with HCL and untreated

In the same way, according to the data in fig. 7.14 we can state that the traditional ceramic treated with HCL 0,3M solution the minimum aluminium pourcentage eschanged decreases as the granulometry increases, so that for a granulometry of 1,5-2,5, compared to the 3,5-6,5 the aluminium pourcentage decreases from 92,1% to 55,3%. The tendenacy is reversed for the untreated traditional ceramic, where we notice that the aluminium pourcentage exchanged increses direct proportionally with the increase of the granulometry. Thus, for a granulometry of 1,5-2,5mm, compared to 3,5-6,5mm, the aluminium pourcentage exchanged increases proportionally from 83,8% to 99,2%.

The same tendency is noticed for the industrial ceramic as well. Thus, the treated industrial ceramic presented for the granulometry 1,5-3,6 compared to 3,5-6,5 mm a pourcentage of iron exchange in decrease from 95,2% to 57,8%, and for the untreated one the effect was reversed, the value of the pourcentage eschanged increased from 85,7% to 99,8%.

Initially, the ionic exchange capacity was studied for all the 5 industrial ceramic and the 7 traditional ones, from all these only the acid ceramic ($CI_a$ și $CT_a$) presented a good reproducibility of the results. The respective ceramic have been used for ionic exchange as wellof other cat ions, considered vulnerable to overcome the limit level of toxicity, such as: $Hg^{2+}$, $Pb^{4+}$, $Pb^{3+}$, $Ni^{2+}$, $As^{3+}$ etc., but their results did not present a resembling reproducibility as in the case of $Fe^{3+}$ and $Al^{3+}$. This is explained by the acide-base action and the rdox of the ceramics with the caustic mode, where the poliedric microstructures are dominant Si(IV), Ti(IV) and Fe(III) which give a redox behavior and which allow through the redox processes the elimination of the harmfull effect of some molecular structures with retention after the purification processes, such as: molecular chlorine which is reduced at the chlorione ion and a serioes of cat ions ($Hg^{2+}$, $Pb^{3+}$, $Pb^{4+}$, $As^{5+}$ etc.) which are reduced to hard soluble structures (Hg(I), Pb(II), As(III) etc.) retained by the ceramic. We would expect a cumulative effect, but the nonhomogenity of the surface pores and the interior ones, responsables for the absoption and portance (transfer and elimination), did not have the expected results. As the domain is actual for the science as well as for technology, the research in the area must be analysed in another doctor's thesis.

The present study has allowed the selection of the optimal ceramic which can be used in the chemoabsorption in the final stage of filtration from the surface and groundwater water treatment for purification, namely in ovtaining a pure water with special organoleptic characteristics. These ceramic items have been the fundament of a new procedure of purification of waters used in the present city and municipal stations. [*Sandu și colab., 2014*].

## Cap. VIII. THE INVOLVMENT OF CERAMIC MATERIALS IN PURIFICATION OF GROUND AND SURFACE WATER. ELABORATION OF A NEW PROCESS

### 8.1. Modern processes in water purification, which correspond to the present norms

Gemerally, the technological processes of water treatment sre elaborated based on the physical-chemical and microbiological properties of the source water, as well as the conditions of quality requested by the consumer. The choice of the treatment processes take into condiertaion on one hand the concentration of the insoluble materials, named also in the charging of physical-mechanical dispersion, then the concentration in the soluble compounds or the chemical charge, as well as the microbiological charge. In this way, through treatment we must eliminate the insuluble materials of diferent dimensions, from mechanic dispersions up to the coloidal ones (by retention on bolts/ grids and through sand filtration, sedimentation, coagulation, rapid or slow filtration, reaching to ultra-filtration and micro-filtration), but also the soluble ones, reducing to minimum the durity (through softening, ionic exchange or chemical desinfection, using the chlorine processes, ozonization, iradiation with ultraviolet radiations etc.).

After the coagulation, there is the decantation with the help of suspensional separators which allow the sedimentation and concentrate evacuation as mud. After the decantion it is mandatory o filtrate the treated water which is based on a process of deparation of the suspensions and colloidal dispersions from the water by pouring the mix through a mushy material, which will retain them leaving the filtrant clear, this being the last step of clearance in the process of obtaining the drinking water. The filtering materials used in the filtration process are: quartyuos sand, ballast, broken granite, granule anthracite, filtering canvas, expanded polistiren, membranes, etc.

The filtration is made generally in the last stage, in two steps: the filtration through the quartzous materials (sands) and respectively, the filtration through active vegetal coal, both in various granulometries, disposed gradually in the filtration stage [*Manzatu si Lucaci, 1981; Kumazawa, 1984*].

These processes have a series of disadvantages related to the low degree of purity, as far as the soluble chemical charge is concerned as well as the coloidal one, by the presence of chlorinated organic compounds formed during the treatment, by the organoleptic characteristics unwanted of the water and by the complexity of the physical-chemical processes involved.

We know, also, processes that use polimeric milipor filters, cellulosic or ceramic, on the for of membranes disposed in diafragmes, cartouches or on special barrels, static or dynamic, with or without generation systems of ions $Ag^+$, respectively with UV lamp or a device for producing ozon by smooth ebullition, using autonomes installations of reduced capacity (maximum 10...100L/zi) [*Kumazawa, 1984; Kyung Taek, 2007; Wirstiuk, 1998; Stoquart si colab., 2012; Yamamura, 2002; Bergen, 1996; Tracuks, 2005; Yankovskyi si Stepanov,2004*], which offer a very high degree of purification, comparable with the instalations or industrial stations, but they have the great disadvantage of low water volumes treated and of very high costs for treatment.

The closest invention to the elaborated process by our team, uses in order to obtain the drinking water, besides the classical materials based on quartz mass and active coal, various granules for the filtration from ceramic materals, with a high porosity and ionic exchange capacity such as: rings of porous ceramic type as „redoxite" **[***Borzenkov si colab., 1998; 2000***],** granules of expanded ceramic and granules from vitrified ceramics with argentic glass films, disposed in containers which are immersed in the adduction channels, between the last stage of filtration and the tampon device, frm the treating station, in order to eliminate totally the cations of transitional metals and the dispersed chlor **[***Prokofiev si Ivaschenko, 2000***]**, both systems being able to present or not at the the inferior part of the filtration basin and the mud collecting channels. [*Bobylev, 2003; Sandu si colab., 1999***].**

These inventions have the disadvantage of some complex installations which need the periodical reactivation of ceramic granules for purification and overstructuring of pure water and which use ceramic vitrified materials, nergointensive.

### 8.3.1. The purpose, the problem and the advantages of teh new process

The purpose of the invention lies in obtaining the drinking water, with a high level of purity and with organoleptic characteristics similar to still water from the mountain naturals springs, uncontaminated or of those of great depth, with physical-mechanical, chemical and microbiological charge admitted by the exploitation normes.

The problem that the invention solves lies in the use during the filtration stage, of large spaces, modern, frequently used today for surface and groundwater treatment in the big cities, of some ceramic materials of various granulometries, with great ionic exchange capacity and great porosity, disposed in a third stage of filtration, after the filtration through sand and the one with coal.

The problem is solved by introducing in the final system of desinfection, with $ClO_2$ or $O_3$, and the tampon system of deposit (from where it is sent to the consumers) of a compartment of filtration which uses as filtering layer ceramic granules, with open porosity, greater than 40%, with granulometries having a diameter 0,5 and 20,0mm, the surface to the bottom. These granules are obtained from the burnt brick falls from the industrial production processes, by breaking, smooth divisation and sorting on four levels with the help of some vibrating boltswith inclination, having the meshes 0,5; 2,0; 5,0; 10,0 and 20,0mm. We use ceramic in pale yellow, with a content of $TiO_2$ between 2 and 4%, until the red ones, with content in $Fe_2O_3$ between 3 and 6% and which per total have a report $SiO_2/Al_2O_3$ (caustic module) taht varies between 2,5 and 3,0 and which come from very low carbonated clays; which induce after burning a content under 2% of MgO and CaO, and during the processing there cannot be used organic plastifying aditives, but only wood dust from soft essence or straw powder. These ones, after the breaking- grinding and sorting, are separately washed on the four sorts of immersion-agitation in deionized water, then they are essorated and dried (the humidity content lower than 5%) and eventually, they are put in bags abd sent to the treating station. In realising the invention we use a modern station that ahs the following working stages: pre-chlorination,(with $ClO_2$), coagulation (with $FeCl_3$, adding $KMnO_4$), rapid filtration (with the following filtering stages: 0,4m hidroantracite, 1,0m quartzous sand, 0,2m ion support on the adduction), post-chlorination(with $ClO_2$), filtration on active coal (granular active coal, on the support as a layer of 0,2...0,5m quartzous ballast), final desinfection (with $ClO_2$ or $O_3$) and final filtration on ceramic. The last stage for final filtration uses a constructive and functional system resembling the other two rapid filtration stages, where the ceramic granules are disposed in successive layerson the support grid, supported by the longitudinal adduction and collecting channels of residual mudfrom the bottom of the filtering basin.These channels have the sectionunder a U form and present at the deversing head in the collecting channel a mobile hatch,of the type of barrier of „too full", which allow the realisation of a stationary zone of sedimentation of the residual mud. This mud eliminates periodically itself with the help of an auger.

By application, the invention brings a series of advantages, among which: it ensures an advanced purification of the water with a capacity of conservation in time of the physico-natural and mineral-chemical characteristics; a still water is obtained with superior organoleptic characteristics which can be used by animals and people, in alimentation, without the existence of some risks of rapid contamination; the water, through its passage through porous ceramic, besides the elimination of all the cations and anions susceptible at ionic exchange and the elimination through absorption or degasification of the ClO2 traces, will restructure itself through the process of acvatemplation in stable oligomers (pentahidrol and hexahidrol), which have antimicrobian effects for long depositation periods, offering a good resitance to contamination; it can be applied to the technologies where the desinfection is made Cl2, as it allows the elimination of these through absorption and degasification, it eliminates the doping processes of the active coal with ceramic materials or powder of feric hidroxid' it allows the valorisation of the brick fall from the process of fabrication and elimination of more expensive materials such as: silicium, zeolites, bentonites, caolin, fluoride, diatomites or Kieselgur.

## Cap. IX. MATHEMATIC MODELING OF THE SPATIO-TEMPORAL EVOLUTION OF THE PHYSICAL-CHEMICAL CHARGE OF THE SURFACE WATERS AS "RIVER " TYPE SYSTEM

The mathematic modeling of the spatio-temporal evolution of the "river " type systems play an important role for the prognosis of the behavior of these systems. Knowing the distribution of the concentration field of the pollutant in time and space will significantly contribue to the prediction of the exceptional phenomena.

A special role for human health is played by the fluor. This is an important chemical element, necessary for the corect development of teeth and bones of the skeleton. [Ani şi colab. 2009; Ciobanu şi Florea, 1999], but also toxic when the limits of oligoelemnt are passed.

It is well-known that, monitoring the pollution of the water in rivers is made through the informatic controlling systems of the pollution level of the environment in time and space. A special component involved in this step is the modelling and the prognosis of the state in the examined area.

The purpose of this chapter is related to the development of the mathematic model of hidrodynamic and that of the pollutants dispersion in the "river " type systems in order to determine the spatio-temporal evolution of fluor on a sector of the river Prut from Ungheni with the help of SMS.

For the water flowing modelling on a sector studied of the river Prut we have used the ecuation system of Navier-Stokes under the Reynolds form (1) şi (2) together with the continuity equation (3), which describe completely the water dynamic in the rivers with turbulences. The numeric models have been elaborated with the help of Surface-water Modeling System (SMS), which represents a package of programs for the efficient management of the whole process of surface waters: from the topographic and hidrodynamic import data to the visualisation and solution analysis. The determination of the pollutants dispersion evolution has been realised in two stages. In the first stage the numeric model of the flowing of the water has been generated using SMS Resource Management Associates (RMA) 2 programme.

In second stage, at the hidrodinamic resulted from RMA2 a fost aplicat modulul RMA4, with the help of which the evolution of the fluor concentrations field has been determined

## Cap. X. GENERAL CONCLUSIONS

The doctor's thesis is structured in two parts: *the theoretical part and the experimental part.*

The second group of objectives have focused on the *four experimental protocoles*, namely: selection of the geographic areas by including in the research activities the wells/ drillings for the monitoring of the ground water evolution and the station for sampling water from the bedriver of some rivers in the hidrographic basins Siret and Prut; selection of the analytical methods and techniques in order to determinate on one side the chemical characteristics and the physical-structural characteristics of the ceramic materials, and on the other hand of the indicators regarding the chemical, microbiological and physical-mechanic charge of ground and surface waters, next to the optimal parameters of the purified waters; the elaboration and the practical realization of a technology to treat underground and surface waters to the final end of potabilization, patented by AGEPI Chișinău and being currently in process of being patented OSIM Bucharest; the evaluation of the selected ceramic materials' impact following the research concerning the chemical nature, the physical structure and the morphology of the granules, on the retaining capacity, the physical structure and the morphology of the granules, on the retaining capacity of the $Fe^{3+}$ and $Al^{3+}$ traces which remain after the coagulation-floculation processes of the treatment; the processing of the experimental data and writing the works; that have been the object of communications sent to seven national (4) and international scientific manifestations as well as of some articles published (9), among which one has been published in magazines CNCSIS B+, five in the volumes of the simposiums, another three in ISI magazines; taking part in 2 national inventions salons and 6 international salons, with the new water treatment procedure patented, where this has been appreciated by international boards, with: Diploma and Gold Medal (9), Silver (1), and Bronze (2) at the the British Invention Show, 2014 - London, International Young Invention Contest (IYIC) 2014 - Seoul, International Salon of Inventions and New Technologies „NEW TIME", Sevastopol - 2014 și 2013, Macao International Innovation and Invention Expo, China - 2014, International Engineering Invention and Innovation Exhibition, i-ENVEX Dewan Peperiksaan Pauh Putra, University Malaysia Perlis - 2014, European Exihibition of Creativity and Innovation EUROINVENT, Iasi - 2014 and 2013, International Exhibition of Research, Inovation and Invention, Cluj Napoca - 2014, National Exhibition with International participation of Research and Inovation Bacău - 2014, Ugal Invent Exhibition 2014 - Galati.

General conclusions, regarding the most important results obtained following the research made, are grouped in the two parts of the thesis, but they will be presented only in part II, Experimental Part.

## 10.4. The chemism of the surface waters from the hidrographic basins Siret and Prut

Concerning the study made on the collecting drainage basins Siret and Prut, realized on the basis on some chemical parameters (salinity, pH) and connected to the correlation between the nature of the geologic sublayer (underground and surface deposits) and the chemical composition of the surface waters, a series of very important conclusions have been drawn regarding the charge of these surface waters of the hydrographic basins, which have been used in the selection protocols of the ceramics involved in potabilization.

### 10.5. The evolution of the quality of the Suceava River between 2008-2010

Following the monitorisation of the three sections of the Suceava river between 2008-2010, a series of conclusions have been drawn regarding the evolution of the chemical and physical charge of this river, which have been also used in the selection protocol of the ceramics involved in potabilization.

### 10.6. The Monitorisation of the groundwater quality in the vulnerable places in Botosani county.

Concerning the information related to the values of the ground waters characteristics in the areas vulnerable to the pollution of the observing drainings or the monitrisation of the chemical charge in Botosani county, a series of conclusions have been drawn regarding the chemical and physical charge of this river which also have been used in the selection protocol of selection of the ceramics involved in potabilization.

### 10.7. The study of some domestic ceramics from burnt clay used for water potabilization

This chapter is, together with the last three, the most important for the thesis. The present study which was made on two lots of freshly made ceramic, industrial type ( bricks that come S.C. Brikston Iași) as well as industrial type ( pots that are burnt by pottery masters in Stavnic Schit) in order to select the optimal type from and acid-base criteria for the use in the chemoabsorption processes that take place in the final stage of filtration within the ground and surface waters treatment, has allowed that based on the fundaments of the ceramic materials science to select those types which can be used in water potabilization, taking into consideration some physical-chemical and morpho-structural characteristics.

The ceramic materials studied, unlike other filtration materials, have a series of advantages, among which we mention: the good mechanic resistence, acid-base chemical stability and rdox, thermical and photo-chemical stability, but also a big series of very important characteristics for these applications, such as: apparent density and specific weight, compression resistence, maximum quantity of absorbed water; frost cleftness or the phenomenon of mechanic deterioration, etc.

Another great advantage of the industrial or technical ceramics is represented by the minimum concentration in the soluble components in water systems, from this point of view, the granules used in treating waters are initially subject to some laundry processes by dispersion in containers with deionized water- light acid, these being previously kept in this environment for some minutes, after which the water is cleaned, and the ceramics are dried in warm air.

As we know, the ionic exchange capacity of the normal clay ceramic is due to the marginal hydroxidic Al–OH and to the acid ones of the type Si(Ti)–$O^-$ $H^+$, which confer them a certain caustic mode, which is given by the Si/Ti ratio. Also, an important role in purification is played by the granulites with a band structure, with a redoxite behavior, which lead through the electrons giving/receiving feed-back system to elimination of the chlorine traces from the water, which will pass through the $Hg^{2+}$, which passes through Hg(I) - precipitated, $Fe^{3+}$ passes in Fe(II) – precipitated etc.

The acid-base character, given by the marginal groupings varies within very large limits, from acid (pH = 4,5), to basic (pH = 9,5);

In order to determine the composition of every lot, we have taken a sample of various pieces of the two ceramic types. The elemental chemical composition and the interna structure has been determined through the technique of the electronic deflection, coupled with the X ray spectrometry (SEM-EDX), using the image of secondary electrons (SE) or retrodiffused (BSE). Then to these tests we have determined the free acidity, which has been correlated with the elemental chemical concentration evaluated based on the EDX spectra.

For the determination of the retention capacity of the $Fe^{3+}$ and $Al^{3+}$ ions by the two ceramic types ( industrial and traditional) we have used three groups of tests of various granulometries, indexed, as it follows: *industrial witness ceramic* ( not treated with chlorine hydride watery solution for unstable components solubilisation); *treated industrial ceramics with chlorine hydride watery solution 5M*; industrial witness ceramic (as well not treated with chlorine acid for the unstable components solubilization) and *treated traditional ceramic.*

The retention capacity of $Fe^{3+}$ and $Al^{3+}$ ions from the watery solutions of 0,5M has been done through the dispersion in 100 mL solution of 90 g ceramic granulesc, under light agitation at the room temperature, for 20 minutes, the we have determined the iron and residual aluminium quantity from the cleaned solution, using absorbtion atomic spectroscopie.

From the ceramics we have chosen in order to evaluate the chemo-absoption capacity of the $Fe^{3+}$ and $Al^{3+}$ ions the most acid samples, $CI_a$ and

$CT_a$, with the caustic module between 1,2 and 2,8. This experiment has validated the fact that the $Fe^{3+}$ and $Al^{3+}$ traces, which remained after treatment, have been eliminated with the help of untreated ceramic with granulometry of over 97%.

Based on these studies, the ecramics with the caustic module between 1,2 and 2,8 have been used for the retention through ionic exchange of other cations as well, considerate vulnerable to overpass the toxicity level, such as: $Hg^{2+}$, $Pb^{4+}$, $Pb^{3+}$, $Ni^{2+}$, $As^{3+}$ etc., but their results id not present a reproducibility, resembling that of $Fe^{3+}$ and $Al^{3+}$. This has been explained by the acid-base and redox action of these ceramics, differentiated by microgranules, in which the poliedric micro-structures of Si(IV), Ti(IV) and Fe(III), are dominating, which confer a behavior of ionic and redoxite exchange, which allows through retention the purification of some ions and molecular structures that remained after the potabilization processes, such as: molecular chlorine which is reduced to chlorine ion and a series of cations (Hg(I), Pb(II), As(III) etc.), retained by the ceramic. We would have expected a cumulative effect, but the non-homogenity of the surface and interior pits, responsible with the adorption and portance (transfer and elimination), did not allow the procurement of the desired results for all the cations

The study has allowed the selection of the optimal ceramics which can be used in the chemoabsoprtion processes from the final stage of filtration from the ground and surface water treatment for potabilization, respectively the acid graules noted $CI_a$ and $CT_a$,. These ceramics have been the basis of the elaboration of a new procedure of potabilization of waters using the existing city or municipal stations.

## 10.8. Involving ceramic materials in surface and groundwaters potabilization. Elaboration of a new process

Concerning the new process for surface and ground water treatment, which is the object of the two inventions patents, which in the final stage, after the final filtration with coal uses a constructive and functional system resembling the other two rapid filtration steps, with ceramic granules disposed in successive layers with the aprox thickness of around 200 mm for the granules sort between 10,0 şi 20,0mm and respectively of around 50mm for those between 0,5 and 2,0mm, thus, on the supporting grill, backed up by the longitudinal collecting channles from the bottom of the filtration basin, is firstly arranged the first sort of granules (10,0...20,0mm) in a thick layer of aprox. 200mm, then second layernof aprox. 100mm from the second sort (5,0...10,0mm), the following thick of 50mm with the third sort (2,0...5,0mm) and the last one thick of aprox.

50mm with the finest sort (0,5...2,0mm). As a filtrating layer, we have used granules of normal ceramics $CI_a$ and $CT_a$, with open porosity through breaking, offering a global porosity between 40 and 55%. These are obtained from the industrially burnt brick falls by breakdown, fine divisation and sorting on four levels with the help of some vibrating bevelling vibrators, having the loops of 0,5; 2,0; 5,0; 10,0 and 20,0mm. The ceramic granules have been washed separately on the four sorts (0,5...2,0mm; 2,0...5,0mm; 5,0...10,0mm and 10,0...20,0mm) by immersion and agitation in deionized water, for as long as 20...30min, than 5%) and finally they are packed in paper, gunny, raffia, or polimeric fibers bags,interwoven and transported t apoi sunt esorate şi uscate (conţinutul de the treating station.

So, in the final filtration basin, after settling the supporting grills on the mud collecting channels, and closing the "too full" hatch, the ceramic granules have been disposed on the for gradually disposed layers, in ascending order of the diameters from the surface to the base.

The new treating process of underground and surface waters for the potabilization brings a new series of novelties which allowed us to revendicate them, being patented with AGEPI Chişinău and in course of patenting with OSIM Bucureşti.

## 10.9. Mathematic shaping of the spaciou-temporal evolution of the physical- chemical charge of the surface waters as a "river" type system.

This shaping study has led to the elaboration of a mathematic model of the evolution of the fluor ions charge, composed from the geometrical attributes of the area studied, the forces that act in the field and the physical characteristics. From the conceptual model, two other numeric models have been generated, for the prediction of the distribution of the fluoride anion, which have been applied on a sector of the Prut river in the city of Ungheni.

## 10.10. Personal conttributions

When elaborating the doctor's thesis we have taken into account more groups of objectives which have been wholly accomplished, such as: bibliographic analysis and synthesis based on which we have elaborated the experimental objectives of the thesis and the working protocls, with original contributions.

Starting with the first year of the stage for the preparation of the thesis, we have made a great number of documentation mobilities in the field and experiments, initially at the monitoring points of the groundwaters through drainage and to those od water sampling from the rivers bottoms from the hydrographic basins Siret and Prut, with a focus on Suceava and Prut river in Botosani. Then we have made the literature study in the Chemistry Library– Syscom 18, Bucharest and experiments in the Laboratory of Ecological Chemistry of the Chemstry Institute of the Science Acadamy of Moldova and the three laboratories of the „Alexandru Ioan Cuza" University in Iaşi ( The Scientific Investigatipn Laboratories and the Geoarheology from the Interdisciplinary ARHEOINVEST platform and the Hydrology Laboratory of the Geography- Geology Faculty and the Analytical Chenistry of the Chemistry Faculty). In parallel, we went and took samples of burnt clay ceramic from S.C. Brikstone Iași and the potters from the Stavnic Schit, com. Voinești, jud. Iași, which have been chemically, physical-structural and morphological analysed, and in the base of the caustic mode, we have studied the ionic exchange capacity and the redoxidic one for the elimination of some ions and molecular structures wity retention in drinking water (remained after the treatment processes). These final studies have been made in the Scientific Investigation Laboratory of the interdisciplinary Platform for Education and Research ARHEOINVEST. During the research, we have elboarted a new procedure for treating the surface and groundwaters in order to be patented.

Also, during the preparatory and elaboration period of the doctor's thesis, within more mobilities for the experimentation, we have undergone various trainings on certain techniques, based on which we have made a series of analysis.

Concerning the practical objectives, which subscribe to the present reserach directions of reserach emphasized in the documentary synthesis, we have realised a series of experiments, rigourouslly elaborated and with a careful processing of the results obtained from which I will mention the following: the selection of the geographic areas by including in the research activities the wells/ drains for monitoring the evolution of ground waters and the prelevation points from the riverbeds in the hydrograohic basins Siret and Prut; selecting some methods and techniques for determining on one side the chemical and physical-structural of the ceramic materials, and on the other side the indicators regarding the chemical charge, microbiological and physical- mechanical of the ground and surface waters, together with the limits of the optimal parameters of the potabilized waters; the elaboration and the practical realization of a treatment technology for the surface and groundwater for potabilization, patented by AGEPI Chișinău and now in course of being patented by OSIM Bucharest; the evaluation of the impact of the selected ceramic materials following the research regarding chemicak nature, physical structure and the morphology of granules, on the capacity of retaining the $Fe^{3+}$and $Al^{3+}$, which remain after the coagulation- flocculation processes from treating. The processing of the experimental data and writing of scientific paperwork and inventions patents.

The obtained information within the experimental part have generated a series of conclusions connected to the novel contributions of the research, from which one as pioneer which as: the ceramics with caustic mode between 1,2 and 2,8 have been used also for the ionic exchange of other cations, considered vulnerable to overcome the toxicity level, such as: $Hg^{2+}$, $Pb^{4+}$, $Pb^{3+}$, $Ni^{2+}$, $As^{3+}$ etc., but the results of which did not present reproducibility, resembling the $Fe^{3+}$ and $Al^{3+}$. This has been explained by the acid-base and redox action of these ceramics, differentiated in microgranules, where the poliedric microstructures of Si(IV), Ti(IV) and Fe(III) are dominating, which give a behavior as ions and redoxite exchange, which allow through retention, etc., the purification of some ions and molecular structures which remained after the potabilization processes, such as: molecular chlorine which is reduced from chlorine ion and a series of cations ($Hg^{2+}$, $Pb^{3+}$, $Pb^{4+}$, $As^{5+}$ etc.) which are reduced to structures hard soluble (Hg(I), Pb(II), As(III) etc.), detained by ceramic. We would have expected a cumulative effect, but the non-homogeneity of the surface and interior pits, responsible for adsorption and portance (transfer and elimination), did not allow to obtain the desired results for all cations

## Perspective directions

Based on the results obtained, throughout the reserach for the elaboration of the thesis, we have open new directions in the developping of this field.

A special attention has been given to ceramic materials made aut of burnt clay, with dominant micro-structures dominated by nanopoliedres with generating ions on basis Si(IV), Ti(IV) and Fe(III), which give acid-base processes of ionic exchange and redoxite, which allow the elimination of some ions and various undesirable molecular structures, remained after the potabilization operations.

The great perspective of these materials is represented the eliminations of the cations $Fe^{3+}$ and $Al^{3+}$, which remain in water after the coagulation- floculation processes from the treatment within the potabilization stations, which in the drinking water causes through accumulation in human body a series of chronicle diseases (for example: Alzheimer).

The continuation of the research will allow the elaboration of small autonomous stations, for each neighbourhood of individual, or of some domestic devices which will be patented in very many countries and will ope directions for research in partnership.

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