VERSITA 10.2478/auoc-2013-0022
Ovidius University Annals of Chemistry Volume 24, Number 2, pp. 131-137, 2013

The framing of the raw materials used for manufacturing some rough ceramic materials into polinary oxide systems

Anna-Maria SZŐKE

University Babeş-Bolyai, Faculty of Environmental Science, Extension Sf.-Gheorghe, Romania

Abstract. In this paper it is presented the framing into polinary oxide systems in the case of optimal design of the oxide composition for obtaining raw ceramic materials. These calculations were carried out on two raw materials, which were the base of the experimental researches, for finding out the potential mineralogical composition. It was also followed, for the two raw materials, the framing options of the composition in oxide systems and the assessment of their belongings to possible subsystems.

Keywords: ceramic masses, oxide systems, sewage sludge

1. Introduction

Wastewater treatment plants produce a great amount of sewage sludge, which in the future cannot be deposited according to EU Directive 2008/98/EC [1]. Concerns for the removal of these residues in the environment without damaging the ecosystem are multiple. One solution is recycling or reusing them. During the recent years, alternative attempts of reusing various types of waste have been made, including the incorporation of products in ceramic clay [2,3,4,5]. Raw materials with heterogeneous chemical and mineralogical composition can be used in ceramic industry. These materials are formed by clay raw materials with a very wide range composition. For this reason, this industry sector is suitable for valuation and use of sewage sludge coming from wastewater treatment plant.

This work offers an alternative for wastewater sludge disposal by incorporating of this in ceramic materials. The objective of our research is to investigate the framing options of the composition in oxide systems and to assess their belongings to possible subsystems.

2. Experimental

Materials used in the present study are local clay from area Bodoc and sewage sludge from the wastewater treatment plant in Sfantu-Gheorghe, Covasna county, Romania.

These were mixed to obtain the corresponding masses of raw bricks. In our experiments, we used various proportions of sludge (5- 20 %) in the production of building ceramics.

The two mentioned raw materials have a complex oxide composition. The oxide compositions of these raw materials and the losses from the calcinations are mentioned in **table 1.**

Oxide composition was determined SR EN 771/1-2003 from Bodoc clay and STAS 9163-1:73 from sewage sludge, by using the classical wet chemistry method, the main oxides being quantified.

It is noticeable that for the Bodoc clay the main oxide is the silica (71%), followed by alumina (16%) and iron trioxide (5%). The alkaline earth oxides (CaO and MgO) are under 4% and the alkaline ones (K_2O and Na_2O) a bit over 4%-**table 2**.

Based on the chemical analyses of the sewage sludge there can be seen the high percent of SiO_2 (14.06%), CaO (13.32%), Al_2O_3 (3.97%), Fe_2O_3 (1.43%). It also has a content of 3.07% of P_2O_5-**table 3.**

To take down the number of alkaline and alkaline earth oxides, the oxide in a certain category in lower quantity should be calculated as equivalent of the main oxide in that category.

ISSN-1223-7221

Table 1. Oxide chemical composition of raw materials before processing

Nr.	Oxide	Bodoc clay, % wt	Sewage sludge, % wt
1.	SiO_2	67.97	14.06
2.	Al_2O_3	15.41	3.97
3.	Fe_2O_3	4.88	1.43
4.	CaO	1.66	13.32
5.	MgO	1.59	0.73
6.	K_2O	2.43	-
7.	P_2O_5	-	3.07
8.	Na_2O	1.54	0.87
9.	MnO	0.13	0.03
10.	TiO_2	0.81	0.28
11.	P.C.*	-	62.24

P.C.*- loss at calcinations at 1000°C

For example, the calcinated Bodoc clay is composed by seven oxides placed in **table 2** in decreasing order. By similarity the magnesium oxide can be transformed by the equivalent into calcium oxide and finally have a bigger quantity of calcium oxide which contains the magnesium oxide too. The same can be done in the case of the alkaline oxides: the sodium oxide, being in lower quantity is recalculated in equivalent of potassium oxide. As a result, finally the total potassium oxide rises with the quantity of the sodium oxide through equivalence. So, from seven oxides, the list dropped to five oxides.

Table 2. The composition of the calcinated Bodoc clay

Nr.	Oxide	Concentration, % wt.	Calcinated clay, % wt.
1.	SiO_2	71.19	70.15
2.	Al_2O_3	16.14	15.90
3.	Fe_2O_3	5.11	5.03
4.	CaO	1.74	4.00
5.	MgO	1.66	--
6.	K_2O	2.55	4.92
7.	Na_2O	1.61	--
Total		100.00	100.00

Table 3. The oxide composition of the calcinated sewage sludge

Nr.	Oxide	Calcinated sludge, %
1.	SiO_2	37.54
2.	Al_2O_3	10.60
3.	Fe_2O_3	3.82
4.	CaO	35.57
5.	MgO	1.95
6.	P_2O_5	8.20
7.	K_2O	--
8.	Na_2O	2.32
Total		100.00

Table 4. Framing the composition of the Bodoc clay in oxide systems

Nr.	Oxide System	Concentration, % wt					The Subsystem they belong to
		K_2O	CaO	Fe_2O_3	Al_2O_3	SiO_2	
1.	K – A- S	5.41	--	--	17.48	77.11	S- A_3S_2- KAS_6
2.	C – A - S	--	4.44	--	17.66	77.90	S- A_3S_2- CAS_2
3.	F – A - S	--	--	5.52	17.46	77.02	S- A_3S_2- F
4.	K - C – A - S	5.18	4.21	--	16.74	73.87	S- A_3S_2- KAS_6- CAS_2
5.	K – F – A - S	5.13	--	5.24	16.56	73.07	S- A_3S_2- KAS_6- F
6.	C – F – A - S	--	4.21	5.29	16.72	73.78	S- A_3S_2- CAS_2- F
7.	K–C– F– A- S	4.92	4.00	5.03	15.90	70.15	S- A_3S_2- KAS_6- CAS_2- F

Note: K = K_2O; C = CaO; A = Al_2O_3; F = Fe_2O_3; S = SiO_2; A_3S_2 – mullite; KAS_6 – orthose; CAS_2 – anorthit.

Table 5. The potential mineralogical composition of the Bodoc clay in seven oxide versions

Nr.	Oxide system/nr. figure	Concentration, % wt				
		S	A_3S_2	KAS_6	CAS_2	F
1.	K – A- S / **Fig. 1**	51.94	16.24	31.82	--	--
2.	C – A – S / **Fig. 2**	64.61	13.30	--	22.09	--
3.	F – A – S / **Fig. 3**	70.16	24.32	--	--	5.52
5.	K - C – A – S / **Fig. 5**	43.75	4.83	30.47	20.95	--
6.	K – F – A – S / **Fig. 6**	49.20	15.38	30.18	--	5.24
7.	C – F – A – S / **Fig. 7**	61.18	12.58	--	20.95	5.29
8.	K– C– F– A- S	41.53	4.60	28.94	19.90	5.03

The two main oxides in the composition of the clay are the silica and the alumina. For this reason, there will be chosen those ternary and quaternary types of oxide systems, in which besides the two mentioned oxide there are a third and a fourth oxide. So, three types of ternary systems, three types of quaternary systems and one of five oxides can be obtained. The mentioned data are indicated in **Table 4** and **Table 5**.

A very attentive correlation was made among the properties of the raw materials, of their mixture and the final properties of the manufactured ceramic product. To find out the potential mineralogical components there were used thermal equilibrium diagrams in simpler systems: ternary and quaternary ones, which can be graphically represented both in the plan and in the space [

The quantities of minerals were calculated from K_2O=K, CaO=C, Al_2O_3=A, Fe_2O_3=F, SiO_2=S. We solved the system of equations derived from partial balance of ingredients mentioned above.

A ternary systems (it is often called a Gibbs triangle) is a barycentric plot on three variables which sum to a constant. It graphically depicts the ratios of the three variables as positions in an equilateral triangle. Every point on a ternary plot represents a different composition of the three components.

The ratios of the three species in the composition are estimated based on the phase diagram grid. The concentration of each species is 100% (pure phase) in its corner of the triangle and 0% at the line opposite it. The percentage of a specific species decreases linearly with increasing distance from this corner. By drawing parallel lines at regular intervals between the zero line and the corner, fine divisions can be established for easy estimation of the content of a species. For a given point, the fraction of each of the three materials in the composition can be determined by the first. This method can be extended to quaternary or multi-component mixtures [6, 7, 8].

.3. Results and Discussion

The Bodoc clay sampled as A_1, in the case of ternary system K_2O-Al_2O_3-SiO_2 is situated in ternary elementary subsystem S-A_3S_2-KAS_6 (silica-mullite-orthose), according to **Fig.1.**

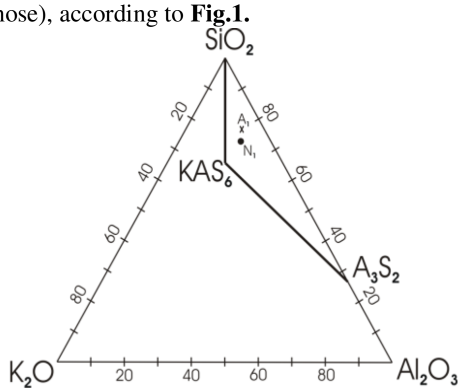

Fig. 1. Clay A_1 and sewage sludge N_1 in ternary system K_2O-Al_2O_3-SiO_2

The $\mathbf{A_1}$ clay and the $\mathbf{N_1}$ sewage sludge are included in elementary subsystem S-KAS_6-A_3S_2 (silica orthose-mullite) belonging to ternary system K_2O-Al_2O_3-SiO_2. So K_2O, is connected to Al_2O_3 and SiO_2 as orthose. One part of alumina together with the corresponding quantity of silica form the mullite and the rest of the silica stays in original form. Similarly it can be found that in ternary system **CaO-**$\mathbf{Al_2O_3}$**-**$\mathbf{SiO_2}$ the $\mathbf{A_2}$ clay is in silica-mullite-anothit subsystem, in spot A_2, as seen in **Fig. 2.**

The first two potential mineralogical compounds are maintained (silica and mullit) and the calcium oxide is totally enclosed in anorthite.

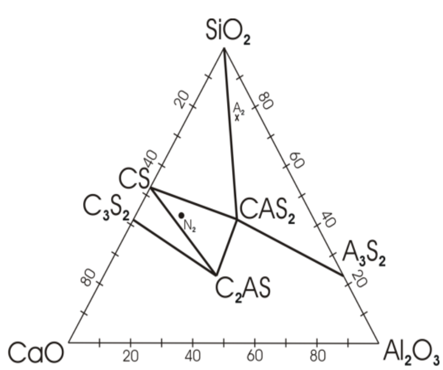

Fig. 2. The $\mathbf{A_2}$ clay and the $\mathbf{N_2}$ sewage sludge in ternary system CaO-Al_2O_3-SiO_2

The $\mathbf{A_2}$ clay is located in S-CAS_2-A_3S_2 (silica-anorthite-mullite) subsystem, and the $\mathbf{N_2}$ sewage sludge in CS-CAS_2-C_2AS (wollastonite- anorthite - ghelenit) subsystem.

In the third ternary system $\mathbf{Fe_2O_3}$**-**$\mathbf{Al_2O_3}$**-**$\mathbf{SiO_2}$, the total alumina can be found together with the silica as mullite and in addition there is free silica and the whole free iron trioxide. The Bodoc clay marked $\mathbf{A_3}$ and the $\mathbf{N_3}$ sewage sludge belong to S-F-A_3S_2 (silica-iron trioxide-mullite) elementary subsystem –see **Fig. 3.**

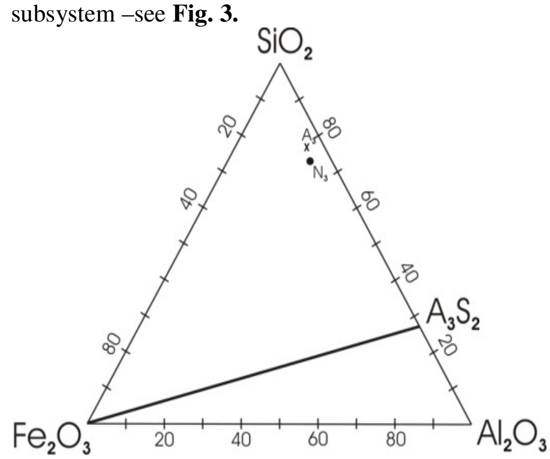

Fig. 3. The $\mathbf{A_3}$ clay and the $\mathbf{N_3}$ sewage sludge in ternary system Fe_2O_3-Al_2O_3-SiO_2

The elementary ternary system $\mathbf{K_2O}$**-CaO-**$\mathbf{SiO_2}$ is not important for the clay, which must contain simultaneously alumina and silica (it is formed, as it is known by hydrated aluminosilicate), **Fig. 4**

The $\mathbf{N_4}$ sewage sludge is located in CS-C_3S_2-KCS (wollastonite-rankinit-double ortosilica of potassium and calcium) subsystem.

Uniting the first two ternary systems along the common side $\mathbf{Al_2O_3}$**-**$\mathbf{SiO_2}$ the $\mathbf{K_2O}$**-CaO-**$\mathbf{Al_2O_3}$**-**$\mathbf{SiO_2}$ quaternary system is obtained, where can the analysed clay moves from the basic plan (spot A_2) to the point of the potassium oxide K=5,18% (at spot $\mathbf{A_5}$) from **Fig. 5**. The elementary subsystem is silica, mullite-anorthit-orthose). The $\mathbf{A_5}$ clay is located in S-A_3S_2-KAS_6-CAS_2 subsystem (silica-mullite-orthoze-anorthit), and the $\mathbf{N_5}$ sewage sludge in CS-C_3S_2-C_2AS-KC_3S_6 (wollastonite-rankinite-ghelenit-potassium devitrit) subsystem.

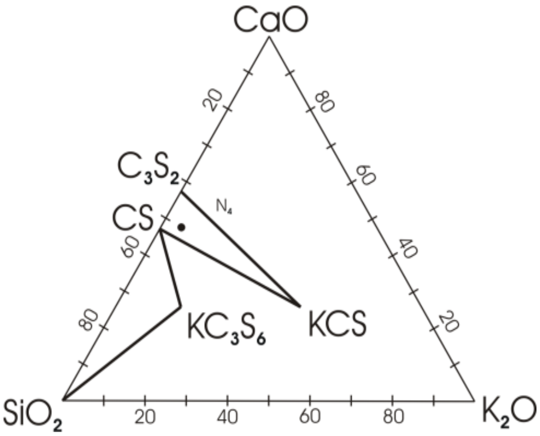

Fig. 4. The position of N_4 in ternary system K_2O-CaO-SiO_2**.**

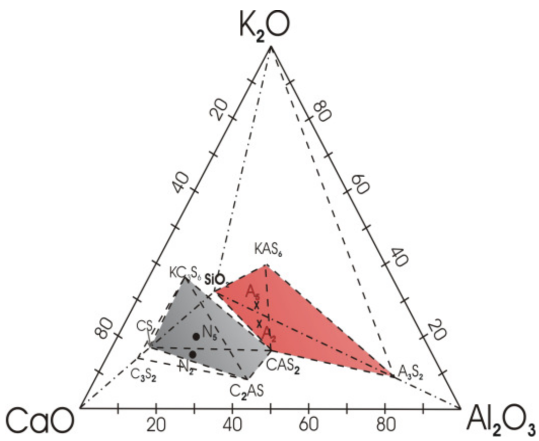

Fig. 5. The position of A_5 clay and of the N_5 sewage sludge in K_2O-CaO-Al_2O_3-SiO_2 quaternary system

Passing to **K_2O-Fe_2O_3-Al_2O_3-SiO_2** quaternary system we get in the same way the spot **A_6**, meaning spot **A_1** raised to the level of Fe_2O_3= 5,24 %. It belongs to the elementary subsystem silica-mullite-orthoza-iron trioxide, **figure 6.** The **A_6** clay and the **N_6** sewage sludge are located in the same S-KAS_6-A_3S_2-F (silica-orthose-mullite-iron trioxide) subsystem.

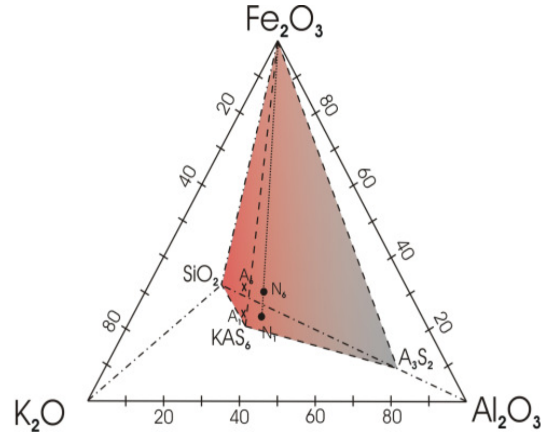

Fig. 6. The position of **A_6** clay and of the **N_6** sewage sludge in quaternary system K_2O-Fe_2O_3-Al_2O_3-SiO_2

The last quaternary system **CaO-Fe_2O_3-Al_2O_3-SiO_2** from **Fig. 7**, gives the position of the clay in the basic plan **CaO-Al_2O_3-SiO_2** (spot A_2), respectively at the level of Fe2O3= 5,29 %, meaning spot A_7.

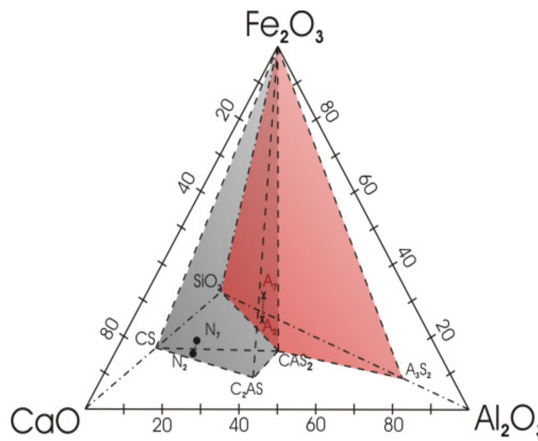

Fig. 7. The position of **A_7** clay and **N_7** sewage sludge in quaternary system CaO-Fe_2O_3-Al_2O_3-SiO_2.

The clay **A_7** is located in S-CAS_2- A_3S_2-F (silica-anorthit-mullite-iron trioxide) subsystem, and the **N_7** sewage sludge in another subsystem: CS-C_2AS-CAS_2-F (wollastonite- ghelenit- anorthit-iron trioxide).

In the last version, that one with five oxide, it is difficult to locate the Bodoc clay, but it is possible to calculate the potential mineralogical position, as seen in **table 5**.

In the case of the Bodoc subject on heat treatment, in the condition of reaching a balanced mineralogical composition (an ideal case), the components from **table 5** can be noticed. The silica react with other oxides, theoretically forming mullite, orthose and anorthite, but it can be found also alone. On the other hand the iron trioxide stays in free state and plays the role of a fondant (it takes down the temperature of the liquid phase in the system).

In a similar way, the framing of sewage sludge composition was done in eight versions and the results were the following.

The sewage sludge provided by the waste water plant from Sfantu-Gheorghe town has the same complex oxide composition. Unlike the Bodoc clay it does not contain potassium oxide but it has another oxide present: P_2O_5.

To harmonize the compositions of the two raw materials we proceeded as it follows from **table 3** (the P_2O_5 being expressed as potassium oxide equivalent). So the clay and the sewage sludge practically contain the same oxide, but in different proportions.

Table 6. a – Versions of framing of the sludge in oxide systems

Nr.	Oxide system/nr.fig	Concentration, % wt					The subsystem they belong to
		K_2O	CaO	Fe_2O_3	Al_2O_3	SiO_2	
1.	K –A-S/fig. 1	6.83	--	--	20.53	72.64	S-A_3S_2-KAS_6
2.	C –A-S/fig. 2	--	44.31	--	12.27	43.42	CS-CAS_2-C_2AS
3.	F –A-S/fig. 3	--	--	7.34	20.42	72.24	S-A_3S_2-F
4.	K–C–S/fig. 4	4.44	48.26	--	--	47.30	CS-C_3S_2-KCS
5.	K–C–A-S/fig. 5.	3.92	42.57	--	11.79	41.72	CS-C_3S_2-C_2AS-KC_3S_6
6.	K–F–A-S/fig. 6	6.36	--	6.88	19.12	67.64	S-A_3S_2-KAS_6-F
7.	C–F–A-S/fig. 7	--	42.44	4.23	11.75	41.58	CS-CAS_2-C_2AS-F
8.	K–C–F–A-S	3.76	40.84	4.07	11.31	40.02	CS-C_3S_2-C_2AS-KC_3S_6-F

Note: K= K_2O; C= CaO; A= Al_2O_3; F= Fe_2O_3; S= SiO_2;
A_3S_2-mullite; CS–wollastonite; KAS_6 –orthose; CAS_2–anorthit; C_2AS–ghelenit;
C_3S_2-rankinit; KCS – double ortosilica of calcium and potassium; KC_3S_6- potassium devitrit.

Table 6. b- The potential mineralogical composition of the sludge in six oxide versions

Nr.	Concentration, % wt									
	S	A_3S_2	KAS_6	CS	CAS_2	C_2AS	F	C_3S_2	KCS	KC_3S_6
1.	41.46	18.36	40,18	--	--	--	--	--	--	--
2.	--	--	--	66.91	7.42	25.67	--	--	--	--
3.	64.22	28.44	--	7.34	--	--	7.34	--	--	--
4.	--	--	--	69.12	--	--	--	20.97	9.91	--
5.	--	--	--	20.86	--	31.69	--	21.49	--	25.96
6.	38.62	17.09	37.41	--	--	--	6.88	--	--	--
7.	--	--	--	64.08	7.08	24.60	4.23	--	--	--
8.	--	--	--	19.95	--	30.40	4.07	20.68	--	24.90

Note: K=K_2O; C=CaO; A=Al_2O_3; F=Fe_2O_3; S= SiO_2;
A_3S_2-mullit; CS–wollastonite; KAS_6–orthose; CAS_2–anorthit; C_2AS–ghelenit; C_3S_2- rankinit; KCS– double ortosilica of calcium and potassium; KC_3S_6- - potassium devitrit

The methodology for the examination of the oxide and mineralogical composition of the treated sludge in the eight versions (four ternary systems, three quaternary ones and that with five oxide) was similar to the examination of the Bodoc clay. An exception is the ternary system **K_2O-CaO-SiO_2** used just for the sludge, its position being given by spot **N_4** located in elementary subsystem **CS- C_3S_2- KCS** wollastonite-rankinit-potassium devitrit. (see **figure 4**).

In the case of the ternary system **K_2O-Al_2O_3-SiO_2** the **N_1** sludge is included in the same subsystem with the Bodoc clay, silica-mullite-orthose, see **figure 1**.

Unlike the previous, the CaO-Al_2O_3-SiO_2 ternary system is located in the spot N_2, as seen in **Fig. 2**, because of high concentration in CaO and very low SiO_2, comparing to the Bodoc clay.

In figure 3. which contains the ternary system **Fe_2O_3-Al_2O_3-SiO_2**e the common belonging of the clay and of the sludge to the elementary subsystem **S-A_3S_2-F** (silica-mullite-iron trioxide) can be observed.

In the case of the three quaternary oxide systems, just at one of them: **K_2O-Fe_2O_3-Al_2O_3-SiO_2**, both raw materials are located in the same elementary subsystem: **S-A_3S_2-KAS_6-F** (silica-mullite-orthose-iron trioxide) in spots **A_6** and **N_6**, (**Fig. 6**).

The other two quaternary systems: **K_2O-CaO-Al_2O_3-SiO_2** (**Fig. 5**.), and **CaO-Fe_2O_3-Al_2O_3-SiO_2** (**Fig. 7**.) contain the clay and the sludge in different oxide subsystems.

Framing the Bodoc clay and sludge into oxide systems based on the harmonization of the two raw materials compositions, it shows their compatibility. Both Bodoc clay and sewage sludge basically contain the same oxides, but in different proportions, as are noticed in **table 6.a**. and **table 6.b**.

4. Conclusions

It is noticeable that in the Bodoc clay subject the main oxide is the silica (71%), followed by alumina (16%) and iron trioxide (5%). The alkaline earth oxides (CaO and MgO) are under 4% and the alkaline ones (K_2O and Na_2O) just over 4%.

The sewage sludge provided by the waste water plant from Sfantu-Gheorghe town has the same complex oxide composition.

Based on the chemical analyses of the sewage sludge it was noticed the high percent of SiO_2 (14.06%), CaO (13.32%), Al_2O_3 (3,97%), Fe_2O_3 (1.43%). In addition, it contains 3.07% wt P_2O_5.

The framing of the Bodoc clay and of the sewage sludge in oxide systems, based on the harmonization of the compounds of the two raw materials suggests their compatibility. Both the Bodoc clay and the sludge practically contain the same basic oxide but in different proportions.

5. References

* E-mail address: mariszoke@yahoo.com

[1].***www.arpm7c.ro/documents/planuri/PRGD.pdf, (2006)

[2] S.R. Teixeira, G.T.A. Santos, A.E. Souza, P. Alessio, S.A. Souza and N.R. Souza, Applied Clay Science, **53**(4), 561-565, (2011)

[3] M.Geri´c, Gajski G., Anin V. O., Kollar R. and Garaj-Vrhovac V., Journal of Environmental Science and Health Part A, **47**, 1521–1527, (2012)

[4]. M.Devant, Cusidóa J.A. and Soriano C., Applied Clay Science, **53**(4), 669-675, (2011)

[5]. El-Fadaly E.,. Bakr I. M, Abo Breka M.R., Journal of American Science, **6**(10), 241-247, (2010)

[6]. S. Solacolu, *Physical chemistry of silicates techniques (In Romanian)*, Second Edition, Ed. Tehnica, Bucharest, (1968)

[7]. Em. A. Bratu*, Operations and equipment in chemical industry, (In Romanian)* Vol. II, Ed. Tehnica, Bucharest, (1970)

[8]. D. Becherescu, V. Cristea, I. Menessy and Fr. Winter, *Solid state chemistry*, vol. II, Ed. Stiintifica si Enciclopedica, Bucuresti,(1987)

Submitted: September 25th 2013
Accepted in revised form: November 22th 2013