Kinetic and energetic aspects of the reaction between sodium carbonate and lateritic kaolinite

C.J. Ngally Sabouang, M. Signing Nganda, T.B. Makon, J.A. Mbey[*], Liboum, D. Njopwouo

University of Yaoundé 1, Department of Inorganic Chemistry, P.O. Box 812 Yaoundé, Cameroon

ABSTRACT

This study reports some kinetic and energetic considerations of the firing of a mixture of a kaolinite laterite with sodium carbonate as a precursor for geopolymerization. The variation of the firing temperature, the sodium carbonate/kaolinite ratio and the mixing way, show that, for a sodium carbonate/kaolinite ratio of 1.5, the reaction kinetic is optimal at 660 °C with a reaction progress of 80 %. Previous mixing with water and previous firing of the kaolinite soil slowdown the reaction. For firing at 660 °C, an attempt to evaluate the energy consumption was done and it is found that, for the preparation of 1 kg of precursor, the energy consumption is 216 kJ.

1. Introduction

Cementitious materials are of great importance in building and construction. They are mainly prepared from earth material after thermal and/or chemical treatment. Portland cements are the most commonly used materials. The environmental issues associated to the production of Portland cement are now driving the research towards the production of alternative cementitous material. Geopolymers are one of the most investigate alternative cements products. The geopolymerization is usually done through chemical route involving the use of strong bases at high concentration for silico-aluminate preparation that are involved in the formation of the geopolymer network. Kaolinites are commonly used materials for this purpose after conversion into meta-kaolinite through thermal treatment at 700-750 °C [1, 2]. The use of some mineral ashes from the combustion of various organics compounds and volcanic ashes are also investigated [3]. Most of the research is focused on the identification of new materials for geopolymer production and the evaluation of the mechanical performance of the products rather than on the fundamental aspects affecting or accompanying the reaction.

The reaction of kaolinite with salts at temperature lower than 600 °C is reported by Heller-Kallai (1978) [4]. In this study, the authors report that the reaction of the alkali metal salt with kaolinite lead to the formation of modified amorphous metakaolinite phase incorporating the alkali metal without the formation of detectable metakoalinite as intermediate. The products of such reactions are of interest in ceramic and cement. This study is a pioneer work that establishes fundamental information on the intermediate phase formed in the thermal treatment of kaolinite in the presence of alkali salt. This intermediate can be used in geopolymers or in ceramics production. It is well established that fundamental studies in the comprehension of reactions involved in cement or ceramics from clayey materials are still challenging due to the variety of initial raw clayey materials involved, their heterogeneity and to the fact that equilibrium is rarely achieved given that preparation conditions are open and the influence of associated minerals is difficult to identify and separate from the global observations.

In the present study, we are focused on the optimization of the reaction of a kaolinite soil with sodium carbonate for the production of silico-aluminate as a precursor for geopolymerization. The considered aspects are the kinetic and the energy consumption. The temperature and the sodium carbonate amount are investigated

as parameters affecting the kinetics of the reaction. The energetic aspect is evaluated through the calculation of the energy consumption for the optimal reaction progress.

2. Materials and methods
2.1. Materials and samples preparations
The material used is a kaolinite of a laterite soil collected atMessamendongo (Yaoundé – Cameroon). Its chemical and mineralogical composition are given in table 1 and the kaolinite content estimated from both chemical and thermal analyses, is 63 % [5]. The material was crush and sieved at 100 μm.

Table 1: Chemical and Mineralogical composition of the soil used

Oxides	Percentage	Minerals	Percentage
SiO_2	46.42	Kaolinite	63.0
Al_2O_3	25.29	Quartz	17.0
Fe_2O_3	14.95	Microcline	2.0
MnO	0.05	Goethite	15.0
MgO	0.08	Titanium oxide	1.2
CaO	<dl*	Florencite	0.7
Na_2O	<dl	Zircon	0.5
K_2O	0.20		
TiO_2	1.15		
P_2O_5	0.13		
LOI	11.08		
Total	99.70		99.4

*dl: detection limit

The sodium carbonate used is an analytical grade product from PROLABO and it was used as purchase. 1 g of the kaolinite soil and 0.5g of sodium carbonate was dry mixed using a Selecta mixer for 30 min at a rate of 12 rpm/min.

For the humid mixture, the carbonate was dissolved in distilled water with a minimum amount of water and the laterite was added to obtain a paste that was further dried in an oven at 105 °C for 24 hours. The obtained pellet was then used as the reactive mixture. The humidification is used as a way to allow better diffusion of carbonate within the kaolinite soil and a comparison between humid and dry mixture reactivity was done. For the dry mixture, the laterite sample and the sodium carbonate were ground together in a mortar to obtain a mixed powder sample. The influence of the temperature and the sodium carbonate/clay ratio were investigated as well as the influence of a previous thermal treatment of the lateritic kaolinite prior to reaction. The temperature of thermal treatment was taken as the temperature of maximum reaction progress from the influence of the temperature on the reaction.

The reactions were carried out in ceramic crucible previously heated at 900 °C and kept dried over silica in a desiccator. A muffle furnace with temperature controlled of ± 5 °C was used.

II.2. Experimental set up for kinetic study
The study focused on the heterogeneous solid-solid reaction between kaolinite and sodium carbonate. The study temperature range was taken from 500 °C to 700 °C, to avoid sodium carbonate melting and its reaction with silica [6].

The X-ray analysis (not presented) of fired product of a mixture of kaolinite soil with excess sodium carbonate at 700 °C during two hours in a muffle furnace indicates the formation of sodium silico-aluminate. Sodium ferrite that was also expected at this temperature was not observed. The iron content in the chemical analysis was assumed to be both from structural iron within the kaolinite layer and from low reactive iron oxide up to 700 °C. From this, it was assumed that the main reaction was the reaction of kaolinite with sodium carbonate at temperature lower than 700 °C. The considered reaction is given bellow:

$$Al_2O_3.2SiO_2.2H_2O(s) + Na_2CO_3(s) \longrightarrow Al_2O_3.2SiO_2.Na_2O(s) + CO_2(g) + H_2O(g) \qquad (1)$$

In order to follow up the reaction of conversion of the kaolinite soil, the measurement of the unreacted sodium carbonate was monitored. The unreacted carbonate was extracted by dissolution with distilled water of the unreacted sodium carbonate follow by a filtration. After Beman (1922)[7], the hydrolysis of sodium ferrite in water produced soda that should be taken in account during titration by HCl. Alexéev (1980)[8] proposed two methods for a titration of a mixture of sodium carbonate and soda. The method used was the precipitation of carbonate. Two identical portions of the solution was taken. The first was used to titrate with HCl using heliantine as the indicator and the other portion was used to precipitate carbonate in presence of

Baryumchloride. Without filtrating, the solution was then titrated in presence of phenolphthalein using HCl. In the first titration, the volume V1 of HCl used was the volume needed for the titration of both carbonate and Soda. In the second titration, the volume V2 of HCl used was only associated to soda. Hence the difference V1 – V2 give the amount of HCl for the titration of carbonate.From this volume, the amount of unreacted sodium carbonate is calculated (m_1) and the difference to the initial amount (m_i) of carbonate leads to the amount of carbonate that has reacted ($m_2 = m_i - m_1$). From reaction equation (1) the amount of carbonate needed for the total reaction (m_o) can be calculated and hence, the reaction progress(α) is calculated as followed:

$$\alpha = (m_i - m_1)/m_o \tag{2}$$

From the reaction equation (1), using an ideal kaolinite molecular formula with a molar mass of M = 258.2 g/mol and sodium carbonate with M = 105.99 g/mol, the needed amount of sodium carbonate for total reaction is $m_o = 0.41$g, therefore sodium carbonate is in excess when 0.5g is used.

2.3. Thermodynamic consideration

The calculations of the energy needed for the preparation of 1 kg of sodium silico-aluminate is done based on the Kirchoff laws for the calculation of the heat needed to increase the reactants temperature from room temperature to the reaction temperature (or final temperature) (equation (3)) and the heat adsorbed or liberated by a reaction which is given through the reaction enthalpy calculation equation (4).

$$Q = n_i \int_{T_i}^{T_f} C_{pi} dT \tag{3}$$

$$n_i \Delta H°(T) = n_i \Delta H°_f(298K) + n_i \int_{T_i}^{T_f} C_{pi} dT \tag{4}$$

In these equations, n is the number of mole of the specie i having a thermal capacity C_{pi}
$\Delta H°$ is the change in standard enthalpy; ΔC_{pi} refers to the algebric sum of the molar thermal capacities at constant pressure of reactants or products i.

The following solid compounds in the mixture were considered as main sources of energy consumption in this process: iron oxide (FeOOH); Kaolinite ($Si_2O_5Al_2(OH)_4$); Quartz (SiO_2) and Sodium Carbonate (Na_2CO_3).

These compounds undergo heating accompanied with some transformations from 298 K (25 °C) to 933 K (660 °C). For the iron oxide reaction with sodium carbonate, the most stable phase ($NaFeO_2$) of the Na-Fe-O diagram [9] was considered as the resulting products. In Table 2, the equations associated to the heating process and the companion transformations are given. The reaction equations due to the reaction at 933 K of sodium carbonate with kaolinite, to form sodium silico-aluminate, and with iron oxide, to form sodium ferrite, are also given (Table 2) [4, 10].

Table 2: Transformations involved in the firing process of the mixture of lateritic kaolinite and sodium carbonate

Compounds*	Proposed reactions upon heating	Comment (energy)
Iron oxide (Ir)	$2FeOOH(s)$ (298 K) $\longrightarrow$ $Fe_2O_3.H_2O(s)$ (500 K)	Heating (Q_1)
	$Fe_2O_3.H_2O(s)$ (500 K) $\longrightarrow$ $\alpha Fe_2O_3(s) + H_2O(g)$ (500 K)	Dehydration (Q_2)
	$\alpha Fe_2O_3(s)$ (500 K) $\longrightarrow$ $\alpha Fe_2O_3(s)$ (933K)	Heating (Q_3)
Kaolinite (K)	$Si_2O_5Al_2(OH)_4(s)$ (298 K) $\longrightarrow$ $Si_2O_5Al_2(OH)_4(s)$ (813 K)	Heating (Q_4)
	$Si_2O_5Al_2(OH)_4(s)$ (813 K) $\longrightarrow$ $2SiO_2.Al_2O_3(s) + 2H_2O(g)$ (813K)	Dehydration (Q_5)
	$2SiO_2.Al_2O_3(s)$ (813K) $\longrightarrow$ $2SiO_2.Al_2O_3(s)$ (933K)	Heating (Q_6)
Quartz (Q)	$\alpha SiO_2(s)$ (298 K) $\longrightarrow$ $\alpha SiO_2(s)$ (846K)	Heating (Q_7)
	$\alpha SiO_2(s)$ (846K) $\longrightarrow$ $\beta SiO_2(s)$ (846K)	Conversion (Q_8)
	$\beta SiO_2(s)$ (846K) $\longrightarrow$ $\beta SiO_2(s)$ (933K)	Heating (Q_9)
Reactions equations of kaolinite and hematite with sodium carbonate and associated energy designation		
Sodium aluminum silicate**	$2SiO_2.Al_2O_3(s) + Na_2CO_3(s) \xrightarrow{933K} Al_2O_3.2SiO_2.Na_2O + H_2O(g) + CO_2(g)$ (Q_{10})	
Sodium ferrite	$\alpha Fe_2O_3(s)$ (933K) $+ Na_2CO_3(s) \xrightarrow{933K} 2NaFeO_2(s) + CO_2(g)$ (Q_{11})	

* Ir = iron oxide; K = kaolinite and Q = quartz; **$Al_2O_3.2SiO_2.Na_2O \equiv 2$ $NaAlSiO_4$

For the preparation at 933 K of 1000 g of precursor, 892 g of laterite soil and 318 g of sodium carbonate was needed. The respective molar mass of each compound is calculated using the 2007 IUPAC atomic mass [11]. In the laterite soil, the percentage content of kaolinite (molar mass 258.16 g/mol), iron oxide (159.69 g/mol) and quartz (molar mass 60.09 g/mol) are respectively x = 0.63; y = 0.15 and z = 0.17 (see table 1). Hence the respective number of mole for each component can be calculated:

n_K = 2.18 mole; n_{Ir}= 0.84 mole and n_Q = 2.53 mole.

The total amount of carbonate that is consumed for both reactions, is $n_C = n_K + n_{Ir}$, hence n_C= 3.02 mole. For the energy calculation, the enthalpy of formation and the heat capacity equation retrieved from the literature are given in table 3. The sodium aluminum silicate phase is taken as nepheline ($NaAlSiO_4$) and for the iron oxide reaction with sodium carbonate, the $NaFeO_2$ phase was considered.

Table 3: Enthalpies of formations and specific heat capacities of compounds in the mixture

Compound	$-\Delta H_f^\circ$ (298 K) (kJ)	C_p (J/K.mol)	C_p Temperature range [ref]
FeOOH(s)	560.46	$106.671-0.83486*10^{-2}T-21.198*10^5T^{-2}$	298-500K [12, 13]
αFe_2O_3 (s)	824.782	$79.74+92.88*10^{-3}T-32.84*10^5T^{-2}$	298-956K [14]
$Si_2O_5Al_2(OH)_4$(s)	4033.45	$240.22+147.6*10^{-3}T-32.9*10^5T^{-2}$	298-1773 [15]
αSiO_2(s)	877.38	$46.90+34.28*10^{-3}T-11.29*10^5T^{-2}$	298-1773 [15]
βSiO_2(s)	877.38	$60.23+8.11*10^{-3}T$	298-1773 [15]
Na_2CO_3(s)	1129.2	$113.40+65.29*10^{-3}T-19.98*10^5T^{-2}$	298-1124K [16,17]
H_2O(g)	241.80	$27.06+17.6*10^{-3}T+2.77*10^5T^{-2}$	298K-2500K [17]
CO_2(g)	393.51	$88.11-269.8*10^{-3}T+7.232*10^5T^{-2}$	298-2200K [17]
$2SiO_2.Al_2O_3$(s)	3208.15	$229.27+36.78*10^{-3}T-14.55*10^5T^{-2}$	298-1773[15]
$NaAlSiO_4$	2090.4	$112.09 -67.11*10^{-3}T$	457-1180K [17]
$NaFeO_2$	698.18	$100.77+18.6*10^{-3}T-14.79*10^5T^{-2}$	298-1000K [9]

From Q_1, Q_4, Q_6 Q_7 and Q_9 (see table 2), the energies involved are calculated using equation (3) and for the others, equation (4) is used.

3. Results and Discussion

3.1. Kinetic study

In figure 1 below, the results on the influence of the mixing mode (wet or dry) are presented. The reaction is carried out at 600 °C. It is obvious from figure 1 that the reaction progress is better for the dry mixed sample. The dried mixtureleads to about 85 % conversion while the wet mixed sample conversion is limited at about 60 % after 90 min reaction. The reaction strat up for both samples is almost the same and the difference in reaction rate clearly appear after 30 min. Given that the wet mixed system is a compact solid (a pellet) and that the dry mixed is a powder, the reaction difference is attributed to the limitation of the heat diffusion in the compact system in comparison to a powder dispersed system. From these results, the subsequent preparations were all done in dry mode.
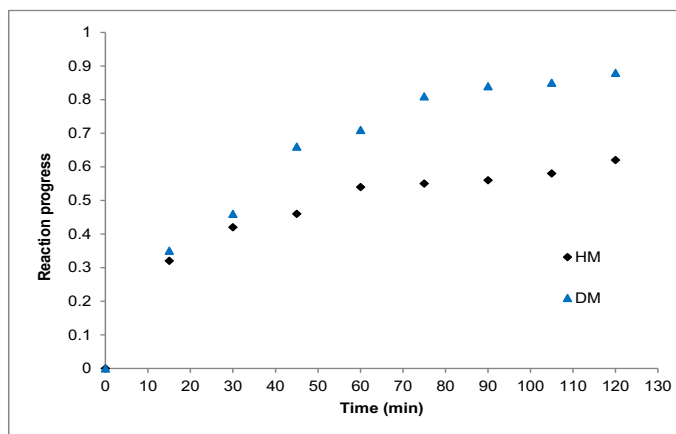

Figure 1: Influence of the mixing mode on the reaction progress
HM: humid mixing; DM: dry mixing

The influence of the reaction temperature is monitored from 500 to 660 °C in order to avoid or limit reaction of sodium carbonate with silica [6, 18].

The results are presented in figured 2. From this figure, it is observed that the temperature increase results in an increase of the reaction progress. From 500 °C to 600 °C, the reaction progress increases as follows: less than 20 % (at 500 °C),about 25 % (at 560 °C) and 55 % (at 600 °C) after about 3 hours (180 min) of reaction. For the same duration, the reaction progress is more than 80 % at 660 °C. For temperatures between 500 ° and 600 °C, the low diffusion on the thermal energy in the system may account for the low reaction rate at the start of the reaction for all the temperatures. After 100 min, the system at 600 °C show an improved reaction rate while for lower temperatures (500 ant 560 °C), the reaction is at its maximum. The temperature of 660 °C is then retained for further tests.
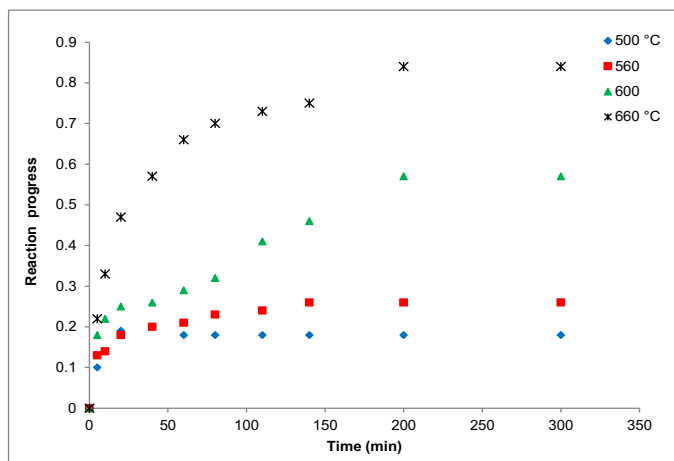
Figure 2: Influence of the reaction temperature on the reaction progress

For the optimization of the reaction, an evaluation of the influence of previous thermal treatment of the laterite was done using a raw and pre heated laterite at 660 °C. The results obtained are depicted is figure 3. It is obvious,from the results, that the thermal treatment lead to a less reactive sample. The pre heated sample lead to a maximum conversion of about 65 % after 3 hours reaction while for the raw the reaction progress is about 80 % for the same reaction time. This observation is in agreement with the proposed catalytic role of the water liberated by dehydration in the reacting system proposed by Heller-Kallai (1978) [4]. The water, released, during the reaction of the raw clay-sodium carbonate system, act as a catalytic agent by dissolving sodium carbonate which diffusion in the system enhances the reaction.
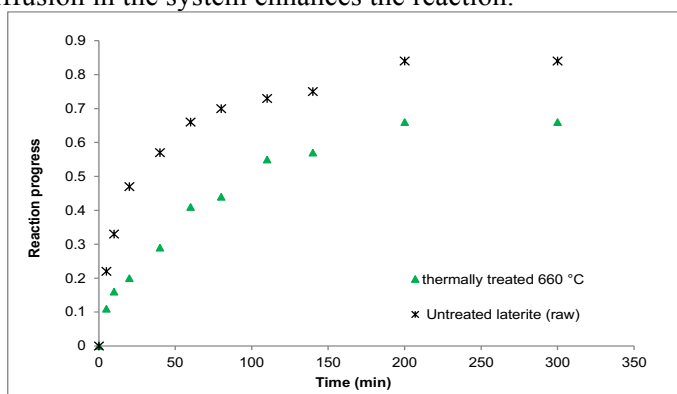

Figure3: Effect of previous thermal treatment of the laterite on reaction progress

Three ratio (R) of sodium carbonate/laterite (0.5; 1; 1.5 on dry basis) are used to evaluate its influence on the reaction progress. The results obtained are presented on figure 4.
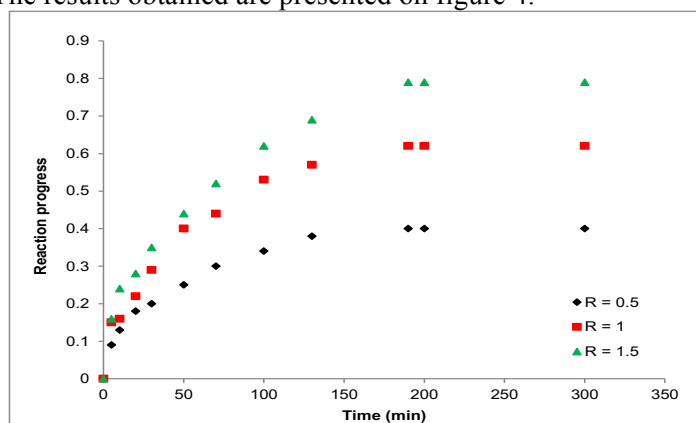

Figure 4: Influence of the sodium carbonate/laterite ration on the reaction progress

It is observed that the maximum reaction conversion is increasing with increasing R. For all the value of R, the minimum time needed to achieve maximum conversion was 120 min and the maximum time needed was about 180 min for all system. From these results, it is extrapolated that optimal conversion of the kaolinite is

achieved for a reaction time of 180 min (3 hours) at 660 °C with a reaction progress of 80 % and the ratio of sodium carbonate/laterite should be greater than 1.2.

3.2. Energetic consideration

The energy nedded for the preparation of 1 kg of precursor from the reaction of lateritic kaolinite with sodium carbonate was done using the thermodynamics consideration previously recalled (see thermodynamic consideration). It is obtained that for 1 kg precursor, the energy needed is about 166 kJ. Assuming that the calculation leads to an under estimation of 30 % because of loss and open conditions of work, the energy needed may reach 216 kJ/kg which corresponds to 0.06 kWh for the production of 1 kg of precursor. This energy consumption is low and agree with the low energy cost of geopolymerization process.

Conclusion

- The present study was examining the kinetic and the energetic aspects of the reaction between a lateritic kaolinite soil and sodium carbonate upon firing from ambient to 660 °C. The following conclusions are drawn from the study:
- Previous humidification of the mixture slowed down the reaction because the compact structure of the pallet limits the heat diffusion within the mixture. Hence, dry mixing is preferred.
- The increase of the temperature,increased the reaction rate. The firing at 660 °C of the lateritic soil, prior to reaction with sodium carbonate, also slowed down the reaction and this indicate that the hydration water in the soil material has a catalytic role for the reaction.
- The sodium carbonate to laterite ratio must be > 1, for an optimization of the conversion of kaolinite, sodium carbonate/laterite is taken at 1.5 and lead to a reaction progress of 80 % for a reaction time of 3 hours.
- The energetic consideration leads to a consumption of 216 kJ/kg which agrees with the objective low energy cost process.

Dedication: To Dr. Liboum, retired Senior Lecturer of the University of Yaounde 1, whom teaching, creativity and research endeavor are the sources of this work.

References

1. A. Elimbi, H.K. Tchakoute, D. Njopwouo, *Constr. Build. Mater.* 25 (2011) 2805.
2. H.K., Tchakoute, A. Elimbi, J.A. Mbey, .C.J. Ngally Sabouang, D. Njopwouo, *Constr. Build. Mater.*35 (2012) 960.
3. B.I. Djon Li Ndjock, A. Elimbi, M. Cyr, *J. Non-Cryst. Solids* 463 (2017) 31.
4. L. Heller-Kallai, *Clay Miner.* 13 (1978) 221.
5. M. SigningNganda, *Matériaux latéritiques de Messamendongo: characterisation et étude cinétique de la reaction avec le carbonate de sodium*, Memoire de DEA, Université de Yaoundé 1, (2008), 50p.
6. N.N. Greenwood, A. Earnshaw, Chemistry of the Elements (2nd ed.). Butterworth-Heinemann.ISBN 0-08-037941-9 (1997).
7. W.J. Beman, The Löwig process for caustic soda using trona as a raw material.Bachelor's thesis, California Institute of Technology (1922). Online athttp://resolver.caltech.edu/CaltechETD:etd-04192004-143549
8. V. Alexéev, Analyse quantitative, Editions Mir, Moscou (1980) 583p.
9. J. Huang, T. Furukawa, K. Aoto, *Thermochim.Acta*. 405 (2003) 67.
10. X-B. Li, F. Niu, J. Tan, G-H. Liu, T-G. Qi, Z-H. Peng, Q-S. Zhou, *Trans. Nonferrous Met. Soc. China.*26 (2016) 1419.
11. M.E. Wieser,M. Berglund, *Pure Appl. Chem.* 81(11) (2009) 2131.
12. I. Diakonov, I. Khodakvsky, J. Shott, E. Sergeeva, *Eur. J. Miner.*6 (1994) 967.
13. R.J. Lemire, U. Berner, C. Musikas, D.A. Palmer, P. Taylor, O. Tochiyama, Chemical thermodynamic of iron part1. *In Chemical Thermodynamics*, vol. 13a, OECD publications, (2013) Paris, France, 1082p.
14. S.K. Sexena, Systematization and Estimation of Thermo chemical Data on Silicates.In *Modelling in Aquatic Chemistry*. OECD Publications, (1997) 724 p., ISBN 92-64-15569-4
15. N.C. Schieltz,M.R. Soleman, *Proc. 13th Natl. Conf. on Clays*, Madison, Wisconsin, Pergamon press, Monograph, No.25, ed. by Earl Ingerson (1966) 419.
16. K.K. Kelley, *U.S. Bureau. Mines Bull.*584 (1960) 232 p., U.S. Govt. Print.Off., Washington.
17. R.A. Robie, Hemingway B.S., *U.S. Geol.Surv. Bull.*, 2131 (1995) 461 p.
18. W.R. Ott, *Ceramurgia. Int.* 5(1) (1979) 37.

(2018) ; http://www.jmaterenvironsci.com