ENERGY REQUIREMENT FOR FIRING PORCELAIN

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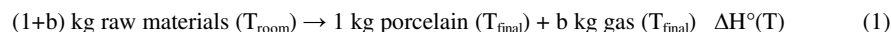[2]Faculty of Sciences, University of Pretoria, Private Bag 0003, Pretoria, South Africa

ABSTRACT. Results from studies on the ternary system Ribaué kaolin–Carapira feldspar–Marracuene quartz sands were used to test a procedure that we developed for calculation of the energy requirement for firing porcelain. Results obtained vary between 1300 and 1800 kJ/kg porcelain. These results differ largely from the ones obtained using Hennicke's procedure.

KEY WORDS: Porcelain, Energy requirement for firing porcelain, Kaolin–feldspar–quartz sands

INTRODUCTION

We used in the present work part of the results obtained in laboratory experiments for production of porcelain from Ribáuè kaolin–Carapira feldspar–Marracuene sands to test a procedure that we developed for calculation of the energy requirement for firing porcelain.

In analogy with the definition adopted in [1-3], the energy requirement for firing porcelain can be defined as the enthalpy change associated with the transformation of the raw materials (feldspar, quartz and kaolin) at room temperature T_{room}, into the final product (porcelain), at a temperature T_{final}, and can be described by following equation

$$(1+b) \text{ kg raw materials } (T_{room}) \rightarrow 1 \text{ kg porcelain } (T_{final}) + b \text{ kg gas } (T_{final}) \quad \Delta H°(T) \qquad (1)$$

The determination of $\Delta H°(T)$ has received a special attention since $\Delta H(T)$ represents the fraction of the amount of energy supplied to the kiln that is used in the transformation of raw materials into the final products. The remaining parts of the supplied energy represent a) the amount lost by the gases leaving the kiln at a high temperature and b) the amount lost through the kiln structure (walls and other kiln elements).

The enthalpy change $\Delta H°(T)$ includes the energy necessary to raise the temperature of raw materials and intermediary phases, formed during the process, until their reaction or transformation temperatures, the correspondent heats of reaction or transformation, melting enthalpy of certain components, solution and mixing enthalpies.

A review of available literature show that this thermodynamic quantity has received some attention in the case of glass and cement production [1, 3-11], while for porcelain we found only Hennicke's estimate of this quantity [12]. This may be attributed to the grater experimental difficulties by the experimental determination of $\Delta H°(T)$ in the case of porcelain.

$\Delta H°(T)$ has been experimentally measured for glass [1, 5, 7, 9] and cement [11] using calorimetric methods. The use of a similar procedure for porcelain do not give good results, basically because of the long firing programme adopted for porcelain and the strong dependence of the composition of the fired product (porcelain) from the firing programme adopted.

For that reason attempts are made here to develop a procedure for calculation of this quantity. In order to achieve this objective it is important:

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1. To characterize very well the raw materials and the fired products (porcelain). These represent the initial and final (thermodynamic) state and are necessary in each determination of an enthalpy change related to a certain process. Characterization of raw materials and final products was carried out using X-ray fluorescence, X-ray diffraction and rational analysis. The amount and composition of the vitreous phase present in the fired porcelain was calculated as a difference of the amount and composition of final product and of all crystalline phases present in porcelain.

2. To connect the initial and final state by thermochemical equations. The sequence of thermochemical equations suggested was derived from results of firing experiments carried out with our samples and from results of studies carried out by Hennicke [12], Brindley and Nakahira [13], Lundin [14], Schűller [15] and Schmidt [16] about transformations occurring during firing of porcelain. Thermochemical data necessary for the calculations were basically extracted from Knacke *et al*. [17]. Data not available in this publication were taken out from Spencer [18], Babushkin *et al*. [7], Hennicke [12] and Conradt [8].

During the development of this procedure, and based on the periodicity of chemical properties, we treated feldspar on one side as K-feldspar and on the other side as a mixture of K- and Na-feldspar. Since $K_2O.Al_2O_3.6SiO_2$ and $Na_2O.Al_2O_3.6SiO_2$ are feldspars formed by two group I elements, we expected both types of feldspars to have a similar contribution on the value of the energy requirement.

EXPERIMENTAL

Transformations assumed in our procedure

The results of the chemical composition and rational analysis of the raw materials (see Table 1 and 2, respectively) show that Marracuene sand contains 99.44% quartz, Carapira feldspar contains 97.88% feldspar (divided in 72% K-feldspar and 26% Na-feldspar) and 1.58% quartz, and Ribáuè kaolin contains 71.11% kaolinite, 20.61% Na-feldspar and 9.20% quartz.

Table 1. Chemical composition of the raw materials in mass %.

Component	Marracuene sand	Carapira feldspar	Ribáuè kaolin
SiO_2	99.44	65.74	54.79
TiO_2	0.06	0.01	0.1
Al_2O_3	< 0.03	18.19	31.29
Fe_2O_3	< 0.02	0.03	0.33
MnO	< 0.01	< 0.01	0.01
MgO	< 0.08	< 0.08	< 0.08
CaO	< 0.01	< 0.01	0.01
Na_2O	< 0.02	3.04	1.34
K_2O	0.13	12.14	1.49
P_2O_5	< 0.02	< 0.02	< 0.02
Cr_2O_3	< 0.02	< 0.02	< 0.02
NiO	< 0.02	< 0.02	< 0.02
H_2O	0.08	0.17	2.07
LI[*]	0.15	0.30	8.21
Total	99.86	99.62	99.64

[*]Loss on ignition.

Table 2. Rational analysis of the raw materials in mass %.

Phase	Carapira feldspar	Ribáuè kaolin
Clay mineral	0.04	71.11
Feldspar	97.88	20.61
Fe_2O_3	0.03	0.34
MgO	0.08	0.08
MnO	0.01	0.01
CaO	0.01	0.01
TiO_2	0.01	0.01
Quartz	1.58	9.20
P_2O_5	< 0.02	< 0.02
Cr_2O_3	< 0.02	< 0.02
NiO	< 0.02	< 0.02
CO_2	0.30	-1.52
Total	100.00	100.00

The characterization of the fired samples gave the mineralogical composition presented in Table 3. While quartz and mullite were obtained from quantitative X-ray diffraction, the amount of vitreous phase was obtained from the difference: % vitreous phase = 100% - Σ % crystalline phases present. The fired samples were prepared from batches with the compositions given in Table 4.

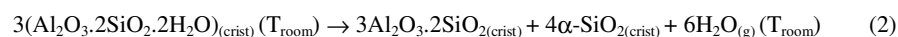Table 3. Mineralogical composition of porcelain samples in mass %.

Sample	Quartz	Mullite	Vitreous phase
N2-1250	19.02	3.71	77.27
N3-1250	50.86	2.01	47.13
N4-1250	35.14	2.17	62.69
N14-1250	62.79	7.99	29.22
N15-1250	39.05	10.01	50.94

Table 4. Composition of the batches used in these studies in mass %.

Sample	Caolin	Feldspar	Quartz
N2	45	40	15
N3	30	36	34
N4	40	36	24
N14	40	20	40
N15	50	20	30

Based on these results, we assume following mechanism:

- Kaolinite is decomposed by room temperature to give mullite, silica and water. Part of the mullite dissolves in the feldspar melt. Decomposition of kaolinite, which takes place in several steps, can be resumed by following equation

$$3(Al_2O_3.2SiO_2.2H_2O)_{(crist)} (T_{room}) \rightarrow 3Al_2O_3.2SiO_{2(crist)} + 4\alpha\text{-}SiO_{2(crist)} + 6H_2O_{(g)} (T_{room}) \quad (2)$$

- The mullite, silica and water obtained in equation (2) are heated up to final temperature. Part of the mullite is dissolved in the feldspar melt. The amount of mullite dissolved is obtained as the difference of the amount of mullite obtained by the decomposition of kaolinite minus the mullite determined by XRD.
- Quartz (99.44% from Marracuene sand, 1.58% from feldspar and 9.20% from kaolin) is heated up to the final temperature T. Part of it is dissolved in the feldspar melt. The amount dissolved in the feldspar melt is calculated as the difference of the total amount of quartz minus quartz determined by XRD in the fired samples and that existent in mullite.
- Feldspar melts at about 1100 °C and dissolves part of the quartz and mullite. It forms the basis of the vitreous phase present in porcelain.

The transformations described here represent a simplification of the real mechanism, a choice assumed for simplicity and convenience in using available thermodynamic data, and based on the fact that ΔH is a state function. For that reason, its determination depends only from knowledge of the initial and final state and not necessarily from the steps that the process undergoes.

Procedure for calculation of the energy requirement

In our procedure and based on Hess's law, $\Delta H°_1(T)$ is calculated as a sum of the ΔH-values of the thermochemical equations suggested here to connect the initial and final state. We consider here following contributions to the $\Delta H°_1(T)$ values:

Decomposition of kaolinite. Decomposition of kaolinite at room temperature is given by equation (2). The enthalpy effect associated to equation (2), $\Delta H°_2(298K)$, is calculated from standard enthalpies of formation products and reactants
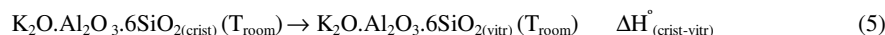
$$\Delta H°_2(298K) = \Delta_f H°(3Al_2O_3.2SiO_{2(crist)}) + 4\Delta_f H°(SiO_{2(Q)}) + 6\Delta_f H°(H_2O_{(g)})$$
$$- 3\Delta_f H°(Al_2O_3.2SiO_2.2H_2O_{(crist)}) \tag{3}$$

Transformation of feldspar. Feldspar at room temperature, $T_{initial}$, is transformed in a melt of the same composition at a temperature $T = T_{final}$. In the case of K-feldspar, this process is represented by following equation

$$K_2O.Al_2O_3.6SiO_{2(crist)}(T_{room}) \rightarrow K_2O.Al_2O_3.6SiO_{2(melt)}(T) \qquad \Delta H°_3(T) \tag{4}$$

For a better use of available data and since the vitreous phase is formed during cooling of the melt, equation (4) was divided in 2 steps:
a) Transformation of crystalline K-feldspar into its vitreous form at room temperature

$$K_2O.Al_2O_3.6SiO_{2(crist)}(T_{room}) \rightarrow K_2O.Al_2O_3.6SiO_{2(vitr)}(T_{room}) \qquad \Delta H°_{(crist-vitr)} \tag{5}$$

b) Heating up the vitreous phase formed until formation of a melt at a temperature $T = T_{final}$.

$$K_2O.Al_2O_3.6SiO_{2(vitr)}(T_{room}) \rightarrow K_2O.Al_2O_3.6SiO_{2(melt)}(T) \qquad \Delta H° = \int_{298}^{T} C^o_{p(vitr)} dT \tag{6}$$

The enthalpy change associated with the transformation of the feldspar is then given by the relation

$$\Delta H^\circ_3(T) = \Delta H^\circ_{(crist\text{-}vitr)}(298K) + \int_{298}^{T} C_P^o\left(K_2O.Al_2O_3.6SiO_{2(vitr)}\right)dT \tag{7}$$

In case of Na-feldspar equation (7) assumes the form

$$\Delta H^\circ_4(T) = \Delta H^\circ_{f(crist\text{-}vitr)}(298) + \int_{298}^{T} C_P^o\left(Na_2O.Al_2O_3.6SiO_{2(vitr)}\right)dT \tag{8}$$

Transformation of mullite. The enthalpy change corresponding to the transformation (heating up to T_{final}) of the mullite present in crystalline form is given by

$$\Delta H^\circ_5(T) = \int_{298}^{T} C_P^o\left(3Al_2O_3.2SiO_2\right)dT \tag{9}$$

For mullite dissolved in the melt last equation is extended to include thermal effect during dissolution. In analogy to equation (7), equation (10) is written as following

$$\Delta H^\circ_6(T) = \Delta H^\circ_{(crist \to vitr)}(298K) + \int_{298}^{T} C_P^o\left(3Al_2O_3.2SiO_2\right)_{(vitr)}dT \tag{10}$$

Transformation of quartz. Hereby we consider quartz coming from Marracuene sand, feldspar, kaolin and from decomposition of kaolinite in equation (2). Like in the case of mullite, we consider here two fractions: a) quartz present in crystalline form and b) quartz dissolved in the melt that originates the vitreous phase.
a)   Transformation of quartz present in crystalline form follows equation (11)

$$\alpha\text{-}SiO_{2(crist)}(T_{room}) \to \beta\text{-}SiO_{2(crist)}(T) \qquad\qquad \Delta H^\circ_7(T) \tag{11}$$

$$\Delta H^\circ_7(T) = \int_{298}^{847} C_P^o\left(SiO_{2(Q)}\right)dT + \Delta H^\circ_{(\alpha \to \beta)}(847K) + \int_{847}^{T} C_P^o\left(SiO_{2(Q)}\right)dT \tag{12}$$

b)   For quartz dissolved in the feldspar melt one has to consider additionally the heat of dissolution. Equation (12) is extended to include this effect

$$\Delta H^\circ_8(T) = \int_{298}^{847} C_P^o\left(SiO_{2(Q)}\right)dT + \Delta H^\circ_{(\alpha \to \beta)}(847K) + \int_{847}^{T} C_P^o\left(SiO_{2(Q)}\right)dT + \Delta H^\circ_{dissol} \tag{13}$$

The energy necessary to raise water temperature from room temperature up to the final temperature T is given by

$$\Delta H^\circ_9 = \int_{298}^{T} C_P^o\left(H_2O(g)\right)dT \tag{14}$$

The energy requirement is obtained as a sum of the contributions of ΔH values in equations (3), (7), (8), (9), (10), (12), (13) and (14). We neglected hereby the mixing enthalpy of Na- and K-feldspar, since both compounds are similar: Na_2O and K_2O have a mole fraction of 1/8 in the respective feldspars; they are elements of the same group and are expected to have a similar behaviour:

$$\Delta H^{o}(T) = \sum_{i=1}^{8} \frac{m_i}{M_i} \Delta H^{o}{}_i(T) \tag{15}$$

m_i in equation (15) represents the mass of compound involved in the transformation while M_i represents the mass of a mole of that compound. Thermodynamic data necessary to calculate the energy requirement according to equation (15) are given in Table 5 and 6. They have been taken basically from Knacke *et al*. When data for a certain transformation were not available we used the further sources indicated in Table 5 and 6.

Table 5. Standard enthalpies of formation, $\Delta_f H_i$, and selected heats of transformation, ΔH_i, used in the calculation.

Compound	Enthalpy (J/mol)
$\Delta_f H^{\circ}_{i\ SiO2(Q)(crist)}$	-910856[1]
$\Delta_f H^{\circ}_{i\ Al2O3(crist)}$	-1675692[1]
$\Delta_f H^{\circ}_{i\ Na2O(crist)}$	-415052[1]
$\Delta_f H^{\circ}_{i\ K2O(crist)}$	-361501[1]
$\Delta_f H^{\circ}_{i\ H2O(g)}$	-241856[1]
$\Delta_f H^{\circ}_{i\ Al2O3.2SiO2.2H2O(crist)}$	-4095843[1]
$\Delta_f H^{\circ}_{i\ 3Al2O3.2SiO2(crist)}$	-6820800[2]
$\Delta_f H^{\circ}_{i\ 3Al2O3.2SiO2(vitreous)}$	-6632410[2]
$\Delta_f H^{\circ}_{I\ Na2O.Al2O3.6SiO2(crist)}$	-7841230[1]
$\Delta_f H^{\circ}_{I\ Na2O.Al2O3.6SiO2(vitr)}$	-82006[3]
$\Delta_f H^{\circ}_{I\ K2O.Al2O3.6SiO2(crist)}$	-7912366[1]
$\Delta_f H^{\circ}_{i\ K2O.Al2O3.6SiO2(vitr)}$	-153134[3]
$\Delta H^{\circ}_{(\alpha\text{-}SiO2\rightarrow\beta\text{-}SiO2)}(847K)$	728[1]
$\Delta H^{\circ}_{dissolução}(SiO_2)$	159[4]

[1]Extracted from [17]. [2]Extracted from [19]. [3]Extracted from [18]. [4]Extracted from [12].

Table 6. Coefficients a_i, b_i and c_i of the Cp (T) equation.(Cp is given in $J.mol^{-1}.K^{-1}$).

Phase I	a_i	b_i	c_I
$\alpha\text{-}SiO_{2(Q)(crist)}$ [1]	40.497	44.601	-0.833
$\beta\text{-}SiO_{2(Q)(crist)}$ [1]	67.593	2.577	-0.138
$H_2O_{(g)}$ [1]	34.376	7.841	-0.423
$Al_2O_3.2SiO_2.2H_2O_{(crist)}$ [1]	229.492	36.819	-1.456
$Na_2O.Al_2O_3.6SiO_{2(crist)\ fase\ A}$ [1]	516.306	116.315	-12.560
$Na_2O.Al_2O_3.6SiO_{2(crist)\ fase\ B}$ [1]	565.677	81.672	-17.180
$Na_2O.Al_2O_3.6SiO_{2\ (vitr)}$ [2]	256.521	75.312	–
$K_2O.Al_2O_3.6SiO_{2\ (vitr)}$ [2]	259.241	71.797	–
$3Al_2O_3.2SiO_{2(crist)}$ [1]	480.574	43.430	-15.230
$3Al_2O_3.2SiO_{2(vitreous)}$ [3]	81.382	3.008	-24.080
$K_2O.Al_2O_3.6SiO_{2(crist)}$ [1]	286.060	38.660	-9.523

[1]Extracted from [17]: Cp follow equation of the type $Cp = a + b.10^{-3}T + c.10^{6}T^{-2}$. [2]Extracted from [18]: Cp follow equation of the type $Cp = a + b.10^{-3}T + c.10^{-6}T^{2}$. [3]Extracted from stebins *et al*. [19]: Cp follow equation of the type $Cp = a + b.10^{-3}T + c.10^{6}T^{-2}$.

RESULTS AND DISCUSSION

ΔH values calculated for the samples prepared from compositions in Table 4 are resumed in Table 7.

Table 7. Values of the energy requirement $\Delta H_1(T)$ in kJ/kg porcelain.

Sample	$\Delta H^0(1523)_I$	$\Delta H^0(1523)_{II}$	Deviation (δ %)
N2-1250	1798	1806	0.44
N3-1250	1309	1314	0.38
N4-1250	1396	1402	0.43
N14-1250	1482	1489	0.47
N15-1250	1691	1696	0.29

I: Feldspar treated as K-feldspar. II: Feldspar treated as a mixture of K- and Na-feldspar.

Deviation is given by $\delta = \dfrac{\Delta H_{s\acute{e}rieII} - \Delta H_{s\acute{e}rieI}}{\Delta H_{s\acute{e}rieII}} \cdot 100\%$ ·

The samples with the largest contents of kaolin seem to give the highest results. This may be explained by the amount of energy required to dissociate kaolinite and to heat the products resulting from this dissociation up to final temperature. Quartz seems to have the lowest contribution on the $\Delta H_1(T)$ value.

The simplification we introduced, treating feldspar as K-feldspar, results in similar $\Delta H_1(T)$ values, as when we consider the feldspar as a mixture of K- and Na-feldspar, as can be seen from deviation values listed in Table 7. Last approach is more in agreement with the mineralogical composition of the Carapira feldspar, which contains approximately 72% of the K-feldspar and 26% of the Na-feldspar.

Results obtained in this study are higher than the ones calculated using Hennicke's procedure. An appreciation of Hennicke's paper shows that Hennicke adopted a definition of the energy requirement different from the one given in equation (1). His definition considers basically the transformation of raw materials into products at room temperature.

In order to have comparable results, we used our procedure to calculate $\Delta H_1(298K)$ using the transformations suggested in this study and compared resulting values with the values calculated by applying Hennicke's procedure to our compositions. Results obtained were again higher than Hennicke's results.

A calculation of the enthalpy of dissociation of kaolinite shows further that also the source of data used by Hennicke's is partially responsible for the differences on the $\Delta H_1(T)$ value. While according to Hennicke we obtained 516 kJ/kg kaolinite for the dissociation of kaolinite, using our data we came to a value of 1448 kJ/kg.

ACKNOWLEDGEMENTS

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