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Optimization of firing cycle for different porcelain bodies of sanitaryware: the influence of feldspar

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ABSTRACT: Four formulas of sanitaryware porcelain were studied. The influence of soda feldspar on the reduction of firing cycle is particularly highlighted. The samples were prepared and treated thermally at various temperatures and holding times and then characterized in terms of water absorption, total shrinkage and flexural strength. The results affirm that it is possible to reduce the firing temperature thirty degree Celsius (30°C) less than the usual temperature which is 1220°C, with a ratio of sodium oxide compared to potassium oxide equal to 5,744.

KEYWORDS: Soda feldspar, water absorption, firing, porcelain, shrinkage, flexural strength.

1 INTRODUCTION

In ceramic sanitaryware sector, tunnel and intermittent kilns are the biggest consumers of thermal energy. The estimated percentage of this energy in the production costs is about 30% [1], [2], [3].

That is why manufacturers try to reduce the cost of this energy by optimizing the cycle of firing.

In this context, we have thought about studying suitable bodies formulas in order to lower the temperature of firing or reduce the holding time.

Accordingly, three new compositions of porcelain bodies were developed starting from standard formula of an industrial use which is fired at 1220°C and at 30min of holding time. The latter were developed, by mixing usual raw materials then firing them at various temperatures and various holding time.

The choice of the formulas is based on the increase of the proportion of fusible phase brought by sodium oxide which exists in soda feldspar to the detriment of potassium oxide which exists in mixed feldspar potash-soda. This said, after the thermal treatment the physical and mechanical characteristics must satisfy the standards.

2 EXPERIMENTAL

The raw materials used in this work were two kaolins (K1 and K2), two clays (A1 and A2), two feldspars (Fel1 and Fel2) and quartz (Q1). The chemical analysis was performed by means of x-ray fluorescence spectroscopy (Axios de Panalytical) and the results are given in table 1.

Four compositions were prepared according to the formulas shown in table 2. From the chemical analysis of the raw materials (Table 1) and the formulas (Table 2), we applied the relation of "Seger" [4] (Table 3) which gives us major information: Evolution of the rate of sodium oxide compared to potassium oxide Na_2O/K_2O by keeping the ratio of silicate oxide compared to alumina SiO_2/Al_2O_3 almost fixed. This relation will be used later to interpret the results.

Twenty-kilogram batch of each were weighed out. Formula n°1 refers to the base compound of this work being similar to the composition of porcelain of sanitaryware used in the factory. In the subsequent formulas (Formula 2 to formula 4), mixed feldspar progressively is eliminated and substituted by soda feldspar. The non-plastic proportion of each batch was wet-ground in a boll mill with 50% of water, for a duration of 4–4,5 h to achieve a fineness of ~99% passing through a 75 µm sieve. Subsequently the plastic raw materials were added to the crushed products in a separate container with small quantities of deflocculent agents which are 2 ‰ of sodium silicate (Na_2SiO_3) and 0,1 ‰ of sodium carbonate(Na_2CO_3). As a result the slip produced was ready for casting in plaster molds to obtain rectangular samples of dimension 200mm×20mm×10mm. These samples were dried in stove at 100°C +/-10 and then thermally heated in an electric laboratory kiln at the rate of 20 ◦C/min at different peak temperatures 1220°C, 1190°C, 1160°C and 1130°C changing for each one the holding time to 10, 30 and 60 min.

After firing, all specimens were subject to the test of water absorption, and those fired at the holding time equal to 30 min were subject to the tests of linear total shrinkage, flexural strength as well.

Table 1. Chemical analysis of raw materials

	Clays :		kaolins :		Feldspars :		Quartz Q1
Chemical elements	**A1**	**A2**	**K1**	**K2**	**Fel1**	**Fel2**	
SiO_2	58,60	54,10	48,11	46,93	77,02	73,09	99,21
Al_2O_3	26,26	30,50	36,14	37,52	12,86	15,99	0,37
Fe_2O_3	1,00	1,33	1,22	0,96	0,60	0,37	0,08
TiO_2	1,26	1,04	0,05	0,30	0,04	0,14	0,01
CaO	0,12	0,08	0,00	0,00	0,21	0,23	0,01
MgO	0,33	0,28	0,27	0,19	0,06	0,32	0,00
K_2O	2,04	1,71	1,90	0,96	4,68	0,09	0,20
Na_2O	0,34	0,21	0,09	0,04	3,82	9,04	0,03
Loss on the ignition	9,92	10,61	12,12	13,04	0,67	0,64	0,11

Table 2. Formulations of the prepared batches

Formulas n° :	A1	A2	K1	K2	Total plastics	Fel1	Fel2	Q1	Total non-plastics	Total
1 (mass%)	18	7	13	13	51	29	9	11	49	100
2 (mass%)	18	7	13	13	51	20	18	11	49	100
3 (mass%)	18	7	13	13	51	11	27	11	49	100
4 (mass%)	18	7	13	13	51	0	38	11	49	100

Table 3. Formulas « SEGER »

Formulas n° :	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SiO_2/Al_2O_3	Na_2O/K_2O
1	5,062	0,978	0,022	0,021	0,009	0,021	0,110	0,146	5,177	1,332
2	4,968	0,979	0,021	0,021	0,009	0,024	0,087	0,181	5,077	2,082
3	4,878	0,980	0,020	0,022	0,009	0,026	0,065	0,215	4,979	3,318
4	4,789	0,980	0,020	0,022	0,009	0,028	0,043	0,248	4,884	5,744

2.1 PROTOCOL OF MEASURMENT OF WATER ABSORPTION

This procedure is based on the standard UNE 67001:2008 (AENOR), which consists of drying the samples at 110°C for 180+/-5 minutes in drying stove cooling them down at room temperature, weighing each sample with an accuracy balance of 0,05g recording its weight (m_0) and then entering the samples in the bath containing demineralized water to prevent the samples from touching the bottom or sides of the bath. We heat water to boiling temperature (100°C) maintaining that temperature for 120+/- 5minutes,then, we stop the heating process and keep the samples immersed for 20 +/- 1h. Afterwards, we remove the samples from the bath and dry them immediately with an absorbant paper. Finally, we weight the samples immediately and record its weight (m_1). The value of water absorption is calculated according to the following equation:

$$WA = 100 * m_1\text{-}m_0/m_0 \quad (1)$$

Where :

WA: is the water absorption coefficient, expressed

in % to tow decimal places.

m_0: is the mass of the dry sample, expressed in g.

m_1: is the mass of the sample after testing.

The final result is the calculation of the average of the three tested samples.

In the case of ceramic porcelain of sanitaryware items, the absorption of water must be less than 0,5% [5], [6], [7], [8].

2.2 Protocol Of Measurment Of Total Linear Shrinkage

After firing, we measure the length of samples with a caliper with accuracy of 0,1 mm (L_2).

The percentage of total linear shrinkage is expressed in % to one decimal places and given by the expression:

$$(L_0\text{-}L_2)/2 \quad (2)$$

Where :

L_0 : The initial length of the sample which is 200 mm.

L_2 : The length of the sample after firing.

2.3 Protocol Of Measurment Of Three-Point Flexural Strength (Module Of Rupture)

Mechanical resistance is calculated as module of rupture (MOR). This measures the maximum force that a rectangular material with withstand before it breaks when it is under a load in a three-points bending setup.

To determinate the “module of rupture” of the studied bodies we used the NETZSCH equipment reference 401. This parameter is expressed in MPa as stated by the following formula:

$$MOR= 0.015*P*L/a^2*b \text{ (MPa)} \quad (3)$$

Being:

a: Hight (cm) of specimen in the break area.

b: Width (cm) of specimen in the break area.

P: Load of rupture for the tested specimen, directly read on the arm of the machine (Newton “N”)

L: Distance between supports of the specimen (cm).

3 Results And Discussion

The temperature usually used in production of ceramic sanitaryware is 1220°C with holding time of 30 min. We will also have the results of the study for three other temperatures: 1190°C, 1160°C and 1130°C. The values in the tables below represent the average of measurements from four samples.

3.1 WATER ABSORPTION

3.1.1 FORMULA N°1

Table 4. The water absorption (%) of the formula n°1 according to the holding time at various temperatures of firing.

	Temperatures (°C)			
Holding time (min)	**1130°C**	**1160°C**	**1190°C**	**1220°C**
60	7,26	2,01	0,98	0,07
30	8,60	3,31	3,11	0,25
10	9,85	5,25	3,55	0,74

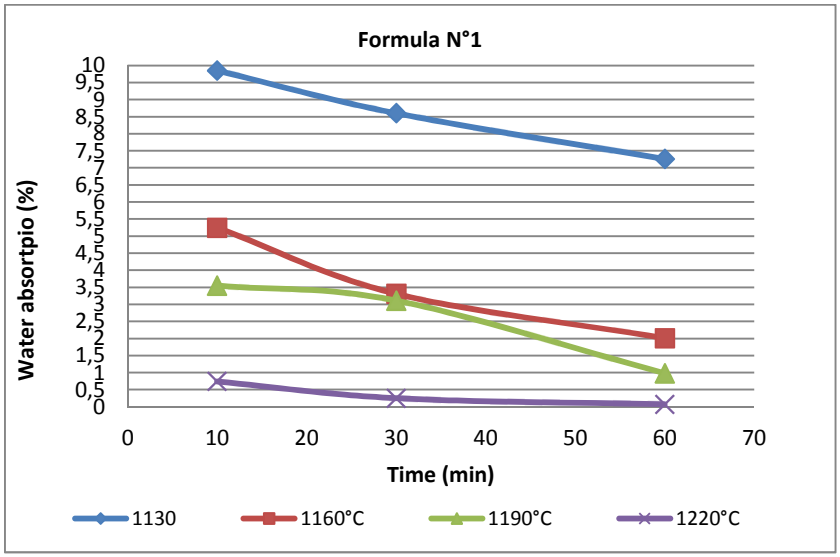

Fig. 1. Evolution of the water absorption of the formula n°1 according to the holding time at various temperatures of firing

With the formula n°1 in which the ratio Na_2O/K_2O is equal to 1,332, the porcelain reaches a porosity lower than 0,5%, only when the thermal treatment is performed at 1220°C at holding times of 30 and 60 min. Therefore it is excluded to work at lower temperatures or soaking times because the material is not vitrified enough.

3.1.2 FORMULA N°2

In the formula n°2, the ratio Na_2O/K_2O increase to 2,082 and we made the same study as that done with the formula n°1.

Table 5. The water absorption (%) of the formula n°2 according to the holding time at various temperatures of firing

	Temperatures (°C)			
Holding time (min)	**1130 °C**	**1160°C**	**1190°C**	**1220°C**
60	7,15	1,84	0,35	0,07
30	8,44	3,00	2,43	0,12
10	9,22	4,08	2,15	0,42

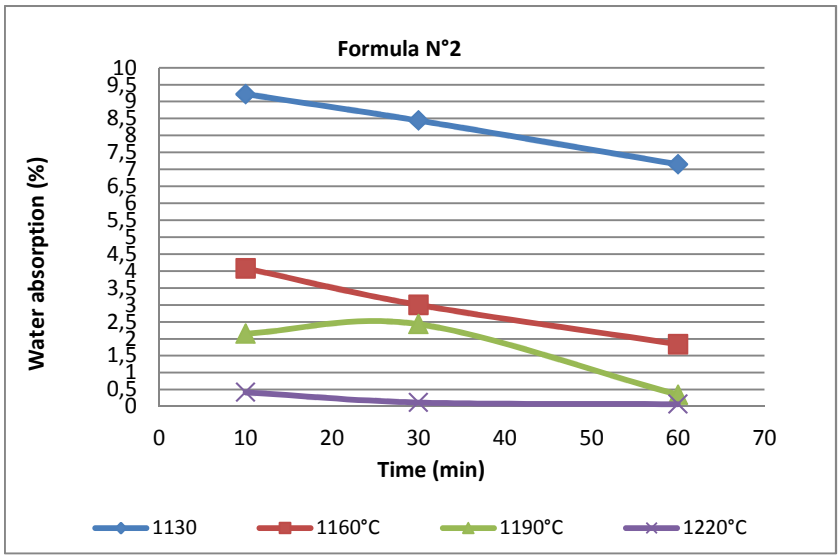

Fig. 2. Evolution of the water absorption of the formula n°2 according to the holding time at various temperatures of firing

Fig. 2 shows that the increase of liquid phase allows the material to be treated thermally at 1190°C but with relatively slow holding time (60min) compared to the usual one which is generally about 30 min.

3.1.3 FORMULA N°3

To achieve better results, we propose to continue our study in order to establish the same abacuses for formula n°3 in which we increase soda feldspar on mixed one to reach a ratio Na_2O/K_2O equal to 3,318. The results are as follows:

Table 6. The water absorption (%) of the formula n°3 according to the holding time at various temperatures of firing

	Temperatures (°C)			
Holding time (min)	**1130 °C**	**1160°C**	**1190°C**	**1220°C**
60	6,32	1,60	0,28	0,06
30	8,12	2,07	0,93	0,08
10	8,59	4,03	1,57	0,22

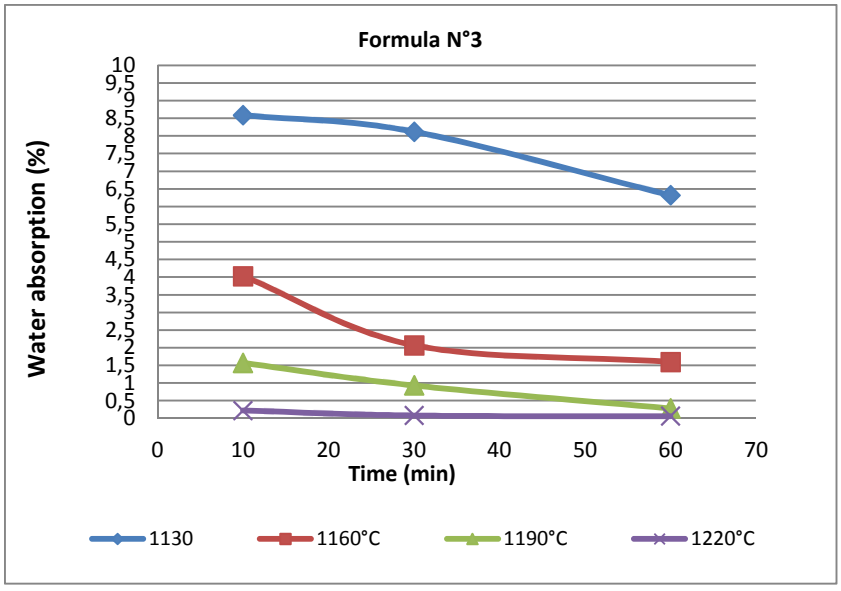

Fig. 3. Evolution of the water absorption of the formula n°3 according to the holding time at various temperatures of firing

Concerning this figure, the porosity drops according to the increase of temperature, but it still impossible to work at temperatures lower than 1190°C.

However, as in the formula n°2, with 1190°C it is possible to reach a satisfactory result after 60 min of holding time. For the same reasons mentioned above, we try to work with the last formula to be able to treat the specimen faster and at low temperature.

3.1.4 FORMULA N°4

Table 7. The water absorption (%) of the formula n°4 according to the holding time at various temperatures of firing

	Temperatures (°C)			
Holding time (min)	**1130°C**	**1160°C**	**1190°C**	**1220°C**
60	6,02	0,39	0,10	0,06
30	8,10	1,68	0,44	0,04
10	8,34	3,61	0,92	0,11

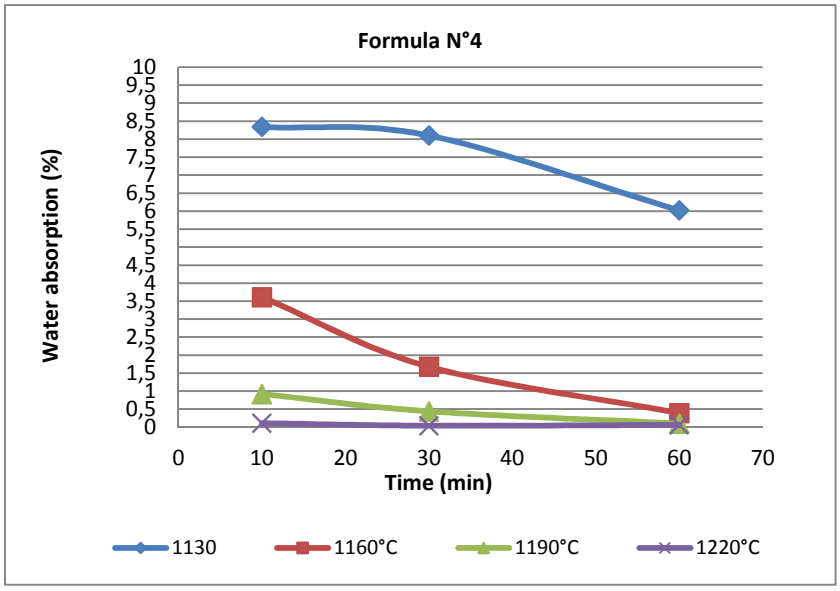

Fig. 4. Evolution of the water absorption of the formula n°4 according to the holding time at various temperatures of firing

With this formula we reached a threshold in which the rate of Na_2O/K_2O is equal to 5,744 (five times more than the usual one). The latter allows to have a vitrified material with a rate of water absorption equal to 0,44% and this at 1190° during a 30 min of holding time.

3.2 ABSORPTION OF WATER AT HOLDING TIME EQUAL TO 30 MIN

To summarize the results, we put in the same table the evolution of the water absorption of the four formulas according to all temperatures but only in 30 min of holding time. The results are as follows:

Table 8. The water absorption (%) of the four formulas according to the temperature with the holding time of 30 min

	Temperatures			
Formulas	**1130°C**	**1160°C**	**1190°C**	**1220°C**
F1	8,60	3,31	3,11	0,25
F2	8,44	3,00	2,43	0,12
F3	8,12	2,07	0,93	0,08
F4	8,10	1,68	0,44	0,04

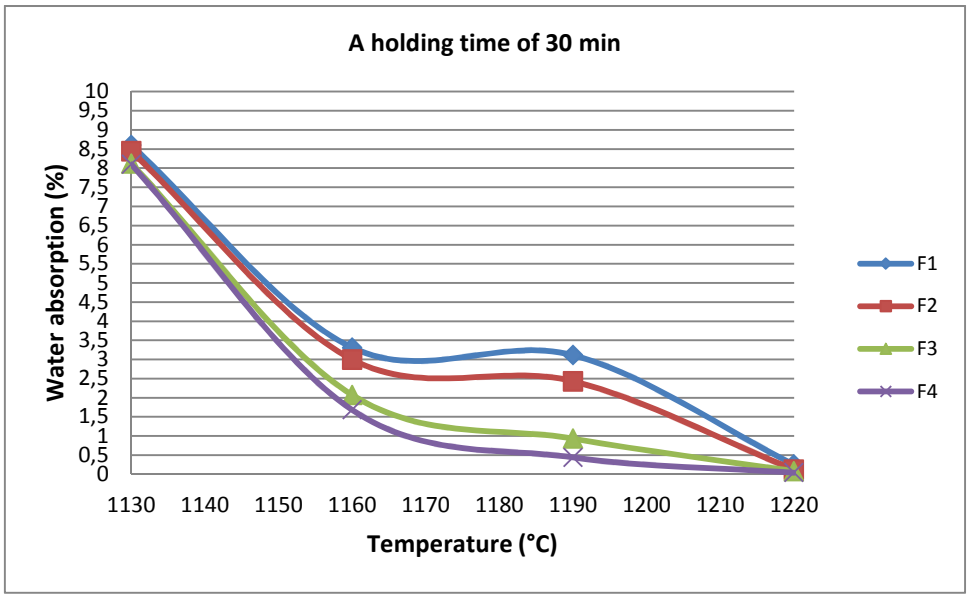

Fig. 5. Water absorption (%) of the four formulas according to the temperature at holding time equal to 30 min

This curve shows that at holding time equal to 30 min, all the bodies resulting from the four developed formulas are vitrified at 1220°C; and that the porosity is lower than 0.5%.

With the formula n° 4, it is clear that we can have water absorption less than 0,5%, yet at temperature of 1190°C.

Generally, porosity decreases with the rise of temperature or the rise of the fusible phase due to the contribution of fluxing agents allowing the formation of eutectics at low temperature. The diameter of the pores starts by increasing with disappearance of the small ones, then while approaching the temperature of sintering, the diameters and the number of open pores fall with formation of one-eyed pores, then of closed pores of small diameter.

In parallel to the study of the influence of soda feldspar on the evolution of water absorption, we have also measured the total shrinkage of four materials treated at various firing temperatures.

3.3 THE TOTAL LINEAR SHRINKAGE AT HOLDING TIME EQUAL TO 30 MIN

Table 9. Total shrinkage (%) of the four formulas according to the temperature at holding time equal to 30 min

	Formulas			
Temperature (°C)	**F1**	**F2**	**F3**	**F4**
1130	8,6	8,7	8,7	8,9
1160	9,8	10,2	10,7	12,0
1190	10,1	10,5	11,0	12,3
1220	11,7	11,5	11,5	12,5

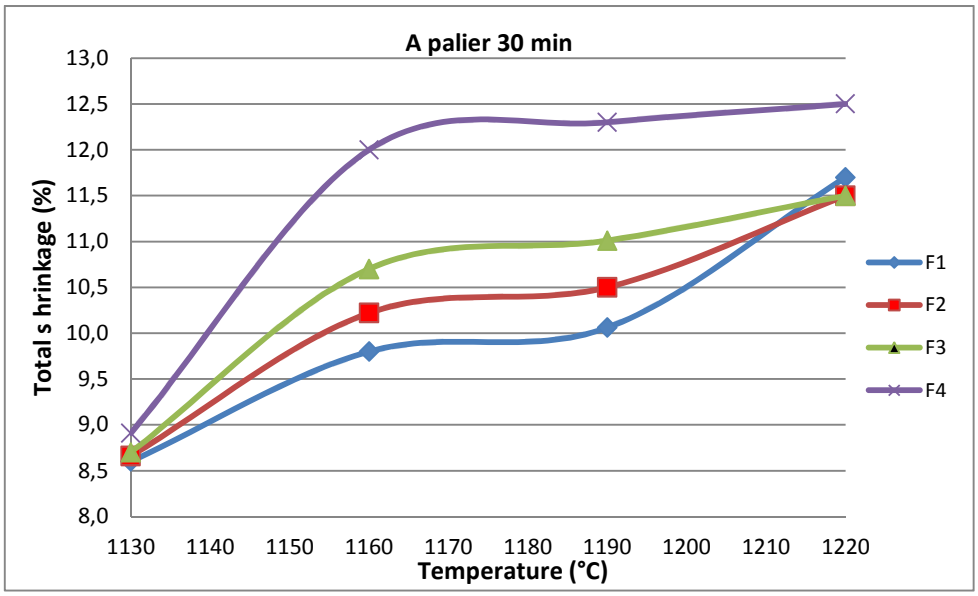

Fig. 6. The evolution of total shrinkage (%) of the four formulas according to the temperature at holding time equal to 30 min

During sintering, the reduction in the volume of the materials is generally due to the progressive disappearance of porosity.

The fig. 6 illustrates the variation of the total shrinkage of the four formulas at various temperatures with holding time equal to 30 min.

It is noticed that the rate of the shrinkage varies in a coherent way. However it is always higher for the formula n°4 compared to the rest of formulas. We can say that the liquid phase appears at lower temperature for this formula and becomes more abundant at high temperatures (1220°C).

3.4 The Flexural Strength At Holding Time Equal To 30 Min

In order to obtain materials not only sintered but also mechanically resistant, we measured the flexural strength for each developed ceramic body at the same holding time (30min).

The mechanical properties of ceramic depend on the surface defects. Among the most important factors influencing these properties there is:

- The porosity;

- The temperature of sintering;

- The volume of the fusible phase in material;

With regards to fired porcelain, the flexural strength reaches its maximum when apparent porosity tends towards zero [5], [9]. Commercial sanitaryware under our experimental conditions yields modulus of rupture values of about 48,26 MPa (mega-Pascal) [10] and this may be compared with experimental body values shown in table 10.

Table 10. The flexural strength (MPa) of the four formulas according to the temperature at holding time equal to 30 min

	Formulas :			
Temperature (°C)	**F1**	**F2**	**F3**	**F4**
1130	28,10	32,40	33,36	38,72
1160	38,80	44,56	48,80	51,98
1190	48,30	52,82	54,11	55,17
1220	61,92	62,33	62,21	65,53

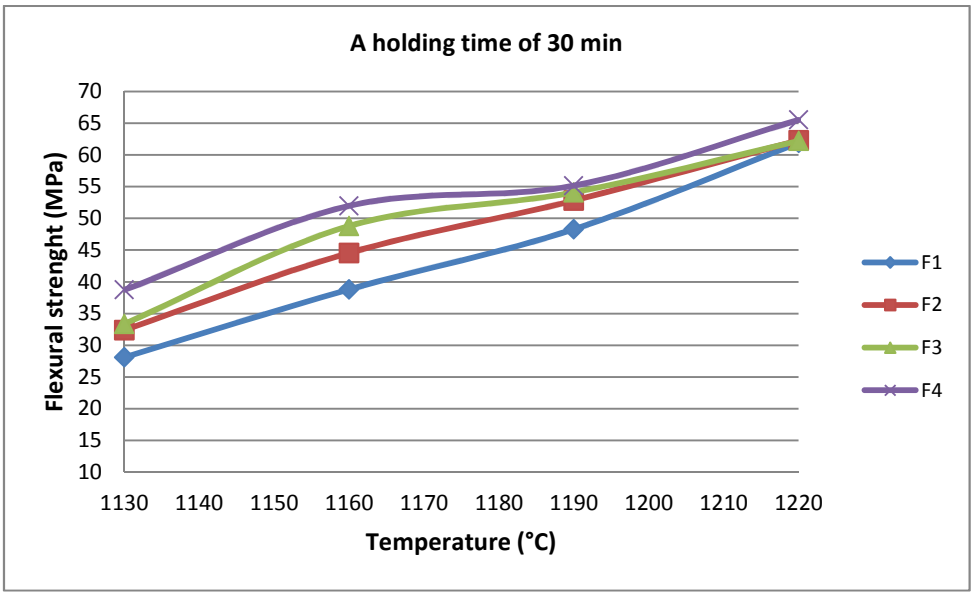

Fig. 7. The evolution of flexural strength of the four formulas according to the temperature at holding time equal to 30 min

The fig. 7 illustrates the variation of the flexural strength of the four compositions at the temperatures: 1130°C, 1160°C 1190°C and 1220°C at holding time of 30 min.

At 1220 °C, the mechanical resistance reaches its maximum between 62 and 65, 53 MPa at all formulas.

With lower temperatures, only the formulas having a high volume of vitreous phase have a relatively important mechanical resistance, especially the formulas n°3 and n°4 which reach the limit of the mechanical resistance at 1160°C. Below this temperature, the materials for the entire compositions become fragile and present a flexural strength lower than the standard.

4 CONCLUSION

During sintering, the growth of the quantity of liquid phase is strongly influenced by the rate of existing sodium oxide in the composition. This oxide decreases the viscosity of glass during the firing of the body and consequently supports the formation of eutectics at low temperature. Taking into account its proportion raised in the formula n°4 to about 0,248 according to the stoechiometric composition “Seger” and which is 1,7 times higher than that in the standard formula, we have successfully reached an optimal firing at a maximum temperature of 1190°C with a holding time of 30 min.

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