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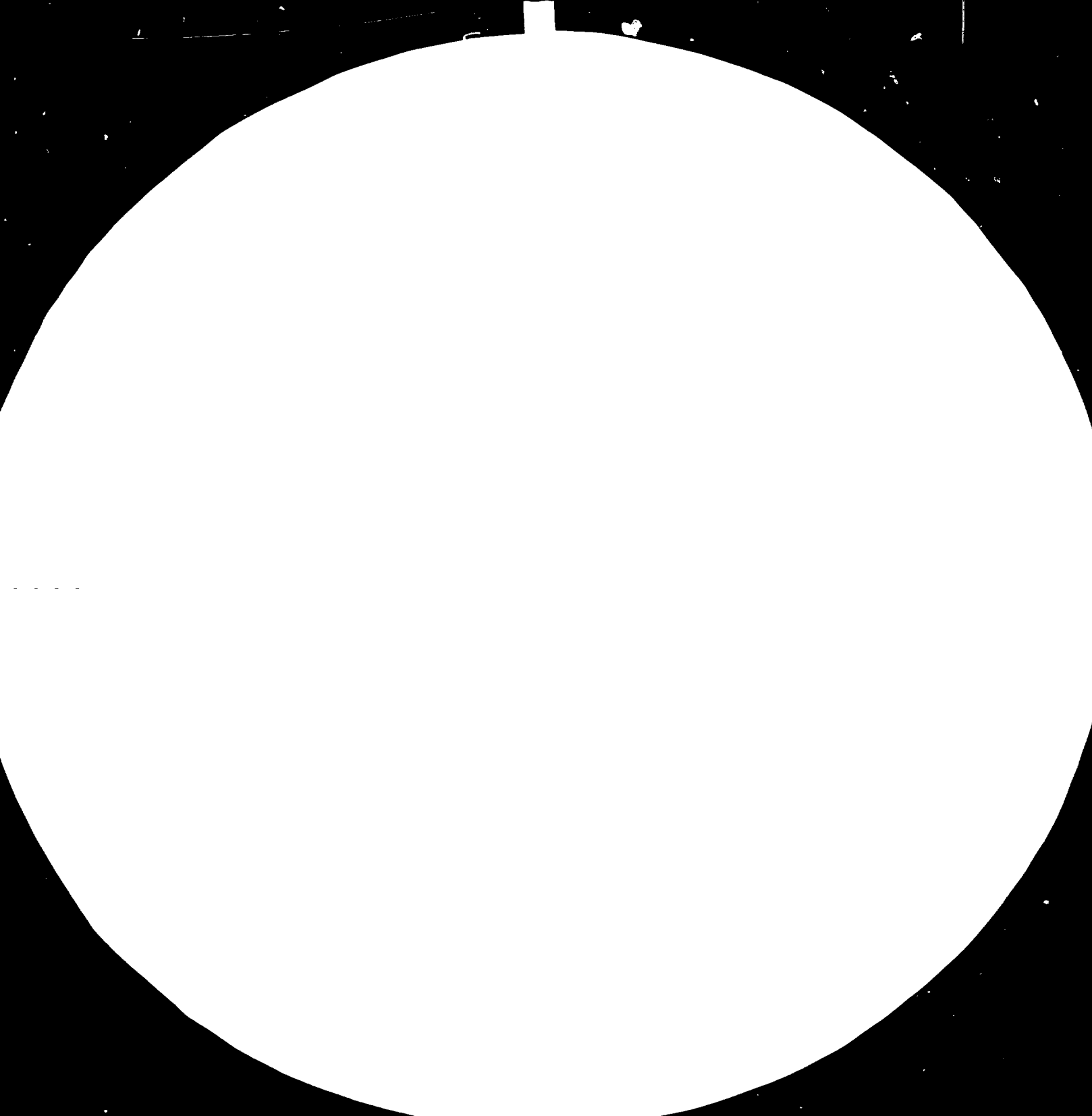

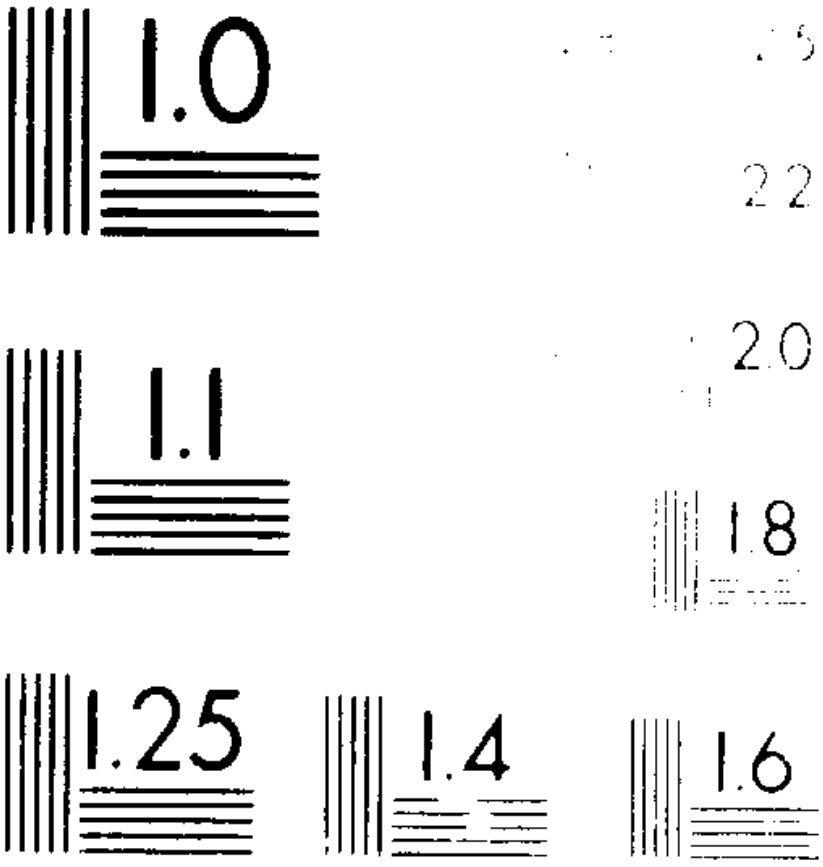
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LIBYAN CEMENT CORPORATION

TF/LIB/82/002

14018

Libya. RED BRICK CLAYS FROM BENGHAZI.

TECHNOLOGICAL TESTS.

DEFINED BY: LIBYAN CEMENT CORPORATION

PERFORMED BY: RESEARCH INSTITUTE FOR CERAMICS, REFRACTORIES AND RAW MATERIALS, PILSEN CZECHOSLOVAKIA

IN CO-OPERATION WITH: UNIDO-CZECHOSLOVAKIA JOINT PROGRAMME FOR INTERNATIONAL CO-OPERATION IN THE FIELD OF CERAMICS, BUILDING MATERIALS AND NON-METALLIC MINERALS BASED INDUSTRIES, PILSEN, CZECHOSLOVAKIA

PILSEN

CZECHOSLOVAKIA

JUNE 1984

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I. INTRODUCTION

During his visit to Libyan Cement Corporation Mr. May, Deputy Director DIO/UNIDO, was requested to assist the corporation in having raw material samples from the brickworks in Benghazí tested. With these tests, special attention was to be paid to the sensitivity to drying. The samples were transferred through UNIDO to the Research Institute for Ceramics, Refractories and Raw Materials in Pilsen, where main physico-chemical tests (DTA, thermodilatometry, chemical analyses) and appropriate technological tests (particle size distribution, plasticity, binding power and mechanical properties after drying and firing) were performed.

According to demand of the Libyan Cement Corporation, emphasies were laid on the testing of properties concerning the behaviour of the samples during drying. The tests were carried out with original samples and also with these samples mixed with different portions of grog. As grog served the Libyan sand G, delivered together with the plastic samples.

The results of tests have shown that there are possibilities consisting in decreasing the sensitivity of the body to drying either by the addition of quartz sands or by the change of the composition of plastic clays.

II. CONCLUSIONS AND RECOMMENDATIONS

Physical, chemical and technological tests of raw materials (sand G, clays M, H, GF) from Benghazi brickworks, Libya were carried out. From the results of these tests following conclusions and recommendations were drawn.

1. Basic Characterisiics of Raw Materials

1.1 Sand G

Siliceous sand is strongly polluted by limestone, the portion of which amounts to 27 per cent by weight. Content of fractions having the grain size below 0,2 mm is very high, whereas the portion of particles with size above 0.5 mm is rather low. This sand can be used as grog in the body but its quality is reduced by limestone.

1.2 Clay M

The main component in this clay is illite. Beside that also quartz and other minerals are present. The temperature of sintering is lowered by alcali like K_2O and by CaO and MgO. This raw material shows a medium plasticity and sensitivity to drying. Being fired above the temperature of 750 ^{o}C it achieves considerable strength. It is suitable for brickmaking.

1.3 Clay H

The chemical and mineralogical composition is similar to that of clay M. Basic component is also illite but the content of limestone is higher reaching the value range of 12 - 15 per cent by weight. It shows medium plasticity and sensitivity to drying. After firing at 750 ^{o}C it gains considerable strength. This clay can be used for the manufacture of bricks but its high sensitivity to drying, content of limestone and lower plasticity reduce substantially the quality of products.

1.4 Clay GF

Illite and limestone in 1 : 1 ratio form substantial portion of clay GF. Alkali, Ca and Mg are contained as well. This raw material has high plasticity and sensitivity to drying. The sensitivity to drying cannot be reduced even by the addition of grog. After firing over 750 °C this material attains considerable mechanical strength.

High content of limestone and high sensitivity to drying deteriorate its quality, so that this clay is not suitable as main plastic component in the body. It can be applied only in small quantities for the modification the properties of the body both before and after firing.

2. Geological Exploration of Reserves

Clay M seems to be suitable for the brickmaking and as the substitute for clay H. It is recommended to carry out a detailed geological exploration of the deposit and semi-industrial evaluation of the clay M.

3. Technological Adjustments Aiming at the Reduction of Rejected Products Within the Drying Process

Taking into the consideration the physical and chemical properties of the raw materials, following measures in the technological process are recommended to be taken.

3.1 To substitute Clay M for Clay H because Clay M is of higher plasticity, lower sensitivity to drying and lower content of limestone than clay H.

3.2 To reduce the portion of clay GF to the minimum content. This clay has extraordinary high sensitivity to drying and its additions to the body have negative influence with respect to drying.

3.3 Humidity of the body ought to be as low as possible during shaping. In this way the drying process can be better accomplished and the rise of cracks in the green bricks will be reduced.

3.4 It is recommendable to increase the portion of grog in the body, especially in case of thick-wall products, up to 20 per cent by weight.

3.5 The portion of the fraction 0,5 - 2 mm in case of thick-wall products ought to be also increased by the addition of crushed fired rejects.

3.6 By creating bigger stocks before driers to lengthen the time of natural drying.

3.7 The drying parameters should be optimized by lowering the temperature at the entry of the drier below 40 ^{o}C and eventually by raising relative humidity of drying medium (controlled humidity drying).
Proposed adjustments in the points 3.2 - 3.5 result in decrease of plasticity. For this reason the following principles ought to be kept to:

3.8 Perfect homogenization of the body, especially with respect to introduction of grog.

3.9 Sufficient maturing of the humid body containig the moisture necessary for shaping.

3.10 Maintaining the maximum possible vacuum during the forming process on the auger press.

4. Pilot Plant Tests of the Raw Materials

Recommendations mentioned above aught to be supported by the semi-industrial tests which would enable to determine the content of the individual components in the body with sufficient accuracy.

At the same time the specific conditions in the technological process whould have to be taken into consideration in case of further testing.

To carry out considerable pilot plant tests, the delivery of approximately 150 kg of plastic clays M and H, 150 kg of sand G and some 50 kg of clay GF would be necessary.

UNIDO-Czechoslovakia Joint Programme for the International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Bazed Industries and the Research Institute for Ceramics, Refractories and Raw Materials in Pilsen are ready to carry out all the necessary technological tests and to provide any technical assistance in implementing new technologies by the Libyan Cement Corporation.

III. TECHNOLOGICAL TESTS OF RED BRICK CLAYS FROM BENGHAZI

1. Sample Specification and Extent of Testing

Four samples of different raw materials were delivered, each having the weight of approximately 0.7 kg.
The samples were labelled in following way:

customer's mark	mark used in this report
I/4/84 Sand - G	G
I/4/84 Clay - M	M
I/4/84 Clay - H	H
I/4/84 Clay - GF	GF

Sample G
was fine sand of yellow colour containing bigger gray/ yellow grains of quartz

Samples M and H
consist of powder portions with solid granular aggregates of red/brown colour

Sample GF
consists of powder portions with solid granular aggregates of grey colour

Laboratory tests were carried out with the samples mentioned above.

Survey of tests carried out on the samples

kind of test	sample			
complete chemical analyses	G	M	H	GF
differential thermal analyses	G	M	H	GF
dilatometric analyses	-	M	H	GF
particle size distribution	G	-	-	-
oversize (mesh 0,063 mm)	-	M	H	GF
mixing water	-	M	H	GF
plasticity number	-	M	H	GF
binding power	G_x	M	H	GF
Bigot curve	G_x	M	H	GF
shrinkage at drying	G_x	M	H	GF
firing	G_x	M	H	GF
physical properties after firing	G_x	M	H	GF
strength after firing	G_x	M	H	GF

G_x = sample was used as grog in case of raw material testing

2. Chemical and Physical Properties Analyses

Chemical and thermal analyses of samples were carried out to verify their basic chemical and mineralogical characteristics. The content of usual oxides in the ceramic body was estimated by means of chemical analyses. The results of these analyses including the loss on ignition are as follows:

Chemical analyses of the samples /per cent/

Component/sample	G	M	H	GF
SiO_2	66.82	59.17	51.91	29.49
Al_2O_3	1.90	16.82	14.38	9.63
Fe_2O_3	0.55	6.95	6.06	3.80
TiO_2	0.13	1.00	0.84	0.50
CaO	15.34	2.85	8.96	26.75
MgO	1.13	1.47	2.41	2.57
K_2O	0.56	2.41	2.50	1.84
Na_2O	0.36	0.51	0.75	0.48
L.O.I.	13.06	8.34	12.07	25.31
Total	99.85	99.52	99.88	100.37

The determination of the individual oxide contents was accomplished by the classical chemical analyses.

Results of DTA were obtained with the air dried samples, particle size of which was below 63 /um. DTA procedures were performed on the equipment Netzsch 402/E. Graphical results are shown in Fig. 1 - 4. They are supplemented by dilatometric measurements during heating in order to improve the accuracy of the mineralogical composition estimation and to determine the behaviour of the samples within the firing process. The dilatometric curves are plotted together with DTA curves (see Fig. 2, 3, 4). Chemical and physical testing of the samples leads to the following results:

Sample G

Free SiO_2 is the preponderant component in the sample (see the holding time on the DTA curve at 573 °C). Decomposition of limestone is responsible for the endothermic reaction in the temperature range from 850 to 900 °C. Obviously magnesite and dolomite is also present in small quantities. Exothermic deflection in the temperature range 100 - 400 °C proves that organic compounds form small portion as well.

The basic components of the sample contain usual impurities in tenths of per cent.

Sample M

Main component in this plastic sample is illite. This assertion is supported by the typical sourse of DTA curve having the endothermic holding times at 100 °C and 520 °C. Characteristic course of dilatometric sample changes at heating accompanied by the firing expansion up to 700 °C with subsequent fast shrinkage above 900 °C proves the presence of illite as well. The decomposition of illite crystal lattice and rise of spinels takes place in this temperature range. Al_2O_3/SiO_2 ratio in the sample corresponds to the stoichiometric ratio of these oxides in illite. Endothermic holding time at 730 °C is due to the presence of magnesite whilst the exothermic effect at the temperature of 320 °C is caused by a considerable portion of organic compounds. The peak on the DTA curve at the temperature 570 °C corresponds to the polymorphic transformation of quartz. There are also ferrous impurities and an increased content of K_2O in the sample.

Sample H

DTA curve and the dilatometric changes are similar, to the great extent, to those of the sample M. Clay mineral illite forms here the basic component as well. But the limestone content is substantially higher with this sample which corresponds to the endothermic holding time at the temperatures above 800 °C.

Exothermic effect at the temperature of 900 °C correlates with the decomposition of the illite crystal lattice. The content of other oxides is not too different from that of sample M.

Sample GF

From the course of the DTA curve and estimated CaO content it can be inferred that sample contains up to 45 per cent by weight of limestone. Further important mineral in the sample is illite which implies from the appropriate endothermic reaction on the DTA curve. On the contrary the exothermic reactions at the temperatures of 250 °C and 870 °C correspond to the presence of organic compounds and the decomposition of the structural lattice.

High content of limestone the decomposition temperature of which corresponds to the temperature of lattice breakdown with illite obviously promotes the decomposition of illite and the formation of new compounds.

The content of further oxides does not differ too much from that of previous samples. Due to high limestone content there is a considerable high L.O.I. value.

3. Technological Test of the Modified Samples

3.1 Determination of the Particle Size Distribution

The results of the determination of the particle size distribution with the sample G, used as grog are:

Particle size distribution of the sample G

mesh /mm/	oversize /per cent/
4	0.0
3	0.0
2	0.9
1	14.2
0.5	17.8
0.315	7.7
0.20	11.0
0.09	33.4
under 0.09	15.0

The result of mesh analyses shows that there is a relatively high portion of particles having size below 0,2 mm, whereas the particles with size from 1 to 4 mm are negligible.

3.2 Determination of Workability in the Plastic State

The informative evaluation of workability and rheological properties was carried out using the results of the determination of oversize on the mesh 0,063, mixing water and plasticity number. Plasticity and mixing water determination was accomplished by means of Pfefferkorn equipment. Plasticity number according to Pfefferkorn is defined for the deformation ratio 3.3.

The binding power of the raw materials was evaluated by measuring the green strength of briquettes containing the various portions of grog (sample G). The measured values of these tests were considerably high even in case of 70 per cent of grog, which is demonstrated by the following figures:

Determination of the bending strength after drying

sample	bending strength (MPa) addition of grog (%)		
	0	40	70
clay M	1.75	2.35	1.84
clay H	2.98	2.75	1.49
clay GF	3.78	3.28	1.93

The binding power of all plastic samples was very good which is demonstrated bellow:

Workability properties and plasticity of tested samples

sample		clay M	clay H	clay GF
oversize /mesh 0,063 mm/	(%)	2.91	5.58	4.31
mixing water x)	(%)	25.6	24.4	32.3
plasticity	(%)	23.0	20.1	25.4

x) mixing water is expressed as absolute humidity related to the weight at the dry state of the sample.

The highest values of the plasticity number and the mixing water has the sample GF. Sample M shows the better quality with respect to the mixing water and plasticity comparing with those of sample H.

3.3 Sensitivity to Drying

Due to the negative experiences with the drying of clays at the factory in Benghazi, special attention was paid just to this problem. With respect to drying following procedures were carried out:

1/ studying the shrinkage on the briquettes
2/ estimation of Bigot curves
3/ modified method of Poggi

The average values of shrinkage at drying are as follows:

sample		clay M	clay H	clay GF
shrinkage at drying	(%)	6.7	6.4	9.0

Bigot curves are shown in Fig. 1 and 2. From these curves the coefficients of sensitivity to drying have been estimated and attached to the plotted curves. (See Fig. 1 and 2.) The sample GF has the high coefficient of sensitivity to drying whereas those of the samples M and H have medium ones. Addition of 20 per cent of grog to the clays transformed the course of their Bigot curves but the values of coefficients above mentioned have been changed only slightly.

Coefficients of Sensitivity to Drying According to the Course of Bigot Curves

sample	clay M	clay H	clay GF
original clay	1.2	1.1	1.8
clay with 20 % of grog	1.4	1.7	2.2

The highest values of coefficients were those of clay GF which is the most sensitive clay to drying. The values of this coefficient for clays M and H are practically the same ones.
The growth of the sensitivity-to-drying coefficients caused by the addition of grogs does not correspond to the practical experience.
According to modified method of Poggi dependence of the bending strength of bricks on the temperature of drying at the strictly defined conditions was studied.
Exceeding of the maximum rate of drying is evaluated according to the strength of the test specimens. To attain more objective assesment of this phenomenon, information about the degree of macroscopic destructions of specimens is attached in Fig. 3, 4, 5 according to following criteria:

degree of deformation	state of test specimen
0	without cracks
1	microcracks on the edges
2	microcracks on the edges and surfaces
3	big cracks on the edges
4	big cracks on the edges and surfaces

Drying has been carried out on the laboratory drier equipped with the automatic temperature control and circulation of drying medium. Testing briquettes of dimensions 8 x 4 x 1,8 cm were used to determine the sensitivity to drying and also for firing tests. Test specimens made from the body having the humidity equal to that of mixing water were put into the drier after half an hour of stay in the air. The results of measurements and the evaluation of the influence of the drying on the specimens are given in Fig. 7, 8, 9 including the information about drying conditions. Safe drying temperature data according to results from Fig. 7, 8, 9 are as follows:

Safe Drying Temperature of Test Specimens (^{o}C)

sample	clay M	clay H	clay GF
original clay, Fig. 7	30	20	<20
original clay with 20 % of grog	40	30	20
original clay with 40 % of grog	>40	>40	20

>safe drying temperature is greater than 40 °C
<safe drying temperature is smaller than 20 °C

From the date given above it can be seen that the sample M shows the smallest sensitivity to drying. Real safe drying temperature values can be even lower due to actual shape of the product.

Following conclusions can be drawn from the testing: sample GF shows extremely high sensitivity to the drying. Lowering of the sensitivity to the drying in this case cannot be accomplished even by the addition of big portions of grog or by slow drying. The samples M and H are substantially less sensible to the drying process. Addition of grog causes the lowering of the sensitivity to drying with both samples but the sample M shows better results in this respect and it can be said that this sample has the lowest sensitivity to drying comparing with sample H and GF.

3.4 Technological Test of Plastic Samples after Firing

The briquettes for firing were prepared both from original plastic clays and with the addition of 20 - 40 per cent by weight of sample G as grog. The extent of these tests were limited due to the delivered quantity of samples. Holding time of 2 hours at the maximum temperature of firing was kept to in all firing tests. Shrinkage on firing and physical properties including the bending strength were evaluated on all fired specimens.

3.4.1 Properties after Firing - Sample M (without the addition of grog)

property	temperature of firing (holding time 2 hours)			
	750 °C	900 °C	1000 °C	1100 °C
shrinkage on firing (%)	0.00	1.69	2.68	5.71
water absorption (%)	17.8	15.4	13.8	8.3
porosity (%)	32.1	13.8	27.1	18.0
bulk density ($kg.m^{-3}$)	1805	1970	1970	2170
bending strength (MPa)	3.94	10.2	-	-

Properties after firing - Sample M

(addition of 20 per cent by wt. of sample G as grog)

property		temperature of firing 900 °C (holding time 2 hours)
water absorption	(%)	19.0
porosity	(%)	34.4
bulk density	($kg.m^{-3}$)	1810
bending strength	(MPa)	3.37

The test sample showed good strength already when it was fired at 750 °C. After firing at 900 °C very good values of water absorption and mechanical strength were achieved. Besides this the tests proved that the samples showed the broad interval of sintering, which is advantageous for the attainment of the uniformity of the fired products.

The addition of 20 per cent of grog caused the deterioration of the strength, but despite this the results are acceptable in this respect.

If 40 per cent of grog was added to the clay, test specimens broke down during the water absorption test. The sample M is suitable for the production of bricks. But the appropriate attention must be paid to the problem of optimum grogging.

3.4.2 Properties after Firing - Sample H
(without the addition of grog)

property	temperature of firing (holding time 2 hours)			
	750 °C	900 °C	1000 °C	1100 °C
shrinkage on firing (%)	0.02	2.07	0.53	4.28
water absorption (%)	19.8	17.0	18.2	12.1
porosity (%)	34.6	31.1	33.1	23.9
bulk density ($kg.m^{-3}$)	1750	1830	1820	1980
bending strength (MPa)	5.2	11.3	-	-

Properties after Firing - Sample H
(addition of 20 per cent by wt. of sample G as grog)

property		temperature of firing 900 °C (holding time 2 hours)
water absorption	(%)	18.5
porosity	(%)	33.8
bulk density	($kg.m^{-3}$)	1830
bending strength	(MPa)	5.11

Properties after firing are practically identical with those of the sample M. Limestone content couses higher porosity and also firing expansion at the temperature of 1000 °C.

3.4.3 Properties after Firing - Sample GF (without the addition of grog)

property		temperature of firing (holding time 2 hours)			
		750 °C	900 °C	1000 °C	1100 °C
shrinkage on firing	(%)	0.00	2.93	2.85	1.46
water absorption	(%)	24.1	20.8	27.7	26.3
porosity	(%)	38.7	33.0	42.6	41.6
bulk density	($kg.m^{-3}$)	1600	1580	1540	1580
bending strength	(MPa)	3.49	12.7	-	-

Considerable strength has been achieved already if the samples were fired at the temperature of 750 °C. Fired bricks have higher values of water absorption as the result of the secondary porosity caused by the decomposition of limestone.

IV. FINAL NOTE

High percentage of rejects in the brickworks Libyan Cement Corporation is caused by the extraordinary high sensitivity to drying of the used clays. The problem can be solved by means of technological adjustments but at the same time the installed technological equipment must be taken into consideration.

For this reason the pilot plant tests must be carried out. Special attention must be paid to the content and sort of grog. The UNIDO-Czechoslovakia Joint Programme for International Co-operation in the Field of Ceramics, Building Materials and Non-metallic Minerals Based Industries in Pilsen and the Research Institute for Ceramics, Refractories and Raw Materials in Pilsen are ready to accomplish further tests on larger scale including the large scale introduction of new raw material bodies in the factory.

V. REFERENCES

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VI. ANNEX

Figure 1

Sample Sand G

DTA Analyses

_____ T (°C)

weight-in quantity:
0,4 g

rate of heating:
10 °C/min.

sensitivity:
0,08 °C/mm

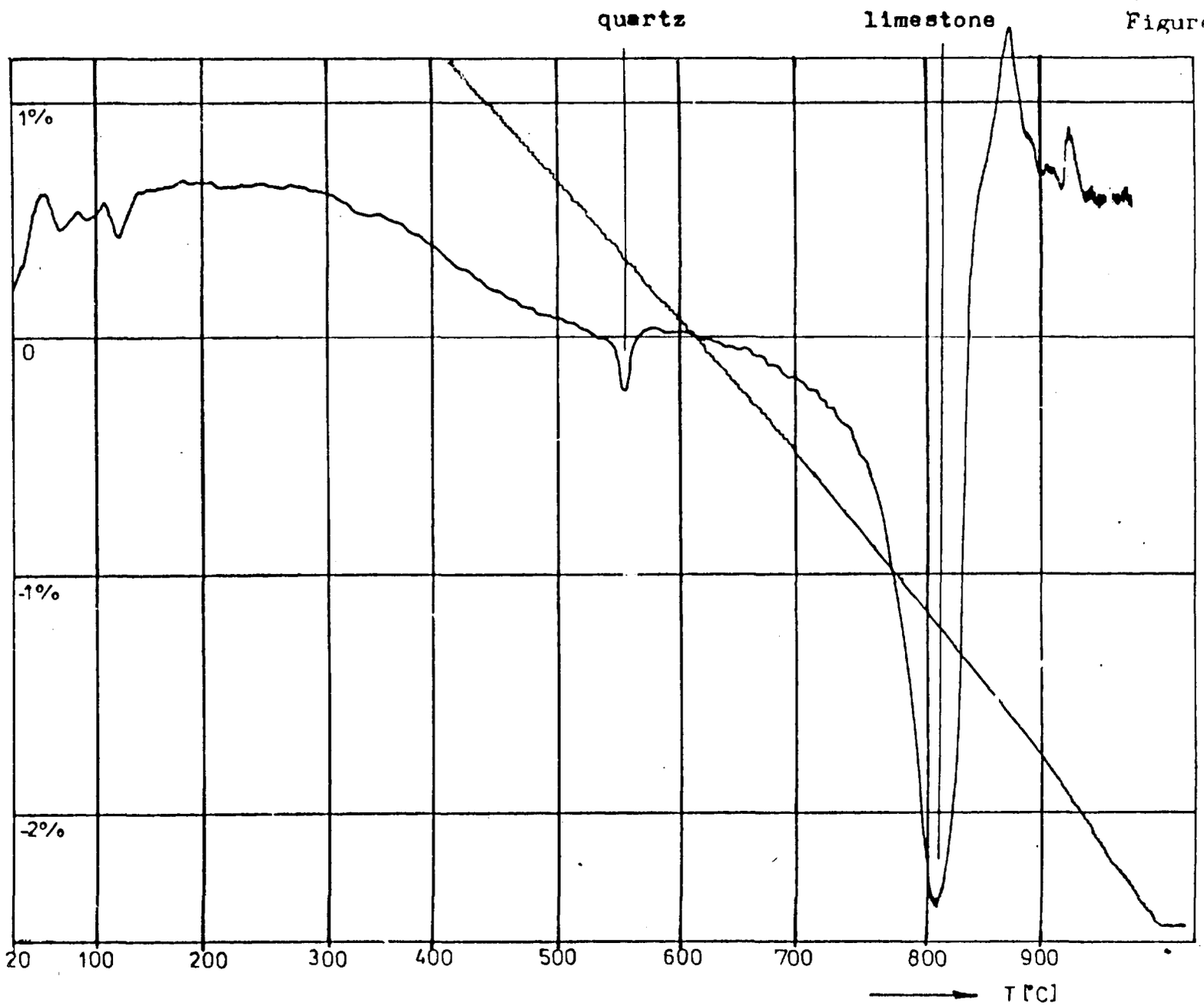


Figure 2

Sample Clay M

DTA Analyses

——— T (°C)

Weight-in quantity:
0,4 g

Rate of heating:
10 °C/min.

Sensitivity:
0,08 °C/mm

Dilatometric Changes

-------- D (%)

Specimen length:
30,2

Rate of heating:
5 °C/min.

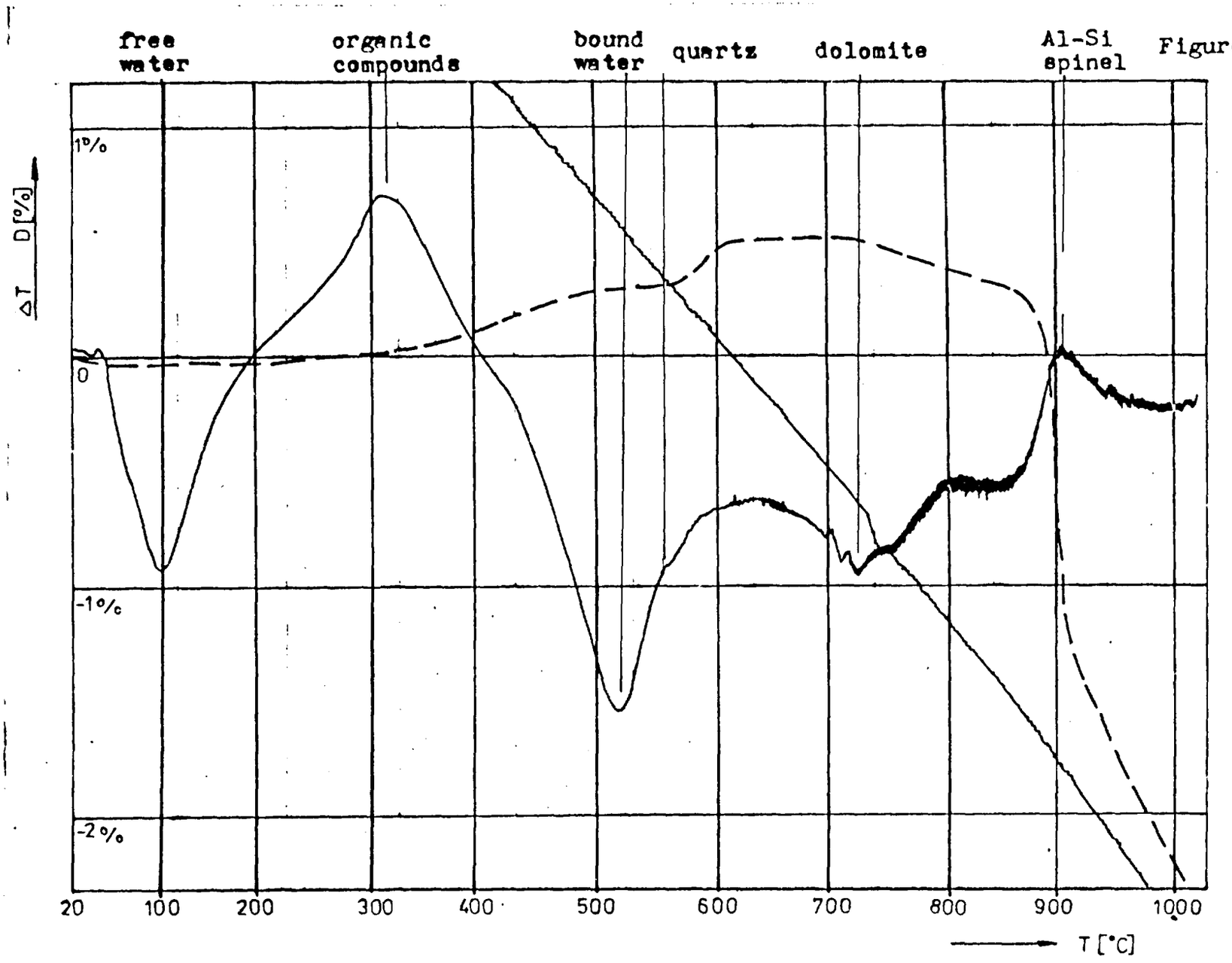


Figure 3

Sample Clay H

DTA Analyses

_____ T (°C)

weight-in quantity:
0,4 g

rate of heating:
10 °C/min.

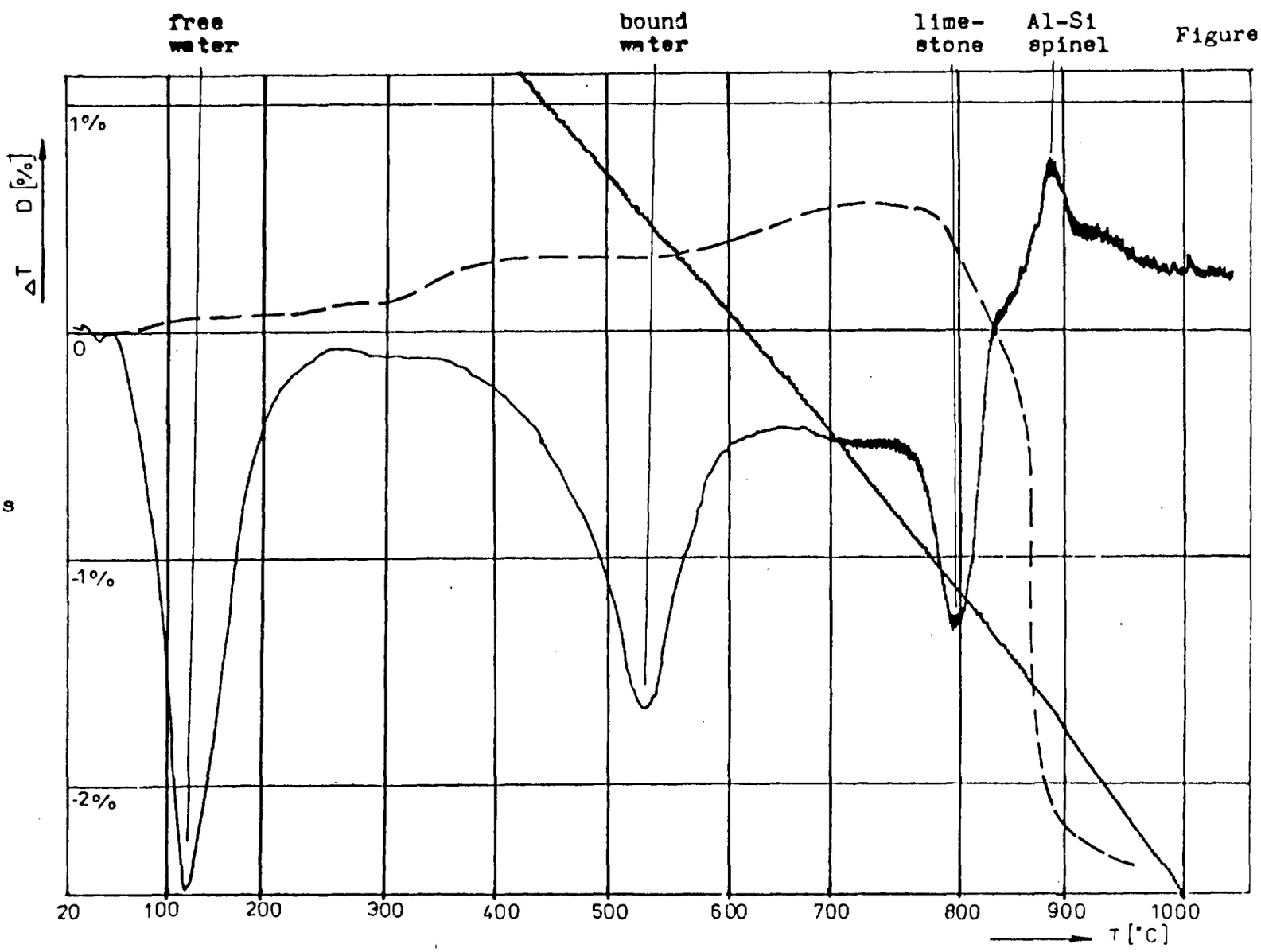
sensitivity:
0,08 °C/mm

Dilatometric Changes

------ D (%)

specimen length:
30,3 mm

rate of heating:
5 °C/min.



Sample Clay GF

DTA Analyses

——— T (°C)

rate of heating:
10 °C/min.
sensitivity:
0,08 °C/mm
weight-in quantity:
0,4 g

Dilatometric Changes

------- D (%)

specimen length:
30,2
rate of heating:
5 °C/min.

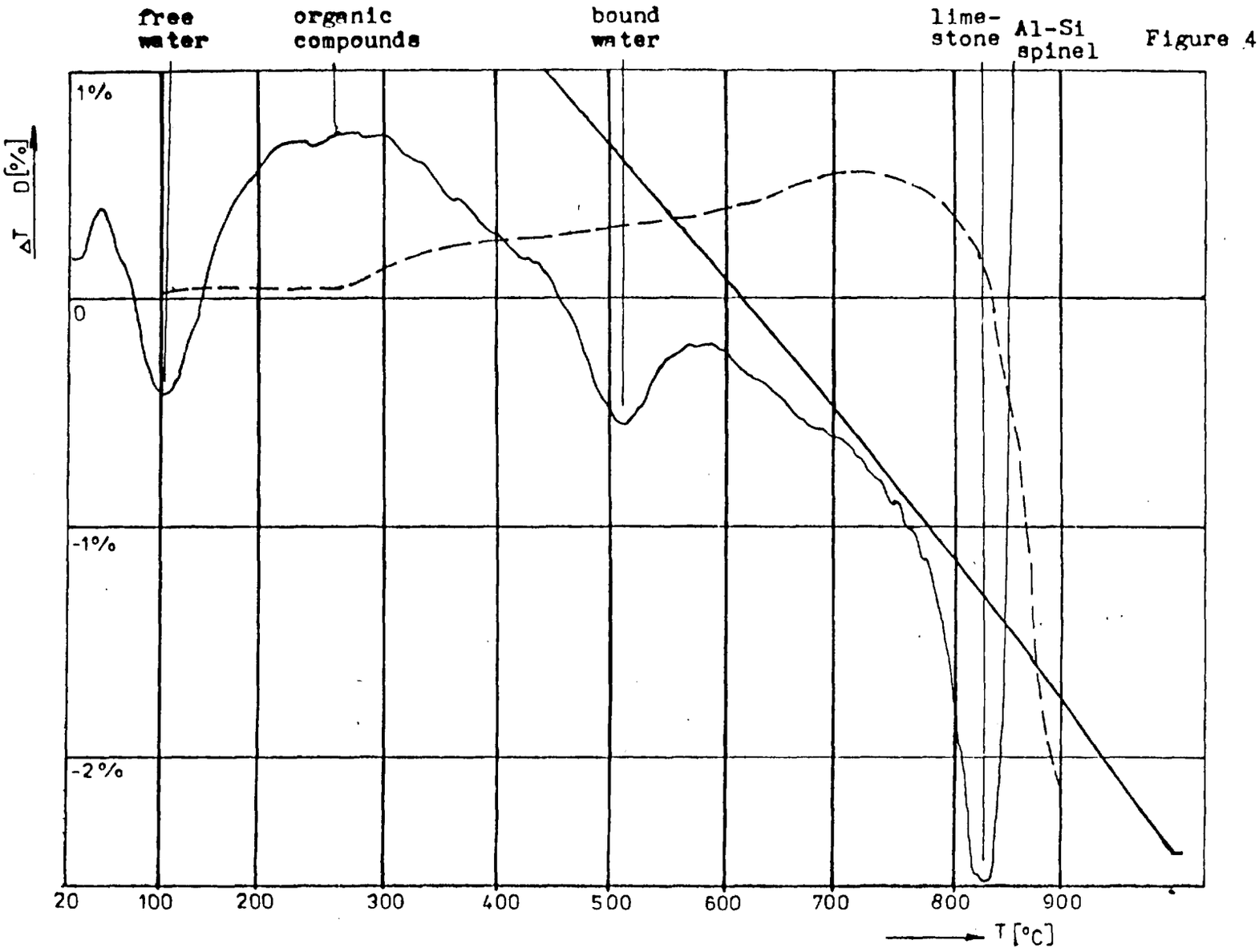
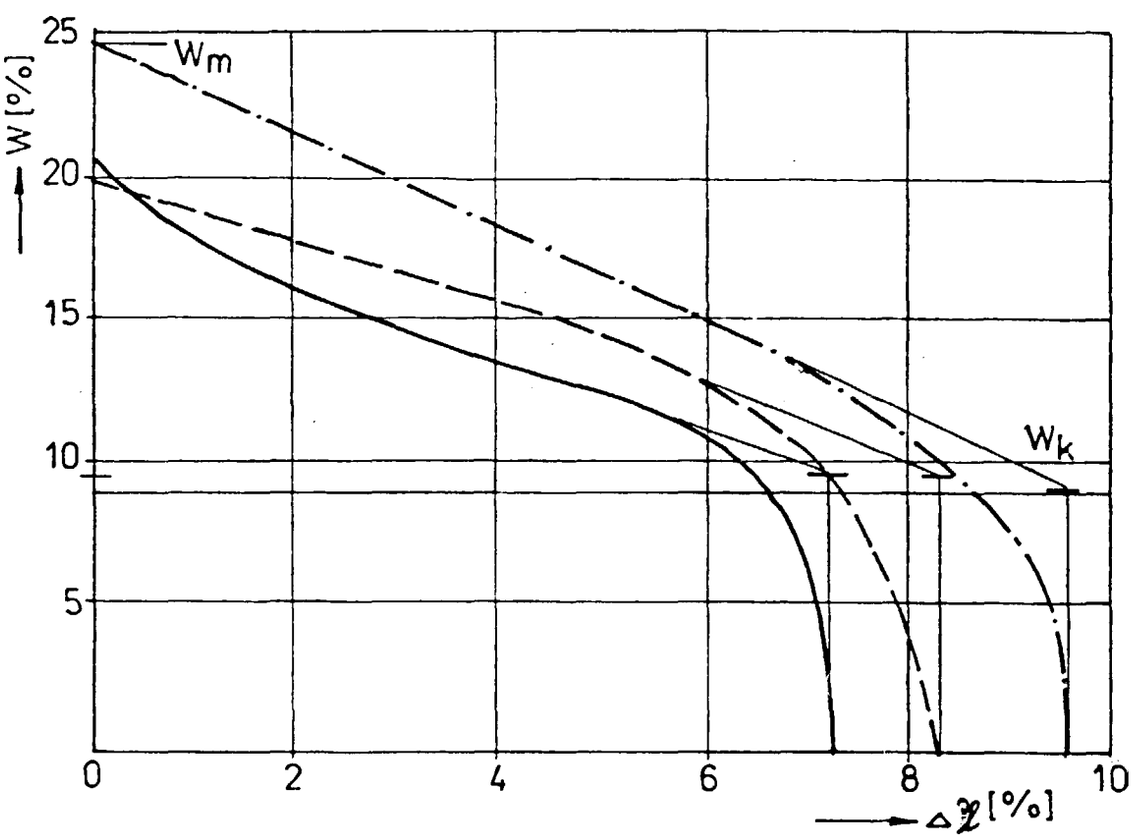


Figure 4

Figure 5

Bigot curves of drying (samples M, H, GF)
- dependence of relative moisture of the sample W on the shrinkage Δl

clay			M ——	H – – –	GF —·—
maximal moisture	W_m	[%]	20,9	19,9	24,64
critical moisture	W_k	[%]	9,5	9,5	8,8
drying sensitivity	K_s	[1]	1,2	1,1	1,8

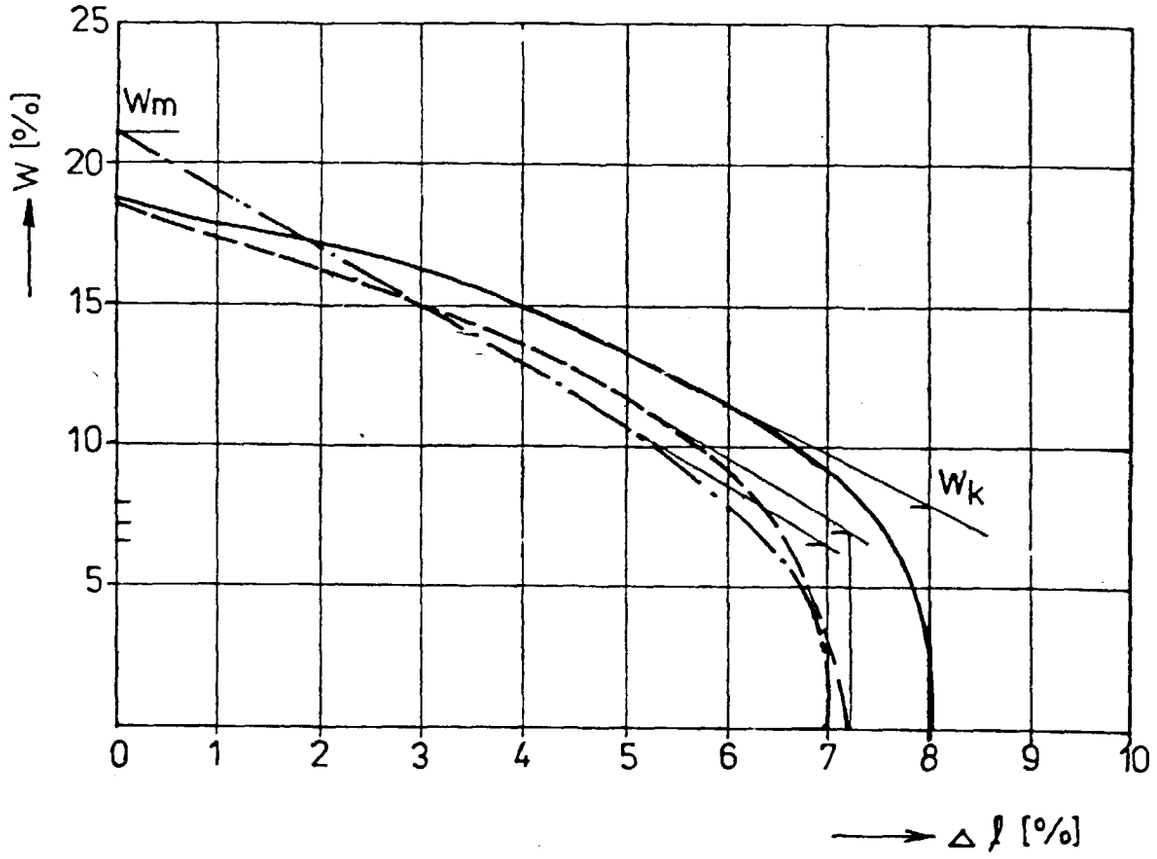


$$K_S = \frac{W_m - W_k}{W_k} \qquad [1]$$

Figure 6

Bigot curves of drying (samples M, H, GF + 20 % of grog)
- dependence of relative moisture of the sample W on the shrinkage Δl

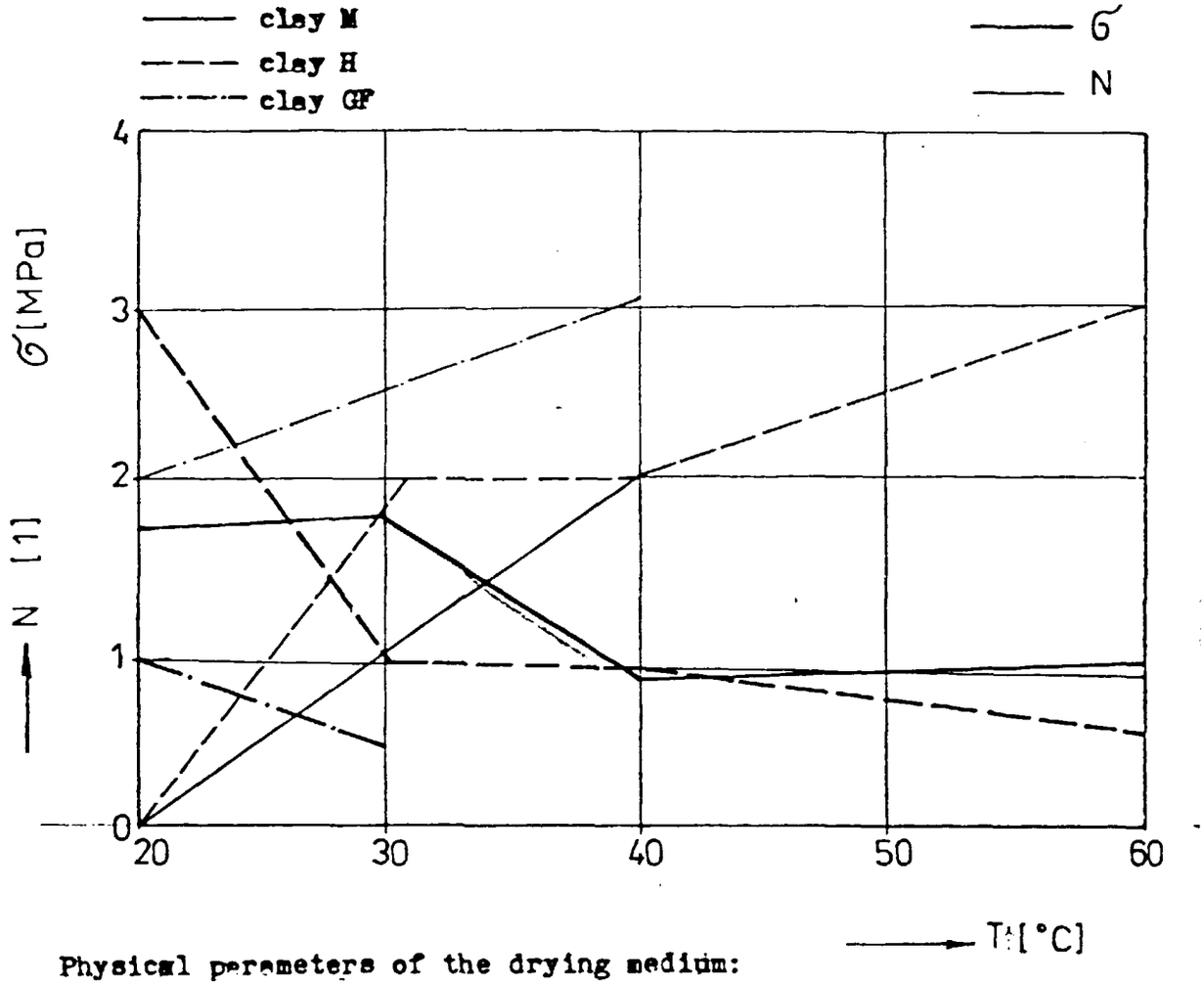
clay + 20 % sand G			M ——	H– – –	GF —·—·—
maximal moisture	W_m	[%]	19,2	18,9	20,8
critical moisture	W_k	[%]	8,0	7,0	6,5
drying sensitivity	K_s	[1]	1,4	1,7	2,2



$$K_s = \frac{W_m - W_k}{W_k} \qquad [1]$$

Figure 7

Dependence of dry bending strength σ and rate of macroscopic destruction of test specimens in the course of drying N on the drying medium temperature T



Physical parameters of the drying medium:

temperature T	°C	20	30	40	60
relative moisture	(%)	52	29	20	5,8
rate of flow	(m/s)	0,0	0,25	0,25	0,25
average rate of drying	(g H_2O/h)	0,81	2,1	3,0	5,5

Figure 8

Dependence of dry bending strength σ and rate of macroscopic destruction of test specimens in the course of drying N on the drying medium temperature T

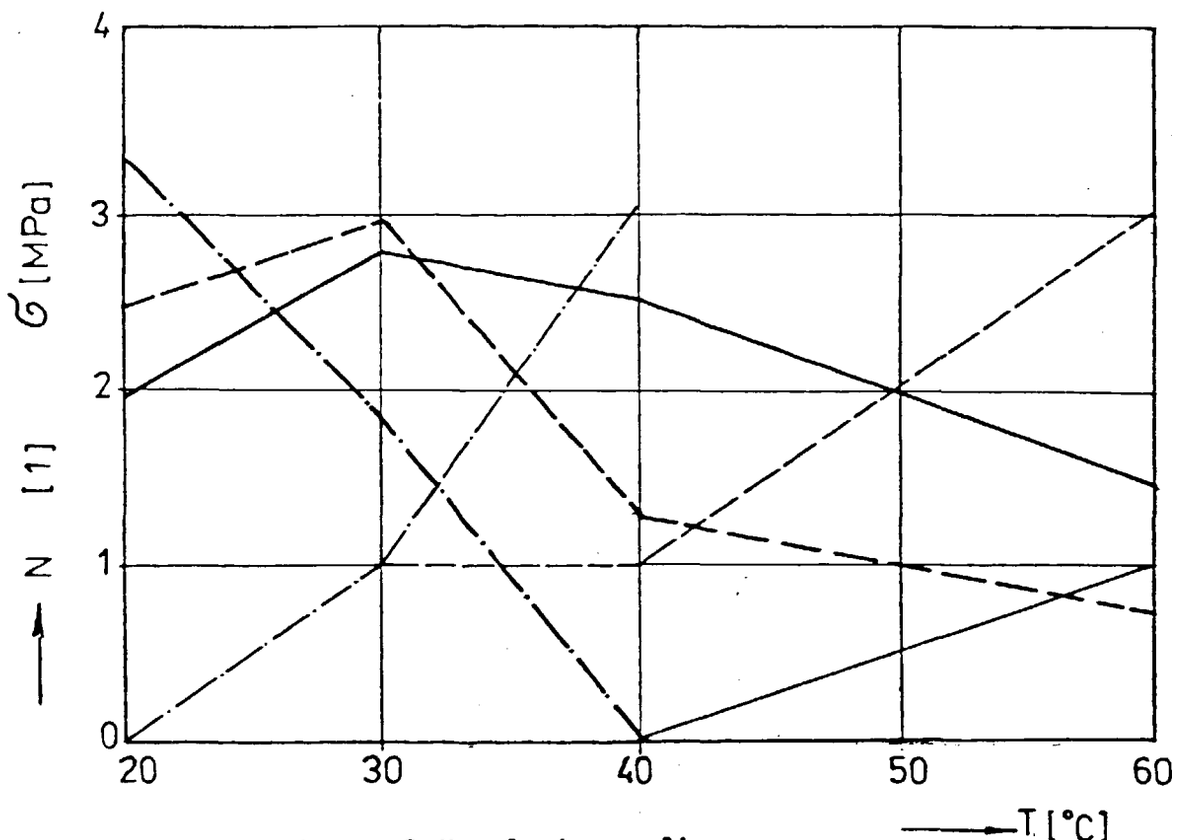
——— clay M + 20 % sand G

– – – clay H + 20 % sand G

——— clay GF+ 20 % sand G

——— σ

——— N

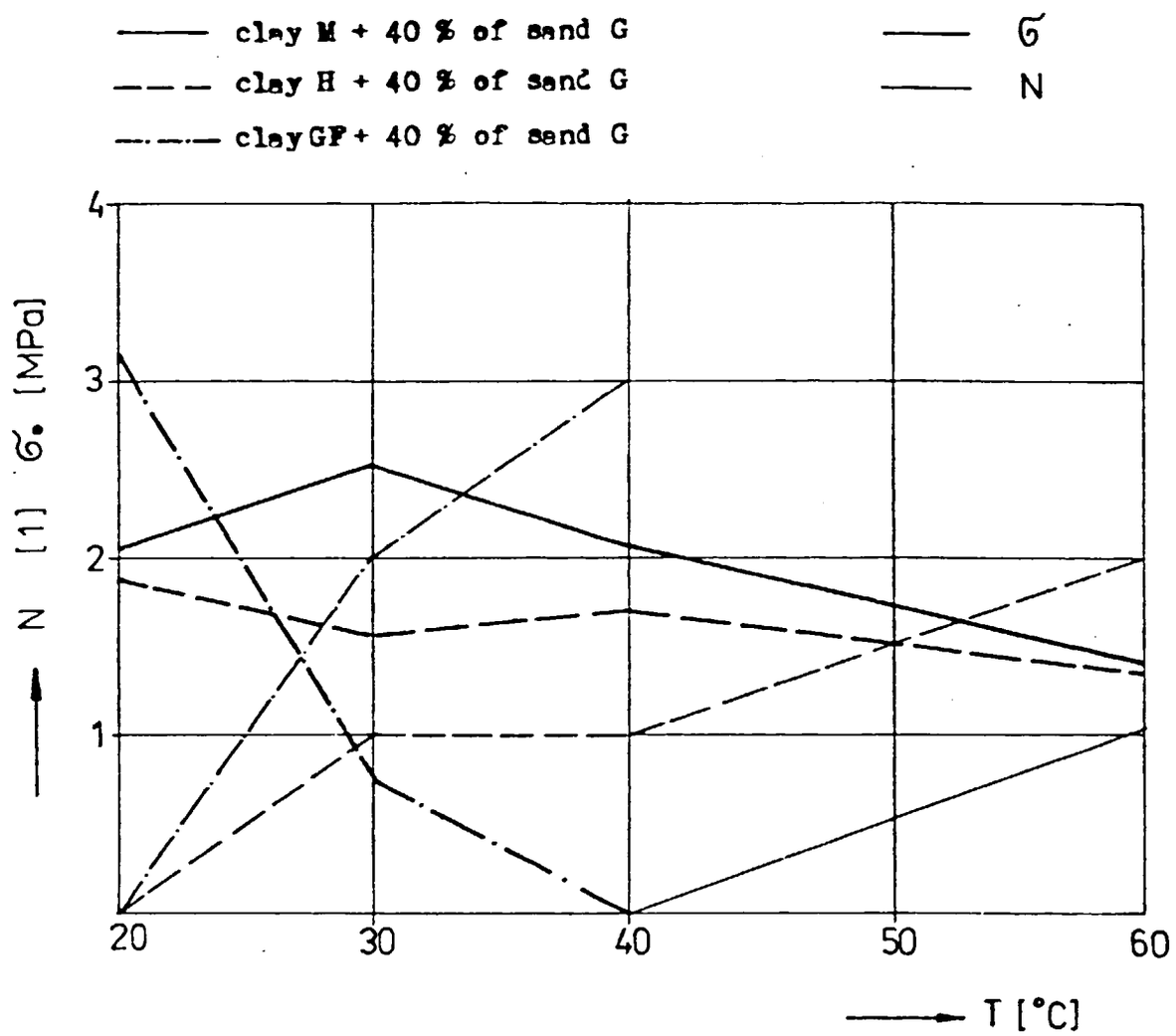


Physical parameters of the drying medium:

temperature T	°C	20	30	40	60
relative moisture	(%)	53	29	20	5,9
rate of flow	(m/s)	0,0	0,25	0,25	0,25
average rate of drying	(g H_2O/h)	0,68	2,1	3,2	5,2

Figure 9

Dependence of dry bending strength σ and rate of macroscopic destruction of test specimens in the course of drying N on the drying medium temperature T



Physical parameters of the drying medium

temperature T	(°C)	20	30	40	60
relative moisture	(%)	55	30	23	6,4
rate of flow	(m/s)	0,0	0,25	0,25	0,25
average rate of drying	(g H_2O/h)	0,71	2,1	2,4	4,7