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Melting Behavior of Flat Glass Batches with Additions of Hydrated Alumina,
Nepheline Syenite and Calumite

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This work concerns the melting of flat glass batches with increases in alumina content from 0.35 to 0.45 to 0.7% Al_2O_3 . The alumina was provided by hydrated alumina, nepheline syenite and Calumite.

The introduction of blast furnace slag (Calumite) showed the most advantageous melting behavior. The use of Calumite had advantages over the other sources particularly through a decrease of the soda ash in the batch. Nepheline syenite showed no advantage over hydrated alumina either in melting behavior or viscosity-temperature relation.

Energy costs become more and more important in the process of glass melting. The energy consumption of a big flat glass furnace was discussed by Ehrlich (1). In an earlier essay, Kroger (2) showed that only about 20% of the melting energy was used in the actual process of the chemical reactions and 80% for preheating the reaction products to 1500°C in order to homogenize the melt by osmosis. Pugh (3) managed to essentially reduce the temperatures for the process of the chemical reactions by substituting oxide and hydroxide raw materials for carbonates. The present essay examines the melting process of different aluminum oxide bases in glass batches in light of energy savings and decreasing soda in favor of Dolomite.

1. Research proposal and procedure of the experiment

The following had to be checked or determined: the sintering process of the aluminum oxide bases hydrated alumina, nepheline syenite and Calumite; the melting process of 12 different batches at 1350 and 1400°C at different points of the reaction; the exchange of soda for dolomite in the batch to reduce the cost of raw materials; the viscosity of the molten glass as a function of temperature; the rate of growth of the crystal and the increase in the seed growth of the experimental melts and finally, the spectroscopic porosity of the glass.

The batches listed in chart I were melted from dried raw materials. The resulting glass compositions are compiled in chart II. Chart III shows the chemical analyses of the applied nepheline syenites and the introduced blast furnace slag (Calumite). In picture I the grain density of the two aluminas have been entered.

The sintering process of the aluminas was examined under a thermal microscope to DIN 51 730 (4). The melting reaction of the different batches was determined



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in a process developed by the Department of Glass and Glasswork Science at the Rhenish-Westphalian Technical University at Aachen. 20g of glass were melted at a time in melting pots with a volumetric capacity of about 20ml. In this process, the entire batch was put into a cold melting pot and the melting pot was inserted into a prefitted bore in a firebrick, which had already been placed in the furnace at the temperature of the experiment. The brick served as a muffle and assured that all of the melting pots of one phase of the experiment underwent the same temperature treatment (picture 2).

They were taken out in the same order in which they had been inserted. Thus the time differences at the beginning of the experiment were compensated for by a corresponding handling at the end of the experiment.

After a short cooling period at room temperature to a temperature of 800°C, the melting pot was put into a lehr preheated to 720°C and cooled at a rate of 10.5K/min. The wall of the melting pot was mechanically removed after the cooling. After this, the vitreous bodies were embedded in synthetic resin. Two cuts, both symmetrical and parallel to the axis of the melting pot, made it possible to lift out 5mm plane parallel slices which were embedded with immersion fluid between glass covers and judged optically.

Batch I, which had 0.35% Al_2O_3 in the glass and contained hydrated alumina, served as a reference sample. The following melting temperatures and times were recorded:

1350°C - 1h, 2h, 3h, 4h

1400°C - 1h, 2h

The viscosity of the different glasses was determined with two direct viscosimeters. Since only slight variations in the temperature-viscosity reactions were expected for the different melted glasses, the devices were standardized with the standard glass I of the DGC. According to its composition, this glass is a drawing glass and serves as a calibration standard¹⁾. After the standardization of the devices, viscosity-temperature curves were found to be within the margin of error. The producer of the devices allows for a maximal margin of error of ±3% relative to the viscosity measured in dPa s.

In order to determine a possible evaporation loss of Na_2O at the time of the viscosity measurement, the Na_2O content was checked with the help of an emission spectral analysis after the viscosity of every glass had been determined and this reading was then compared with the calculated Na_2O content. The variations were within the margin of error given for the standard glass. After every temperature change of 25K, a glass sample of 50mg was tempered for 20 minutes in a funnel-shaped holder made out of platinum foil in a barrel furnace in order to determine the devitrifying range.

The evaluation was made exclusively under the microscope, that is the nucleus formation by counting the crystal centers within a certain area and the rate of growth of the crystal by measuring the longest crystal needles with a calibration scale.

2. Discussion of experimental results

The evaluation of the results were obtained with the thermal microscope. The three examined aluminae showed for the temperature reactions characteristic points, compiled in Chart 4.

The sintering reaction, found in the tests that were described here can be explained with the phase diagrams $Na_2OAl_2O_3SiO_2$ (nepheline syenite) and $CaOAl_2O_3SiO_2$ (Calumite). According to the first-mentioned diagram for the composition of the nepheline syenite, as it was found in the chemical composition, one can expect a melting point of about 1400°C. According to the chemical analysis, Calumite lies in the area of Gehlenite $2CaO-Al_2O_3-SiO_2$. This was confirmed, since in tests to



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devitrify Calumite, Gehlenite was found radiographically. If one enters the analytically determined chemical composition in the phase diagram $\text{CaOAl}_2\text{O}_3\text{SiO}_2$, there is a dot at the phase border with Gehlenite and Calcium-Silicate with a melting point of about 1440 to 1450°C. The grain density of the nephelite syenite is much lighter than that of the Calumite (Picture 1). It is even below that of sand. Thus this raw material has a very big surface area which is important for the melting reaction. The grain density of the glassy Calumite is much coarser and can more easily be counted among the grain size density of the Carbonatic raw materials, such as dolomite and limestone.

The melting reaction of the different batches was optically examined as described in paragraph I. At a temperature of 1350°C of the experiment and after one hour of melting time, the samples No. 9, 10 and 11 show the best melting reaction, with sample 10 already almost totally melted. Sample 8 melted particularly slowly. This is the sample with 0.7% Al_2O_3 and the exchange of 1% Na_2O for 1% MgO . After two hours, the samples no. 10 and 11 have totally melted. Sample no. 6 and 8 still show large, unmelted areas. After three hours, samples no. 7, 9, 10, and 11 (Alumina Calumite) are totally melted and mostly non-porous. All the other samples still contain unmelted batch parts and bubbles. After 4h, the samples No. 6 and 8 still contain the highest amount of unmelted batch. Samples No. 7, 9, 10 and 11 have totally melted and except 7 are also totally nonporous. The other sample still contains but small amounts of unmelted material, but still show a strong bubble formation.

At a temperature of 1400°C for the experiment, batches no. 2 and 7 were for practical reasons not melted any more. After one hour of the experiment, one notices again the very good melting property of batches No. 10 and 11. For example, no. 8, however most of the batch is still not melted. After two hours almost all samples have totally melted. Only the samples no. 1, 8, and 12 show small amounts of batch residue. Only the samples no. 9, 10, and 11 also show a nonporous melt.

The results of the experiment clearly show a better melting property of those samples that contain Calumite as alumina, compared to those with nephelite syenite and hydrated alumina. Even though pure nephelite syenite melts at about 40K below the melting temperature for blast furnace slag and also shows a much lighter grain density by comparison, batches containing Calumite show a much better melting property.

One also notices that a higher Al_2O_3 content (samples No. 10 and 11; 0.7% Al_2O_3) does not affect the good melting property. The samples that contain nephelite syenite as alumina do not show a much different reaction from traditional hydrated alumina. Only sample No. 8 with 0.7% Al_2O_3 and an additional exchange of 1% Na_2O for 1% MgO shows, apart from the 2 hr. experiment at 1400°C, a much worse melting property than all other samples. Should a substitution of Na_2 by MgO be nevertheless desirable in order to cut costs, it is in any case preferable to use Calumite as alumina.

The very good melting property of sample No. 11 proves this. It is also necessary to consider the very good refining reaction of the melted batches when Calumite is used rather than nepheline syenite and hydrated alumina.

The viscosity-temperature reaction of the molten glasses is graphically represented in pictures 3 to 6. Pictures 3 to 5 show this correlation for glasses with the same alumina content and different alumina in the batches. Picture 6 shows the viscous temperature reaction for glasses with increasing Al_2O_3 content but always the same alumina (Calumite).



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As can be seen in picture 3, sample No. 7 with an Al_2O_3 content of 0.35%, is throughout the whole temperature range, higher in viscosity than the reference glass (sample No. 1). The temperature difference as to the different viscosities is about 15 with lower viscosity range and increases to about 18K in the upper viscosity range.

Picture 4 shows the comparison of the glass samples No. 2, 4, 5 and 9 (0.45% of Al_2O_3 content) with the sample No. 1 (0.35% Al_2O_3 content). Sample No. 5 shows the highest viscosity readings, since in this glass not only the alumina content was increased but also 1% of Na_2O was substituted for 1% of MgO . The glass sample No. 2 comes closest to the reference sample No. 1, as to its viscosity-temperature reaction. The average temperature difference for the same viscosity values is 20K. Compared to sample No. 2, the samples No. 4 and 9 show only a slight increase in viscosity. The differences, though, are within the margin of error of the test data. The viscosity-temperature curves, entered in picture 5 for glasses with an Al_2O_3 content of 0.7% show higher viscosity differences among themselves than the glass samples depicted in picture 4. It is noticeable that the viscosity curves of the samples No. 10 (Calumite as alumina) and 12 (nepheline syenite as alumina) are congruent. The glass sample 8 shows the largest difference. This glass was melted with nepheline syenite as alumina and 1% MgO was exchanged for 1% Na_2O . Looking at the viscosity-temperature curves in picture 6, one notices that even though there is an increase in the alumina content and a substitution of 1% Na_2O for 1% MgO , the differences in viscosity of the different samples are within the accuracy of the measurement. The maximum temperature difference between sample No. 7 (0.35% Al_2O_3) and sample No. 10 (0.7% Al_2O_3) is 8K, and the temperature difference between sample No. 7 and sample No. 11 (substitution of 1% Na_2O for 1% MgO with 0.7% Al_2O_3) is at the most 12K. The glass samples compared here were all melted with Calumite as alumina. When comparing the glass samples in picture 6, one clearly notices that, when using Calumite, the alumina content can be increased from 0.35 to 0.7% Al_2O_3 , if, at the same time, 1% Na_2O can be substituted for 1% MgO .

The viscosity-temperature curve of the glass sample No. 8 shows, however, that much higher temperatures are needed when Na_2O is substituted for MgO in the presence of nepheline syenite as alumina for comparable viscosity data.

When hydrated alumina is used as alumina in the batches, one always gets lower viscosity readings at the same temperatures than when using nepheline syenite and Calumite. This difference becomes very clear, when the glasses show the same chemical compositions. This deviation can only be explained by the structure of the melted glasses.

The rates of crystalline growth of the samples No. 1, 11 and 12, which are relevant for the practice, is indicated in picture 7. The rates of crystalline growth show no important differences. The nucleus formation numbers, though, show great differences. If one equates the nucleus formation of the glass sample No. 1 in a temperature field between 875 and 1000°C, with reference to one, then the sample No. 12 (nepheline syenite as alumina) shows double to triple, and sample No. 11 (Calumite as alumina with a decrease of alkaline oxide) fivefold the number of nucleus formations. The reason for the strong nucleus formation reaction in sample No. 11 was not further examined in the experiment. Maybe the results can be explained with the results of Seifert's experiments on silicate melts containing alkaline oxide earth.



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Picture 8 gives the example of transmissions between two glasses with 6mm layer thickness that were melted with nepheline syenite and Calumite. Because of the relatively high content of FeO and sulfide sulfur in Calumite, a shifting of the transmission in the IR-range of 0.7% from Calumite, if no oxidizing agents are added to the melt. In a glass of 6mm thickness under maximum absorption at 050nm (Fe^{2+}) it is about 6.0%. This difference in transmission is reduced in the visible area to 2%.

3. Summary

With an increase in the Al_2O_3 content in flat glasses from 0.3 to 0.7% hydrated alumina is replaced by nepheline syenite in the batch for economic reasons. The present tests show, though, that a batch containing nepheline syenite has no melting advantage over a hydrated alumina batch. Calumite, though, influences the melting process of the examined batches favorably; the higher the content of Calumite in the batch, the better.

Since nepheline syenite has a lower grain concentration and thus a larger reactive surface than Calumite, as well as a lower melting temperature, according to the sintering experiment, a better melting property of the batches containing nepheline might have been expected.

The favorable melting and refining property of the batches containing Calumite can be attributed to the glassy condition and the relatively high sulfide sulfur content of this raw material. Since almost 70% of today's batch costs can be traced to the soda content, it was attempted to reduce sodium oxide in the glass in favor of magnesium oxide. As the tests show, such a substitution can, in the presence of nepheline syenite as alumina in the batch, only be effective by using higher melting temperatures. But in the presence of Calumite, the substitution works very well, because of a property in this raw material which accelerates the melting process.

In practice, the laboratory tests were proven to be correct. The viscosity-temperature readings show that in the melting as well as the forming process the melting temperatures of the glasses melted with hydrated alumina lie at most 20h below those of the glasses that were melted with Calumite or nepheline syenite. In the same chemical analysis, the melts containing nepheline syenite and Calumite are the same, within the margin of error as far as their viscosity-temperature reaction is concerned.

All devitrifying tests of melt No. 11 (alumina Calumite and substitution of Na_2O by MgO) show a higher number of nucleus formation as compared to similarly composed glasses with the aluminae nepheline syenite or hydrated alumina in the batch. It can be assumed that Calumite causes the nucleus formation here. A systematic examination of the nucleus formation number as a function of the Calumite concentration in the batch was not conducted.

Calumite contains more iron than nepheline syenite. The iron (II) - iron (III) correlation is very much shifted in favor of the bivalent iron ion. This can be noticed in the transmission of the glass, when the amount of Calumite is used, that creates an Al_2O_3 content of 0.7% in the finished glass. When comparing the transmission of a 6mm thick glass, the glass with Calumite as alumina shows a transmission loss of 6% during the maximum absorption of 1050nm. This should not influence the melting process negatively, though.



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4. Literature

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CHARTS AND ILLUSTRATIONS

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CHART I: BATCHES WITH DIFFERENT ALUMINAE IN REFERENCE TO 100 G. OF GLASS

Chart No.	1	2	4	5	6	7	8	9	10	11	12
<u>Components</u>											
Sand	71,539	71,503	70,840	70,818	71,405	71,129	71,384	70,93	70,293	70,290	70,200
Soda	23,322	23,227	22,893	21,238	23,306	23,292	21,652	23,60	23,555	21,820	23,310
Dolomite	19,970	19,960	19,960	24,954	16,488	19,771	21,481	19,64	19,290	24,200	19,897
Limestone	6,014	6,011	5,981	3,134	6,120	5,138	3,274	4,66	3,506	0,699	5,900
Natrium Sulfide	0,919	0,915	0,915	0,850	0,943	0,919	0,877	0,53	0,533	0,536	0,533
Hydrated Alumina	0,276	0,429	-	-	-	-	-	-	-	-	-
Nepheline Sylenite	-	-	1,172	1,138	2,185	-	2,151	-	-	-	2,156
Calumite	-	-	-	-	-	1,213	-	1,886	3,442	3,388	-

CHART 2: CHEMICAL COMPOSITION (IN %) OF THE MELTED GLASSES (SAMPLE NO. BATCH NO. FROM THE BATCHES (CHART I)

Sample No.	SiO ₂	SO ₃	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Cl ⁻
1	71,48	0,30	14,04	0,029	9,61	4,055	0,35	0,062	0,045	0,030
2	71,44	0,30	13,98	0,029	9,61	4,053	0,45	0,062	0,045	0,030
4	71,44	0,30	13,88	0,133	9,61	4,052	0,45	0,063	0,046	0,030
5	71,44	0,30	12,88	0,130	9,61	5,053	0,45	0,070	0,046	0,028
6	72,55	0,26	14,21	0,219	8,60	3,351	0,68	0,058	0,045	0,030
7	71,47	0,30	14,03	0,030	9,61	4,054	0,35	0,063	0,057	0,030
8	72,54	0,26	13,21	0,316	8,60	4,351	0,68	0,065	0,045	0,028
9	71,49	0,30	14,04	0,040	9,61	4,050	0,45	0,047	0,056	0,031
10	71,36	0,30	14,02	0,060	9,56	4,030	0,68	0,070	0,070	0,031
11	71,36	0,30	13,02	0,060	9,56	5,030	0,68	0,070	0,070	0,031
12	71,36	0,30	14,02	0,215	9,55	4,040	0,68	0,063	0,044	0,030

CHART 3: CHEMICAL ANALYSIS OF NEPHELITE AND CALUMITE (COMPOSITION IN %)

	Nepheline Syenite	Calumite
SiO ₂	56,4	33,00
Na ₂ O	7,7	0,45
K ₂ O	8,7	0,85
Al ₂ O ₃	23,7	15,00
CaO	1,4	45,00
Fe ₂ O ₃	0,105	0,20
MnO	-	0,30
TiO ₂	-	0,60
MgO	-	3,50
	-	0,65

Screen Analysis, See Illustration 1.



August 1983

Einschmelzverhalten von Flachglasmengen unter Einsatz von Tonerdehydrat, ... Glastechn. Ber. 199

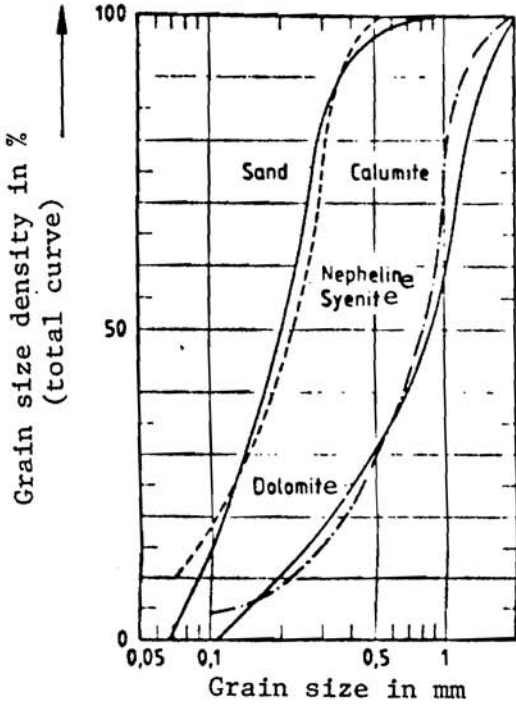


Illustration 1. Grain density analysis of melting sand, nepheline syenite, dolomite and calumite.

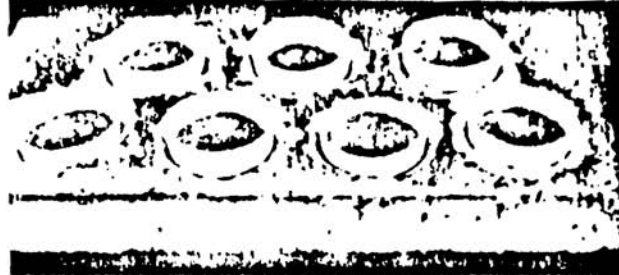


Illustration 2. A fireproof brick with batch samples.

CHART 4: TEMPERATURE REACTION OF THREE DIFFERENT ALUMINAE

	Nepheline Syenite	Calumite	Hydrated Alumina
Sintering Start	1280 °C	1410 °C	} There was no change in the sample in the 1500°C measuring range.
Melting Point	1310 °C	1420 °C	
Hemispheric Point	1380 °C	1435 °C	
Point of fluency	1400 °C	1440 °C	

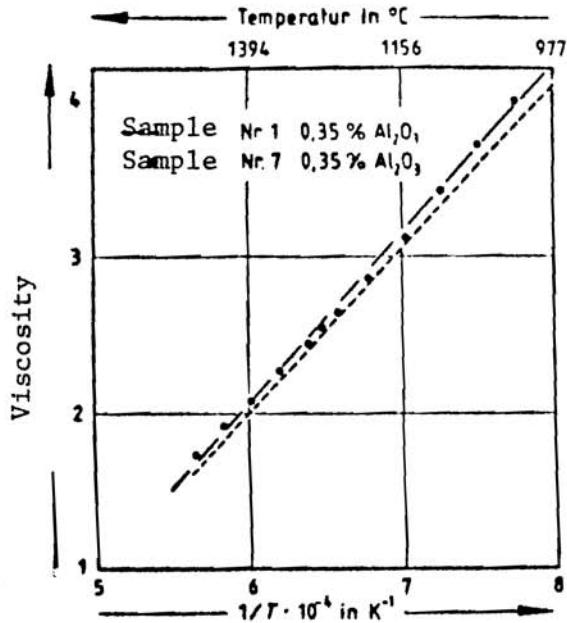


Illustration 3. Viscosity-temperature reaction of glasses containing aluminum oxide with different aluminae in the batch.

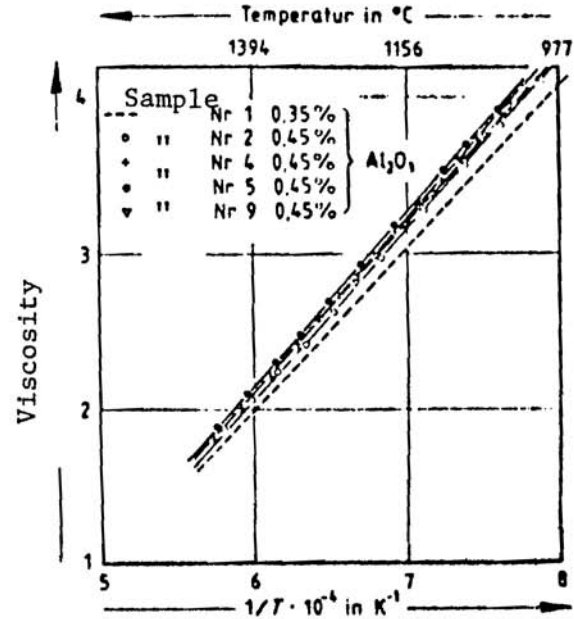


Illustration 4. Viscosity-temperature reaction of glasses with the same aluminum oxide content (sample nos. 2, 4, 5, and 9) compared to sample no. 1 (0.35% Al_2O_3) with different aluminae in the batch.

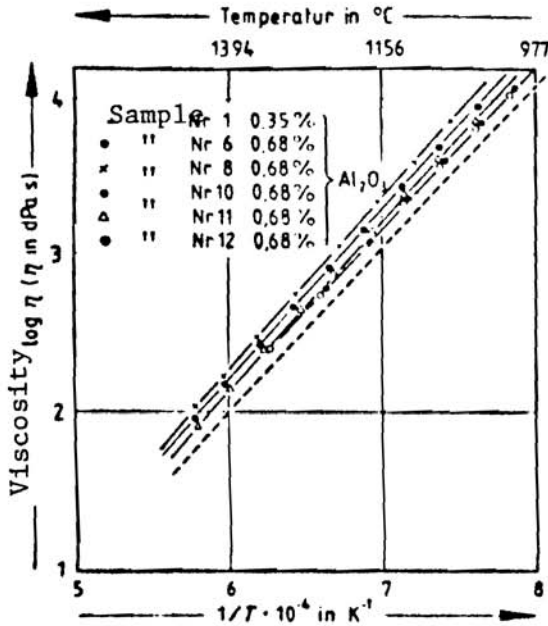


Illustration 5. Viscosity-temperature reaction of glasses with the same aluminum oxide content (sample nos. 6, 8, 10, 11 and 12) compared to sample no. 1 (0.35% Al₂O₃) with different aluminae in the batch.

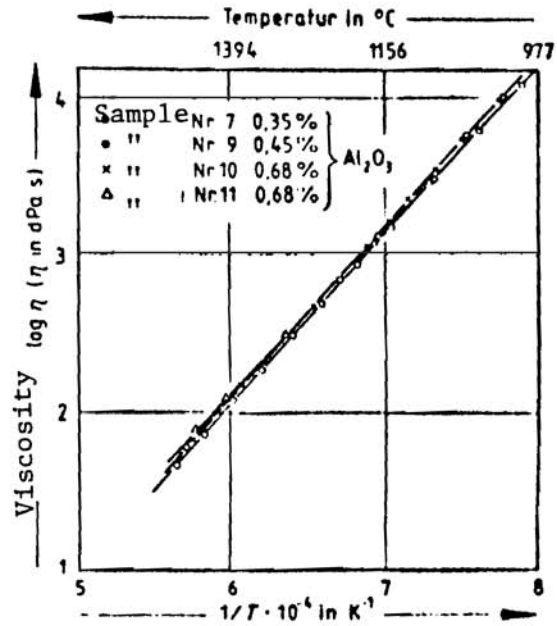


Illustration 6. Viscosity-temperature reaction of glasses with different aluminum oxide content and calumite as alumina in the batches.

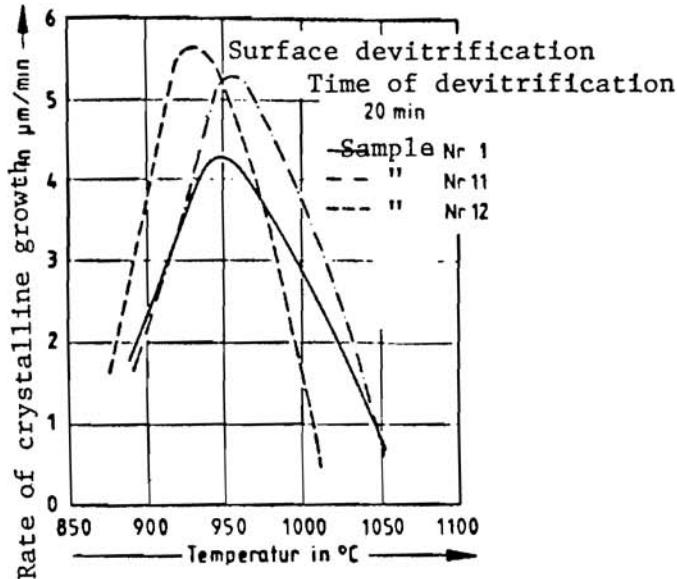


Illustration 7. Rate of crystalline growth of three glasses (sample nos. 1, 11 and 12), depending on the temperature.

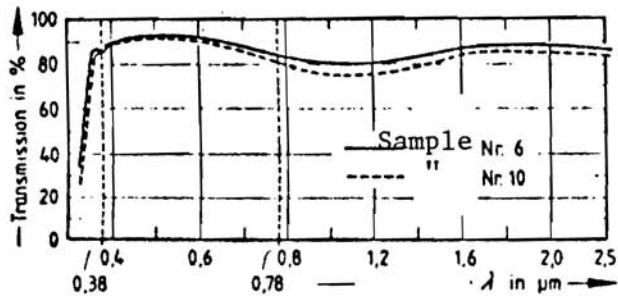


Illustration 8. Transmission wave of two glasses (sample nos. 6 and 10) with a glass thickness of 6 mm.