Original Paper

Influence of different Al_2O_3-containing batch materials on melting, fining and properties of soda–lime–silica glass[1])

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Proceeding from the composition (in wt%): 72.5 SiO_2, 1.5 Al_2O_3, 10.5 CaO, 2.5 MgO, 12.5 Na_2O, and 0.5 K_2O the batch raw materials calcined and hydrated alumina, nepheline syenite, Calumite, and Ecomelt, respectively, were employed in order to introduce aluminum oxide to the glass. Batch calculations assured constant chemical composition, sand/sulfate ratios, sulfate/carbon ratios, redox numbers, and total sulfur contents. The glasses and melts obtained were investigated with respect to different properties, e. g. viscosity, homogeneity, optical transmission, and residual sulfur content. The results display similarities, however, partly also significant differences with respect to the Al_2O_3 source used. Thus especially the glasses containing the blast furnace slags revealed distinct characteristics compared to glasses with nepheline syenite and hydrated alumina. With increasing melting time the differences are reduced.

Ifluß verschiedener Al_2O_3-Gemengerohstoffe auf Schmelzen, Läutern und Eigenschaften von Kalk-Natronsilicatglas

Ausgehend von der Zusammensetzung (Massengehalt in %): 72,5 SiO_2; 1,5 Al_2O_3; 10,5 CaO; 2,5 MgO; 12,5 Na_2O und 0,5 K_2O wurden die Gemengerohstoffe Tonerde und Tonerdehydrat, Nephelin-Syenit, Calumite bzw. Ecomelt als Al_2O_3-Träger im Glas eingesetzt. Durch Gemengeberechnungen wurde abgesichert, daß konstante chemische Zusammensetzungen, Sand/Sulfat- und Sulfat/Kohle-Verhältnisse, Redoxzahlen und Gesamtschwefelgehalte eingehalten wurden. An den erhaltenen Gläsern und Schmelzen wurden sodann verschiedene Eigenschaften bestimmt, z. B. Viskosität, Homogenität, optische Transmission und Restschwefelgehalt. Die Ergebnisse zeigen Ähnlichkeiten, zum Teil aber auch deutliche Unterschiede in Abhängigkeit vom eingesetzten Al_2O_3-Rohstoff. Insbesondere weisen die Gläser und Schmelzen, die die Hochofenschlacken enthalten, im Vergleich zu solchen mit Nephelin-Syenit und Tonerdehydrat zum Teil deutlich unterschiedliche Charakteristika aus. Mit zunehmenden Schmelzzeiten werden die Unterschiede allerdings merklich geringer.

1. Introduction

Aluminum oxide (Al_2O_3) is an essential constituent both of various industrial and many specialty glasses and affects several glass properties strongly. Thus a certain amount of Al_2O_3 gives rise to an improved chemical stability of the glasses, the mechanical strength is increased, furthermore the tendency to ase separation and devitrification is reduced. In most cases this desired influence is achieved by an Al_2O_3 content of the glasses as low as 0.5 to 2 wt%. The introduction of this important glass component is possible by different sources of Al_2O_3-containing raw materials. The industrial practice shows that the employment of a distinct Al_2O_3 source implies characteristic attributes concerning the properties both of the glass melt and the finished glass product, besides economical points of view. On the background of environmental stipulations the emission control of certain polluting substances becomes another important issue. Thus the determining factors for the proper choice of the Al_2O_3-containing raw material are, besides others, the

- total alumina and alkali contents;
- level of contamination and discharge of pollutants;
- availability and constancy of chemistry;
- dissolution behavior;
- reduction of soda ash consumption, and
- increase in melting rate and workability.

The present paper deals with the application of the different natural and technical Al_2O_3-containing batch raw materials, calcined Al_2O_3, hydrated alumina ($Al(OH)_3$), nepheline syenite, and the blast furnace slags Calumite and Ecomelt, respectively. Subsequent laboratory studies both on the glass melts and the glasses obtained are reported and conclusions with respect to melting, workability and properties are made.

2. Experimental

2.1. Preparation of the glasses

The choice of the base glass composition was made in compliance with industrial practice. The compo-

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[2]) Now with: VGT-DYKO Industriekeramik GmbH, Düsseldorf (Germany).

Table 1. Calculated batch compositions for 100 g glass. The glasses are denoted by the way the Al_2O_3 source is introduced.

batch components	glass type (denoted by the way the Al_2O_3 source is introduced)							
	Al_2O_3	$Al(OH)_3$	Calumite	Ecomelt	nepheline syenite	C5[3])	E5[4])	N5[5])
sand	72.1	72.1	69.1	68.08	69.3	70.92	70.82	69.66
Al_2O_3	1.35	–	–	–	–	0.63	0.84	0.15
$Al(OH)_3$	–	2.08	–	–	–	–	–	–
Calumite	–	–	9.39	–	–	5.0	–	–
Ecomelt		–	–	13.14	–	–	5.0	–
nepheline syenite	–	–	–	–	5.1	–	–	5.0
limestone	13.05	13.05	6.65	6.07	12.94	9.64	10.39	12.95
dolomite	11.1	11.1	9.28	6.15	11.17	10.17	9.26	11.17
K_2CO_3	0.73	0.73	0.60	0.59	–	0.66	0.68	0.05
Na_2CO_3	19.83	19.82	14.84	11.56	19.11	17.18	16.69	19.20
Na_2SO_4	0.98	0.98	0.53	0.09	0.93	0.74	0.64	0.94
$NaNO_3$	1.28	1.28	9.64	15.43	1.23	5.72	6.65	1.24

[3]) 5 g Calumite + x g Al_2O_3/100 g glass. [4])5 g Ecomelt + x g Al_2O_3/100 g glass. [5]) 5 g nepheline syenite + x g Al_2O_3/100 g gla

sition (in wt%) was 72.5 SiO_2, 1.5 Al_2O_3, 10.5 CaO, 2.5 MgO, 12.5 Na_2O, and 0.5 K_2O. First, the chosen batch materials were characterized chemically and physically [1]. The raw materials sand, limestone, dolomite and nepheline syenite were of technical grade and were provided by H. Heye Glasfabrik, Obernkirchen (Germany). The raw materials soda ash, pot ash, calcined and hydrated alumina, sodium sulfate, and sodium nitrate were of analytical grade (Merck, Darmstadt (Germany)). The blast furnace slags Calumite (Trademark, Calumite S. A., Esch-Sur-Alzette (Luxembourg)), and Ecomelt (Trademark, Krupp Stahl AG, Werk Rheinhausen (Germany)) were provided by agency of H. Heye Glasfabrik, Obernkirchen (Germany).

Refining of the melts was achieved by the addition of sodium sulfate and carbon. The chemical base glass composition and the total sulfur content were kept constant with the ratios sand/sulfate = = 100/1.4 and carbon/sulfate = 1/20. Furthermore an invariable redox number of the batch of + 15 was set. For reasons of comparison the initial conditions were changed at times, thus the redox number could be changed by adjusting the $NaNO_3$ content. After careful pulverization and mixing, the batch raw materials for 25, 50 or 100 g glass were melted at 1450 °C in Pt/Rh(20) crucibles in an electrically heated furnace for variable melting times. The melting atmosphere was air. Batch formulas are given in table 1.

2.2. Property measurements

The dynamic viscosity of the glass melts obtained was determined at 900 to 1420 °C with a rotational viscometer (Rotovisco RV12, Haake, Karlsruhe (Germany)), using the DGG standard glass I for calibration [2]. For that the pulverized and homogenized batch raw material for 50 g glass was melted for 15 min in a Pt/Rh(20) crucible at 1450 °C in an electrically heated furnace in air atmosphere. Th air-quenched glass was pulverized and 35 g of th homogeneous glass powder was inserted into th preheated viscometer. Viscosities were recorded . 5 K steps during cooling.

The homogeneity of the glasses was measure using the Christiansen-Shelyubskii method [3]. Th homogeneity factor, σ, obtained is proportional t the variance of the refractive index, Δn. The glasse investigated were made in 25 and 50 g melt portion respectively, at 1450 °C. The glasses were anneale for 120 min at 570 °C. The bulk material of the glas samples was used only. A glass fraction of 0.315 t 0.5 mm grain size was taken for the measur ments.

The residual total sulfur content of the glass wa obtained by means of a colorimetric titratio (Coulomat 702-SO/CS/E, Ströhlein, Kaarst (Germ ny)). A preliminary scattering in the data could b overcome, and a comparison with data obtained b H. Heye Glasfabrik, Obernkirchen (Germany), fina ly showed good coincidence. Moreover, it had to b assured that the test samples for the colorimetr titration had to be taken from the bulk of 50 g gla portions. Samples taken from the surface par displayed lower values.

To determine the molar ratio of Fe^{2+}/Fe_{tot} th hot digestion method with CO_2 as a protecting a mosphere, in combination with α, α'-dipyridyl as complex forming agent, was used [4 to 6]. Here aga only test samples of the bulk glass could be use Samples from the surface of a 50 g glass bloc displayed a totally different Fe^{2+}/Fe_{tot} ratio. It cou further be shown that the results do not va significantly whether an Al_2O_3 or a Pt/Rh(20) crucil is used for melting of the glasses. This is in co trast to literature results [7]. If one varies the total Al_2 content of the glasses, one obtains a maximum in t Fe^{2+}/Fe_{tot} ratio at about 4.5 wt%, as was four earlier [8]. In a further series the redox number w

changed to + 7.5 and 0, respectively. The results show an increasing Fe^{2+}/Fe_{tot} ratio with decreasing redox number, reaching about 35 % for a redox number 0.

The optical transmission spectra were recorded with a computerized 2-beam spectrophotometer (Omega, Bruins, München (Germany)) on samples of 5 mm thickness in the wavelengths region between 260 and 1800 nm. Moreover, the infrared transmittance of the samples was studied between 2500 and 5000 nm using a PU-9700, Philips, Kassel (Germany). Glass samples from 50 g batches were used.

The dissolution behavior of the Al_2O_3-containing raw materials was studied in a high-temperature centrifuge [9]. For that either the melted (Calumite, Ecomelt) or compacted (calcined Al_2O_3) body was contacted with a block of the Al_2O_3-free base glass as a sandwich. This sandwich was then subjected to a temperature program, ending at 1400 °C with holding times of 10, 20 and 30 min, respectively. After cooling the samples were prepared for analysis with an electron microprobe (JXA-5, Jeol, Tokyo (Japan)) and the interdiffusion profiles of Na^+, Ca^{2+}, Al^{3+}, and Si^{4+} ions were determined.

The number of gas blisters was determined in the following way. Glass batches for 100 g glass were melted for 15 min at 1450 °C. Then the melts were air-quenched within 4 min in the crucible and the resulting glasses were annealed for 30 min at 570 °C. Glass surfaces of 15 cm^2 were prepared by sawing, grinding, and polishing. Then the sizes of the gas blisters were measured microscopically and evaluated according to Saltikov [10].

To measure the surface tension of the different glass melts, the maximum pull on cylinder method [11] was used. To do so, the pulverized batch for 50 g glass was heated either for 4 h at 1450 °C or for 30 min, pulverized again and heated for 15 min. After that the melt was air-quenched, pulverized and heated again for 15 min at 1450 °C. Due to this procedure the glasses obtained were essentially free of blisters. The surface tension measurements were made at 1100 to 1450 °C.

The oxygen activity was measured by Rüssel [12] on a variety of melts using a ZrO_2 oxygen sensor. For the measurement the oxygen sensor was inserted into a finely pulverized glass batch which was heated in a Pt/Rh(20) crucible at 10 K/min to 1450 °C. Above about 800 °C the electromotoric force signal obtained could be converted to activity.

Further experimental details may be taken from [1].

3. Results and discussion

3.1. Viscosity

Figure 1 shows a plot of the dynamic viscosity, η, as a function of temperature, ϑ (955 to 1070 °C). In order

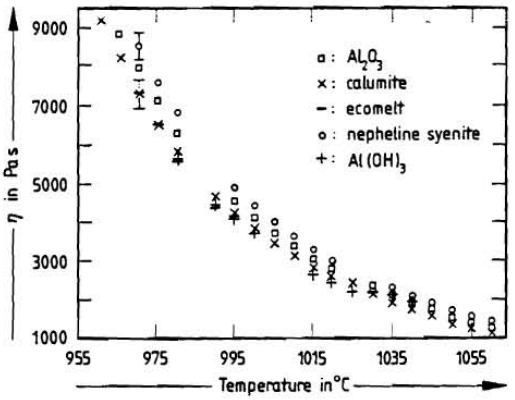


Figure 1. Viscosity-temperature curves of a soda–lime–silica glass melt containing different Al_2O_3 raw materials.

Table 2. Constants A, B and T_0 of the Vogel-Fulcher-Tammann equation at 910 to 1410 °C

glasses with different sources of Al_2O_3	A	B in °C	T_0 in °C
nepheline syenite	−1.677	4600	273.28
Al_2O_3	−1.945	4972	244.1
$Al(OH)_3$	−1.909	4865	251.69
Calumite	−1.530	4282	299.74
Ecomelt	−1.660	4277	319.31

to enhance the effect, the total Al_2O_3 content was increased here to 2.5 wt%. The melt with nepheline syenite shows the highest viscosities, whereas that with Calumite as an Al_2O_3 source displays the lowest viscosities. The other melts are in between. The increase in viscosity is particularly strong at low temperatures.

Previous investigations using a model glass (composition (in wt%): 74 SiO_2, 16 Na_2O, 10 CaO) showed a similar tendency [13]. There too a glass melt with nepheline syenite had the strongest increase in viscosity at low temperatures. This then was attributed to an early dissolution of that Al_2O_3 source with a corresponding increase in viscosity. A further reason for a differing viscosity may be seen in some kind of "memory" effect [14]. Thus the dissimilar structural bonding of the Al_2O_3 raw materials still influences a property like viscosity, although the overall homogeneities are already matching. At lower temperature the size and the distribution of Al_2O_3-containing clusters are decisive. Higher temperatures and/or longer melting times reduce the mentioned influences.

To evaluate the temperature dependence of the viscosity, the Vogel-Fulcher-Tammann equation

$$\lg \eta = A + B/(\vartheta - T_0) \qquad (1)$$

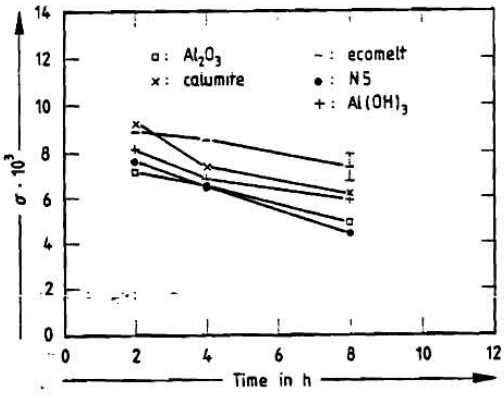


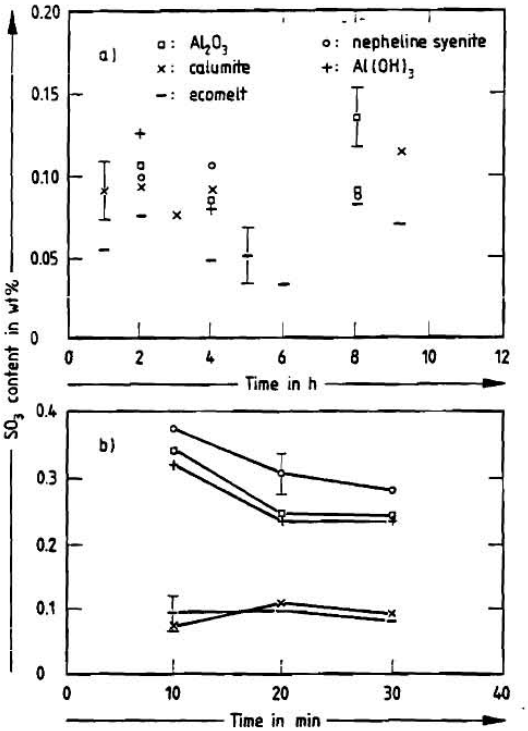
Figure 2. Homogeneity factor, σ, as a function of the melting time of a soda–lime–silica glass containing different Al_2O_3 raw materials using 50 g samples with grain sizes < 0.315 mm.

with A, B, T_0 = constants, and ϑ = temperature in °C, was applied. Three viscosity points at 910, 1160, and 1410 °C were chosen and table 2 contains the constants A, B, and T_0 of equation (1) for the glass melts with the respective Al_2O_3 sources. Here a similar tendency holds.

3.2. Homogeneity

Preliminary studies with 25 g samples of Calumite-containing glasses displayed an unexpected strong scattering of the homogeneity factor, σ, as well as of the mean value, $\bar{n}$, of the index of refraction [1]. It could be shown that there is a narrow correlation between the sizes of the limestone and dolomite grain fractions and the homogeneity factor. In order to overcome this masking effect it had to be assured that these raw materials were used only with grain sizes < 0.315 mm. Then the homogeneity factor measurement became reproducible and could be applied to elucidate the influence of the different Al_2O_3 raw materials. A grain size effect was already found by Dietzel et al. [15], who showed the absence of cords when using a grain size < 0.2 mm for limestone and dolomite.

A further factor can influence the homogeneity measurement. Stained glasses show absorption bands which may effect the transmittance of a Christiansen filter. This is also the case when glasses are prepared containing the blast furnace slags Calumite and Ecomelt, respectively. Correcting the transmission curves for that absorption effect, one obtains the results shown in figure 2. There are still some small homogeneity differences, with the lowest homogeneity of the Ecomelt-containing glasses. However, even these differences disappear if the pulverization of the raw material is further enhanced. Then the homogeneity factor of a 50 g glass reaches the final values of $\sigma = (2 \text{ to } 3) \cdot 10^{-3}$ already after about 30 min of melting [1].



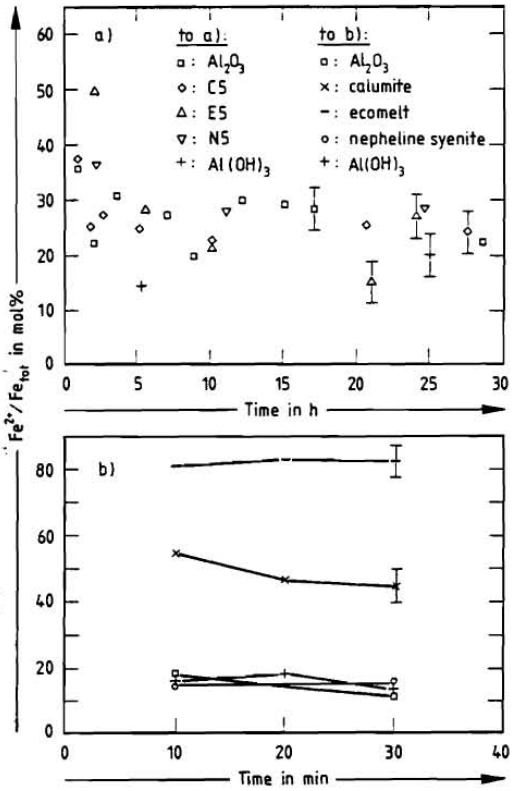
Figures 3a and b. SO_3 contents as a function of melting time of a soda–lime–silica glass containing different Al_2O_3 raw materials, a) long melting times (0 to 12 h), b) short melting times (0 to 40 min).

3.3. Residual sulfur content

Since most of the technical glasses are fined using sulfates, they do contain some residual sulfur. Thus the average SO_3 content of flint glass is 0.19 wt%, green glass shows 0.1 wt%, and amber glass has 0.02 wt% [16]. Figure 3a displays the SO_3 contents obtained in this study. The data lie between 0.04 and 0.13 wt%, and there is no distinct dependence on the Al_2O_3 source used. Similar high scattering of SO_3 data has been reported elsewhere [17]. If shorter melting times are used, the SO_3 contents split up in two groups (figure 3b). Glasses with the Al_2O_3 sources calcined Al_2O_3, $Al(OH)_3$, and nepheline syenite show higher SO_3 contents, whereas the glasses with Calumite and Ecomelt display values of about 0.1 wt%, which already are near the equilibrium SO_3 contents.

3.4. Ferrous-ferric ratio

One of the most important quantities for obtaining glasses of high quality is the redox state, characterized by the Fe^{2+}/Fe_{tot} ratio. There are many factors which may influence this ratio, e.g. melting temperature and time, melting atmosphere, content of oxidizing or reducing agents in the raw materials,



Figures 4a and b. Molar Fe^{2+}/Fe_{tot} ratios as a function of melting time of a soda–lime–silica glass containing different Al_2O_3 raw materials (25 g samples), a) long melting times (0 to 30 h), b) short melting times (0 to 40 min).

content of other polyvalent ions, crucible material, total iron oxide content, and cooling rate. Undesired scattering of the Fe^{2+}/Fe_{tot} ratio may result in changes of viscosity, heat transfer, fining behavior, and color [18 to 20].

Figure 4a shows this Fe^{2+}/Fe_{tot} molar ratio as a function of melting time for glasses containing the raw materials of different Al_2O_3 sources. Despite the scattering in the data it can be seen that a certain equilibrium value is reached at longer times, irrespective of the Al_2O_3 source. However, for short melting times there do exist differences depending on the Al_2O_3 raw materials. Thus especially Ecomelt- and Calumite-containing glasses are characterized by a high portion of divalent iron ions. This can be understood from the fact that both raw materials contain the majority of their iron ions as Fe^{2+} already in the as-received state. Figure 4b elucidates this dissimilar behavior for shorter melting times. Whereas glasses containing calcined Al_2O_3, $Al(OH)_3$, and nepheline syenite, respectively, are characterized by a Fe^{2+}/Fe_{tot} ratio < 20 mol%, glasses with Calumite and Ecomelt display much higher ratios, even up to 80 mol% for Ecomelt.

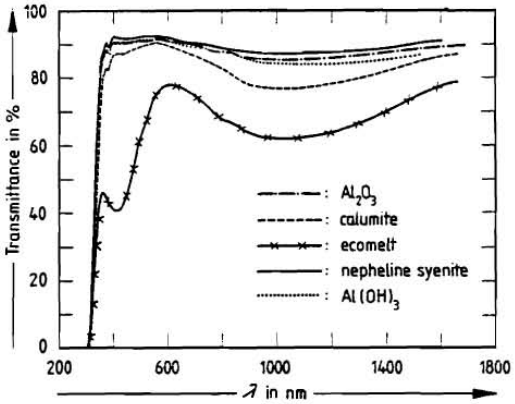


Figure 5. Optical transmission spectra of a soda–lime–silica glass containing different Al_2O_3 raw materials with a redox number of +5 and a melting time of 4 h.

3.5. Optical transmission

Iron oxide impurities in the raw materials are by far the most important constituents on this level. They can give rise to an undesired color tint or, depending on their ratio Fe^{2+}/Fe^{3+}, may influence the overall melting behavior strongly. To elucidate the influence of different Al_2O_3 raw materials on optical and infrared transmission, several series of experiments were conducted. A melting time of 48 h led to optical spectra which differed to some extent at the UV edge depending on the actual Fe^{3+} content. A minor influence can also be found due to the Fe^{3+} concentration at 380 nm, and the spectra also display faint absorptions near 440 nm. If one reduces the melting time to 2 h, then an overall reduction of the transmittance can be visualized, which amounts to 3.1 % for the glass with Ecomelt, E5. This effect is strongly enhanced, if the total Al_2O_3 content is introduced as Calumite and Ecomelt, respectively (figure 5). Moreover, the glass with Ecomelt shows a strong absorption peak at 411 nm, which probably might be related to the amber chromophore. However, the spectrophotometric determination of the Fe^{3+} ion is not yet obvious thus far [17]. Reducing the redox number of the batch to + 5 by adjusting the sodium nitrate content leads to a further reduction of the transmittance of the slag-containing glasses and an even stronger amber color can be evidenced, ending up in a totally nontransmitting behavior of the glasses in the short wavelengths part of the optical spectrum.

On the other hand, there are no distinct differences in the infrared transmittance of the glasses between 2500 and 5000 nm, irrespective of the Al_2O_3 raw material used.

3.6. Dissolution behavior

The dissolution behavior of Al_2O_3-containing materials has been investigated already several times [13,

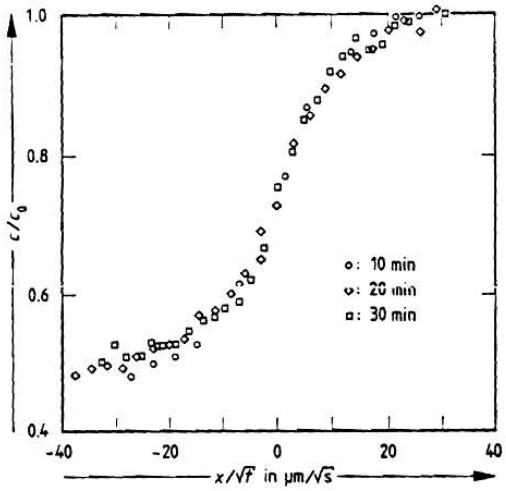


Figure 6. Ca^{2+} interdiffusion profiles as a function of $x/\sqrt{t}$ for different times at a reaction temperature of 1400 °C and a centrifuge acceleration of ≈ 46 g (g = 9.81 m/s²).

21 and 22]. Thus Al_2O_3-containing model cords have been studied [21], as well as the dissolution of different Al_2O_3 raw materials in melts [13 and 22]. In the latter cases dissolution profiles were obtained [13] and the number of undissolved grains was taken as a measure of the dissolution progress [22], respectively.

Figure 6 shows some typical Ca^{2+} interdiffusion profiles, plotted as $c = f(x/\sqrt{t})$, where c = concentration, x = penetration depth, and t = time. From the coincidence of the data points for the different times a conclusion with regard to the consistence as a diffusion process may be drawn. Similar dependencies were found for the other profiles at 1450 °C, and table 3 contains the mean penetration depths, $\bar{x}$, for the different components, where $\bar{x}$ is defined as the half-width of the interdiffusion zone. According to

$$\tilde{D}_{\text{eff}} = \frac{\bar{x}^2}{4 \cdot t} \qquad (2)$$

an effective interdiffusion coefficient, $\tilde{D}$eff, governing the overall dissolution process, can be described (table 3). Although the dissolution is a coupled multicomponent process, the mean effective interdiffusion coefficients of the individual species cluster at ≈ $1.3 \cdot 10^{-8}$ cm²/s (calcined Al_2O_3), ≈ $18 \cdot 10^{-8}$ cm²/s (Calumite), and ≈ $15 \cdot 10^{-8}$ cm²/s (Ecomelt), respectively. The dissolution of calcined Al_2O_3 is more slowly than that of the slags. This can be understood by the fact that in the case of Al_2O_3 the Al^{3+} ions have to be dissolved first, before they are able to diffuse. Since the slags are already glassy, the Al^{3+} ions can diffuse more readily from one melt to the other.

The use of the high-temperature centrifuge prevented the influence of any convection process. In the earlier study such convective processes overlapped the diffusion, making an interpretation of the overall process much more difficult [13]. However, also in the dissolution process of this study indication of uphill diffusion could be found, similar to that of the earlier investigation [21].

3.7. Blister analyses

The statistical blister analysis provides the following results. The glass with calcined Al_2O_3 has the highest number of bubbles (3850 bubbles/cm³) with 50 % of them ≤ 75 µm. The glass with nepheline syenite shows 2180 bubbles/cm³ and 50 % of them are ≤ 110 µm. Both hydrated alumina and Calumite display similar total numbers of blisters (1370 and 1430 bubbles/cm³, respectively), their 50 % values are lying ≤ 130 and ≤ 80 µm, respectively. Melts with Ecomelt developed the smallest number of blisters found, namely 960 bubbles/cm³, with 50 % of them ≤ 80 µm. A change from redox number + 15 to + 5 did not show a significant influence on the data of Ecomelt-containing glass.

Although gas bubble analyses have not been performed, one may speculate that the main gases involved are SO_2, O_2, and CO_2, respectively. SO_2 is provided by the decomposition of the fining agent Na_2SO_4 [23] and the sulfides contained in the slag materials. O_2 mainly stems from the fining process reactions, too, and CO_2 comes from the decomposition of the carbonates. It is difficult to explain the experimental findings in detail. However, some guidelines can be set. As has been shown earlier, melts with nepheline syenite do show the highest viscosities. This means that the rise of the bubbles is

Table 3. Mean penetration depths, $\bar{x}$, and effective interdiffusion coefficients, $\tilde{D}_{\text{eff}}$, for the dissolution of different Al_2O_3-containing bodies in Al_2O_3-free melts

	Al_2O_3				Calumite				Ecomelt			
elements	Si	Ca	Al	Na	Si	Ca	Al	Na	Si	Ca	Al	Na
$\bar{x}$ in µm	70	90	80	60	220	340	200	380	250	140	170	420
$\tilde{D}_{\text{eff}}$ in 10^{-8} cm²/s	1.1	1.8	1.4	0.7	10	24	8.5	30	13	4.3	5.8	37

hindered. As oxygen activity measurements showed [12], melts with this Al_2O_3 raw material displayed the highest oxygen activity in the melt during the entire melting process. This means that the fining process is less efficient, and from both tendencies a medium total number of bubbles can be understood qualitatively.

Ecomelt, on the other hand, shows a strongly reducing action and also provides a low-viscosity melt. This enables a low-temperature decomposition of the sulfates and a more rapid rise of the bubbles to the surface. The high amount of sulfide in this raw material even enhances this process. Moreover, since this batch contains the highest amount of $NaNO_3$ (necessary to fix the redox number at + 15), the formation of silicates and the decomposition of Na_2CO_3 are shifted to lower temperatures [24]. All these effects favor a low number of bubbles.

According to similar lines the findings for the melts with the other Al_2O_3 raw materials may be discussed [1].

3.8. Surface tension

The surface tension of glass melts is an important property both during melting and finishing. It is weakly dependent on composition of the melt and the temperature, and strongly dependent on the melting atmosphere [25].

Figure 7 shows the surface tension results, obtained for the glass melts with the different Al_2O_3 raw materials. Within the error range (± 6 mN/m) there is no clear dependence on the different Al_2O_3 sources. Moreover, there is also no influence on the results whether 1.5 or 2.5 wt% of Al_2O_3 were used, and whether the redox number was set on + 5 or + 15. One may understand the coincidence of the surface tension values irrespective of differing raw materials and redox numbers due to the fact that the melt surface is rapidly brought to an equilibrium with the furnace atmosphere with the consequence of identical conditions.

4. Conclusions

Five different Al_2O_3-containing raw materials were introduced into a typical flint glass composition. Already from their chemical and mineralogical characteristics, from their contents of reducing agents, and from their grain sizes and morphologies differences in melting and properties are to be expected. However, with increasing melting times these differences are reduced and finally disappear. The half-life of the "memory" effect thus is restricted.

The introduction of the sulfide-containing slags Calumite and Ecomelt leads to an early and strong liberation of SO_2 in combination with a high Fe^{2+}

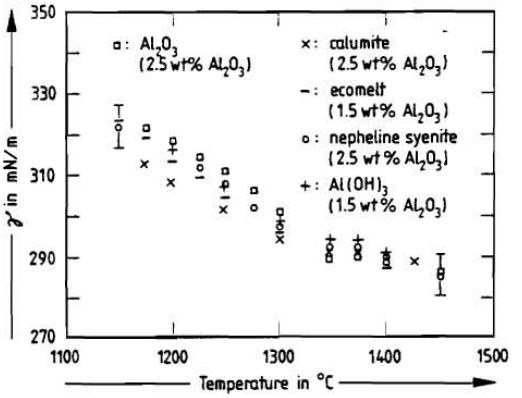


Figure 7. Surface tension, γ, as a function of temperature of a soda–lime–silica glass containing different Al_2O_3 raw materials.

content. This action is especially pronounced for Ecomelt, thus its use in flint glass batches is restricted. This slag material seems to be more appropriate for amber glass.

Melts with nepheline syenite display the highest viscosities, followed by those with Al_2O_3, and $Al(OH)_3$. The melts with the slag materials show the lowest values of viscosity. This viscosity behavior gives a pronounced evidence for the "memory" effect with a strongly different lifetime of the structural Al_2O_3 clusters present in the melts. Of course, workability is influenced by this behavior.

Calcined Al_2O_3 is the most stable component against dissolution. Moreover, it also shows the highest number of gas bubbles developed. Compared to that Calumite and hydrated Al_2O_3 are very reactive, and Ecomelt shows the easiest dissolution and fining behavior of all the Al_2O_3 raw materials investigated. One reason for that ranking is viscosity, however, early decomposition and gas release are also important factors.

Optical transmission spectra, Fe^{2+}/Fe_{tot} ratios and oxygen activities are totally in line with the residual sulfur contents.

Homogeneity and surface tension are the properties which are least influenced by the different Al_2O_3-containing raw materials. Thus the homogeneity is strongly determined by the grain size of the raw materials and the surface tension mainly is a function of the melting atmosphere.

In conclusion, although Al_2O_3 is a minor constituent of technical glasses only, its melting behavior is complex and the suitability of the different raw materials has to be checked. There are distinct advantages and disadvantages which have to be taken into account.

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