NATURAL ALUMINOUS RAW MATERIALS IN GLASS MELTING

Leena Hatakka

Department of Chemical Engineering
Åbo Akademi
Finland 1987

Preface

The work reported in this thesis has been done at the Laboratory for Inorganic Chemistry at Åbo Akademi during the years 1983-1987.

I am deeply indepted to the head of the Laboratory, Professor Kaj H. Karlsson for his guidance and advice throughout the course of this work. His enthusiasm and encouragement have been invaluable.

I am grateful to Professor Tapio Westerlund for a pleasant co-operation with the development of the glass optimization method. I am also grateful to my colleagues at the Department, especially to Dr. Mikko Hupa for many valuable discussions and criticism during my work.

Further, I wish to express my appreciation to Lohja Corporation Minerals, particularly to Mr. Carl-Johan Skand, the research manager, for a good co-operation and financial support. I am also grateful to Wärtsilä Nuutajärvi Glass and Ahlstrom Corporation Insulation Materials Industry for providing me the opportunity to perfom melting experiments on an industrial scale. Further I wish to thank Mrs. Ann Christin Waller for assisting with the English language and Mr. John Lassus for drawing the figures in the manuscript.

The financial support from The Academy of Finland and The Research Institute of the Åbo Akademi Foundation (Stiftelsens för Åbo Akademi forskningsinstitut) is gratefully acknowledged.

Åbo, November 1987

Leena Hatakka

Abstract

The work deals with replacement of silica sand by aluminous silicates in commercial soda lime glasses. Special attention is paid to the raw materials felspar and petalitic pegmatite. An increased replacement leads to new batch and glass compositions and also to changed glass properties. The melting behaviour of the glasses changes accordingly. Thus, when the sand content of the glass batch is decreased, the batch composition must be totally changed to guarantee a good production and to avoid a deterioration of the glass quality.

The first part of this work deals with the testing of a computer program developed to find the batch composition that minimizes the raw material costs for a glass that is to provide specified physical properties. The computer program was proved to be an excellent tool when developing new glass batch compositions. The estimated property values were in good agreement with the experimentally tested values with the exception of liquidus temperature. As no models are available, the melting behaviour of the glasses must be experimentally tested.

The computer program was used in calculating batch compositions with aluminous silicates as the main raw material. Test runs in a 70 ton/day tank indicated that introducing 8 wt% alumina as pegmatite in an insulating wool glass gave no disturbances in the melting process. Tableware glasses containing 4-13 wt % alumina introduced as felspar showed a vigorous foaming when melted in a pot furnace. Foaming could be suppressed if higher charging temperatures were used or if fluorspar as a fluxing and refining agent was introduced. The suggested saving of melting energy when sand content of a glass is decreased was not verified by these test runs. On the other hand, no efforts were made to optimize the melting parameters.

Finally, batch melting reactions and melting behaviour of glasses containing a high content of one of the aluminous silicates felspar, nepheline syenite or petalitic pegmatite were tested by thermal analysis and laboratory meltings. The thermal analysis of the batches indicated that the temperature for the commencement of the initial batch melting reactions decreases when sand is replaced by the aluminous silicates. Further, the laboratory meltings showed a decrease in the batch-free time with an increased replacement of sand. Felspar was found to be the most suitable of the raw materials tested to replace sand in conventional soda lime glasses as regards the batch-free time only. Fluorspar gave a good refining of the glasses with a high felspar content. The laboratory experiments gave no further information on the formation of the foam observed in melting the tableware glasses. Thus, in some melting conditions foaming may set upper limits for the content of aluminous silicates in the batch.

INTRODUCTION

Most commercial glasses are mixtures of several components. Typically for a glass, each component contributes to the physical and chemical properties in a way that is specific for the component and its relative amount in the glass. The "classic" approach was always from composition to properties, not vice versa, although the latter is more useful. The component proportions that yield the optimum glass properties are usually solved by some statistical method (West and Gerow 1971, Huff and Call 1973, Kiessling and Dressel 1979, Gan et al 1981, Salvagno et al 1983, Lakatos 1983, Chick et al 1984, 1986). After finding a proper calculation method for mixture problems, the accuracy of the solution mainly depends on the validity of the models used to describe the glass properties.

The relations between physical properties and glass composition are usually described by empirical models, which are valid only within the composition range examined. The narrower the range the more accurately the properties can be described by empirical models. Experimental property measurements confirm the well-known glass structure theories according to which the structure sensitive properties show non–linear dependence on the chemical composition. Using master models for a broad composition field inevitably means uncertainty in some physical properties but gives a possibility to investigate unconventional compositions with predicted, conventional values.

In practice, all glass properties are not of equal importance. The user expects the mechanical strength, thermal shock resistance, durability and transparency of the glass to meet the requirements commonly set on glass. On the other hand, to the manufacturers the processing of the glass puts limits to the viscosity-temperature relation, liquidus temperature, heat transfer properties, surface tension etc. The more special usage the glass is meant for the more the properties restrict its composition. The requirement of a good homogeneity is common to all glasses. Besides leading to variations in the important glass properties, inhomogeneities also give rise to visual defects in the glass. Homogeneity is a dynamic property reflecting the melting behaviour of the glass. Glass

melting can be divided into stages where one type of reactions is dominant at a time. During the vigorous initial solid-liquid reactions carbonates are converted into silicates by reacting with sand. The following stage involves a diffusion controlled dissolution of residual quartz in the silicate melt. After complete dissolution of all solid matter the melt still contains blisters and seeds which must be removed before working the glass. This refining stage is followed by the homogenisation stage during which the differences in the chemical composition of the melt are smoothed.

The glass satisfying the properties specified both by the usage and the working process must also meet the requirement of reasonable production costs. The production costs can be roughly divided into raw material, energy and other costs consisting of labour, administration, capital etc. In the production of bulk commercial glasses in small and medium size plants none of these costs has a predominant role but savings all over the line should be considered. However, in large plants the raw material costs become more important. It is easy to calculate the effect of a change in the batch composition on the raw material costs. However, the batch composition that gives a glass with desired physical properties to the lowest production costs can be calculated with respect to the raw material costs only. The batch melting properties and partly both the energy consumption and the life of the furnace depend on the batch composition. Kröger (1953, 1956, 1958) gives thermodynamic data for calculating the heat requirement for melting a container glass. However, the thermodynamic data available are insufficient for calculating the heat requirement of melting batches with another composition than the typical soda-lime glasses with sand as the main raw material. Likewise, the influence of fluxes and refining agents on melting properties is only qualitatively described in the literature. Besides being dynamic and difficult to evaluate, the melting properties of a batch are also furnace specific.

The aim of the present work is to evaluate how replacing sand by aluminous silicates affects quality, processing and costs of commercial soda-lime glasses. Special attention is paid to the domestic raw materials, felspar and pegmatite. An increased replacement of the main raw material, sand, leads besides to new batch compositions but also to changed glass properties. A simple reduction in the sand content changes both the working properties and the quality of the glass. Thus, the glass composition must be totally changed in order to produce a satisfactory alternative. A computerized method of calculation was developed to find the batch composition that minimizes the raw material costs for a glass that is to provide specified physical properties. The calculation method was tested by melting some glasses in full-scale. Besides on the experiences from these meltings the evaluation of the melting properties is based also on thermal analysis of the initial batch melting reactions and on observations from systematic laboratory meltings.

The thesis consists of the present summary part and the following seven parts:

I   Westerlund, T., Hatakka, L. and Karlsson K. H., A model for optimizing glass batch compositions, Journal of the American Ceramic Society, **66** (1983), 574-579.

II Hatakka, L., Kvaliteten som funktion av glasets fysikaliska egenskaper, Glasteknisk Tidskrift, **40** (1985), 39-44.

III Hatakka, L. and Karlsson, K.H., Optimisation of batch costs for an industrial furnace, Glass Technology, **27** (1986), 17-20.

IV Hatakka, L., Melting kinetics and physical properties of tableware glasses with high alumina contents, Collected papers, XIV International Congress on Glass, Volume-III (1986), 29-34.

V   Hatakka, L., OGBC - a program for batch optimisation, Glass, **63** (1986), 449-450.

VI Hatakka, L., Thermal analysis of glass batches containing aluminous silicates, Åbo Akademi, Laboratory for Inorganic Chemistry, Report No. 60 (1987), pp 26.

VII Hatakka, L., Melting rates of glass batches containing aluminous silicates, Åbo Akademi, Laboratory for Inorganic Chemistry, Report No. 61 (1987), pp 36.

The papers will be referred to in the text by their Roman numerals.

Calculation method

The interest in finding methods suitable for calculating batch and glass compositions to meet specified physical properties has lately increased. West and Gerow (1971) reported a method of estimating glaze properties using linear programming. The method allows changes in the composition so that the properties of the optimized glaze can meet a set of specified constraints. Huff and Call (1973) used non–linear programming to deduce glass compositions from properties. The program calculates the glass composition giving the best fit with the values desired within the composition range where the models for the physical properties are valid. Each property is assigned a maximum or minimum allowed value and a penalty function describing the relative importance of the property. Penalty functions are used also to ensure that the properties are calculated within the compositional validity range of the models. The composition giving the least total deviation from the properties desired and from the compositional range allowed is optimal. As several solutions can be found in a multi-component system, the search of the absolute minimum requires a good starting guess.

The optimization methods described in Parts I and III of this thesis use non–linear programming for calculating the glass composition. The models used to describe the relation between properties and composition are taken either directly from the literature or from statistical modifications of models given in the literature (Scholze 1977, Lakatos et al 1972 a, 1972 b, 1974, 1976 a, 1976 b, Kalsing 1955.) Some relations are experimentally extended to the compositional range desired (Hatakka 1984). The validity range for the models is

Oxide	lower limit	upper limit
B_2O_3	0	15 %
Al_2O_3	0	15 (8 % in Part I)
Li_2O	0	3
Na_2O	10	17
K_2O	0	9
MgO	0	6
CaO	4	14
BaO	0	16
ZnO	0	10
PbO	0	12
SiO_2	60	77

The validity range of the models is fairly wide. As the description of non–linear properties usually involves some inaccuracy when their compositional validity range is wide, also the accuracy of the models used in this work is decreased. However, master models are essential in search of new alternative compositions for glasses with conventional properties.

The method described in Part I finds the optimal composition by minimizing the squares of the errors between the desired and calculated properties. The relative importance between different feeds is taken into account by introducing weight factors for each property. The glass composition is not automatically restricted in the calculation algorithm, although the models used to describe the different properties are valid only within the given range. The program indicates whether the calculated composition is outside this range. However, the possibility to calculate glasses with compositions outside the range but with specified calculated properties can be of interest in research and development as the effect of the composition on each property is taken into account simultaneously. The error in the calculated values depends on the amount and type of the oxide exceeding the range and on the property examined. The calculated values of physical properties should be verified experimentally whenever there is any doubt about the validity of the models. When needed, the glass composition can be restricted by fixing the feed of one or more raw materials or by introducing lower and higher limits for the raw material feeds. The number of equally good solutions depends on the definition of the actual problem, i.e. on the number of given properties compared to the number of oxides in the available raw materials (III, IV, V). The mixture restriction of the oxides summing up to 100 % reduces the number of unknown concentrations of oxides in the glass by one. Thus, if the number of specified properties is less than the number of oxides minus one, these properties can be achieved by several compositions. When choosing between these different compositions the calculation algorithm described in Part I uses the minimum batch costs as an optimization criterion. Another possibility is to choose the composition that gives the least random variations in the properties caused by the random variations in the batch material compositions. The same optimization criteria can also be used when none or only one composition meets the requirements set by the glass properties. If savings in the batch costs can be achieved without losing much in the properties desired, the cheaper batch is chosen. However, cheaper batch compositions causing deviations from the desired property values are refused if the desired properties are weighted heavily.

The optimization method briefly discussed in Parts III, IV and V differs from the earlier method in Part I in allowing the physical properties to vary within a specified range. From a practical point of view it is sufficient if the properties meet some minimum or maximum requirements. The range allowed is separately specified for each property but can of course also be set to a single value. Thus, it is easier to find several equally good solutions in a multi-component system. The definition and solution of the problem in a two-oxide system with two properties desired are illustrated in Figure 1 of Part V. The cost optimization routine chooses the least expensive one between the compositions suggested by the first optimization. As the least expensive batch does not necessarily give the least expensive glass, the cost optimization routine allows the minimization of either the batch or the glass costs. As the printouts of the optimization according to Tables II and III in Part I are somewhat hard to interpret, the format of the printout was changed to give, besides all the data needed for an optimization, the glass and batch compositions and the calculated properties as well as a cost analysis of the optimized glass composition. The complete printout of the optimization of the glass referred to as 'Second' in Part V is given on the next page.

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Rawmaterials
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	Price	B2O3	Al2O3	Li2O	Na2O	K2O	MgO	CaO	Fe2O3	SiO2
Soda ash	115.00GBP/TON	0.000	0.000	0.000	58.200	0.000	0.000	0.000	0.000	0.000
Limestone	9.00GBP/TON	0.000	0.000	0.000	0.000	0.000	0.450	55.200	0.030	0.000
Anhydrite	25.00GBP/TON	0.000	0.000	0.000	0.000	0.000	0.000	29.500	0.000	0.000
Calumite	25.00GBP/TON	0.000	12.000	0.000	0.600	0.700	7.200	41.500	0.100	35.500
Feldspar	44.00GBP/TON	0.000	18.200	0.000	5.200	7.500	0.000	0.600	0.050	68.000
Dolomite	25.00GBP/TON	0.000	0.050	0.000	0.000	0.000	20.700	31.400	0.095	0.000
Sand	16.00GBP/TON	0.000	0.230	0.000	0.100	0.040	0.000	0.000	0.035	99.700
Batch	37.16GBP/TON	0.000	2.845	0.000	11.388	1.145	0.150	9.165	0.030	59.932
Glass	43.90GBP/TON	0.000	3.361	0.000	13.452	1.352	0.178	10.826	0.036	70.796

Glass price has been minimized   Glass to batch ratio is   0.85

	Min	Feedrate	Max	Batch price	Glass composition	Oxide price	Glass price	in %	Remark
Soda ash	0.00	18.14	100.00	20.86	12.47	197.59	24.64	56.14	
Limestone	0.00	15.79	100.00	1.42	10.39	16.16	1.68	3.83	
Anhydrite	0.00	0.80	100.00	0.20	0.28	84.75	0.24	0.54	Fixed
Calumite	0.00	0.00	100.00	0.00	0.00	25.61	0.00	0.00	
Feldspar	0.00	15.00	100.00	6.60	17.64	44.20	7.80	17.76	Fixed
Dolomite	0.00	0.38	100.00	0.10	0.24	47.85	0.11	0.26	
Sand	0.00	49.88	100.00	7.98	58.99	15.98	9.43	21.48	
Total		100.00		37.16	100.00		43.90	100.00	

Properties
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	Unit	Weight	Min	Actual value	Max
Viscosity at 600C	log(dPas)	1.00	11.400	11.420	11.500
Viscosity at 700C	log(dPas)	1.00	8.300	8.343	8.400
Viscosity at 800C	log(dPas)	1.00	6.400	6.451	6.500
Viscosity at 1100C	log(dPas)	100.00	3.500	3.547	3.550
Viscosity at 1200C	log(dPas)	100.00	2.950	3.000	3.000
Viscosity at 1450C	log(dPas)	10.00	2.000	2.042	2.100
Thermal expansion	10**-5 1/K	100.00	0.800	0.962	1.000
Young's modulus	10**4 MN/m**2	0.00	7.000	7.111	8.000
Poisson's ratio		0.00	0.200	0.228	0.300
Durability(P-value)	cm**3 HCl/g	1.00	0.100	1.240	1.350
Liquidus temp.	10**3 C	1.00	0.950	1.054	1.050

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Optimization	Function evaluations	Costs	Square sum
1	242	43.9760	0.501777E-05
2	393	43.8959	0.185711E-04

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CPU time 2.70   Elapsed time 30.66

Printout of the optimization of the glass referred to as 'Second' in Part V.

Kiessling's and Dressel's (1979) calculation method also includes both the optimization of the glass composition to satisfy the properties desired and the minimization of the batch costs. The properties are, however, described by equations of first order, which are valid usually only within fairly limited composition ranges. However, their method also allows non–linear models. Lakatos (1983, 1984 a and b) uses linear programming in optimizing container glass compositions for the minimum batch price. His non–linear models restrict the use of the program to small deviations from ordinary container glass. It is thus mainly meant for minor adjustments. When using linear programming the optimum composition is always found at the limiting value of some property or allowed composition range. Thus, it can be used in analysing the cost sensitive properties, i.e. properties that have a maximum or minimum value allowed and would give cheaper glasses if the constraints were somewhat relaxed. Westerlund (1986) has developed a linear technique for minimizing the raw material costs of a glass with desired properties. The formulation of the problem is identical with the formulation given in Part III. The problem with non–linear equations is overcome by linearizing the constraints after each iteration. The non–linear method described in this work also give the cost sensitive property if some property reaches the lower or upper constraint value. However, it is often difficult to specify the absolute limiting values and the relative importance of the properties. As some inaccuracy in the calculated values is brought about with the models, properties well within the allowed variation range are preferable, especially when developing unconventional glass compositions.

Part II of this work gives some examples of the problem formulation when optimizing the glass composition. The example with a container glass in Chapter 3.1 indicates that no savings in the raw material costs of the glass may be gained with the given raw materials and prices if the viscosity-temperature relation is kept practically unchanged with respect to the given values between 600 and 1460 °C. The insulating wool optimization in Chapter 3.2 shows, that the cost minimization drastically decreases the glass costs without affecting the glass quality. It should be pointed out that the reference glass, marked by I-1 in Table 6 corresponds to the oxide composition of an industrially manufactured glass. The biggest saving is due to the elimination of barium oxide from the glass. The example in Chapter 3.3 deals with the improvement of durability of a handblown art glass. The durability is increased without changing neither the working properties nor any other quality sensitive properties of the glass. Nevertheless, the raw material costs are unchanged. The examples in Part II are only theoretical calculations of the glass compositions and properties in order to demonstrate some possible uses of the optimization algorithm.

The models used to describe the dependence of the properties on the chemical composition of the glass are an essential part of a calculation algorithm. Although the formulation of the problem and the optimization method used are important in finding a global optimum value, the solution can never be more accurate than the models describing the properties. As the glass compositions given in Parts I, II and V have not been experimentally tested, they cannot be taken as any verification of the reliability of the models. However, some earlier experiments indicate that the properties calculated by the actual models agree well with the experimentally tested values with the exception of the liquidus temperature (Hatakka 1984). The calculated liquidus temperatures for

soda lime type glasses with 10-14 % alumina were found to be 20-100 °C higher than the actual values. However, liquidus temperature is described by a model that does not take into account different primary phase fields hence involving some unceratainty in the prediciton of liquidus. The calculation method has also been tested in optimizing glaze compositions. Although the conventional glaze compositions are outside the validity range of the models, the results from laboratory experiments were very encouraging.

2

Experiences from laboratory and full-scale experiments

Initial batch-melting reactions

The initial batch-melting reactions were investigated by thermal analysis of a number of binary and complex batches containing aluminous silicates (VI). The thermal effects recorded in a mixture of soda ash and silica sand were in good agreement with the results reported by Wilburn and Thomasson (1958), i.e. finely grained raw materials show chemical reactions at lower temperatures than do coarse grained raw materials. The batches containing aluminous silicates also showed an increased temperature for the onset of chemical reactions with an increasing raw material grain size. However, when using aluminous silicates, the increase was less pronounced than when using sand. The binary systems of coarse grained soda ash and sand showed no or only minor reactions below the melting point of soda ash, while all grain sizes of the aluminous silicates gave chemical reactions at lower temperatures, c.f. Figure 12 in VI.

The largest differences in the temperatures indicating the formation of the first liquid phase were those recorded between sand and potash felspar. For each fraction the binary mixture of soda ash and potash felspar showed about 20 °C lower reaction temperature than the corresponding mixtures of soda ash and sand. Sodium-potassium felspar containing some free quartz shows reaction with soda ash at about 10 °C higher temperature than the corresponding fractions of pure potash felspar. Nepheline syenite reacts with soda ash roughly at the same temperature as does sodium-potassium felspar, but usually the peak suggesting the formation of the first liquid phase is followed by another at about the melting point of soda ash.

It is claimed that lithia raw materials speed up the initial batch reactions. According to Franklin and Klein (1983) the reaction temperatures in a container glass decreased by 5-10 °C when 0.05 wt% Li_2CO_3 was added to the batch. The temperature for the formation of the liquid phase in an insulating fiber glass decreased with about 30 °C when 1.14 wt% of a $Li_2CO_3 - Na_2SO_4$ eutectic mixture was added to the batch (Brown and Boryta, 1983). Afghan (1976) reports petalite to have a beneficial influence on the initial batch reactions. The experiments with commercial grade raw materials indicated a reaction between petalitic pegmatite and soda ash below the melting point of soda ash, while sand was attacked only by molten soda (VI). Thus, the lithia in petalitic pegmatite has not such a pronounced effect as the one reported for the carbonates. In fact, there were no essential differences in the temperatures for chemical reaction in batches containing petalitic pegmatite, felspar or nepheline syenite.

The thermal analysis of complex batches consisting of commercial grade raw materials gave results analogous to the experiments with binary batches: the reactions in solid state proceeded longer in a batch containing a high content of aluminous silicates than in a batch with silica sand as the main raw material. Secondly, the temperatures for the chemical reactions decreased with 10-20 °C when aluminous silicates gradually replaced sand.

Batch-free time

In most glasses the residual sand grains are the most difficult to dissolve. Cable (1980) predicts decrease in batch-free time when decreasing the content of silica added as sand. According to Afghan (1976) batches containing petalite have shorter batch-free times largely because of their lower sand content. Hedvall and Åberg (1942) found that the batch-free time decreased when 10 wt% of the sand was replaced by felspar in a soda lime glass. Similar results were recorded also by Östlund and Stübner (1945).

Parts III and IV deal with the experiences of melting some glasses with an increased content of aluminous silicates in full–scale. The sand content in an insulating fibre glass melted in a 70 ton/day tank was gradually decreased by introducing more pegmatite in the batch (III). The alumina content of the glass was increased from the normal 3.6 to 8.2 wt% corresponding to 50 wt% pegmatite in a batch with no cullet. During the test runs a normal cullet level of 30 wt% of total feed mixed with the raw materials was fed into the furnace. Compared to a normal run, no essential differences in the batch-free time or in the energy consumption of the glass could be detected. It should be pointed out that the viscosity of the final glass all the time was kept unchanged from that of the normal glass with 3.6 % alumina, despite the changed glass and batch compositions. However, the batch blanket behaved in a slightly different way during the test runs. Normally, the glass is covered by batch from the back of the furnace up to the bubblers. When the content of pegmatite in the batch was increased, the batch cover was partly lost. The batch piles moved rapidly forward in the furnace and in some cases even passed the bubblers. Whether this new behaviour of the batch blanket could be taken as an indication of a faster melting could not be verified on the basis of the test runs.

Manring and Conroy (1968) report the batch blanket to disappear with high cullet contents. They found that the glass surface temperature and the bridgewall temperature increased as well as the melting rate. Cullet may be considered a silicate raw material. In the test runs reported in Part III, the silicate content of the batch was increased from the normal 30 % cullet to about 30 % cullet plus 36 % pegmatite. The crown temperature was found to increase with increased content of silicates. This gives reason to believe that the heat consumed by the batch melting reactions has decreased, which would mean a shorter batch-free time with the higher melting temperature. The increased crown temperature can as well be explained by a decreased heat transfer into the glass.

Some problems with the foaming of the melt arose during the melting of the tableware glasses reported in Part IV. As a result the effect of the increased felspar content on the batch-free time of the glasses could not be explicitly verified. However, after solving the foaming problems, the melting time of the glasses with a high felspar content was about the same as that of the ordinary production glasses used as references. Because the profile of the melting process was changed, the glasses can no longer be directly compared in terms of batch-free time. The foaming problem is separately discussed later.

The laboratory meltings reported in Part VII showed that the batch-free time was noticeably decreased when sand was replaced by aluminous silicates in a soda–lime

glass. The aluminous silicates not converted to a melt by reacting with carbonates were found to melt and mix in the bulk melt. Sand behaved differently; i.e. the residual sand grains slowly dissolved in the bulk melt. No essential differences were detected in the melting behaviour of felspar, nepheline syenite or petalitic pegmatite when an equal amount of respective silicate replaced sand. However, when silicates replaced sand so that the viscosity-temperature relation was kept unchanged from that of the reference glass, the ratio of carbonates to silicates in the batch affected the batch-free time. If the increased content of aluminous silicates changes the glass composition so that less soda ash is needed to satisfy a specified viscosity-temperature curve, it is likely that the batch-free time of the glass will be longer than is expected from the actual content of aluminous silicates in the batch. This explains why felspar was found to be the most suitable one of the tested raw materials for replacing sand in conventional soda–lime glasses when considering only the batch-free time.

Refining and homogenisation

Increasing the content of aluminous silicates in the batch inevitably gives an increase of the alumina content of the glass. In soda–lime glasses the influence of the increased content of alumina on the viscosity of the glass is roughly compensated for by a corresponding decrease in the silica content. However, the acidity of the glass changes. This may also lead to a changed gas solubility. The refining of aluminous silicate glasses is thus likely to cause problems when using additives that are working properly in ordinary soda–lime glasses. Zschimmer et al (1926) report sodium sulphate to cause problems in the refining of glasses with a high alumina content. According to Arnot (1937) the refining is accelerated by small replacements of sand by felspar. The positive effect is supposed to depend on foaming of the melt caused by felspar. With greater felspar additions the foaming is so intense that it disturbs the melting process. Bauermeister et al (1977) detected an intense bubble nucleation in glasses containing felspar. However, they detected no foaming, probably because of the relative low felspar content. They reported the bubble nucleation to aid in getting a glass with a good homogeneity. A good homogeneity of felspar glasses was also reported by Hedvall and Åberg (1940).

A poor refining is usually easier accepted at insulating glass wool plants than at other bulk glass plants. The glass is allowed to contain some seeds and inhomogeneities as long as those do not disturb the working process or diminish the mechanical or chemical properties of the fibers. Defects can be critical for the fiber length, too. However, the ordinary insulating wool glass is melted without refining agents. No differences could be detected in the amount of bubbles nor in the homogeneity between the ordinary glass and the glasses containing a high pegmatite content, Part III.

Good refining and homogeneity are essential properties for a tableware glass. In the early experiments the quality of the felspar glasses described in Part IV decreased because of a heavy foaming in the melt. Actually two different types of foaming were detected during the melting of these glasses. Primary foaming was produced during the fusion of the batch and secondary foaming suddenly appeared in a batch-free melt at a late stage

of the refining. The primary foaming could be overcome with higher temperatures at charging. The refining agents normally used were ineffective in minimizing the secondary foaming. However, fluorspar was found to be effective both in suppressing the primary foaming and in refining the glass. Although fluoride somewhat decreases the viscosity and the surface tension of the glass, its positive effect on the melting process is likely to depend on the formation of a eutectic melt of a low viscosity at low temperatures (Mulfinger 1980). The visually classified homogeneity of the felspar glasses was better than that of the two reference glasses.

Although no foaming was detected in the experiments under laboratory conditions, fluoride introduced as fluorspar was found to give a satisfactory refining result of glasses with a high felspar content. The enviromental regulations restrict the use of fluoride in many countries. Thus, despite the small amounts needed to bring about this refinement it is advisable to look for alternative refining agents. One additional important property of the refining agent to look for is its capacity to form primary melts of a low viscosity at low temperatures.

Physical properties

Some calculated properties of the glasses described in Parts III and IV were experimentally tested. The insulating glasses (Part III) were also analysed with respect to their chemical composition.

The actual spinning temperature of the insulating glasses was in good agreement with the calculated value, c.f. Table 5 in Part III. From the very beginning no problems that could be traced back to the glass composition were observed during the test runs. Therefore, the other properties used as optimization criteria were not experimentally tested. Also the analysed glass composition agreed well with the calculated composition. Thus, if there were discrepancies in the actual property values, they most likely depended on the accuracy of the models used to describe them. The insulating wool test run successfully verified both the suitability of pegmatite as a raw material for glass making and the applicability of the optimization method.

The method of working the tableware glasses given in Part IV, handblowing, gives a rapid indication of the glass quality. As the glasses behaved as expected, there was no need to test the viscosity-temperature relation experimentally. It was found that the earlier verified viscosity values of some other soda–lime glasses with a high alumina content agreed well enough with the calculated values (Hatakka 1984). The estimation of the liquidus temperature was, however, poor. The model used to describe the liquidus temperature from the oxide composition always gave a higher calculated temperature than the actual, measured temperature. Hence, until better models are available it is advisable not to use the liquidus temperature as an optimization criterion when calculating glass compositions.

Foaming

Foaming was detected between 900 and 1200 °C in thermal analysis of binary soda ash mixtures with nepheline syenite and felspar, Part VI. During the melting of the tableware glasses with a high felspar content foam appeared when the batch was charged into the furnace at 1300 °C and also during the refining, Part IV. The primary foaming of the tableware glasses could be suppressed by using higher charging temperatures. No foaming was detected during the melting of the insulating glasses (Part III) and of the glasses with different aluminous silicates (Part VII). As the charging temperature was high, about 1400 °C, for these glasses, it is likely that foaming during the first part of melting is avoided when the batch is rapidly heated up to the melting temperature.

The foaming during the melting of the tableware glasses could be suppressed by adding fluorspar to the batch (Part IV). According to Mulfinger (1980), fluoride gives a eutectic melt at about 550-600 °C and thus has a positive effect on the 'initial reaction' of sand grains. Further, the carbonates are decomposed at lower temperatures and the viscosity as well as the surface tension of the melt are decreased by fluoride additions. Fluoride was also found effective in eliminating the foaming of felspar glasses by Östlund and Stübner (1945).

Despite extensive research, the foaming process seems still to be too complex to be grasped with one single explanation. For instance a division into a primary foaming and a secondary foaming could sometimes be fruitful. Foaming is a common phenomenon also in the melting of soda–lime glasses, but normally it does not disturb the melting process. Kappel et al (1987) have recently discussed the foaming behaviour of glass melts. According to them foam is mostly caused by gases liberated in the chemical reactions of the batch, i.e. CO_2 and SO_2. The foam stability and decay were found to depend on the temperature of the melt, material transfer between melt surface and furnace atmosphere, pressure imposed on foam lamellae and on the gas content of the bubbles. No clear correlation was found between the surface tension of the melt and the foam stability. Cable and Akhtar (1968) also concluded that a change of surface tension is not a necessary part of foam production or destruction. Waldecker (1983) reports the stability of the foam to depend also on the surface tension and on the viscosity of the melt.

The stable foam detected in the melting of the glasses with a high content of aluminous silicates is thus likely to be only partly due to the increased alumina and the simultaneously increased surface tension of the melt. Compared to an ordinary batch with sand as the main raw material, a primary melt phase is formed at lower temperatures when aluminous silicates replace sand (Part VI). The batches with a high content of aluminous silicates are likely to form a eutectic melt with a high viscosity. The air inclusions in the batch and the gases liberated by the chemical reactions will be entrapped by the highly viscous melt and thus cause the foaming of the melt. The rate of heating the batch up to the melting temperature is likely to be an important factor for the foam formation. The heat transfer to the batch is faster in a tank than in a pot furnace, a fact that explains the faultless operation of the tank during the melting of the insulating wool (Part III).

A secondary foaming of a melt is usually connected with a changed gas solubility as a result of a changed temperature of the melt or a changed melting atmosphere. However, a secondary foaming was detected during the melting of the tableware glasses although the melting conditions were constant. This gives reason to believe that the production of the foam depends either on a late liberation of gases or on reaching a homogeneous melt with a gas solubility different from the one in a melt consisting of liquid layers of different composition. Goldman (1986) reports that a conversion of 0.1 wt% of ferric to ferrous iron in a nuclear waste glass can evolve a volume of oxygen greater than the entire melt volume. Fuchs and Förster (1982) observed up to 150 % increase in volume when remelting solid basalts in a heating microscope. The increase in volume correlated with the content of MgO, CaO, SiO_2 and Fe_2O_3 in the basalt. Meyer (1965) reports felspar to have a similar increase in volume at 1300-1500 °C, depending on the chemical composition. The increase in volume was caused by a heavy release of gases. The bubbles contained mostly nitrogen and oxygen. The foaming increased with the Fe_2O_3-content of the felspars. At high temperatures the Fe_2O_3 gave off oxygen, which liberated chemically combined nitrogen by reacting with it. Kranz (1967) confirms Meyer's results. He spectrometrically determined that the gases entrapped in felspars consisted both of organic gases (lower hydrocarbons, organic amines and ammonia) and of inorganic gases (hydrogen, argon, nitrogen, carbon dioxide and water). During oxidizing firing the ammonia and amino-groups built in the felspar lattice are released, thus causing the bubble formation detected during felspar fusion. Emer (1969) detected a lot of small bubbles in phonolite grains at temperatures above 1100 °C. These bubbles containing water vapour caused the foaming of glasses containing phonolite.

Thus the secondary foaming detected in the melting of the tableware glasses (Part IV) is likely to depend on the liberation of gases entrapped in the felspar lattice. The observation of glass discs in a stereo microscope indicated the presence of some gases in the aluminous silicate grains (Part VII). The composition of the gases is unknown.

The experiments reported in Parts III and IV of this work indicate that the production of foam depends on the melting conditions and can be avoided either by using high melting temperatures and small charges or by introducing a fluxing and refining agent in the batch. An effective fluxing agent aids in forming a melt with a low viscosity at low temperatures. Fluorspar was found to be effective both as a fluxing and a refining agent.

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