Melting behavior of recycled cullet; effects of impurity dissolution, pulverisation and solution pre-treatment

Ann-Katrin Glüsing, Reinhard Conradt

Motivation

The reuse of recycled cullet in the production of new glass containers lies above 60%. The cullet ratio depends on the glass colour, the level of impurities, and on availability. As a side effect of cullet waste management, the occurrence of metallic and ceramic impurities can not be avoided. Quality criteria for recycled cullet must comprise these impurities as potential sources of quality defects in the product. The potential of ceramics to generate glass defects contributes to a large extent to economic and technological restrictions for the overall amount of recycled cullet. The impurities in recycled cullet are distinguished by their potential to impair glass quality. In recycling cullet, emphasis must be laid on safe separation of the most critical species. It is the objective of our experimental work to generate a basis which allows to identify the most critical ESP species, and to asses their effect on glass quality.

Relevance for the container glass industry

In order to assure a further increase of the cullet ratio, an optimisation of the cullet quality is required. Presently, a cullet ratio of 30 to 90 % is reached depending on product colour and type. The benefit of cullet use consist, firstly, in energy saving and, secondly, in a reduction of CO_2 emission. Beyond this, the use of cullet accelerates the melting process, thereby improving the efficiency of heat exploitation. Tab 1 gives the relative amounts of energy saving by cullet reuse.

Tab 1 Energy saving by cullet reuse, per wt. % of cullet per t of molten glass [1].

calculated via theoretical heat demand	O.36 %
literature, multiple sources	0.2 to 0.4 %
industrial experience	0.25 to 0.3 %

As to the CO_2 emission: The output is reduced in direct proportion to the energy input (≈ 0.2 kg CO_2 per kWh), and beyond this, to the reduction of primary raw materials (≈ 190 kg CO_2 per t of primary batch). A 10 % increase of the cullet ratio, referred to an annual production of 3.8 Mio. t container glass, is equivalent to an energy saving of $1.7\cdot 10^8$ kWh, and a reduction of CO_2 emission by $1.1\cdot 10^5$ t (1/3 fossil fuel, 2/3 batch gases).

Objective

The impurities in recycled cullet are distinguished by their potential risk to impare glass quality. For this purpose, the local dissolution kinetics of different impurities are determined by high temperature observation tests, put into relation to their physical and chemical properties, and evaluated for the industrial relevance with respect to their residence time distribution of individual tanks. This leads to the formulation of a ranking of different ceramic impurities (with respect to their time demand for total dissolution), and in turn, to the formulation of an acceptance threshold for their sizes. The behavior of ceramic and metallic impurities in contact with flint glass melts is examined in detail. Quantitative data on dissolution kinetics are measured in a high temperature furnace by in-situ observations, video recording and image analysis. Special emphasis is laid on earthenware, stones, porcelains, aluminium, as well as on glass ceramics.

Experimental methods

Video recording of the dissolution behavior

The dissolution of individual particles is recorded by a video camera as a function of time and temperature, demonstrated in fig. 1. Along with the local kinetics of the materials (at given diameter and temperature), the time demand t* for total dissolution is determined, the so-called lifetime.

Fig. 1 Decrease of size of a porcelain particle at 1300 °, $t_{fig.\ 1\text{-}5} = 0, 1, 4, 8, 13$ h

Industrial relevance of these results is obtained by discussing the lifetime with respect to the residence time of the glass melts in individual furnaces. In detail, impurities are mixed into ground cullet and charged on top of a hot melt, or dropped as individual particles onto the melt. Then the dissolution kinetics is monitored. The results present a quantitative view of local kinetics. The decrease of particle size with time and temperature is examined. The evaluation is performed by the aid of an image analyser. The change of size is put into relation to the exposure time.

Results

Local kinetics

We distinguish between linear and diffusion controlled types of kinetics, and different combination of both types. With the identification of the local mechanism, kinetic parameters v and D denoting an effective dissolution velocity and diffusion coefficient, respectively, are determined as explained in [2-3]. The time laws of different types of dissolution kinetics are compiled in terms of: the local reaction progress $\Delta r(t)/r_o$, the particle lifetime t*, and the diameter d_0* associated with the given lifetime.

The decrease of the size of individual particles (with approx. radial habitués) is recorded and evaluated by an image analyser. Among the different evaluation modes, the analysis of the apparent area A(t) of the particle silhouette is the most reliable way. In a next step, the data are analysed with respect to the most probable type of dissolution kinetics. The kinetic parameters for the different types of dissolution kinetics are determined by multiple regression of $\Delta r(t)/r_0$ versus t or vice versa. Then the experimental data are plotted versus the normalized time t/t* and contrasted to the regression curves. This results in highly discriminative plots which allow to select the type of kinetic equation representing best the data set. For example in diagram 1, types A and B can be excluded right away. Finally, type D is preferred to type C because of its better representation of the initial behavior.

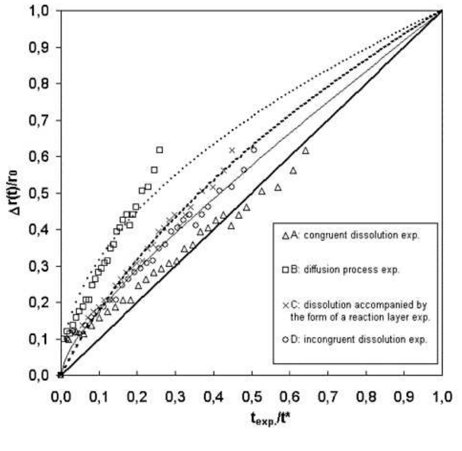
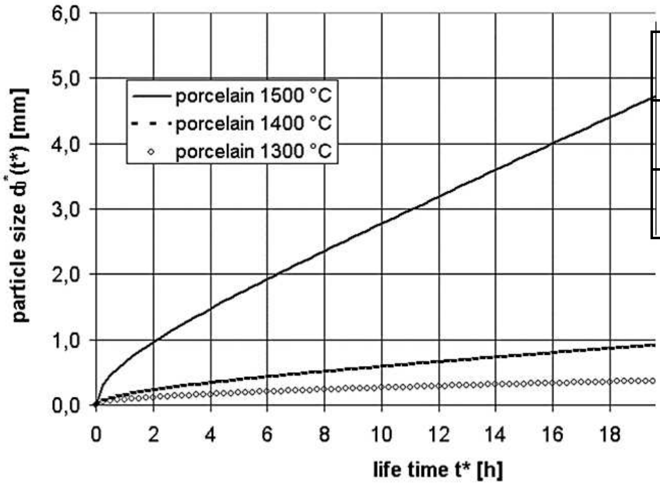


Diagram 1 Decrease of particle size versus normalized time t/t* of a porcelain ceramics at 1500 °C.

So, for a given lifetime t*, the corresponding particle size can be determined. This is shown in diagram 2 for a porcelain. The above data are transformed into plots of particle size versus particle lifetime $d_0^*(t^*)$ at 1300 -1500 °C.



porcelain (1300 °C)	$v = 5.32 \cdot 10^{-8}$ cm/s $D = 1.17 \cdot 10^{-9}$ cm^2/s	r^2 = 0.973
porcelain (1400 °C)	$v = 4.10 \cdot 10^{-7}$ cm/s $D = 4.62 \cdot 10^{-9}$ cm^2/s	r^2 = 0.943
porcelain (1500 °C)	$v = 2.72 \cdot 10^{-6}$ cm/s $D = 6.72 \cdot 10^{-8}$ cm^2/s	r^2 = 0,986

Diagram 2 Particle lifetime t* of a porcelain

Porcelain dissolves incongruently by type D. The dissolution of a porcelain of 1 mm diameter requires 2 h at 1500 °C, 22 h at 1400 °C and 118 h at 1300 °C. The critical particle diameter rises with temperature. The microscopic inspection of residual defects reveals in detail the local mechanisms (dissolution, phase transformation, recrystallisation) generating the kinetic laws is shown in fig. 2.

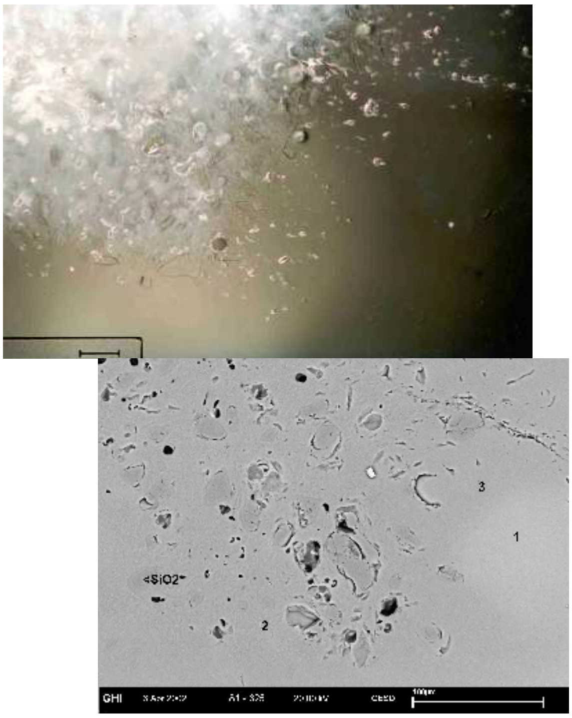


Fig. 2 Microscopic and SEM view of the dissolution of a porcelain after a high temperature exposure at 1400 °C

Around the porcelain core, a diffusion border is formed. The up-take of alkali from the melt and the dissolution and transformation of alumo silicates determine the change of composition in this transition zone. The video monitoring confirms this observation by showing a viscous envelope around the particle. The influence of the increased viscosity by the increased alumina content is responsible for a retarded movement of bubbles and the melt.

The core, the boundary zone and the surrounding glass are analysed by SEM-EDX and evaluated for their normative phase content

- core: quartz grains SiO_2 und mullite felt A_3S_2 in a albitic, glassy bonding phase (NAS_6, SiO_2)
- border: nephelin, silica (NAS_2, SiO_2) with traces of C_2AS_2, KAS_2, A_3S_2
- glass: SiO_2, NC_3S_6, NAS_6, NS_2, KAS_6.

The normative phase content describes the thermodynamic position of a melt, a glass or a crystal in relation to the eq. state at room temperature.

Aluminium as metallic impurity

Aluminium was tested by applying rolled foils from the recycling aggregates and massive cubic particles. Around the foils, a alumina (Al_2O_3) diffusion barrier is generated, generating a Si particle comprising an iron penetration phase. Small foils, by contrast, dissolve completely. Massive cubic particles dissolve under homogeneous Si-brown colouring of the glass with a residual colloidal iron containing phase (fig. 3).

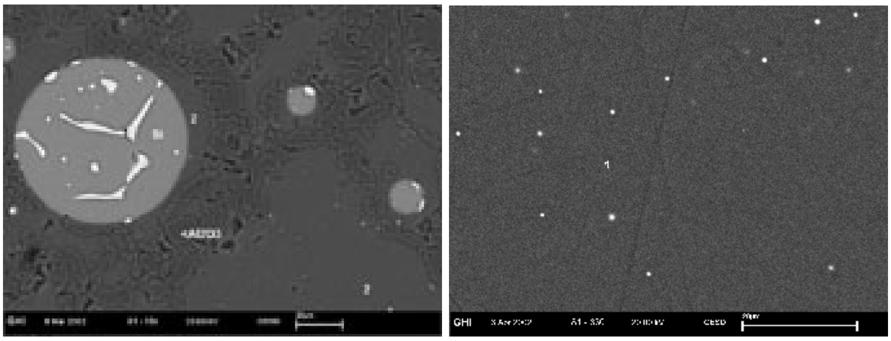


Fig. 3 Dissolution of a aluminium foil into a Si particle with an iron penetration phase surrounded by a alumina oxide barrier and a massive cubic particle with a homogeneous colouring cord

Behavior of impurities in the batch

The behavior of individual particles in the batch is examined, too. For this purpose, coarse ceramic particles with approx. spherical habitus (5 – 2 mm) and needle-shaped ceramic fragments (0.5 - 2 mm) are mixed into batch samples and charged on top of a cullet melt. The aspects of particle size and shape are discussed later under the section "glass powder".

High temperature observation of batch melting behavior

The observation is done in different observation furnaces from above as well as through the melt. Coarse ceramic particles segregate; all needle fragment are orientated in the sinking melt. Rolled shaped Al-foils adhere to the surface of the melt. Impurities like quartz stones behave like sand grains forming agglomerates and bubbles in the batch. Porous ceramic are quickly transformed by dissolution of the bonding phase. The colored glass ceramic directly sinks into the melt and does not participate in the batch reactions.

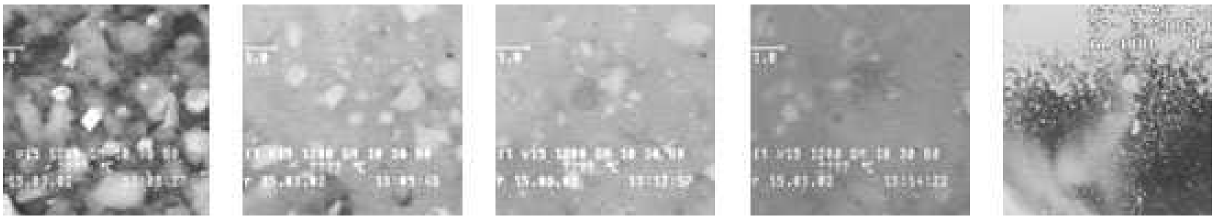


Fig. 4 Rate of batch melting for a with ceramics doted mass glass at 1200 °C,
(view through the melt: outer right image)

Fig. 4 demonstrates a view from the top and through the melt during batch melting. Primary melt formation is accompanied by transport, degassing, and film forming phenomena. The segments in fig. 5 show the phase transformation of a porous ceramic during batch melting, for a quartz stone and the raw materials dolomite and nephelin in the melt.

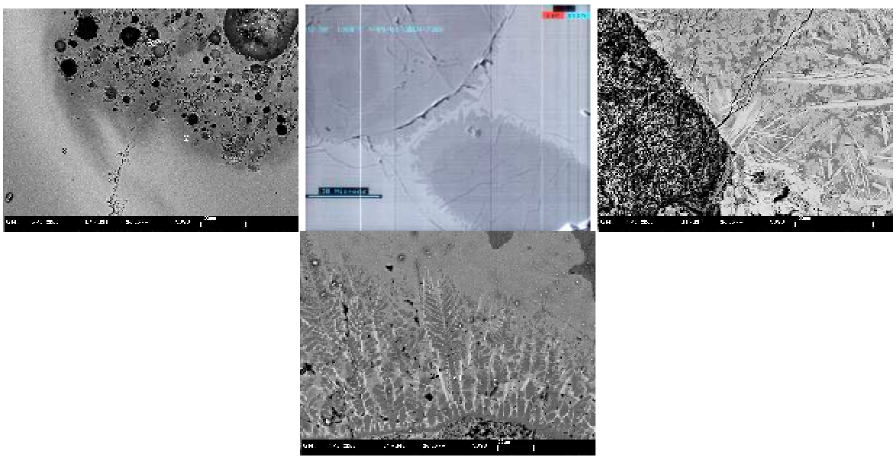


Fig. 5 Transformation during batch melting: porous ceramics, quartz stone, dolomite and nephelin

Pre-treatment of cullet

The pre-treatment of cullet is discussed with respect to the use of glass powder and to the washing of cullet with alkaline solutions. Therefore cullets were classified by size to show the potential of the fine or coarse fractions to generate defects. The grain size distribution and the impurity content, especially the metallic and ceramic impurities, were determined. With respect to the melting behavior, next to the determination of the dissolution kinetics of the cullet impurities, investigations on pulverisation [4] and pre-treatment by alkaline solutions [5] of cullet were performed.

Glass powder by cullet milling

In order to improve the quality of recycled cullets, cullets are classified by size. By this procedure, impurities are accumulated in the fine fractions. It is the objective to demonstrate the glass defect problem related to fine fractions. For this purpose the melting behavior of powder samples as batch component is studied by hot-stage microscopy, and by melting tests performed in an observation furnace. Fig. 6 shows as conclusion of melting cullet and ceramics, relicts for the coarse, bubbles for the fine fraction. Sufficient and total dissolution by increasing the temperature is showing the medium fraction for the fraction of 0.5-0.125 mm. The effect can even be enforced by pelletizing.

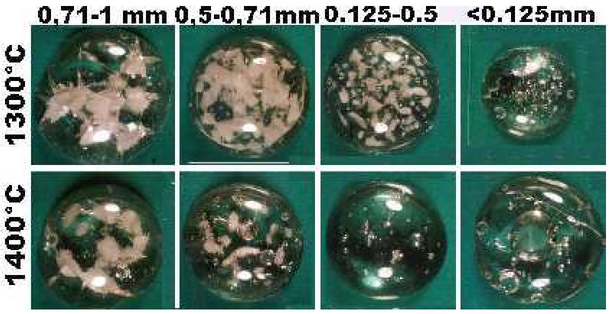


Fig. 6 Melting behavior of different fractions of glass powder and ceramics at 1300-1400 °C

It is shown that the fine cullet fractions enhances the local turnover of the batch reactions while coarse fractions promote convective flow. Additional studies were performed at an industrial site.

Transformation of aluminium

The behavior of metallic impurities in white glass melting through pre-treatment of cullets in alkaline solution was investigated. Technical elimination of impurities through treatment with alkaline solutions applied to non-iron metallic impurities, cullets and mixtures of both, as well as the melting behaviour of the pre-treated mixtures was investigated. The idea of transformation of aluminium into hydroxides or aluminates is realised through the use of alkaline solutions. Solutions were applied as commonly used in the washing process of returnable bottles. Different methods of process application show the effect of time, temperature and concentration on the transformation of impurities into harmless compounds.

Evaluation for industrial furnaces

The lifetime t* is the basis to determine the acceptable particle size d_0 in relation to the residence time in a tank. The materials values are taken from temperature dependent lines as shown in diagram 1. For the unrealistic case of a plug flow reactor characteristics of the tank, the critical diameter d_0 can be taken directly from the lifetime plots e.g. diagram 2. Real furnaces, however show a more complicated mass flow behavior. By tracer experiments, by modelling (or – with certain limitations - by color change campaigns) the residence time spectra for the throughput of volume elements through the basin are determined. By an individual study [6], the following characteristic times were determined: τ_{00} = 6 h (first detection of tracer), τ_{05} = 8 h and τ_{20} = 12 h. The time corresponds to critical particle sizes $d_{crit.}$. The highest security level is related to the time τ_{00}. At τ_{00}, there is no tracer response, hence the entire volume is still contained in the furnace, with no defects being able to reach the end of the feeder. At time τ_{20}, corresponding to 20 % of tracer throughput, 80 % of particles with size d_{20} are still contained in the furnace. These will dissolve for sure. But 20 % of defects of the said size are pulled through the furnace and may cause defects of sizes ranging up to $\Delta d = d_{20}-d_0$. In a production situation, a compromise has to be made. For example, at τ_{05} with a particle size d = 0.8 mm, no more then 5 % of the original amount of ceramic impurities may cause defects. Diagram 3 demonstrates the discussed method.

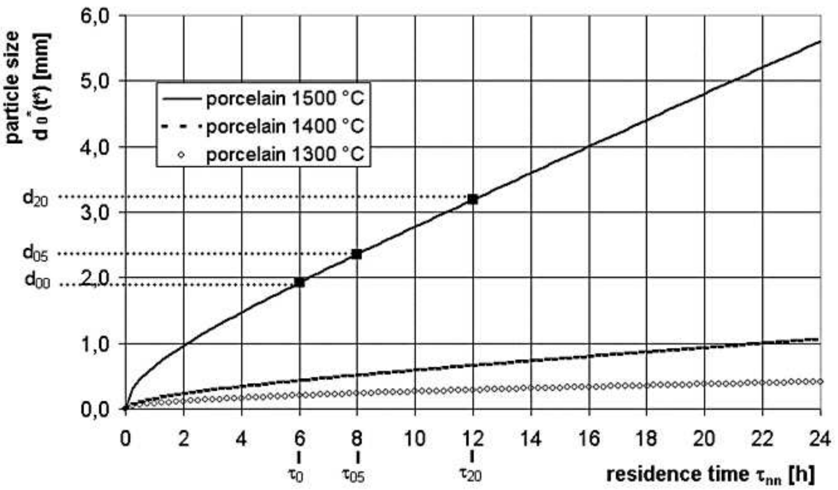


Diagram 3 The lifetime t* and particle size d_{00} for a porcelain including the residence time τ_{nn} and the critical particle size $d_{crit.}$

Conclusion

The discussed paper tries to comprehensively treat the problem of impurities in cullets. This includes the local reaction mechanisms (dissolution kinetics, life time, recristallisation) as well as participation in the global mass flow in the furnace (batch reactions, turn-over to the melt). The results are put into relation to their physical and chemical properties, and evaluated for industrial relevance with respect to the residence time distribution of individual tanks. This can be used to formulate acceptance thresholds for particle sizes of ceramic and metallic impurities. By this, interesting problems solutions are given for combination of particle sizes, the fine and coarse fraction or the pre-treatment by alkaline solutions to minimize the glass defects according to the cullets. As a benefit, glass producers are put into a position to exert quality control, and not to rely on detection of glass defects in the product alone. At the same time, criteria of acceptable particle sizes are given for the recyclers.

---

[1] Research project in preparation on reuse of the fine rest fraction, GHI, 2001

[2] Glüsing, A.-K.; Conradt, R., Dissolution kinetics of ceramic and metallic impurities of cullet, Proc. Int. Symp. Recycling and reuse of glass cullet, Dundee, 2001

[3] Glüsing, A.-K.; Conradt, R., Ranking of ceramic and metallic impurities in recycled cullet with respect to their impact on container glass quality, Proc. 6th Int. Conf. Advances in fusion and processing of glass, Ulm, 2000

[4] Roumeas, V. Prozesstechnische Bewältigung der Verunreinigungen im Altglas durch Feinvermahlung, Diplomarbeit RWTH Aachen, 2001

[5] Dehaudt, M. Prozesstechnische Bewältigung der Verunreinigungen im Altglas durch Lösungsumsatz, Diplomarbeit RWTH Aachen, 2001

[6] Schippan, D. Tracerversuche diskreter Verweilzeiten an einer Hohlglaswanne, Diplomarbeit RWTH Aachen, Mai 1999