

ASSESSMENT OF CONSTITUENT AVAILABILITY OF ANTIMONY-CONTAINING ROLLED PLATE GLASS WITH REGARD TO THE EUROPEAN REACH REGULATION.

A briefing paper by TC13 - The International Commission on Glass' Technical Committee on the Environment.

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Abstract

The TC13 of the International Commission on Glass (ICG) conducted a round-robin analysis of antimony leachability from samples of antimony-containing rolled plate glass manufactured and sold in Europe. Sample preparation followed the method developed by TC13 and based on EN/12457-4. Leachability results were compared with the land-fill criteria in Council Decision 2003/33/EC. The average antimony leachability was lower than the criteria for landfill as non-hazardous waste. This supports the exemption of this type of glass from registration and assessment under the European REACH regulation.

Introduction

This study was conducted to support the work, primarily led by CPIV¹, on the exemption of glass from the European REACH directive. Glass would be exempt if it did not contain any constituents that meet the criteria as dangerous in accordance with Directive 67/548/EC. However, also "*Glass is exempted if conclusive scientific experimental data show that its constituents, meeting the criteria as dangerous in accordance with Directive 67/548/EEC in concentrations above the lowest of the applicable concentration limits set out in Directive 1999/45/EC or set out in Annex 1 to Directive 67/548/EEC, are not available throughout the life-cycle of the substance.*"

This work follows a study by TC13 to develop a suitable test based on the standard method EN-12457 and the landfill criteria in Council Decision 2003/33/EC to prove that certain constituents "*are not available throughout the life-cycle of the substance*". The previous study demonstrated this method is an appropriate test, while assessing the leachability of samples of tableware and cooker top glass.

The test procedure EN 12457 was chosen because it reflects a worse case scenario. It is applied to size-reduced material and the liquid to solid ratio (L/S) of 10 l/kg that is used to elute the sample reflects the release over a relevantly long time frame (H. van der Sloot, 2008).

This study focuses on flat glass. Most flat glass has no constituents potentially deemed harmful and would automatically be exempt from REACH registration. However, some plate glass for the photovoltaic market contains antimony. Although the amount of antimony may be below the "*lowest of the applicable concentration limits set out in Directive 1999/45/EC, or the concentration limit set out in Annex 1 to Directive 67/548/EC*", TC13 considered that it would be useful to study this glass.

¹ CPIV is the standing committee for all the sectors of the glass industry in Europe.

This would both confirm or determine the suitability for its exemption and also further test the assessment method previously used by TC13.

Samples of antimony-containing plate glass manufactured in Europe by the member companies of Glass for Europe² were assessed. All rolled plate glass sold is annealed but some is also toughened. Samples of both types, annealed and toughened, and annealed-only glass were assessed. (Note that for final use the glass is always toughened.)

Method

As noted above, the assessment method followed is described in EN 12457. However, the previous TC13 paper recommended that this is modified by removing fragments smaller than 0.5mm. This is in accordance with the general EN12457 procedure requirement that "*on no account shall the material be finely ground*" and avoids the very fine fragments that are formed when glass, unlike most other materials, is crushed.

Samples both with and without the fines removed were assessed. Because some of the rolled plate glass is toughened, and toughened glass naturally breaks into pieces that are normally all a few millimetres in size, rather than a great range of sizes like un-toughened glass, the specific part 4 of the standard EN 12457-4 was followed. This states that the sample should be prepared to pass through a 10 mm sieve. Much of the broken toughened glass did this without further preparation, but the crushing required by the un-toughened glass produced the fine fragments identified in the earlier TC13 paper and were removed from some of the samples.

Preparation, elution and analysis were done by the following European laboratories:

- NSG Pilkington – England
- SSV – Italy
- AGC – Belgium
- St. Gobain – France
- Şişecam – Turkey
- Schott – Germany
- Arc International – France
- British Glass – England

Each laboratory replicated their work, and various averages were calculated from the collated data. Six samples from four different manufacturers were tested; three samples were toughened and three were not toughened. The analysed antimony (Sb) content in the supplied samples ranged from 0.10 to 0.24 %.

Results and discussion

The average results are summarised in the table below. As well as the Sb leachability, the conductivity, the pH and amount of the whole sample that was in the fine fraction <0.5mm is also shown.

² Glass for Europe is the trade association for Europe's manufacturers of building, automotive, and transport glass, all derived from the base material, flat glass. (<http://www.glassforeurope.com>)

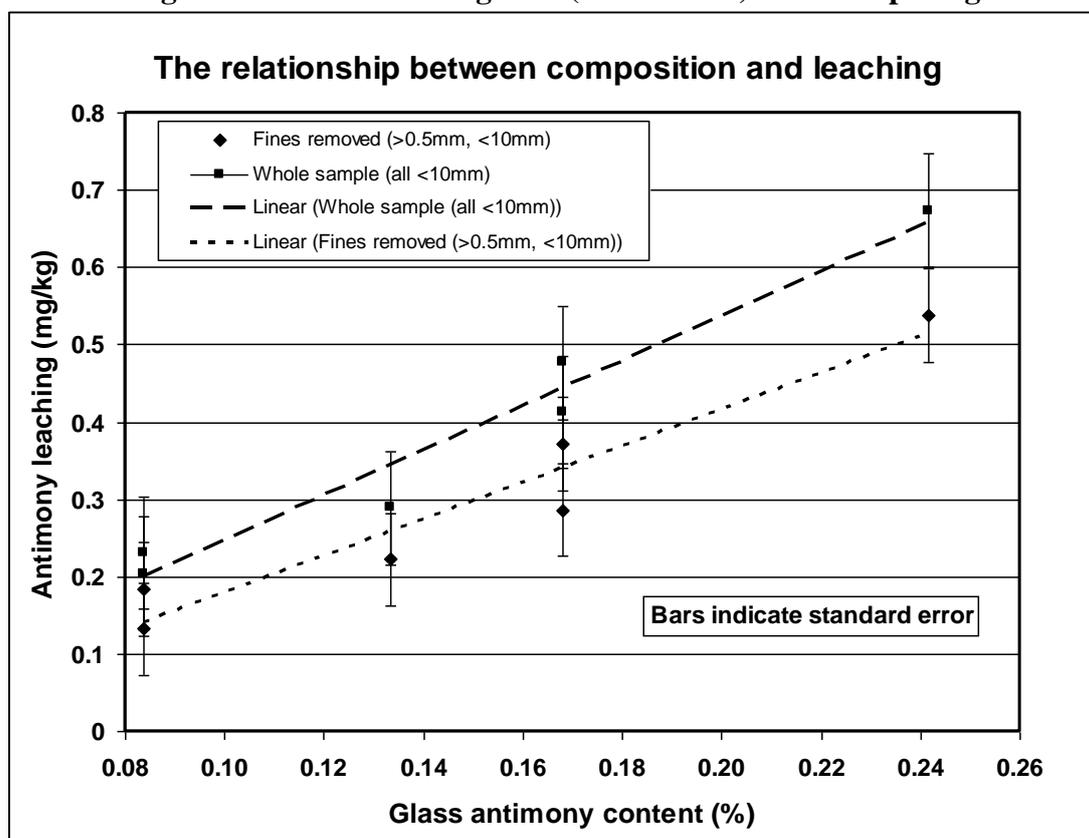
Summary results of leaching tests done on all glass samples.

	All <10 mm	>0.5 mm <10 mm
EC ($\mu\text{S}/\text{cm}$)	38.0	23.7
pH	9.3	8.4
Fraction <0.5mm wt%	8.24	-
Sb leachability (mg/kg)	0.38	0.29

The overall average antimony leaching from all the samples analysed was 0.34 mg/kg. Separately, the average for the whole crushed sample was 0.38 mg/kg, and with the fines removed it was 0.29 mg/kg. The relevant value in Council Decision 2003/33/EC relating to criteria for acceptance to landfill as non-dangerous waste is 0.7 mg/kg. The average Sb leachability is lower than this value indicating that at the end of its life the waste glass could be sent to landfill, and thus demonstrating that the glass should be exempt from REACH registration as no harmful components are “available throughout its life-cycle”.

The higher conductivity and pH of the eluate from the samples containing the fine fragments of glass demonstrates the effect that these small particles have on the elution, and why the EN 12457-4 procedure says that the material should not be “finely ground”. That is why TC13 recommends that the EN procedure is slightly modified when glass is being assessed. (Although in this case even when the fines were not removed from the samples, the average Sb leachability was below the 2003/33/EC acceptance criteria.) On average, just less than 10% of the annealed glass that was crushed to pass through a 10mm sieve was in the <0.5mm fine fraction.

Average results of Sb leaching tests (EN 12547-4) on rolled plate glass.



The Sb content in the tested samples varies from 0.10% to 0.24%. Assessing the different preparations separately demonstrated that the quantity of Sb leached from the sample during the test is directly proportional to that of the starting material (see the figure above).

The difference between the preparations is clear, with more leaching occurring from the samples containing the fine fragments, supporting the observations above and TC13's previous recommendation. All of the antimony-containing rolled plate glass products currently put on the market in Europe have an average Sb elution below the 2003/33/EC landfill criteria and so would be exempt from REACH registration and assessment.

The results of this study should be considered as case-specific and not necessarily applicable to other types of glass. The leachability of Sb from other glass products manufactured by different techniques would not necessarily show the same characteristics as the glasses tested in this study.

Conclusion

The work demonstrates that the antimony in rolled plate glass for the photovoltaic market does not exhibit unacceptable leaching and the glass would be acceptable at landfill for non-dangerous waste. This glass can be considered non-critical from a release to soil, surface water and ground water point of view. The antimony can thus be considered "*not available throughout the life-cycle*" of the glass and so the glass should be exempt from REACH registration and assessment. The work also confirms the applicability of the method recommended by TC13 for assessing glass samples for REACH exemption.

References

EN 12543-4 Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction).

Hans van der Sloot, Joris Dijkstra, Ole Hjelm, Gerd Spanka, Philo Bluysen and Sara Giselsson. Evaluation of a horizontal approach to assess the possible release of dangerous substances from construction products in support of requirements from the construction products directive (tr2). Förderkennzeichen (UFOPLAN) 206 95 384. November 2008.

Council Decision 2003/33/EC. Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC.

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