ASSESSMENT OF CONSTITUENT AVAILABILITY OF SELENIUM-CONTAINING FLOAT 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 selenium leachability from samples of selenium-containing tinted float. Sample preparation followed the method developed by TC13 and based on the European Standard EN/12457-4. Leachability results were compared with the land-fill criteria in European Council Decision 2003/33/EC. Selenium was not detected in the leachate from any of the glass samples. Therefore the average selenium leachability was evidently much 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 regulation. 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*". (TC13, 2009) That study demonstrated this method is an appropriate test, while assessing the leachability of samples of tableware and cooker top glass. A subsequent study to assess antimony leaching from rolled plate glass confirmed the applicability of the methodology. (TC13, 2010)

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.

¹ CPIV is the standing committee for cross-sectoral issues for all sectors of the European glass industry.

However, some grey or bronze float glass for particular automotive and architectural markets contains selenium. Although the amount of selenium used to colour the glass in these products is always 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 informative to study this glass. This would confirm and/or determine its suitability for its exemption and also further test the assessment method previously used by TC13.

Although this study focuses on the REACH regulation, it provides useful information relating to the Construction Products Directive 89/106/EEC and the current work of CEN TC351 on the "Assessment of release of dangerous substances from construction products".

Samples of selenium-containing, tinted, float glass manufactured by the four member companies of Glass for Europe² were assessed. The analysed selenium (Se) content in the tinted glass samples ranged from 15ppm to 28ppm with an average of 21ppm.

Method

As noted above, the assessment method followed is described in EN 12457. However, the EN12457 general procedure requires that "on no account shall the material be finely ground". This poses a problem because unlike most materials when glass is crushed very fine fragments are unavoidably formed. The previous TC13 papers (2009 and 2010) addressed this issue and recommended that the method be slightly modified by removing fragments smaller than 0.5mm.

Some tinted glass products are toughened, and toughened glass naturally breaks into pieces that are normally all a few millimetres in size, rather than a great range of sizes characteristic of un-toughened glass. Two of the samples in this study were toughened and two were un-toughened. To account for this 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 the samples as described above.

Preparation of replicate samples, their elution and analysis were done by the following European laboratories:

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

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. (<u>http://www.glassforeurope.com</u>)

Although the sample preparation and elution processes were identical, the laboratories employed different analytical techniques. Two used graphite furnace atomic absorption spectroscopy; one used hydride generation atomic absorption spectroscopy; two used inductively-coupled plasma optical emission spectroscopy; and two used inductively-coupled plasma mass spectroscopy.

Results and discussion

None of the laboratories detected any selenium in the leachate from any of the samples, irrespective of preparation or selenium content. Therefore, statistical analysis of the results was inappropriate. The detection limit for selenium in the eluate of the four analytical techniques used by the laboratories varied. This variation resulted in an average elution detection limit for selenium of 0.031 mg/kg. Any selenium leaching that did occur was on average lower than this value. In fact, the ICP mass spectroscopy machines had a detection limit that resulted in an elution detection limit of lower than 0.005 mg/kg.

The relevant value in Council Decision 2003/33/EC relating to criteria for acceptance to landfill as non-hazardous waste is 0.5 mg/kg. If any selenium leaching does occur from tinted flat glass it must be very much less than this value. This indicates that at the end of its life any waste glass of this type could be sent to landfill as non-hazardous waste, and thus demonstrates that the glass should be exempt from REACH registration as no harmful components are "available throughout its life-cycle".

The results of this study should be considered as case-specific and not necessarily applicable to other types of selenium-containing glass.

As well as the REACH Regulation, flat glass is also covered by the Construction Products Directive 89/106/EEC and is part of the scope of the mandate of CEN TC351 "Assessment of release of dangerous substances from construction products". The results of this study also demonstrate that even though some selenium is present in the glass, it is not released into the environment and that flat glass is likely to be classified in the "without testing" category of the CPD.

Conclusion

The work demonstrates that the selenium in tinted float glass for the architectural and automotive market does not exhibit unacceptable leaching and the glass could be sent for landfill. This glass can be considered non-critical with regard to release to soil, surface water and ground water. The selenium can 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, and provides information useful to CEN TC351 regarding the Construction Products Directive.

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).

TC13 2009. Preliminary report on a method to determine the availability of glass consituents with regard to the European regulation REACH. This will be available on the TC13 part of the ICG website <u>www.icg.group.sheff.ac.uk</u>

TC13 2010. 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. Issued January 2010. This will be available on the TC13 part of the ICG website www.icg.group.sheff.ac.uk

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