GLASS FOR EUROPE
Building, Automotive, Solar-Energy Glass

The status of Flat Soda Lime Silicate Glass and its raw materials under REACH

(Regulation (EC) No 1907 /2006).

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Index

1. Introduction

This document aims to clarify the status of the Soda Lime Silicate (SLS) glass used for the manufacture of flat glass products[1] and its raw materials in relation to the requirements of REACH[2] and demonstrate that flat soda-lime-silicate (FSLS) glass meets the requirement for exemption of registration and that its raw materials must be considered as intermediates. In this regard, the following will be provided in order to fulfil the requirement of Article 36[3]:

- the chemical identity of the soda lime silicate glass used in flat glass products;
- a description of the relevant chemical reactions taking place in the synthesis of the new substance i.e. the soda lime silicate (SLS) glass;
- a description of the technical role in the process for which the intermediates are used in the manufacturing of the new substance and the functional properties that they bring to the new substance;
- demonstration that the SLS glass manufactured from the intermediate is exempted from registration under REACH.

[1] *E.g. glass for building and automotive, does not cover container or fiberglass, see paragraph 4.2.*
[2] *Regulation (EC) N° 1907/2006.*
[3] *Article 36: Obligation to keep information – under Title IV "Information in the supply chain".*

2. Flat SLS glass under REACH

Flat SLS glass is considered as a UVCB substance (substances of unknown or variable composition, complex reaction products or biological materials). It is covered by the CAS number: CAS 65997-17-3 and EINEC number: EC 266-046-0; Glass, oxide, chemicals[4].

The chemical analysis of glass is not enough to identify thoroughly the substance. Generally the chemical composition is expressed in terms of oxides, although the glass is not a mixture of oxides as glass is an amorphous silicate (see paragraph *The nature of SLS glass* below page 11). To adequately identify the substance additional information are needed such as the mineralogical formula and a X-ray diffraction pattern.

The SLS glass is very rarely put on the market as a substance but rather as articles because the shape, surface or design of the product put on the market determines the function to a greater degree than the chemical composition[5].

REACH Annex V.11 (Amended by Regulation (EC) No 987/2008) provides exemption from the registration, downstream user and evaluation requirements for some glasses:

The following substances unless they meet the criteria for classification as dangerous according to Directive 67/548/EEC and provided that they do not contain constituents meeting the criteria as dangerous in accordance with Directive 67/548/EEC present in concentrations above the lowest of the applicable concentration limits set out in Directive 1999/45/EC or concentration limits set out in Annex I to Directive 67/548/EEC, unless conclusive scientific experimental data show that these constituents are not available throughout the lifecycle of the substance and those data have been ascertained to be adequate and reliable:

Glass, ceramic frits.

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[4] *Regulation No 1907/2006 - Recital (45). The European Inventory of Existing Commercial Chemical Substances (EINECS) included certain complex substances in a single entry. UVCB substances (substances of unknown or variable composition, complex reaction products or biological materials) may be registered as a single substance under this Regulation, despite their variable composition, provided that the hazardous properties do not differ significantly and warrant the same classification.*

[5] *Article 3 (3) Definition. Article: means an object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition.*

3. Intermediates under REACH

3.1. Definition of intermediate

Art 3.15: Intermediate: means a substance that is manufactured for and consumed in or used for chemical processing in order to be transformed into another substance (hereinafter referred to as "synthesis"):

a) non-isolated intermediate: means an intermediate that during synthesis is not intentionally removed (except for sampling) from the equipment in which the synthesis takes place. Such equipment includes the reaction vessel, its ancillary equipment, and any equipment through which the substance(s) pass(es) during a continuous flow or batch process as well as the pipework for transfer from one vessel to another for the purpose of the next reaction step, but it excludes tanks or other vessels in which the substance(s) are stored after the manufacture;
b) on-site isolated intermediate (OSII): means an intermediate not meeting the criteria of a non-isolated intermediate and where the manufacture of the intermediate and the synthesis of (an)other substance(s) from that intermediate take place on the same site, operated by one or more legal entities;
c) transported isolated intermediate (TII): means an intermediate not meeting the criteria of a non-isolated intermediate and transported between or supplied to other sites;

Art. 2.1.c. The Regulation shall not apply to non-isolated intermediates.

Art. 2.8. On-site isolated intermediates and transported isolated intermediates shall be exempted from Chapter 1 of Title II - *Registration of substances*, with the exception of Articles 8 and 9; and Title VII - *Authorisation*.

In the manufacturing of SLS glass intermediates are in general transported isolated intermediates (TII).

3.2. Provisions for intermediates under REACH

If intermediates are manufactured and used under Strictly Controlled Conditions Article 18.4 a) to f)[6], the following applies:

1. reduced information requirements on registration;
2. reduced fee requirements;
3. exemption from dossier evaluation and substance evaluation.

All intermediates (independently from the conditions of use) are:

1. exempted from authorisation - Art. 2(8) of REACH;
2. exempted from restriction (On Site Isolated) - Art. 68(1) of REACH.

[6] *Article 18. Registration of transported isolated intermediates.*

4. Flat Soda Lime Silicate (FSLS) Glass

4.1.Definition

Flat SLS glass products for use in building are regulated by the Construction Product Regulation (CPR - Regulation (EU) No 305/2011) and subject to CE marking. In the frame of the CPR several product standards are developed by CEN[7] in order to characterise flat glass products, define the specifications they must fulfil, and establish test methods for the verification of compliance with the standards.

SLS Glass is defined by several European Standards. EN 572-1 gives the definition and general chemical, physical and mechanical properties of the SLS glass (Table 1 and Table 3).

Oxide Name	Oxide Formula	Proportion
Silicon dioxide	SiO_2	69 % to 74%
Calcium oxide	CaO	5% to 12%
Sodium oxide	Na_2O	12% to 16%
Magnesium oxide	MgO	0% to 6%
Aluminium oxide	Al_2O_3	0% to 3%

Table 1. Range of composition of SLS glass (EN 572-1) expressed in oxide %[8].

In addition to the above general composition, these glasses may also contain small quantities of other substances; e.g. body tinted glass is obtained by the addition of suitable materials.

EN 572-1 is being amended by EN 572-1:2012/prA1:2014.
The basic glass products covered by this European standard are all manufactured from soda-lime silicate glass.
The magnitude of the proportions by mass of the principal constituents of soda-lime silicate glass covered by this standard is given in Table 2:

Constituents	Proportion by mass of element
Silicon (Si)	32 - 35%
Calcium (Ca)	3.5 – 10.1%
Sodium (Na)	7.4 – 11.9%
Magnesium (Mg)	0 – 3.7%
Aluminium (Al)	0 – 1.6%
Others	< 5%

Table 2. Magnitude of the proportions by mass of the constituents of soda-lime silicate glass. Oxygen represents the balance to 100%.

Soda-lime silicate glass is an amorphous inorganic substance obtained from different inorganic raw materials which react at high temperature to form a new random network, where different cations are linked together, typically by oxygen bridges, arranged in such a way that no free oxides are present.

[7] *CEN: European Committee for Standardisation. CEN TC129 Glass in Building.*
[8] *Although the chemical composition is expressed in terms of oxides, it is important to note that the phase composition of a glass is not adequately described by a list of oxide weight percentage. The phase composition refers to the mineralogical formula; an example is given in Table 4.*

Soda-lime silicate glass can best be identified by the mineralogical formula:

$$Na_nCa_oMg_pAl_q......Si_mO_s$$

Where: s = n/2 + o + p + 3 q/2 + ... + 2m.

Characteristic	Symbol	Numerical value and unit
Density (at 18°C)	ρ	2500 kg/m^3
Hardness (Knoop)	HK 0,1/20	6 GPa
Young's modulus (modulus of elasticity)	E	7x10^{10} Pa
Poisson ratio	μ	0.2
Characteristic bending strength	$F_{g,k/k}$	45 x 10^6 Pa
Specific heat capacity	C	0.72 x 10^3 J/(kg.K)
Average coefficient of linear expansion between 20° C and 300° C	α	9 x 10^{-6} K^{-1}
Resistance against temperature differential and sudden temperature change		40 K
Thermal conductivity	λ	1 W/ (m.K)
Mean refractive index to visible radiation (380 nm to 780 nm)	N	1.5
Emissivity	ε	0.837
Minimum light transmittance for clear glass (measured according to EN 410)		0.89 (2 mm) 0.87 (4 mm) 0.85 (6 mm) 0.81 (10 mm)

Table 3. General characteristic values of Soda Lime Silicate Glass according to EN 572-1.

4.2.Utilisation

There are two main types of flat glass produced in the EU: rolled glass and float glass. Although strictly there are other types of flat glass such as drawn sheet glass and channel shaped glass, but they represent a very minor production. The majority of rolled glass is patterned or wired glass and accounts for around 3.5 % of the total sector output. Patterned glass is used for horticultural greenhouses, for decorative purposes and in applications where light is dispersed, for example for glass partitions, bathroom windows and for photovoltaic panels.

Float glass makes up the other 96 % of output and is used principally in the building and automotive industries.

Flat soda lime silicate glass is used in various applications:

- Construction: exterior glazing (windows, doors, guard rails, etc.), and interior decoration (doors, partitions, mirrors, wall coverings, guard rails, etc.)
- Automotive: windshields, side and rear windows, sun roofs, rear view mirrors.
- Industrial: copy machines, oven doors, fridges, vending machines, chilled display cabinets, etc.
- Electronics: TV, computers, etc.

5. The making of Flat SLS Glass

The composition of the glass depends on the specific properties and applications envisaged, as well as technical and economic considerations. The chosen raw materials must be able to be melted and react together to form the glass; they must ensure the requested mechanical, chemical and optical properties of the SLS glass produced as shown in Table 3; and, as flat glass is a mass production product, they must be affordable and available in large quantities.

Flat SLS glass is made from raw materials most of which are from natural origin such as sand, limestone, dolomite, soda ash, etc. The following steps occur (Figure 1):

1. Glass raw material transport (trucks, ship, train or Big Bag, sacks and drums)
2. Raw material storage in silo inside a building (Batch house)
3. Raw material dosing and weighing system
4. Mixer
5. Batch transportation and filling into furnace
6. Furnace

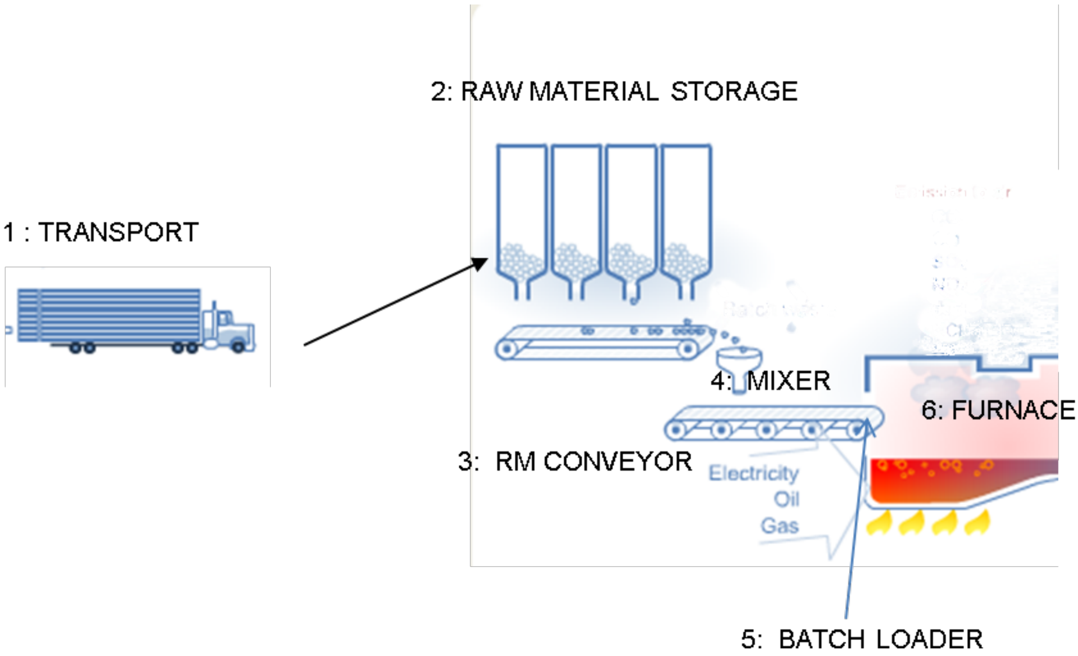

Figure 1. Raw material preparation and feeding to the furnace for the making of SLS glass.

In the furnace, endothermic reactions occur between the different raw materials in order to produce the new substance glass (Table 4 and Figure 2). All ingredients that are brought into the furnace (where the temperature is around 1550°C) are turned into glass with the exception of some gases that are exhausted such as SO_2 and CO_2.

After the reactions have taken place and the glass is synthesised, the glass remains in the furnace for a couple of days before it is withdrawn and shaped into articles. Although the fusion process is always the same there are different shaping processes to produce the flat articles depending on the final use of the products (Figure 3). The characteristics of those articles are defined by European Standards:

- Float glass (EN 572-2);
- Polished wired glass (EN 572-3);
- Drawn sheet glass (EN 572-4);
- Patterned glass (EN 572-5);
- Wired patterned glass (EN 572-6);
- Wired or unwired channel shaped glass (EN 572-7).

6. The nature of SLS glass

6.1. General composition

Flat Soda Lime Silicate glass, although being an UVCB substance according to REACH, has a very precisely defined composition in order to meet the criteria requested by EN 572-1 and other relevant EN Standards and to display the specific properties needed for the different applications. Properties of the SLS glass are of two main types: those that are linked to the structure of the glass and those that are linked to the chemical composition of the glass. So depending on the application, the composition of the glass varies. The principal raw materials[9] of soda-lime silicate glass are: sand, soda ash (synthetic from the Solvay process, or from natural origin), dolomite, limestone, feldspar or nepheline syenite, or phonolite (frequently replaced by slag from the steel industry) and salt cake (Table 5).

Raw materials: several substances	→	Endothermic chemical reactions	→	Glass: one substance
Sand (Quartz SiO_2) **Soda Ash (Na_2CO_3)** **Limestone ($CaCO_3$)** **Dolomite ($CaMg(CO_3)_2$)** **Feldspar ($NaAlSi_3O_8$)** **Salt Cake (Na_2SO_4)** **Slag** **…**		a SiO_2 + b Na_2CO_3 + c $CaCO_3$ + d $CaMg(CO_3)_2$ + e $NaAlSi_3O_8$ + f Na_2SO_4 + …. + energy = $Na_nCa_oMg_pAl_q......Si_mO_s$ + x SO_2 + y CO_2		$Na_nCa_oMg_pAl_q...Si_mO_s$ s = n/2 + o + p + 3 q/2 + … + 2m

Table 4. Three steps of the making of SLS glass.

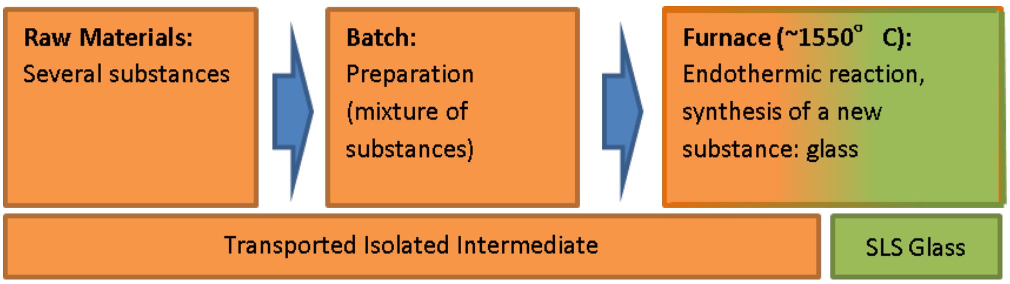

Figure 2. Formation of the substance SLS Glass from raw materials.

[9] *In addition to the raw materials variable quantities of glass cullet (i.e. recycled glass) are also added.*

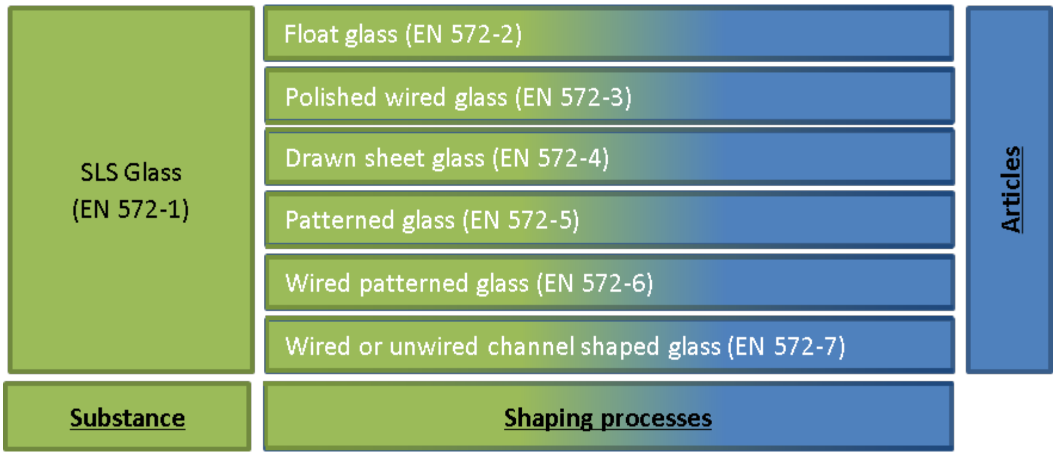

Figure 3. Shaping of the substance SLS glass into articles.

Other ingredients can be added, generally in very low quantities (from less than 10 ppm up to 2000 ppm in rare cases) in order to modify the physical, chemical, and optical properties of the glass for special applications. These ingredients added in small quantities can include:

- colouring agents;
- redox active species;
- other elements to improve specific properties (e.g. modify the refractive index).

Several substances	CAS #	kg	%
Sand (Quartz SiO_2)	14808-60-7	2433	60.2%
Soda Ash (Na_2CO_3)	497-19-8	794	19.7%
Dolomite ($CaMg(CO_3)_2$)	240-440-2	643	15.9%
Feldspar ($NaAlSi_3O_8$)	68476-25-5	85	2.1%
Limestone ($CaCO_3$)	1317-65-3	48	1.2%
Salt Cake (Na_2SO_4)	7757-82-6	32	0.8%
Others		< 2	<0.1%
Total		4037	100%

Chemical composition		One single substance
SiO_2	73.1%	$Na_{1.8}Ca_{0.6}Mg_{0.4}$ $Al_{0.05}Si_5O_{12}$ CAS: 65997-17-3
Na_2O	14.7%	
CaO	6.7%	
MgO	4.2%	
Al_2O_3	1.0%	
Others oxides	< 0.1%	
3379 kg	100%	100%

Table 5. Example of batch formula and resulting SLS glass composition, starting from the raw material to the new glass substance. The chemical composition of the glass is shown as oxide % in the standard way for convenience, even though no oxides are present as such. The resulting substance glass is a silicate.

During the synthesis of the glass, the raw materials react together and disappear to form the new substance. This can clearly be seen from the X-ray diffraction pattern of the raw material (Figure 4) and the one of the formed glass (Figure 5).

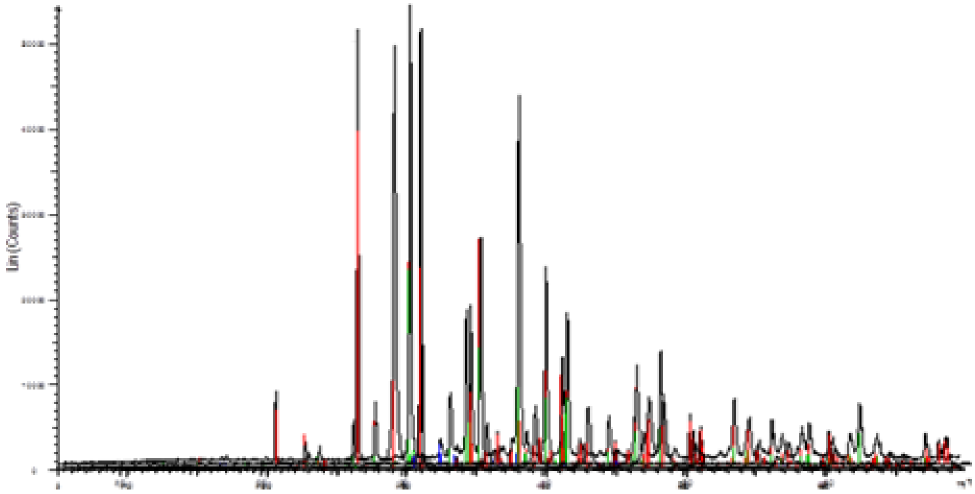

Figure 4. X-Ray Diffraction pattern of a mixture of sand (quartz), soda ash, limestone and dolomite. Horizontal axis: 2ϑ, vertical axis: intensity (counts).

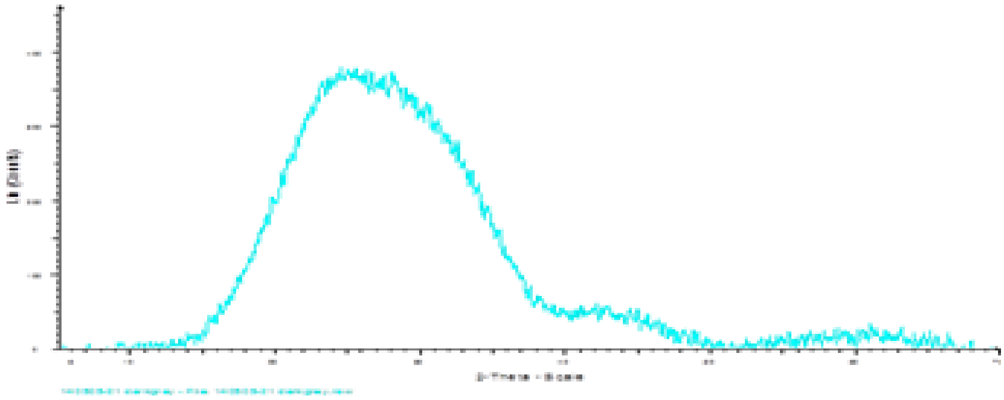

Figure 5. X-Ray Diffraction pattern of soda lime silicate glass. Due to the amorphous glass structure of the substance, no X-ray diffraction peaks appear. Horizontal axis: 2ϑ, vertical axis: intensity (counts).

6.2. Structure of the SLS glass

While all raw materials are crystalline substances, being natural or synthetic, the glass itself is not crystalline but amorphous (Figure 5). Its structure is characterised by a continuous random network of tetrahedrons of oxygen with a silicon ion in the middle (Figure 6). The tetrahedrons are bonded together by oxygen that are shared by two tetrahedrons. These oxygen ions are called bridging oxygen (BO). Those tetrahedrons form a network that is the skeleton of the glass (silicon is called the network former). The introduction in the system of other cations such as Na^{+}, Ca^{++}, Mg^{++}, etc., opens up, i.e. depolymerises, the network formed by the silicon tetrahedrons (network modifiers), so some oxygen ions are no longer shared by two tetrahedrons and become available for other links; these are called non bridging oxygen (NBO).

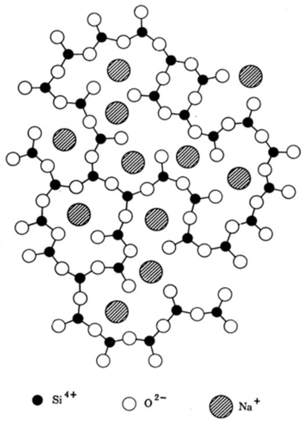

Figure 6. Glass structure showing the silicon tetrahedrons linked together to form the network. Larger ions such as Na^+ are placed outside the tetrahedron. Zarzycki, 1982.

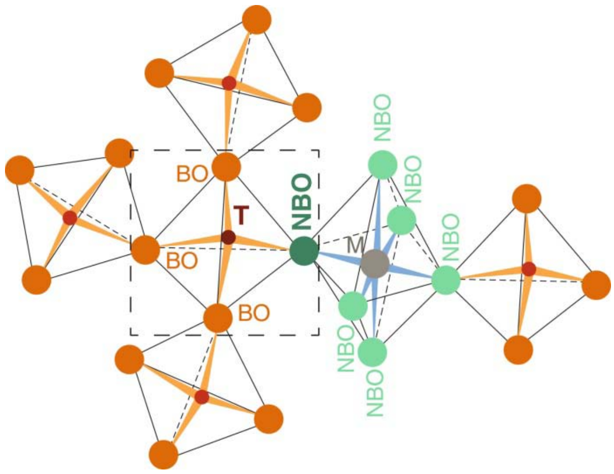

Figure 7. Silicon (red) tetrahedrons with bridging oxygens (BO - orange) and octahedron of non-bridging oxygens (NBO - green) with a metallic cation (grey). Mysen, 2014.

Only small ions with a high number of positive charges such as silicon (Si^{4+}) can form the tetrahedrons and the network of the glass; the other larger cations with smaller number of positive charges are accommodated in larger polyhedrons (e.g. hexahedrons or octahedrons) constituted by non-bridging oxygens (Figure 7). To ensure that all cations are at their highest level of positive charge, SLS glass is generally oxidised.

The non-bridging oxygen to network forming tetrahedral ratio, or the non-bridging oxygen's to tetrahedrally coordinated cations ratio, (NBO/T ([10])) is a measure of the depolymerisation of the network. The parameter Q that is a measure of the polymerisation of the glass is often preferred[11], it represents the average number of BO per tetrahedron. The lower the NBO/T ratio (thus the higher the Q value) the higher polymerisation of the matrix of the silicate glass. Pure silica glass (100% SiO_2) has a

[10] *NBO/T can vary between 0 and 4.*
[11] *Q = 4 – NBO/T.*

NBO/T = 0 (Q = 4, fully polymerized) meaning that all 4 oxygens per tetrahedron are BO and thus linked to another tetrahedron. A pure $Na_2O.SiO_2$ glass has a NBO/T = 2 (Q=2) meaning that each tetrahedron is linked to two others (2 BO) and 2 oxygens (NBO) are available for linking with Na^+. Soda lime silicate glasses have a NBO/T ≈ 0.75 (Table 7) which means that the network is fairly polymerised with ≈3 BO (Q = 3.2) per tetrahedron (which is one of Zachariasen's conditions for the formation of glass[12]) ensuring a strong 3D network and ≈1 NBO available for other cations. For low Q the tetrahedrons will form 2D networks or even chain-like networks. Several very important physical and chemical properties are linked to the polymerisation level of the glass, such as thermal conductivity, electrical conductivity, thermal expansion, viscosity and density.

6.3. Roles of the major elements

Network formers: they are characterised by small ionic radius and higher charges so they can be accommodated within the oxygen tetrahedrons. Although several network formers exist, SiO_2 is the only one used in the production of SLS glass (former of SiO_4 tetrahedrons). It reduces thermal expansion of the glass and increases its mechanical and chemical resistance.

Network modifiers: too large to enter the tetrahedron, they allow the depolymerisation of the silica network and the modification of the properties of the glass and make glass useful for applications. Na_2O is the most utilised, although it reduces the chemical resistance of the glass. Inversely, CaO increases the chemical resistance of the glass.

Element	Valence Z	Ionic radius (CN=6) Å	Most frequent CN	Ionic distance for oxides Å	*F* Field strength at distance of O^{2-} ions Z_c/a^2	Function in glass structure
K	1	1.33	8	2.76	0.13	Network modifiers Z_c/a^2: 0.1-0.35
Na	1	0.98	8	2.42	0.17	
Na	1	0.98	6	2.30	0.19	
Ca	2	1.06	8	2.48	0.33	
Ca	2	1.06	6	2.38	0.35	
Mg	2	0.78	6	2.10	0.45	Intermediates Z_c/a^2: 0.5-1.0
Mg	2	0.78	4	1.97	0.51	
Al	3	0.57	6	1.89	0.84	
Al	3	0.57	4	1.76	0.97	
Si	4	0.39	4	1.60	1.56	Network former Z_c/a^2: 1.5-2.0

Table 6. Dietzel's field strength and other parameters of major cations used in the manufacture of SLS glass. (CN: coordination number.) Scholtze, 1990.

These cations are not part of the network but modify the properties of the glass in order to meet the technical requirements for flat glass applications (and requirements of the EN 572-1). The modification of the properties of the glass is linked to the nature of the atoms and to their interactions with neighbouring atoms.

[12] *For a description of Zachariasen's work, see https://en.wikipedia.org/wiki/William_Houlder_Zachariasen; or Zachariasen, 1932.*

Aluminium have an intermediate role (Table 6) as it can act as a network former (in substitution of Si) and act as a network modifier and improve the mechanical and chemical resistance.

The ability of cations to enter the glass network is characterised by their Dietzel's Field Strength $F = Z_c/a^2$ ([13]). It is a measure of the strength of the ionic NBO-M-NBO bridges between Q sites. The network forming cations have high field strength, Z_c/a^2: 1.2 - 2.0, while network modifiers have low field strength, Z_c/a^2: 0.1 – 0.4 (Table 6). The difference between the field strength of the network modifiers and the network formers is important to avoid crystallisation of minerals instead of formation of a glass: the higher the difference between the field strength of the cations the higher the tendency to form a glass. Na and K will form the more stable glass whereas a too high proportion of Ca and Mg could lead to crystallisation (Table 6). Binary systems where the difference in field strength (ΔF) between two cations (NWF and NWM) is greater than 1.33 will readily form a glass. Na will easily form glass with Si (ΔF =1.44) whereas it is more difficult with Ca ($\Delta F = 1.24$) and Mg ($\Delta F = 1.12$). That is why Na is essential to the formation of soda lime silicate glass. However, as Na has a low field strength, Na-Si glass are not very chemically durable, the introduction of cations with higher field strength (Ca, Mg) is necessary to increase the chemical durability of the glass.

FSLS glass	Clear	Clear	Clear	Extra clear	Green
SiO_2	72.60	72.47	71.80	72.70	72.28
Na_2O	13.90	13.41	13.60	13.00	13.47
CaO	8.40	8.81	8.78	8.80	8.78
MgO	3.90	4.19	3.76	4.30	3.98
Al_2O_3	1.10	0.66	1.01	0.60	0.67
K_2O	0.06	0.06	0.60	0.40	0.08
SO_3	0.20	0.29	0.26	0.20	0.17
Fe_2O_3	0.11	0.11	0.10	0.02	0.57
Q	3.27	3.24	3.25	3.24	3.25
NBO/T	0.73	0.76	0.75	0.76	0.75

Table 7. Example of actual flat SLS glass composition and associated Q value and NBO/T ratio.

Physical properties of SLS glasses are greatly affected by the degree of polymerisation (i.e. Q); polymerisation (Q) decreases as SiO_2 and Al_2O_3 (network-formers) concentrations decrease and Na_2O, CaO, MgO, and K_2O (network modifiers) increase. For instance: thermal conductivity, viscosity and transition temperature[14] (T_g) decrease as polymerisation (Q) decreases (NBO/T increases); thermal expansion increases with increasing NBO/T (decreasing Q). Thus it is important for flat SLS to have the right NBO/T (or Q) value in order to meet the technical requirements for the use of flat SLS glass products. For instance, the thermal expansion coefficient of flat SLS glass must be high enough to allow thermal toughening[15] of the glass when high thermal and mechanical resistances or safety properties are requested.

[13] *Z_c = number of charge of the cation, r_c = ionic radius of the cation, $a = r_c + rO^-$.*

[14] *The transition temperature (Tg) is an extremely important characteristic of glass; it corresponds to the reversible glass–liquid transition in amorphous materials from a hard and relatively brittle state into a molten or rubber-like state (ISO 11357-2).*

[15] *Thermal toughening is obtained by heating up the glass above its transition temperature (Tg) followed by rapid cooling with forced air drafts in order to create high internal stresses. This results in an increased thermal and mechanical resistance of the glass. In case of breakage, the glass will shatter into small armless pieces. Thermally toughened safety glass is used in many applications such as building, furniture, industrial and automotive. Properties of toughened glass are regulated by the European Standard EN 12150-2.*

6.4. Role of trace elements

In order to provide specific properties for special applications some metals are added to the generic SLS glass formula. The modifications of the properties of the glass that result from the addition of those atoms are linked to the nature of the atoms themselves, their state of oxidation and to their interactions with neighbouring atoms. Most of the properties impacted are optical properties such as light transmission, colour, etc. The colour of the SLS glass and therefore its optical properties depends generally not on one ion alone but rather on interaction between different ions in their different oxidation states which are a function of the redox state of the glass (see 6.5. Redox and Figure 9). As an example, subtle differences in those parameters produce varying shades of green in flat glass. These metals are generally added at trace level from less than 10 ppm up to around 2000 ppm in rare cases (Table 10).

The Dietzel's Field Strength of the trace elements (Table 8) is relatively high, from > 0.5 up to 1.76. That means that they are strongly bonded into the network, and much more than the network modifiers Na and K. The high field strength of the added cations lowers the leaching rate of the glass and consequently improves its durability.

The trace elements are used not only to produce colours but also to control ultraviolet and infrared transmission. Examples of the impact of colours of glass on its optical properties is given in Figure 8 where the effect of different colours on the light transmission and UV absorption is displayed.

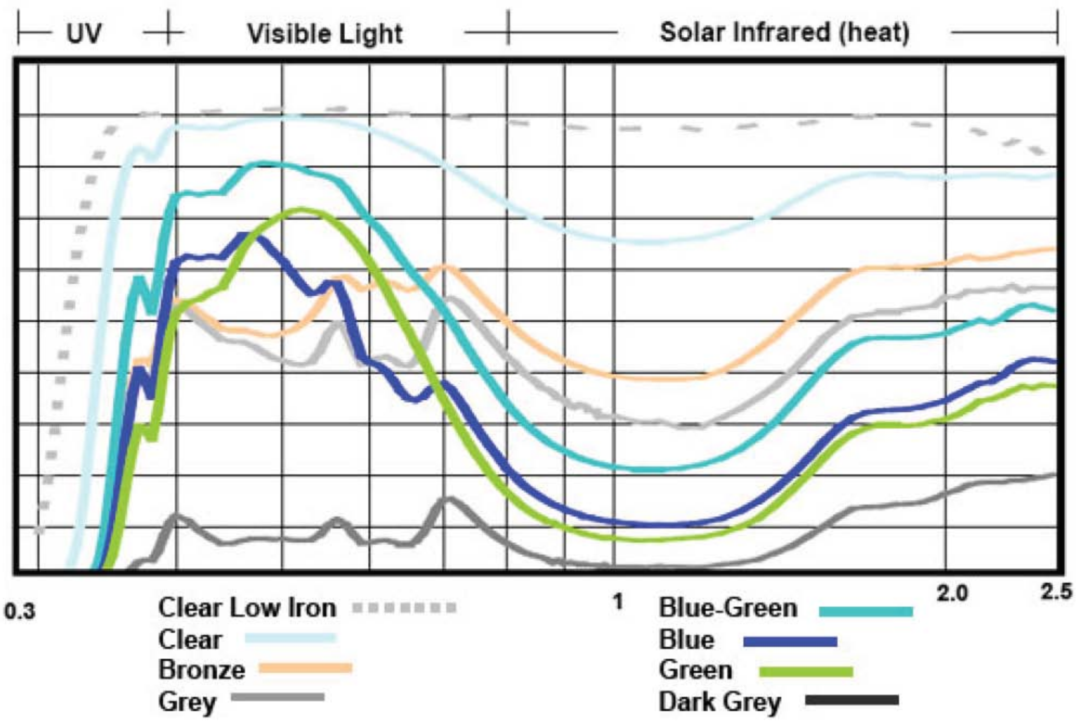

Figure 8. UV, visible, and near infrared transmission (300-2500 nm) of common glass with different colours. Arsenault, 2015.

The colour and light transmission properties are modified depending on the application of the flat glass products:

- Automotive glasses are generally tinted, green, grey or blue in order to ensure protection from UVA damage to passengers and plastics as well as controlling the temperature inside the vehicle.
- Greenhouse glass and Photovoltaic panel covers require a high visible light transmission (400-700 nm) while limiting Infrared heat transmittance (>3,000 nm).
- SLS glass for furniture, shower doors, and many other articles are clear or extra clear.
  Clear window glass typically contains a small amount of iron and have a greenish tint when seen from the edge. However, recently extra clear SLS glass is becoming more popular in building in order to increase comfort by letting more daylight in the building. In warm countries tinted glass helps preventing building overheating.

Element	Valence Z	Ionic radius (CN=6) Å	Most frequent CN	Ionic distance for oxides (Å)	*F* Field strength (Dietzel) Z/a^2
Fe	2	0.83	6	2.15	0.52
Co	2	0.82	6	2.14	0.53
Fe	2	0.83	4	2.03	0.58
Co	2	0.82	4	2.02	0.59
Sb	3	0.90	6	2.22	0.73
Fe	3	0.67	6	1.99	0.91
Co	3	0.66	6	1.98	0.92
Cr	3	0.64	6	1.96	0.94
Fe	3	0.67	4	1.88	1.02
Co	3	0.66	4	1.87	1.03
Sb	5	0.63	4	1.84	1.76
Se	6	0.41	4	1.63	2.25
S	6	0.31	4	1.52	2.60

Table 8. Dietzel's field strength for several trace elements used in SLS glass. CN: coordination number. Scholze, 1990.

6.5. Redox

Iron (Fe) is always present as an impurity from the natural raw materials. The iron content, and particularly the ratio Fe^{++}/Fe^{+++}, must be carefully controlled as it has a strong impact on the final coloration of the glass and hence its light transmission. The redox state of the glass, i.e. the equilibrium between all oxidising and reducing species in the system, can be characterised by the iron redox ratio: Fe^{2+}/Fe^{tot}. Important in the calculation procedure for a batch composition is the batch redox number. A high positive redox number of a batch indicates a batch with high oxygen potential that will produce an oxidized glass (e.g. iron is mainly as Fe^{3+}).

The redox state of the batch and of the glass melt will have a strong influence on the final properties of the glass (notably colour, light transmission, etc.). Oxidizing agents (e.g. sulphates or nitrates) or reducing agents (e.g. coke or slag) are added to the batch to attain the suitable redox of the glass. The Redox number is determined by the quantities of oxidizing or reducing species in batch. Based on empirical data a formula has been derived:

$$R_{total} = \Sigma R_i \times G_i$$ [16] (see Table 9).

Ingredient	Redox factor R_i
Oxidizing ingredients	
Sodium sulphate (Na_2SO_4)	+ 0.67
Sodium nitrate ($NaNO_3$)	+ 0.32
Diiron oxide (Fe_2O_3)	+ 0.25
Fe_3O_4	+ 0.19
Reducing ingredients	
Carbon (C)	- 6.70
Coke (C)	- 5.70
Slag	- 0.071 till - 0.09

Table 9. Redox factors for some raw materials used in the manufacturing of flat SLS glass. Hubert, 2015.

Several reactions occur to contribute to the redox state of the glass (Figure 9):

$$2C + SO_4^{2-} \rightarrow 2CO_2 + S^{2-}$$
$$S^{2-} + 3SO_4^{2-} \rightarrow 4SO^{2-} + 4O^{2-}$$
$$2SO_4^{2-} \leftrightarrow 2SO_2 + O_2 + 2O^{2-}$$

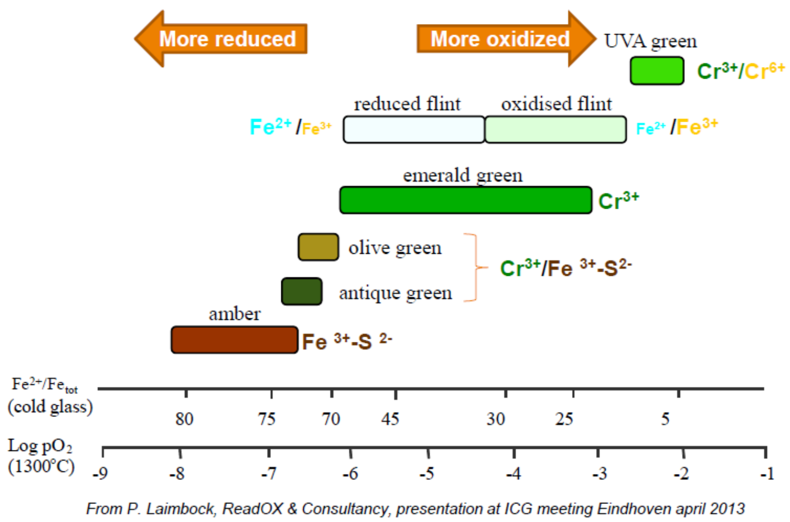

Figure 9. Effect of the redox state of the glass on its colour. Redox vs. colour of Fe & Cr-containing glasses. Hubert, 2015.

[16] *G_i: reducing or oxidizing compound per 2000 kg sand in batch; R_i redox factor .*

6.6. General formula

The resulting substance has the chemical composition of a silicate with the general formula of:

$$Na_nCa_oMg_pAl_qSi_mO_s$$

Where: $s = n/2 + o + p + 3\,q/2 + 2m$ in order to balance all electrical charges.

Clear Flat Soda Lime Silicate glass, which is the most common type of glass put on the market for use in Automotive, Buildings and Industrial applications contains only the general raw materials described above (see also Table 10 and Table 11); trace elements are added to provide additional or modified properties to the SLS glass. The general idealised formula of the Flat SLS glass from Table 7 is:

$$Na_{1.8}Ca_{0.6}Mg_{0.4}Al_{0.05}Si_5O_{12}$$

7. The hazardousness of flat SLS glass

7.1. Meeting the criteria of Annex V.11 for exemption from registration under REACH

Glass can be exempted from registration (Annex V.11) under certain conditions; i.e. if it can be demonstrated that the glass does not display any hazard characteristic:

glasses are only to be exempted if they (as substance as such) do not meet the criteria for classification as dangerous according to Directive 67/548/EEC, and provided that they do not contain constituents meeting the criteria as dangerous (Directive 67/548/EEC) that are present in concentrations above the lowest of the applicable concentration limit (Directive 1999/45/EC or in Annex I to Directive 67/548/EEC), unless conclusive scientific experimental data show that these constituents are not available throughout the life-cycle of the substance (consider the constituents after the production of the glass as constituents could be different than the starting materials).

"Constituents" are not defined in the REACH Regulation. However, a definition can be found in ECHA's guidance document on substance naming[17]: "*Any single species present in a substance that can be characterized by its unique chemical identity*".

A method has been developed by Greim H, Schaeffer H, and Favaro N. (2013) in order to identify the "dangerous constituents" in glass.

Due to the nature of glass, its constituents are closely linked together and are in a specific chemical environment (silica tetrahedrons network), totally different from the initial state (raw materials), and do not occur in simple compounds such as metals or oxides. Any toxicological effects of the constituents present in the substance glass are different from those foreseeable for the raw material substances.

[17] *Guidance for identification and naming of substances under REACH and CLP.*

Type of FSLS glass	Ion of interest	Clear & Extra clear	Green	Coloured	Extra Clear	Function in SLS glass	
Application /Use Raw Material		Building & Industrial	Automotive	Building & Automotive	PV Panels & Greenhouses		
Sand (SiO_2)	Si^{4+}	X	X	X	X	Network former	Major ingredients (%)
Soda Ash (Na_2CO_3)	Na^+	X	X	X	X	Network modifier	
Dolomite ($CaMg(CO_3)_2$)	Ca^{2+} Mg^{2+}	X	X	X	X	Network modifiers	
Feldspar ($NaAlSi_3O_8$), Nepheline Syenite ($NaKAl_2Si_2O_8$)	Al^{3+} Si^{4+} Na^+	X	X	X	X	Network formers Network modifier	
Limestone ($CaCO_3$)	Ca^{2+}	X	X	X	X	Network modifier	
Salt Cake (Na_2SO_4)	Na^+ S^{2-}/S^{6+} O^{2-}	X	X	X	X	Network modifier/former Redox	
Sodium nitrate ($NaNO_3$)	Na^+ O^{2-}			(X)		Network modifier Redox control	
Slag ($Ca_2(MgFeAl)(SiAl)_2O_7$. FeS)	Ca^{2+}, Mg^{2+}, Al^{3+}, S^{2-}	X	X	X	X	Network former &modifier Redox control	
Coke	C^{4+}	(X)	(X)	(X)	(X)	Redox control	Minor ingredients (ppm)
Fe_2O_3	Fe^{2+}/ Fe^{3+}		X	X		Colouring agent (green/yellow)	
Cr_2O_3, Iron chromite ($FeCr_2O_4$)	Cr^{3+}		X	X		Colouring agent (green)	
Sb_2O_3	Sb^{2+}/ Sb^{3+}				(X)	Increase light transmission	
Se, Na_2SeO_3, $ZnSeO_3$	Se^{6+}			X		Colouring agent (bronze)	
CoO, $CoSO_4$	Co^{2+}/ Co^{3+}			X		Colouring agent (blue)	

Table 10. Summary table with uses and function of the principal raw materials for the different types of Flat Soda Lime Silicate (FSLS) glasses. Extracted from the Best Available Techniques (BAT) Reference Document for the Manufacture of Glass. (X) Used in specific products only.

Substance	CAS	Registration	Tonnage Band (tpa)	Year	
Soda Lime Silicate Glass	65997-17-3	Exemption (Annex V.11)[18]			Glass
Sand (quartz, SiO_2)	14808-60-7	Exemption (Annex V.7)[19]			Major ingredients (%)
Sodium carbonate -Soda Ash (Na_2CO_3)	497-19-8	Full	10 000 000-100 000 000	2011	
Dolomite ($CaMg(CO_3)_2$)	240-440-2	Exemption (Annex V.7)			
Feldspar ($NaAlSI_3O_8$)	68476-25-5	Exemption (Annex V.7)			
Nepheline syenite ($NaKAl_2Si_2O_8$)	37244-96-5	Exemption (Annex V.7)			
Limestone ($CaCO_3$)	1317-65-3	Exemption (Annex V.7)			
Salt Cake - Sodium sulphate (Na_2SO_4)	7757-82-6	Full	100 000-1 000 000	2011	
Slag ($Ca_2(MgFeAl)(SiAl)_2O_7$. FeS) (UVCB)	65996-69-2	Full	10 000 000 – 1000 000 000	2011	
Sodium nitrate ($NaNO_3$)	7631-99-4	Full	10 000 – 100 000	2011	
Coke (C)	65996-77-2	Exemption (Annex V.10)[20]			Minor ingredients (ppm)
Diiron trioxide (Fe_2O_3)	1309-37-1	Full	100 000-1 000 000	2011	
Iron chromite ($FeCr_2O_4$)	1308-31-2	Exemption (Annex V.7)			
Chromium$^{(III)}$ oxide (Cr_2O_3)	1308-38-9	Full	10 000 – 100 000	2010	
Diantimony trioxide (Sb_2O_3)	1309-64-4	Full	10 000+	2011	
Sodium selenite (Na_2SeO_3)	10102-18-8	Full	10 – 100	2013	
Zinc selenite ($ZnSeO_3$)	13597-46-1	Full	100 – 1 000	2011	
Selenium (Se)	7782-49-2	Full	1 000 – 10 000	2013	
Cobalt oxide (CoO)	1307-96-6	Full	1 000 – 10 000	2011	
Cobalt sulphate ($CoSO_4$)	10124-43-3	Full	10 000-100 000	2011	

Table 11.Summary registration status under REACH of Flat Soda Lime Silicate glass and its most frequent raw materials extracted from the Best Available Techniques (BAT) Reference Document for the Manufacture of Glass.

[18] *Regulation (EC) No 987/2008.*

[19] *Annex V.7. of REACH exempts the following substances which occur in nature, if they are not chemically modified: Minerals, ores, ore concentrates, raw and processed natural gas, crude oil, coal.*

[20] *Annex V.10 of REACH: The following substances if they are not chemically modified:*
Liquefied petroleum gas, natural gas condensate, process gases and components thereof, coke, cement clinker, magnesia.

On this basis it is possible to state that:

- no single species present in the glass can be characterized by its unique chemical identity and form;
- no single species present in the glass has maintained the form and the chemical characteristics of the raw materials;
- no single species eventually released from the glass has maintained the form and the chemical characteristics of the raw materials.

Therefore it is appropriate to interpret "dangerous constituents" in the glass as elements meeting the criteria for classification as dangerous in all their chemical forms according to Annex I of Directive 67/548/EEC and Annex VI of the CLP (Regulation (EC) 1272/2008); example: Index No 051-003-00-9: *Antimony compounds with the exception of the tetroxide (Sb_2O_4), pentoxide (Sb_2O_5), trisulphide (Sb_2S_3), pentasulphide (Sb_2S_5) and those specified elsewhere in this Annex*.

Based on Annex VI of the CLP (Regulation (EC) 1272/2008) and Annex I of Directive 67/548/EEC and the previous considerations, the following constituents among those normally used to produce Flat SLS glass (see Table 10 and Table 11) are classified as dangerous[21]: antimony (Sb) and selenium (Se), Table 12.

Index No	International Chemical Identification	Classification		Concentration set out in Annex I of Directive 67/548/EEC and Part 3 of Annex VI of Regulation (EC) N° 1272/2008	Lower concentration set out in Annexes II & III of Directive 1999/45/EC
		Danger & risk phrase	Hazard Statement Codes		
051-003-00-9	Antimony compounds, with the exception of the tetroxide (Sb_2O_4), pentoxide (Sb_2O_5), trisulphide (Sb_2S_3), pentasulphide (Sb_2S_5) and those specified elsewhere in this Annex	Xn: R20/22 N: R51-53	H302 H332 H411	Xn: R20/22: C ≥ 0.25 %	Xn: R20/22 C ≥ 0.25 % N: R51-53 C ≥ 2.5 %
034-002-00-8	Selenium compounds with the exception of cadmium sulphoselenide and those specified elsewhere in this Annex	T: R23/R25, R33 N: R50-53	H301 H331 H373 H400 H410		T: R23/R25 C ≥ 3 % R33 C ≥ 1.0%[22] N: R50-53 C ≥ 0.25 %

Table 12. Dangerous constituents in Flat SLS according to Annex I of Directive 67/548/EEC and Directive 1999/45/EC.

Those two constituents are generally present only in specific FSLS glasses such as glass for photovoltaic panel cover and coloured glass, and with a concentration below the thresholds above which the glass would be considered as dangerous (Table 12): Sb is generally < 0.25 % (lower than the limit set in Annex I

[21] *Other constituents are listed as dangerous compounds in all their forms in Annex I of Directive 67/548/EEC: arsenic, cadmium, chromium(VI), lead, beryllium, mercury, thallium and uranium but they are not normally present in Flat SLS glass compositions and for this reason they are not taken into consideration in this document.*
[22] *Annex V of Directive 1999/45/EC.*

of Directive 67/548/EEC and Part 3 of Annex VI of Regulation (EC) N° 1272/2008 and in Annexes II and III of Directive 1999/45/EC) and Se < 50 ppm (0.005% - much lower than the limit set in Annexes II and III of Directive 1999/45/EC). So it can be concluded that Flat Soda Lime Silicate Glasses containing the "dangerous constituents" Sb and Se are meeting the requirement of Annex V.11 for exemption from registration.

7.2. Availability of dangerous constituents throughout the Life Cycle

In the case that a dangerous constituent would be present in a concentration higher than the limit set in Annex I of Directive 67/548/EC (Part 3 of Annex VI of Regulation (EC) N° 1272/2008) or Annexes II and III of 1999/45/EC, it should then be demonstrated that the "constituents are not available throughout the life-cycle of the substance" in an adequate and reliable way. An unequivocal "pass or fail" test is needed. Table 12 shows the main circumstances where FSLS glass could release dangerous constituents into the environment: during its service life on the façade or roof of a building or after the end of its life if the glass is mixed with other Construction & Demolition Waste (C&D waste) and used as backfilling material or dumped into a landfill. For the assessment of the possible release of a constituent during the service life and the end of life, it is considered that leaching tests are the most relevant test methods applicable and that the criteria for acceptance of a material in a landfill for non-dangerous waste as set in Commission Decision 2003/33/EC would be appropriate to decide whether a glass meet the criteria of Annex V.11 or not.

Even though FSLS glasses containing dangerous constituents meet the requirements of AnnexV.11 because the concentrations of antimony and selenium are lower than the limit values set in the annexes of Directives 67/548/EC and 1999/45/EC investigations were carried out in order to assess the behaviour of these dangerous constituents during the life cycle of the products: i.e. during the service life of the product (in a building as a construction product) and at the end of the life of the product (Table 13).

7.2.1. Service Life

Flat Soda Lime Silicate Glasses containing antimony for photovoltaic panel covers were tested according to a standard developed by CEN TC 351[23] in order to assess the possible release of dangerous substances during the life time of the product: the horizontal dynamic surface leaching test, also named the Tank Test (FprCEN/TS 16637-2 and NEN 7375). During the test, sheets of the glass were immersed in water for 64 days. Antimony was analysed in the solution after 6H, 24H, 54H, 72H, 216H, 384H, 864H, and 1536H. All results were below detection limit (< 0.005 µg/cm²), indicating that there is virtually no release of antimony during the service life of the products.

[23] *European Committee for Standardisation, CEN/TC 351 - Construction Products - Assessment of release of dangerous substances.*

Life Cycle Stage	Area of use	Exposure conditions	Suitable characterisation method
Service life	Facades, Roof	Rain water, splash water	Tank test, DSLT, special test methods. FprCEN/TS 16637-2 NEN 7375
After demolition (End of life)	Reuse phase in road construction	Soil/rain water	Granular test. EN 12457-4
	Disposal (landfill)	Ground/percolating rain water	Granular test. EN 12457-4

Table 13. Exposure scenario and test methods for assessment of the possible release of dangerous constituents during the life cycle of Flat Soda Lime Silicate Glass. DSLT: Dynamic Surface Leaching Test.

7.2.2. End of Life

At the end of life, most FSLS glass could be recycled; however in many instances, the FSLS glass is mixed with other Construction & Demolition Wastes and used for backfilling; it may also end up in landfill for inert waste[24]. To assess the availability of potentially dangerous constituents at the end of the life of the product, leaching tests were carried out (Table 13) according to EN 12457-4 on glasses containing Sb and Se by the International Commission on Glass (TC 13: Environment). The European standard for leaching test EN 12457-4 was chosen because it represents a worst case scenario as it requires a ratio of 10 between the volume of leaching agent and the solid (i.e. 10 litres of leachate for 1 kg of material), which corresponds to an exposure of 60 to 100 years in the ground (H. Van der Sloot et al., 2008). The results were compared to the limit values set out in Commission Decision 2003/33/EC for dangerous waste.

The overall average **antimony** leaching from all the samples analysed was 0.38 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 should not be considered as dangerous.

Similarly, **selenium**-containing tinted flat soda lime silicate glass was tested according to EN 12547 by ICG TC 13 and the results compared with the limit set in Commission Decision 2003/33/EC. However, as Selenium content in the glass is very low (< 50 ppm) no selenium was detected in the leachates; all measurements results were below the detection limit (0.005 mg/kg by ICP-MS). 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.

[24] According to Commission Decision 2003/33/EC, glass from C&D waste can be accepted in landfill for inert waste without testing when collected separately.

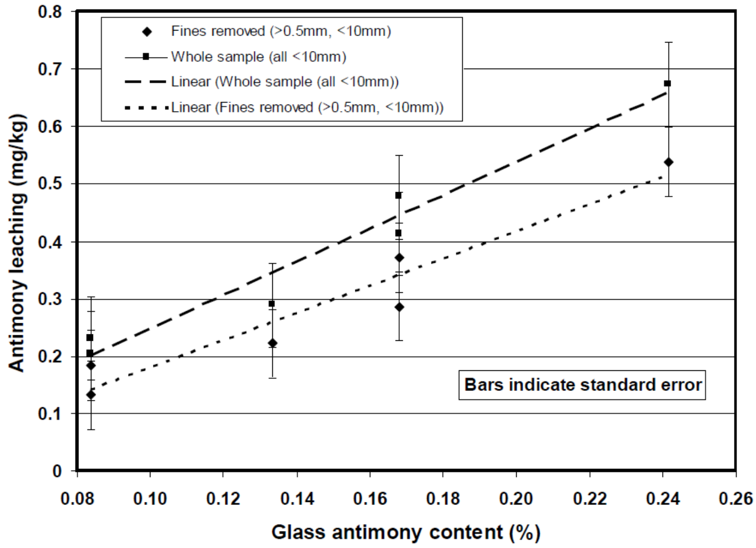

Figure 10. The relationship between composition and leaching. Average results of Sb leaching tests (EN 12547-4) on rolled plate glass for Photovoltaic panel cover. ICG TC13 document, 2010.

7.3. Substances of Very High Concern (SVHC)

Due to their low hazardousness, none of the main raw materials (major ingredients) used for the production of FSLS glass are likely to be included in the Candidate List of Substances of Very High Concern for Authorisation. On the other hand, some of the ingredients used to provide special properties to some glasses containing Sb, Co, Se, etc. might display hazardous properties that might lead to their inclusion in the list of SVHC. Today, the only substance present in the Candidate List of Substances of Very High Concern for Authorisation is cobalt sulphate (CAS 10124-43-3). This substance benefits from full registration and is used in very limited quantity in glass production (the concentration of cobalt (Co) in FSLS glass is < 0.005 %).

7.4. Conclusion on the hazardousness of Flat Soda Lime Silicate Glass

Due to the nature of glass and its structure, any potential hazardousness of the raw materials is not transferred to the SLS substance (Table 14).

Few dangerous constituents (Sb and Se) are used for the manufacturing of Flat SLS glass and these are generally in concentrations below the limits set in Annex I of Directive 67/548/EC and Annexes II and III of Directive 1999/45/EC. Leaching tests performed on the glass containing those dangerous constituents have proved that the metals are not available during the entire life cycle of the product. This is related to the high field strength of these added cations within the glass network, because high field strength of cations lowers their leaching rate from the glass.

Raw material	CAS	Hazard
Major ingredients (%)		
Sand (quartz SiO_2)	14808-60-7	H373
Sodium carbonate (Na_2CO_3)	497-19-8	H319
Dolomite ($CaMg(CO_3)_2$)	240-440-2	None
Feldspar ($NaAlSi_3O_8$)	68476-25-5	None
Nepheline syenite ($NaKAl_2Si_2O_8$)	37244-96-5	None
Limestone ($CaCO_3$)	1317-65-3	None
Salt Cake Sodium sulphate (Na_2SO_4)	7757-82-6	H317
Slag ($Ca_2(MgFeAl)(SiAl)_2O_{7.}$ FeS) (UVCB)	65996-69-2	None
Sodium nitrate ($NaNO_3$)	7631-99-4	H272 H319
Minor ingredients (ppm)		
Coke (Coal - C)	65996-77-2	None
Diiron trioxide (Fe_2O_3)	1309-37-1	H319
Iron chromite ($FeCr_2O_4$)	1308-31-2	None
Chromium$^{(III)}$ oxide (Cr_2O_3)	1308-38-9	H302, H317 H319
Diantimony trioxide (Sb_2O_3)	1309-64-4	H351
Sodium selenite (Na_2SeO_3)	10102-18-8	H300, H317, H331, H411
Zinc selenite ($ZnSeO_3$)	13597-46-1	H301, H332, H400, H410
Selenium (Se)	7782-49-2	H301, H331, H373, H413
Cobalt oxide (CoO)	1307-96-6	H302, H317, H400, H410
Cobalt sulphate ($CoSO_4$)	10124-43-3	H302, H317, H334, H341, H350i, H366F, H400, H410 SVHC on the Candidate List for Authorisation

Glass	Hazard
Soda Lime Silicate Glass idealised formula: **$Na_{1.8}Ca_{0.6}Mg_{0.4}$ $Al_{0.05}$ Si_5O_{12}** CAS 65997-17-3	None

Table 14. Summary of the hazardousness of raw materials used for the manufacturing of Flat Soda Lime Silicate glass and the hazardousness of the manufactured FSLS Glass.

8. Conclusions

Flat Soda Lime Silicate Glass is a unique UVCB substance synthesised by reaction of several substances. Its general formula is that of a silicate, and no oxides are present as such:

$$Na_nCa_oMg_pAl_qSi_mO_s$$

Where: s = n/2 + o + p + 3 q/2 + 2m in order to balance all electrical charges.

The general idealised formula of most common Flat SLS glass becomes:

$$Na_{1.8}Ca_{0.6}Mg_{0.4}Al_{0.05}Si_5O_{12}$$

Raw material substances are not present within the glass. All raw materials used in the synthesis of Flat SLS glass bring a functional property to the FSLS glass product. Flat glass products are regulated by the Construction Product Regulation (CPR - Regulation (EU) No 305/2011) under which several European product standards regulate the characteristics that FSLS must demonstrate.

Even though dangerous substances or SHVC may be used as raw materials, their hazardousness is not transmitted to the SLS glass; and Flat SLS glass fulfils the requirements for exemption of Annex V.11 of REACH.

All raw material substances used for the synthesis of flat SLS glass are consumed during the synthesis of the new substance glass in order to provide specific physical, chemical and optical properties needed for the different applications and uses of the glass and therefore fulfil the definition of intermediates (Transported Isolated Intermediates) under REACH.

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Index of figures

Index of tables