

# GLASS MANUFACTURE

Glass has been manufactured in New Zealand for over one hundred years, and is a common part of our daily lives. It is used commonly in windows, bottles, jars and domestic glassware, as well as as a material for artwork, such as stained glass. It is manufactured from cheap and abundant raw materials, and is readily recycled.

Glass is produced in a two step process, and then shaped to make it suitable for a variety of applications.

## **Step 1 - Batch mixing**

The mixture of ingredients to make up the glass (silica,  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$  and recycled glass, together with small quantities of various other minor ingredients) are mixed in a rotary mixer to ensure an even mix of ingredients and fed into the furnace.

## **Step 2 - Batch melting**

The mixture is heated to  $1500\text{-}1550^\circ\text{C}$ , where the ingredients melt, various chemical reactions take place and  $\text{CO}_2$  and  $\text{SO}_3$  are evolved.

## **Shaping plate glass**

The molten glass is cooled to  $1000^\circ\text{C}$  in a drawing canal, and then drawn up a tower (the drawing tower) where it is pressed into the desired width and thickness, and cools to  $280^\circ\text{C}$ . Individual plates of glass are snapped off at the top of the tower and further cooled before being put into storage ready for sale.

## **Molding glass containers**

Here molten glass is channeled off in forehearths (heated channels) where it is slowly cooled to temperatures of  $1100\text{ - }1150^\circ\text{C}$  to increase its viscosity. Precisely weighed slugs of glass are cut off, molded with compressed air, cooled slowly in annealing lehrs (special ovens) and coated with a special spray to prevent scratching.

## INTRODUCTION

Natural glass, known as obsidian, was widely utilised by prehistoric man, and glass has been made by people for approximately 9000 years. It was first known to be developed in the Middle East around 7000BC, and glass bottles were made in Egypt in 1500BC. By the Renaissance, coloured glass, crystal and mirrors had all been developed and were being made in Venice. Glass has been manufactured in New Zealand since 1870, and continues to be widely used despite the increase in usage of metal and plastic products for containers and windows. It retains its popularity because of its versatility, relative cheapness, and, in an age of depleting resources, its recyclability.

Glass has two important properties. Firstly it does not have a definite melting point but softens gradually over a range of temperatures. Secondly it does not cleave in a plane face like diamond or table salt. The explanation of both these properties lies in the fact that glass has no ordered structure, but is instead a supercooled liquid. A sheet of glass left to stand for a long time, perhaps one hundred years, will actually flow and change its dimensions slightly.

## Raw materials

Glass consists mainly of silica, obtained from the pure sands of the Parengarenga Harbour, just north of North Cape. This sand is washed and sifted to remove shells, stones and exceptionally large grains of sand, before it is mixed with other materials (see **Tables 1 and 2**) which control the colour and other properties, and lower the 1730°C melting point of pure silica. Between 10 and 80% of the finished product is from recycled glass (known as cullet) which is collected both in kerb-side collections and in the approximately 1000 yellow recycling bins established by ACI New Zealand Glass Manufacturers throughout the country.

**Table 1 - Major ingredients used in making glass**

Ingredient	Composition	Source	Annual quantity / kT*
Sand	96 - 98 % SiO <sub>2</sub>	Parengarenga Harbour	40
Soda ash	Na <sub>2</sub> CO <sub>3</sub>	USA	14
Limestone	CaCO <sub>3</sub>	Waitomo	12
Cullet	glass	N.Z. recycling bins and kerbside collections	40

\* The annual quantity refers to that used by ACI New Zealand Glass Manufacturers, New Zealand's major glass manufacturer.

**Table 2 - Minor ingredients used in making glass**

Ingredient	Composition	Source
Saltcake	Na <sub>2</sub> SO <sub>4</sub>	New Zealand
Alumina	Al <sub>2</sub> O <sub>3</sub>	Australia
Magnetite	Fe <sub>2</sub> O <sub>3</sub>	New Zealand iron sand
Iron chromite	Fe <sub>2</sub> O <sub>3</sub> (28%), Cr <sub>2</sub> O <sub>3</sub> (45%), SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>	South Africa
Iron pyrites	FeS	China / Taipei
Carbon	carbon	USA
Selenium	selenium	Japan
Cobalt(II) oxide	CoO	

## Uses of glass

The majority of glass made in New Zealand is either sheet glass or glass molded into jars and bottles. 95% of sheet glass is used for glazing in houses and factories, with the remaining 5% used for making mirrors or is toughened for use in domestic appliances such as ovens, and 40% of the total is exported. Molded glass is largely used for making bottles, and ACI NZGM make 280 million bottles a year (1989).

## THE MANUFACTURING PROCESS

Glass is made from its raw materials in a carefully controlled two-step process, and is then molded to form either sheet glass or bottles. A schematic diagram of this process is given in **Figure 1**.

### Step 1 - Batch mixing

Glass is made of different ingredients in differing proportions depending on the desired end product, but most glass (except for some specialist glass) consists of all the "majors" mixed with small quantities of some of the minors. Thus the minors are weighed first in a special weighing hopper, and added to the majors with a little water. Water is necessary as in a very dry mix the fines can blow off the batch as it enters the furnace and clog up the furnace flues. The two tonne batch is then mixed for between two and three minutes in a rotary mixer, before being transported to a batch hopper, from which it is slowly fed into a furnace.

The mix of raw materials is dependent on the type of glass desired. Window glass is made from 72%  $\text{SiO}_2$ , 13%  $\text{Na}_2\text{CO}_3$  and 12%  $\text{CaCO}_3$ , while bottle glass has more  $\text{SiO}_2$  and less  $\text{CaCO}_3$ . Crystal is made from 45%  $\text{SiO}_2$  and 44%  $\text{PbO}$  with 9%  $\text{K}_2\text{CO}_3$ , and pyrex (used for laboratory equipment and ovenwear because of its heat resistance) from 80%  $\text{SiO}_2$  and 12%  $\text{B}_2\text{O}_3$ . The remainder in each of these mixtures is made up of the various minors.

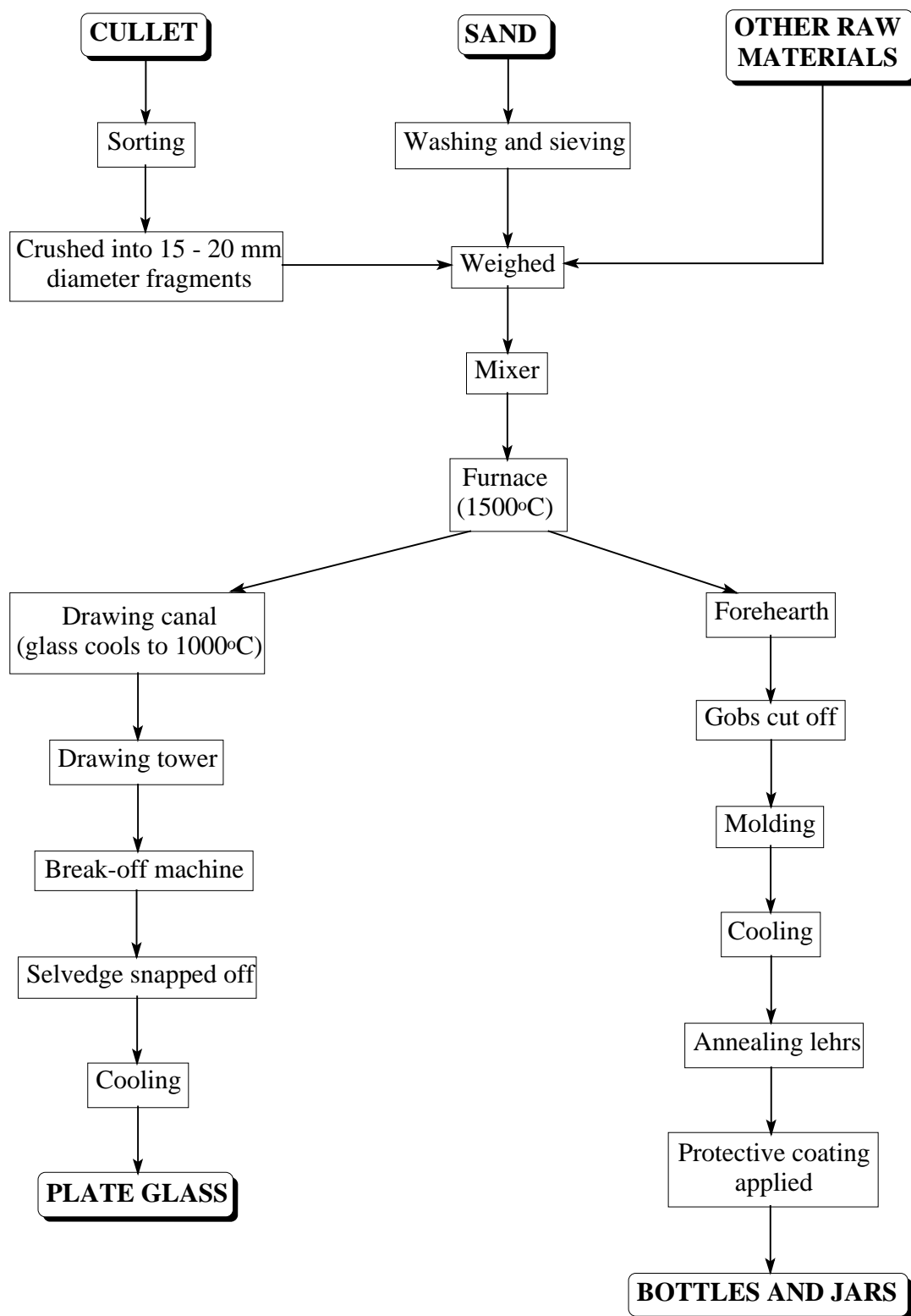
### *Glass colour*

The choice of minors at this point determines the colour of the final product. Colour results from two factors: the oxidation state of the glass, and the specific colourant additives used. Glass oxidation is promoted by the addition of carbon, and the degree of oxidation is measured on an arbitrary scale known as the carbon number. Clear glass has a carbon number of zero, dark green glass is -28 and amber is -52.

Other variations of colour are achieved through the action of coloured materials that act as dyes. For example, the iron (II) ions naturally present in sand results in the green tinge seen in clear glass, and this can be masked by the addition of selenium. Moreover, the amber and green colours of glass bottles are caused not only by the degree of oxidation, but also by the addition of iron chromite and an ironsand / saltcake mix respectively. As glass is fed continuously into the furnaces, each furnace has to be dedicated to producing glass of a particular recipe, and it takes 12-48 hours and a number of steps to alter the mix to change to producing a different type of glass of an acceptable standard.

### Step 2 - Batch melting

The ingredients mixture is fed continuously into a furnace fired by natural gas, boosted by electricity when necessary. The glass is initially heated to  $1400^\circ\text{C}$ , then raised to  $1540^\circ\text{C}$ , at which temperature the mixture melts. The glass is then held above  $1400^\circ\text{C}$  while it is refined and  $\text{CO}_2$  and  $\text{SO}_3$  are evolved. When no more gases are evolved the liquid is ready to be formed into the desired endproduct. The furnaces are kept at these precise temperatures by a cross-fired system which reduces heat loss and promotes a more even heat distribution in the molten glass. It functions as follows:



**Figure 1 - Schematic diagram of the glass manufacturing process**

1. Preheated air (which has been heated by passing up the regenerator packing and so cooling the packing) is blown into the furnace by large fans
2. The air mixes with natural gas and combusts
3. The flow of air pushes the flue gasses across the furnace, over the glass and down the opposite regenerator, heating up its packing

4. After half an hour, the opposite regenerator is used and the cycle reverses

The furnace statistics for two of ACI New Zealand Glass Manufacturers are given in **Table 2**.

**Table 2 - Glass furnace statistics**

	<b>Tank 2</b>	<b>Tank 3</b>
<b>Capacity / Tonnes</b>	200	300
<b>Melting area / m<sup>2</sup></b>	65	81
<b>Gas usage / m<sup>3</sup> year<sup>-1</sup></b>	6 491 000	8 725 000
<b>Electroboost usage / kWh year<sup>-1</sup></b>	114 400	4 221 000
<b>Maximum throughput / T day<sup>-1</sup></b>	200	280

### **Shaping plate glass**

This process is no longer carried out in New Zealand, but it was used by Pilkington in Whangarei until quite recently.

The cooled, molten glass from the furnace flowed into an extension of the tank known as the drawing canal, where it cooled to 1000°C before being drawn up into a tower, the drawing tower, by dipping an iron grille into the glass, onto which the glass stuck. The 2.5 metre wide sheet of glass was drawn up into the tower by asbestos rollers, cooling as it rose. Plate glass can be made as thin as 2mm, with this thickness determined by the speed of its progress up the drawing tower - 2mm thick glass moves up at approximately 170 metres an hour, while the average is about 40 metres per hour.

By the time the glass reaches the top of the tower it is ten metres above the molten glass, and only 280°C. On the top floor of the factory the glass is monitored to ensure its constant thickness, and then scored and snapped off by the break-off machine. The individual sheets weigh 22kg, and are lifted by rubber suction pads and placed on a conveyor belt where they are cooled and have their rough edges snapped off, before being transported to the warehouse for storage.

### **Molding glass containers**

Molten glass is removed from the furnace through forehearths (heated channels) where the glass is cooled to between 1100 and 1150°C, the exact temperature varying depending on the product to be formed. It is then fed into a forming machine where shears cut off weighed "gobs" of red-hot glass, one two or three at a time as required. These are molded in "sections" within the machine, held in the air for a short time to cool (to prevent them from losing their shape immediately) and transported to the annealing lehrs.

The annealing lehrs are a further stage in the cooling process, where the bottles are reheated to 600°C and then slowly cooled to remove stress points and prevent the glass from becoming brittle. Finally the bottles are coated with a shiny, slippery spray-on coating that temporarily protects them from becoming scratched, and they are packed for delivery to clients.

Some information about the production capacity of forming machines at ACI NZGM is given in **Table 3**.

**Table 3 - Forming machine statistics at ACI NZGM**

	Machine	No. of sections	No. of gobs produced simultaneously	Maximum throughput / bottles per min.
<b>Tank 2</b>	2/1	8	1 or 2	260
	2/3	8	1 or 2	220
<b>Tank 3</b>	3/1	10	1 or 2	265
	3/4	10	1, 2 or 3	450 (for beer stubbies)

## THE ROLE OF THE LABORATORY

The laboratory is primarily involved in the determination of the mix of ingredients for each batch of glass. A small sample is taken from each batch and dissolved in hydrofluoric acid and then analysed in an atomic absorption spectrophotometer to determine which elements it contains and their proportions. From this information, the relative masses of the other ingredients to be added is calculated, and a suitable mix made. As the composition of each batch of sand collected is slightly different (even when they were taken from very close areas in the Parengrenga) each batch is kept separate and requires a different mix of additives.

## ENVIRONMENTAL CONSIDERATIONS

The only substances discharged into the environment as a result of this process are the CO<sub>2</sub> and SO<sub>3</sub> released during the batch melting process, and these gases are simply released through a tall plant stack.

However, the glass industry is also working to support the environment by recycling its product. This lowers costs (as cullet is cheaper and easier to melt than silica) and prevents wastage. ACI NZGM have been involved with recycling to a small extent since they were established in 1922, and began using the yellow recycling bins throughout the country in 1973. These bins are now to be found everywhere between Stewart Island and Kaitaia, and on average 35% of all glass produced is recycled, providing 35 000 tonnes/year of cullet. More recently kerb-side collections have been instituted throughout the country to increase the level of glass recycling. The cullet thus collected is then used as a raw material in glass production making up anywhere between 10% (for clear glass) and 80% (for amber or green glass) of the final product. For this reason glass recycling is practised to a much greater extent by manufacturers of glass bottles than manufacturers of plate glass, as they produce a much greater volume of coloured glass.

Article written by Heather Wansbrough from information supplied by Karl Borham (ACI New Zealand Glass Manufacturers) and with reference to:

- Callan, Louise; *Looking into Glass*; New Zealand Geographic; Jan-Mar 1989