1. The History of Glass

Marie-Hélène Chopinet

Glass production is 5000 years old. Until the 1st century BC when blowing appeared in the Middle East, glass objects were mainly ornaments and small containers for cosmetics. Tiberius created a glass industry in Rome to satisfy the local customers more easily. Very soon, the western European glassmakers learnt to make glass themselves instead of importing ingots and processing them in secondary workshops. The collapse of the Roman Empire did not mean the disappearance of a product that has proved so useful. The art of glass was renewed during the Middle Age: stained glass windows appeared in numerous churches and cathedrals that were built all over Europe. The crusades enhanced the movement with new techniques coming from the East.

Glass was still made with sand and a flux but the flux changed from sodium to potassium salts produced by combustion of land plants instead of the Mediterranean coastal plants containing mainly sodium.

This composition was still used with a few improvements like purification of the ashes when industrial soda ash was invented at the beginning of the 19th century. The same century saw very important progress in glassmaking and it led to a huge decrease in price to the point where everyone could buy glass panes for their windows at the end of this period. Melting processes were also much improved. Use of coal was common since the 18th century, but the furnaces themselves had not really changed until the Siemens brothers invented the regenerative gas furnace where gas was produced with a gas producer. Ten years later, the tank furnace, a close ancestor of present-day melting furnaces, was introduced.

The forming processes had been improved since antiquity but the major changes occurred at the end of the 19th century when the processes were mechanized. As a result, the output increased spectacularly even after the end of the First World War, which took the lives of many glassworkers. Throughout the 20th century, the trend towards automation accelerated and melting tanks were applied to all types of glass. The middle of the century saw the revolutionary invention of float glass which laid the foundations for the modern glass industry.

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J.D. Musgraves, J. Hu, L. Calvez (Eds.), *Springer Handbook of Glass*, Springer Handbooks, https://doi.org/10.1007/978-3-319-93728-1_1

Glass has always been the subject of various considerations about its quite special nature and influence on human life. It is interesting to recall an old one and a much more recent one, both providing an overall view of the interaction between glass and the human being.

> Who, when he saw the first sand or ashes, by a casual intenseness of heat, melted into a 'metalline' form, rugged with excrescences, and clouded with impurities, would have imagined, that in this shapeless lump lay concealed so many conveniences of life, as would in time constitute a great part of the happiness of the world? Yet by some such fortuitous liquefaction was mankind taught to procure a body at once in a high degree solid and transparent, which might admit the light of the sun, and exclude the violence of the wind; which might extend the sight of the philosopher to new ranges of existence, and charm him at one time with the unbounded extent of the material creation, and at another with the endless subordination of animal life; and, what is yet of more importance, might supply the decays of nature, and succour old age with subsidiary sight. Thus was the first artificer in glass employed, though without his own knowledge or expectation he was facilitating and prolonging the enjoyment of light, enlarging the avenues of science, and conferring the highest and most lasting pleasures; he was enabling the student to contemplate nature, and the beauty to behold herself. [1.1]

> What is special about glass is that it can provide shelter and storage and combines these and many other practical uses with the ability to extend the most potent of our senses, sight, and the most formidable of human organs, the brains. [1.2]

Glass is a very ancient material. It even exists as a natural one but it is not the subject of this chapter, which will be devoted to the history of its manufacture and uses along the centuries (Table 1.1).

Table 1.1 Milestones in the history of glass manufacturing

Dates	Types of glass and products
5000 BP	Jewels, small containers Blowing process to make containers
Around 2000 BP	Flat glass by casting
500–1000	Cylinder technique to make flat window glass Crown glass technique to make flat window glass Crystal glass invention
End of 17th century	Plate-glass casting
19th century	New raw materials via chemistry developments
1850–1870	Regenerator furnace
1870–1890	Tank furnace
1870–1910	New process to make window glass and roofing
1890–1930	Mechanization of all processes
1920–1930	Forehearth in container glass Textile fiber development
1920–1950	Insulation glass development
1960	Float glass process

1.1 Early Ages: The Invention of Glass

Glass was developed initially for aesthetic reasons: the most ancient glass objects discovered in excavations, beads for instance, date back to between 3000 and 2000 BC. It appeared most probably accidently as glazing on earthenware in the Middle East between Phoenicia (Lebanon), Syria and Egypt. The legendary *Pliny the Elder* [1.4] narrated in his Natural History claims that a ship laden with nitre moored upon the coast near the river Belus between Tyr and Sidon (Lebanon). The Phoenician merchants, preparing their meal on the seashore and finding no stones at hand to hold their cauldrons, used for the purpose some lumps of nitre which they had taken from the vessel. After the fire burnt for the whole night, in combination with the sands of the beach, they observed transparent streams of a liquid hitherto unknown flowing from the hearth: this, it is said, was the origin of glass (Fig. 1.1).

Fig. 1.1 Glass is invented on a Middle-East beach by Phoenician merchants [1.3]

1.1.1 The Flux: Alkali Salts

The main possible sources [1.5] of alkaline salts available to the ancient glassmaker were: (1) large-scale deposits resulting from the evaporation and drying up of former land-locked seas and lakes, and (2) vegetable matter ash.

Deposits from former seas or lakes of interest to the glassmaker are illustrated by the impure carbonate and bicarbonate found in Wadi Natrun, in El Kab in Egypt and in Magadi in East Africa, and by sodium sulfate in Wadi Natrun and other locations all over the world.

It is a natural conjecture that natron (*nitre* in Pliny) from Wadi Natrun may have been used for glassmaking. It had already been used from very early times as a detergent in medicine, and in embalming. Specimens of natron have been found in ancient Egyptian tombs. Analysis of the specimens and of modern soda obtained from Wadi Natrun show that both contain sodium carbonate and bicarbonate up to 95%, sodium chloride up to 40%, and sodium sulfate up to 30%. [1.5]

All the ancient Egyptian glasses contain much more potash than can possibly be derived from natron or natural soda (Table 1.2). It shows that alkali derived from plant ash has long been an important ingredient in glassmaking. The alkali referred to in the tablets of Assurbanipal in the 7th century BC is derived from salicornia and the traditional glass-making mixture, sand plus ash, with a few other minor constituents, was essentially the same until the beginning of the 19th century. Plant ashes have over many centuries also been employed in medicines, detergents, and as the source of alkalis for manufacturing operations such as soap making.

In the ashes, two kinds of alkaline elements can be found, sodium (soda) and potassium (potash). Plants that grow near the sea or in salted deserts are associated with relatively high soda content, whilst those from inland region are relatively rich in potash. Nevertheless, the alkali in coastal and marine plant ash is not wholly soda, nor ashes of inland plants wholly potash, which explains the usual mixture of both alkalis observed in ancient glass samples.

It is legitimate to deduce that the use of ashes as a flux to make glass might have originated from glazing on pottery. In primitive firing methods, the pots were stacked and covered by the fuel, chaff, straw, reeds, or wood, the ash from which reacted with the clay or siliceous material of the pot. The discovery that a crude glaze was thus produced might have given a natural impetus to further experimentation and initiated the long course of development, which ultimately led to the isolation of the glaze, or glass, as an independent material.

1.1.2 Glass Made in Two Steps, Melting and Remelting Before Processing

The earliest glasses were not transparent. In addition to glazing on pottery, glass was mainly used to make replicas of semiprecious stones of various colors. It was processed as beads or as small containers for cosmetics by shaping the glass around a core of sand that is removed after cooling. It was also cast and pressed to make bowls or hollowware.

According to *Pliny*, glass was considered to originate from a region known as Phoenice (present-day Lebanon), close to Judaea (present-day Israel) and enclosed between the lower ridges of Mount Carmelus, a marshy area where

> flows the river Belus, which, after a course of five miles, empties itself into the sea near the colony of Ptolemaïs. The tide of this river is slow, and the

Table 1.2 Glass compositions of various periods. Most of the glasses contain between 0–4 % MgO [1.5]

	Silica	**Alkaline oxides**		**Calcium oxide**	**Alumina**
	SiO$_2$ (wt%)	**Soda Na$_2$O (wt%)**	**Potash K$_2$O (wt%)**	**CaO (wt%)**	**Al$_2$O$_3$ (wt%)**
Thebes (1500 BC)	65	14.3	2.0	6.5	3.0
Tell El Amarna (1370–1350 BC) Colored opaque	62	14–19	1.5–7	7–10	1.5
Tell El Amarna (1370–1350 BC) Transparent clear	63	20–22	0.4–0.8	7–9	1
Nimrude Assyria (800–850 BC)	71.5	12.7	0.9	4.8	0.5
Babylon (250 BC)	65.8	12.1	2.3	6.6	2.1
Alexandria (100 BC)	68	14–15.5	0.1	7–10	4–5
Roman Salona (2nd century AC)	64.5	17	1.5	6.8	3
Roman Cologne (1st–5th century)	67.6	20	0.6	6.7	3.2
Merovingian (6th century)	67	19.3		7.5	3.2
Reims stained glass (13th century	54	1.9	12–15	18–20	3–4
English (16th–17th AC)	56–65	0.4–2	5–12	15–20	1.2
Modern	68–74	12–16	0–1	7–14	0.3–3

> water unhealthy to drink, but held sacred in certain religious ceremonials. Full of slimy deposits, and very deep, it is only during the reflux of the tide that the river shows its sands; which, stirred by the waves, separate themselves from their impurities, and so become clean. It is generally thought that it is the acridity of the seawater that has this purgative effect upon the sand, and that without it no use could be made of it. The shore upon which this sand is gathered is not more than half a mile in extent; and yet, for many ages, this was the only spot that afforded the material for making glass. [1.4]

Therefore, for centuries, glass was produced in primary Middle East workshops, shipped all around the Mediterranean Sea by the Phoenicians, and transformed in secondary workshops [1.6, 7]. This explains why glass has always been recycled throughout history, except perhaps in the middle of the twentieth century!

1.1.3 The Romans Develop a Real Glass Industry

Around the first century BC, in the Middle East again, glass blowing was invented. It involved the use of a long iron pipe, which was dipped into the molten glass to gather a lump that was blown through the tube, the blowpipe, at first without a mold. It obviously required a good metallurgical technique, precise knowledge of molten glass behavior, and preparation of glass with reproducible chemical compositions. This new revolutionary technique made transparent thin glass possible and opened up new fields for its uses.

This development did not escape the notice of Roman rulers, who were at that time the masters of the whole Mediterranean. Rome was traditionally supplied with glass from Egypt and Syria in large quantities. The emperor Tiberius *imported* glassblowers from the Middle East in 14 BC, and made them work in the Italian peninsula using crude glass imported from overseas, thus creating a real local glass industry. Very soon, glass was molded and various types of containers and drinking vessels were produced and sold all over the Roman Empire.

Over time, Roman glassmakers learned that the sand from the Belus was not the only one which could be used:

> At the present day, a very white sand good for the purpose can be found at the mouth of the river Volturnus, in Italy. It spreads over an extent of six miles, upon the sea-shore that lies between Cumæ and Liternum, and is prepared for use by pounding it with a pestle and mortar; which done, it is mixed with three parts of nitre, either by weight or measure, and, when fused, is transferred to another furnace. Here it forms a mass of what is called 'hammonitrum' which is again submitted to fusion, and becomes a mass of pure, white glass. Indeed, at the present day, even throughout the Gallic and Spanish provinces, we find sand subjected to a similar process. [1.4]

According to the accounts, the primary melting step was done in Italy. The process was still completed in two phases, one of melting, and one of remelting and working the glass to give it its shape.

1.1.4 Window Glass

Casting

The Roman glassmakers not only manufactured containers of various sizes and shapes, but also flat glass beginning in the first half of the 1st century AC, as was proven by the finding of window frames and pieces of window glass in Pompeii and Herculaneum excavations [1.8, 9]. The technique was to cast molten glass on a flat slab of stone and spread it as much as possible. The glass was translucent rather than transparent due to its large thickness and relative crudeness.

Cylinder Method

A second method (Fig. 1.2) to make flat glass emerged around the 2nd century [1.10]: the cylinder blowing method. This process involves blowing a large and long glass *bottle* and removing both ends. The resulting open-ended cylinder is then longitudinally slit and flattened to produce a rectangular sheet of glass. The details of the method were significantly improved over the centuries to come but its principle remained the same. The molten glass, cooled to the working consistency and kept at this consistency by reheating when required, was blown into a globe and formed into a shape which, when swung from side to side in a trench and upon being further blown, became a cylinder. The ends of the cylinder were subsequently removed. At first the cylinder was slit when still hot using a cold iron and clumsily opened out (or spread) on an iron plate at the mouth of the furnace. Following an improved method which was developed only around the 18th century, the cylinder was allowed to cool down before being slit from end to end with an iron or a diamond cutter. It was then reheated in a special kiln known as a flattening kiln to a temperature at which it could be opened out using a piece of polished refractory called a lagre with little damage to its surface [1.11, p.80].

Crown Method

The disk blowing method (crown glass) (Fig. 1.3) appeared later around the 4th century, but became the

Fig. 1.2 Flat glassmaking by the cylinder method [1.12]

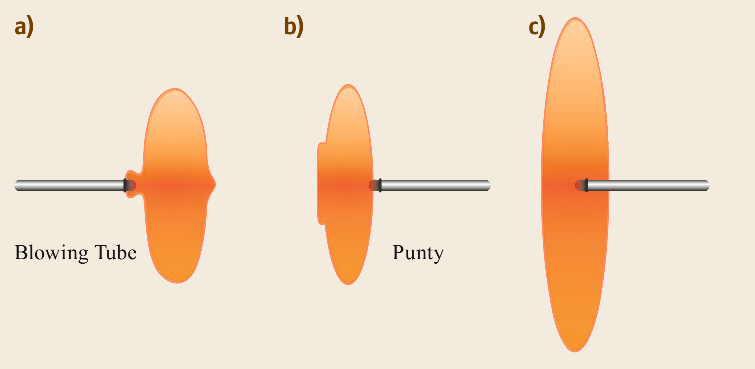

Fig. 1.3a–c Flat glass by the crown method. **(a)** Glass blown into a pear shape, **(b)** after the detachment of the blowpipe a punty is sealed on, **(c)** the glass is spun in a flashing furnace

main process in the Middle East and in northern Africa during the 7th and 8th centuries. [1.10]

The glass was first formed into the shape of a pear by blowing, heating, and rolling on a polished metal surface (known as a marver). The end of the pear-shaped mass at the far end of the blowpipe was then flattened, and an iron rod called a punty was sealed to the center of this flattened surface. The blowpipe was detached and the piece was reheated at a flashing furnace. As the piece began to soften, it was rapidly spun on the punty. Through the action of centrifugal force, the glass was gradually opened out—or flashed—into a flat, circular plate that could extend up to sixty inches in diameter (in the 18th–19th centuries), depending on the rotation speed and amount of glass the gatherer originally collected on the blowpipe. This plate was known as a table of crown glass. The main advantage of this flat glass manufacturing method is that the glass never came into contact with any surface while it was still in a malleable state. As a result, the glass produced this way claims a remarkable polish and lustrous appearance. Conversely, only small panes could be cut from the circular table, and the central *bull's eye* (where the punty was attached) and the selvage at the rim were wasted [1.11, p.51].

The cylinder method remained the cheaper alternative after the invention of crown glass, and both methods were used until the end of the 19th century. The cylinder method is still used in the Verreries de Saint Just in Loire.

1.2 Early Middle Ages

1.2.1 Situation in Western Europe After the Collapse of the Roman Empire

The collapse of the Roman Empire in the 5th century did not mean the complete elimination of glassmaking, simply because glassware was too utilitarian to be forgotten. Even luxury glass was still made on the borders of the Empire that had escaped the invasions from North-Eastern Europe.

The idea that glass had disappeared within the Roman Empire was due to the facts that objects were progressively no longer being buried in graves during the first millennium, that glass was being recycled, and that broken pieces were not recovered during early archeological excavations.

As a matter of fact, many medieval workshops have now been discovered all over Europe (Table 1.3—data for France). Glassmakers were mobile: they needed sands of good quality as well as large supplies of wood as fuel and possibly also ashes containing alkali in later periods. The need for wood was one of the major reasons to migrate once they had consumed all the local resources.

1.2.2 Evolution of the Composition of Glass and Choice of the Alkaline Flux

Until the 9th century, at least in Italy, the glass produced was a soda-lime silica glass. Its composition is quite close to that of a modern glass. It was melted from a mixture of sand (containing impurities such as calcium carbonate, aluminum oxide, and iron oxide) and alkalis from the Middle East (rochetta or polverine, the plant ash imported from the Levant, Syria and Egypt [1.14], which had the advantage of being extracted from plants very rich in alkaline and mainly sodium salts). Calcium carbonate and aluminum oxide were present in the mixture due to their abundance in the earth's crust, and were beneficial to glass because they improve its durability. Glassmakers of this period naturally did not understand these effects but optimal batching of raw materials was identified on a trial-and-error basis.

As we can see from Table 1.2 [1.5], potassium-based glasses appeared during the first millennium AD through the substitution of the traditional sodium flux by land plant ashes [1.15], especially in the north of Europe. Those ashes usually contain a few percent of potassium or sodium salts, carbonates, chlorides and sulfates, together with many other trace elements such as alkaline-earth, metal, phosphates, etc.

In Mediterranean countries, areas where seawater is particularly rich in sodium salts, glasses were still prepared with ashes (soda ash) of plants growing in saline habitats (e. g., the well-known *Barilla* from Alicante in Spain, which refers to ashes of Salsola Kali, Salicornia, seaweeds and other marine plants). Seaweeds were also burnt in Brittany or England to prepare a kind of flux, *Varech* or *kelp*, which also contains mainly sodium salts, but is of lower quality than the Mediterranean Barilla and was considered to be less efficient to melt sand. Those ashes also contain potassium salts (Table 1.4).

Table 1.3 Number of glass workshops discovered in France dating before the 11th century [1.13]

Period	North	South
Protohistory	–	1
1st to 3rd century	12	4
4th to 9th century	8	10
Total	20	15

Table 1.4 Composition of a few alkalis containing ashes where it can be observed that land plants such as the Keli from Syria contains sodium and that marine plants such as seaweeds contain potassium [1.5]

In wt%	Kali or ash from the Syrian desert plant *Chinane*	Kelp (combustion of seaweeds in Orkneys)	Varech (combustion of seaweeds, France 19th century)
Sodium carbonate	45	5.3	0–9.5
Sodium hydroxide	2.5		
Potassium chloride	4.5	19.3	4.1–20
Potassium sulfide	3.0		
Calcium carbonate	34.0	6.4	
Calcium phosphate	4.0	10.5	
Magnesium carbonate	1.0	6.8	
Carbon	1.0		
Potassium sulfate		4.5	18.6–41.5
Sodium sulfate		3.6	0–30.9
Sodium chloride		26.5	29–50.7
Sodium sulfite			0–14.9

In other districts closer to forests, potash glasses were melted with additions of ashes from land plants like ferns, or from trees such as beeches. These two plants are the most often cited in the literature but many others were experimented with as well to determine their fluxing potential towards local sand (Table 1.5).

The choice of raw materials for the glass composition was entirely empirical and dependent on the local resources, which is well exemplified in *Agricola*'s book published in 1556:

> To make glass, fusible stones are used and concrete 'sucs' which have a natural affinity with these stones. Among fusible stones, are preferred those which are white and transparent. That is why the first choice between them is crystal rock. The second choice is stones that do not have the same hardness but are nevertheless white and transparent. The third choice is stones that are neither white nor transparent. First they are burnt, ground and sieved in order to obtain sand. If river sand is available glassmakers are dispensed of calcination and sieving.
>
> Among the concrete 'sucs' the first rank goes to nitre, the fossil salt comes next. If neither is available, it is possible to use the leached salt obtained from the ashes of Anthyllis or any other plant containing salt. Some people place the last one on the second rank... Those who have no salt take two parts of oak, beech or pine ashes added with sea-salt. [1.16]

The resulting glasses were strangely similar, apart from the alkaline element used (sodium or potassium). This can be easily explained by the fact that glassmakers had two opposite aims: (1) melting in the furnace they have at moderate temperatures and keep it in working order as long as possible, (2) and introducing a minimum amount of flux to reduce the price and the work needed. The result is that they usually arrived at similar ratios between sand and flux as being the best compromise. The compositions are quite often not so far from the present-day ones, for similar reasons.

Mixture of both types of glass (sodium and potassium) can be found in excavations due to recycling of old local glass or glass coming from other countries, a practice which never ceased.

Glass compositions remained of this type until the beginning of the 19th century, with or without purification of the flux, depending on the skill of the glassmaker and on the quality of the production his market needed.

Agricola indicated that a purified form of flux could be obtained by extracting the water-soluble alkaline salts from the ashes, separating them from the alkaline earth or metal salts polluting the raw material for glass melting. Earlier in the period, the purification process remained the secret of some glassmakers, especially those of Venice [1.16].

1.2.3 The Melting Process and the Furnace

The most important supply glassmakers needed was fuel, or more exactly at that time, wood. Until the end of the 19th century and the invention of the Siemens furnace, the consumption of fuel was 3 to 7 times more than the amount of glass melted (compared to 1/10 in modern times!). The melting process and working of the glass were usually done in the same place, and no longer in separate primary melting workshops and secondary rework shops.

However, the melting process was very often carried out in two steps because the raw materials require a prereaction before being introduced into the final pot. The prereaction step, known as *fritting*, is necessary to obtain a glass of reasonable quality at the rather low temperatures accessible in the furnaces. The fritting process was still used, especially in container glass, during the 19th century for very difficult types of glass.

Table 1.5 Composition of land ashes [1.5]

Ashes (%)		Chemical composition of ashes							
		SiO_2 (wt%)	CaO (wt%)	MgO (wt%)	Na_2O (wt%)	K_2O (wt%)	P_2O_5 (wt%)	SO_3 (wt%)	Cl (wt%)
Beech trunk	0.55	5.4	56.4	10.9	3.6	16.4	5.4	1.8	
Beech branches	1.23	9.8	48	10.6	2.4	13.8	12.2	0.8	
Beech leaves	3.05	33.8	44.9	5.9	0.7	5.2	4.7	3.6	0.3
Oak	0.51	2.0	72.5	3.9	3.9	9.5	5.8	2.0	
Apple tree	1.1	2.7	70.9	5.5	1.9	11.8	4.5	2.7	
Fern	5.89	6.1	14.1	7.6	4.6	42.8	9.7	5.1	10.2
Rush	4.56	11	9.4	6.3	6.6	36.6	6.3	8.8	14.2
Willow	3.85	71.4	6.0	1.3	0.26	8.6	2.1	2.8	
Heather	3.61	35.2	18.8	8.3	5.3	13.3	5.0	4.4	2.2
Barley straw	4.39	53.8	7.5	2.5	4.6	21.2	4.3	3.6	

Georg Agricola (1494–1555) explained that some glassmakers had three furnaces, a fritting furnace for prereaction, a glass-melting furnace, and the last one being what we would call the annealing lehr [1.17]. The raw material mixture was first fired in the vaulted fritting furnace, until it partly melted and eventually became a partially glassy material. It was extracted and broken after cooling down in order to be introduced into the pots already set in the melting furnace after having been heated up in the fritting furnace.

The second furnace, the melting furnace was generally circular (Fig. 1.4), some ten feet in diameter and eight feet high. It consisted of two chambers, one for the fire (in the lower part) with a narrow orifice in the front to introduce wood into the firebox. In the middle of the vault of this lower part was a large round hole allowing the passage of flame into the upper chamber. Openings were created in the walls around the upper chamber. The larger ones were used to load the preheated pots into the chamber around the flame hole, whereas the smaller ones were designed for the workers to take gatherings of molten glass in the pots. On the backside of the furnace, an orifice allows the heat to be passed to the third furnace, the annealing chamber.

When there were only two furnaces and no furnace in which to conduct the first melting process, the glassmakers introduced the mixture of raw materials into the pots once they had finished working. It melted during the night with boys coming to maintain the fire with dry wood. In most workshops, while blowing was going on, other pots in the same furnace contained the mixture of raw materials currently melting for the next day's work. If only one furnace was present, it had three chambers. The upper chamber was dedicated to cooling of the glass products and was not directly heated, only by the lower chambers.

The furnaces were made from unfired, sun-dried bricks of refractory clay. Their construction was a rather complicated process even though no furnace lasted more than a few months before deteriorating too much and having to be rebuilt. The pots were also made of clay and their appropriate fabrication represented a large part of the technical skills required to be a glassmaker.

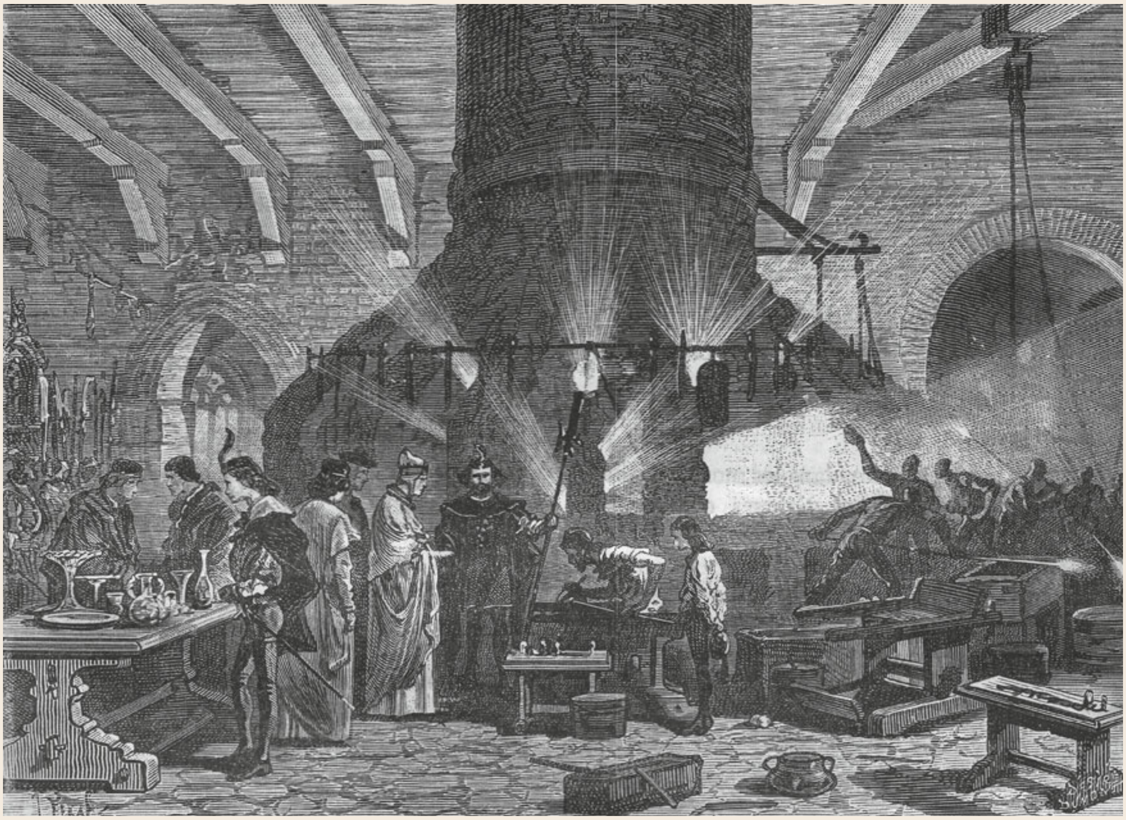

Fig. 1.4 Visit of the Venice Doge to a glass-making factory showing the glass-making furnace and the glass workers (from L. Figuier, Les merveilles de l'industrie, around 1870)

1.2.4 Window Glass: A Commodity Reserved for Wealthy People

The Romans had made use of glass to enclose buildings. Logically, in the northern countries, glass should have been widespread to protect from the cold while letting light enter houses. However, it seems that glass was reserved for churches and a handful of rich people but did not reach the largest part of the population.

Many quotations indicate that the use of sheet glass in dwellings was not common even in the 14th century or even later. For instance, in the counts of the silver of the kings of France in 1554, one can read:

> two yards of oil cloth with which was made a window frame set in the room of the queen in the castle of Melun, plus four chassis of wood to be arranged with paper on the windows of the said room and oil to cover them to make them clear. [1.17]

"In the 18th century, there still existed in Paris a job consisting in setting oiled paper in windows", and as late as 1897, Henrivaux recalled that the paper window pane "begins to be unknown in our villages and the glass-mounted print replaces the rustic image glued to the wall", illustrating the fact that window glass for everybody was a nineteenth century advance.

1.2.5 The Emergence of a New Production: Stained Glass Windows

The Middle Ages are widely known for the huge number of churches that were built across Europe, most of them being decorated with stained glass windows. These windows were apparently produced mainly using the cylinder method, at least in Western Europe.

Stained glass production began well before the end of the 1st millennium AD. Even if traces of it are rather rare nowadays, what is left is unquestionable. Progressively, as careful (because glass is not always immediately visible and has often been missed in the past) excavations are made on various sites, the flat glass-making *landscape* of those early centuries is revealed. Until the 7th century (perhaps as early as the 5th century in some places) only *white* glass was used in church windows and possibly rich settlements. Greenish white stained glasses dating back to the 7th and 8th centuries were found for instance in Notre-Dame de Bondeville, in Normandy, in Ile-de-France, or in the east of France. They are not yet painted but sometimes color appears and their manufacture is more sophisticated. Well-known examples of stained glass windows during the later period around 800–820 include those of the Abbey of San Vicenzo in Volturno in Italy, and at the monastic sites of Jarrow (682–870) and Monkwearmouth in England. These glasses are not painted and not colored, except when recycled glass from the Roman period was used [1.18].

In the 8th century, it is evident that painted stained glass, a new step in the evolution of stained glass, had been developed. The main discoveries were made in Saint-Denis Abbey and in Normandy. The *paint* was a kind of enamel, usually dark brown or black, obtained from a mixture of pigments (ground copper or iron oxide), a frit (powdered glass), and a mixture of various substances (wine, urine or vinegar, and gum Arabic) as the medium. This *paint* was applied on the glass and the enamel was fixed by *firing* the glass in an annealing furnace around 600 °C.

By 1000 AD painted glass is mentioned quite frequently in church records [1.2, p. 20]. It was the Benedictine order in particular that gave the impetus for window glass. Churches used glass as a way of glorifying God and became involved in actual glass window production in their monasteries, injecting huge amounts of manpower and money into its development. The demand for colored glasses increased significantly during the period of Gothic cathedrals in the 11th and 12th century and reached its peak in the 14th and 15th centuries.

This later history is much better documented than that of the 1st millennium, as it is still possible to see today the production of the glassmakers of the Middle Ages in cathedrals and churches all over Europe despite wars and destruction. Some of the largest cathedrals even had their own glass workshop operating on-site during the construction. Just as any other craft, glassmaking organized itself during this period into corporations.

1.2.6 A New Class of Noblemen, the Glassmakers

Glass production underwent major changes during this period, perhaps not much from the technical point of view but its organization was transformed. During the 10th and 11th centuries, noblemen were granted special privileges by the European kings to make and trade glass without being deprived of their status as nobility. They were also granted relief from various taxes that further helped them to refill their treasury emptied by the Crusades. From another point of view, the production of glass in Europe was somehow enhanced during this period with the pilgrims bringing back beautiful objects as well as secrets from Constantinople and the Middle East glassmakers. It also means that glassmaking skills were increasingly passed down only in specialized glassmaker families.

1.3 A New Era, Late Middle Age and Renaissance: 13th to 16th Centuries

At the end of the Middle Ages, with the onset of the Renaissance, many crafts experienced a boost to innovations and glass manufacturing and processing was not an exception.

1.3.1 Emergence of Venice and its Cristallo in the Luxury Glass Market

During this medieval period, the Venetians had been well known for their glassware since the 13th century. The Venetian republic had wide connections with the East Mediterranean countries where luxury glass was still manufactured. From Constantinople where the glass tradition had been preserved, particularly for mosaics, came the renewal of the art of glassmaking. Venice possessed everything that was necessary to make glass: the very islands on which the city stood were composed of silica-rich sand. Beech forests on the Istrian Peninsula across the gulf of Venice provided the best fuel for the furnaces fires and, perhaps more importantly, as a skillful trader, the city was equipped to ship its production to the richest and most distant markets.

The Venetian glassmakers discovered quite early how to purify the ashes by leaching the alkaline salts in water: this efficiently reduces the content of insoluble alkaline-earth elements and iron oxide, the main residual coloring agent of glass, giving its usual green color. Thus, they specialized in very clear glass, which referred to *crystal rock* which represented the archetype for whiteness in everybody's mind. They called it *cristallo* and that was to be the name of various kinds of glasses as *pure* and white as crystal rock in the future.

The secrecy that surrounded the making of Venetian glass was almost as strong a factor in its success as the beauty of the glass itself. The Venetian glassmaker was a master craftsman and a master at intrigue. Those who were not glass-workers came to believe that the glassmakers had knowledge of processes as mysterious as those of the alchemists. A glasshouse was therefore often regarded with the frightened awe that other people might have for houses they thought to be haunted by ghosts (Fig. 1.4).

But in 1291, even the most careful restrictions—and the nervous caution of the public towards the risk of fire, related to the presence of glass furnaces—seemed inadequate to protect the secrets of the Venetian glassworkers. Consequently, the authorities decided that all the glassmakers would be moved into a single place, onto the island of Murano where they could be more carefully guarded. For a long period, heavy penalties were still inflicted upon those who went abroad and taught their art to foreigners.

Despite those precautions, Venetian glassmakers were able to escape their prison-island and proceeded to spread throughout Europe, not only the basic techniques that had survived in spite of history, but the tools and the very broad knowledge of Venice inherited from the east.

Venice, which seemed everlasting until the middle of the 15th century, saw her trade strongly weakened by the Turks at sea on one hand and by the French on land on the other. By the beginning of the 17th century, Venice was rapidly losing her once magnificent role as maker of the world's finest *cristallo*.

There were other important glass-making centers in Italy [1.2, p. 23], particularly the northern town of Altare. Although smaller than those of Murano, the Altare works were particularly influential because their policy was to spread their techniques as widely as possible, rather than retain them as trade secrets as the Muranese attempted. Therefore the Italian techniques, as well as the glass itself, spread out throughout Western Europe, particularly beginning in the 16th century.

1.3.2 Development of Glass in Other Parts of Europe

European glassmakers migrated frequently. The owner of a glasshouse would close up his workshop and move elsewhere because the local fuel supply had dwindled, because he had been offered subsidy somewhere else, or just for the love of traveling, being sure that he would have no difficulty to find work wherever he might go. Bohemia was the first to win a great reputation as a glass center, even before the fame of Venice began to decline. A local glass industry was created in the 13th century by Venetian glassmakers and was encouraged during the 16th century by the Bohemian rulers. Apart from the Venetian-type crystal, its specialty was gold ruby glass.

Similar types of glass were made in many different parts of Europe: French, Dutch, Flemish, German, or Spanish glasses were largely the same, their specificity being more in uses and therefore in shapes and colors than in the nature of the material. In every country, for instance, drinking habits strongly influenced glass production. The only major variation was the type of ashes, either sodium-containing from marine plants or potassium-containing from terrestrial plants, obviously depending on the situation of the glass workshop.

1.4 Modern Times: 17th and 18th Century to Beginning of the 19th Century

Many important evolutions characterized this period. In particular, a real glass industry was developed all over the European continent. These advances were largely due to the beginning of a real *scientific* mind and improved analysis of the problems, even if the most important revolutions in this domain were to occur in the 19th century.

The raw materials were chosen with more care, the glass composition was more stable, the glassmaker *dynasties* were in place which brought about better transmission of glass-making skills, furnaces were more efficient, and transportation of men and merchandize was faster despite the numerous wars.

1.4.1 Use of Coal Instead of Wood in Furnaces: The First Trials in England

By the early 17th century [1.11, p. 34] in England, attempts were already made in metallurgy to separate the coal from the iron ore by using the reverberatory principle of furnace design. In this type of furnace, the fuel and the ore are kept apart, and the flames were made to strike back from the arched roof of the furnace upon the materials to be smelted. The reverberatory furnace was found to meet the glassmaker's needs. Using certain types of coal, and placing a cover over the pots, the batch could melt without filling the molten glass with impurities. By the early months of 1612, green glass for windows was being imperfectly made at a coal-fired furnace in Southwark.

The new furnace and glasshouse design differed from its predecessors (Figs. 1.5 and 1.6) because it incorporated a long, underground tunnel feeding fresh air from outside the glasshouse to a grate for the coal in the center of the furnace. As this would often make the grate too long, a dividing wall (*bridge*) was built in the center of the trench, supporting the inner ends of the grates (Fig. 1.6). The furnace itself was built over this central grate in the shape of an inverted funnel with a curved crown to reflect the flame from the fire down on to the pots that were arranged around the waist of the furnace on a circular course of brickwork, or on two longitudinal ones on both sides of the grate in a rectangular furnace. This masonry part was called the siege or bench [1.19]. The pots were often covered to protect against soot, smoke, and black drops which fell from the crown. In the case of British window glass production, it was common practice to construct the outer building in the same shape as the furnace itself, in this case, a circular one.

With the appearance of the new furnace, which allowed use of a cheaper kind of fuel, the days of wood firing were numbered. The end came more rapidly than

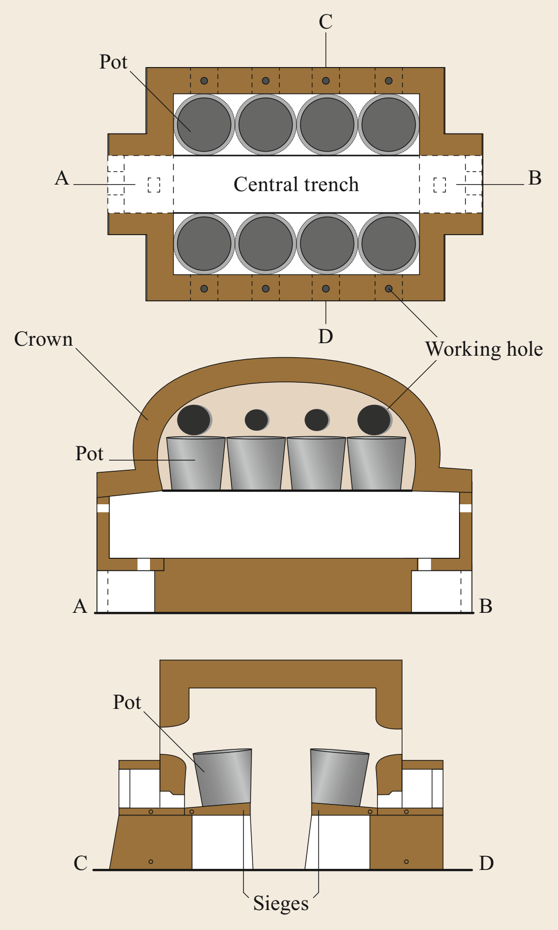

Fig. 1.5 Wood-fired furnace (after [1.19])

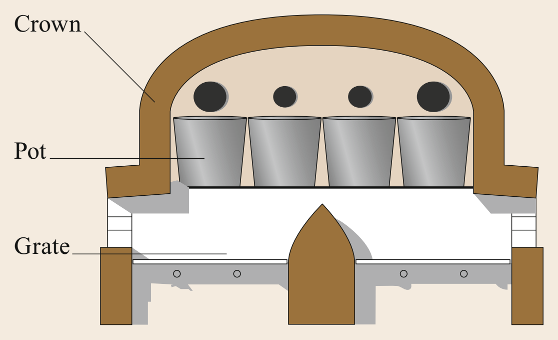

Fig. 1.6 Coal-fired furnace (after [1.19])

even the most pessimistic would have ventured to forecast. On May 23, 1615, King James I passed a sort of death sentence on furnaces using wood. Anxious to preserve the forests, he decreed that, in future, glass was to be made in coal-fired furnaces. The control of the furnaces was already in the hands of those who held Letters Patent for their use. By the royal proclamation of 1615, the patentees were given monopolistic control not only of the furnaces but of the industry as well. One of them was Sir Robert Mansfield (or Sir Robert Mansell as he came to be known) and he soon bought out the other partners and thus gained absolute authority over most of the glass industry in England.

From this time, English glassmakers and, later, their continental counterparts began to seek sites for their furnaces elsewhere than in forests, in places where coal was available. This was a major change in the glassmaking preoccupations. It was the birth of the glass industry in the North-East of England, near Newcastle, which became a great center for the manufacture of English window glass. The problem of plate glass was different because it was a different market and it has to be close to its customers, not too far from London or other big cities, for instance.

1.4.2 Flint Glass: A Revolution in England

Glassmakers (and their customers) have always been attracted either by brilliantly colored glass or by very white glass similar to crystal rock. For years or centuries, new mixtures had been experimented with to find a glass as *pure* as the Venetian *cristallo*. About the year 1675, George Ravenscroft's ingeniousness produced England's famous "flint" glass by additions of more lead oxide than what had ever been done before. Chemically, this glass is based upon the usual potassium silicate glass with calcium oxide being replaced by lead oxide, most probably because the British Isles have always been a place for lead mining, at least since the Roman times. This new glass proved to be easier to work and engrave which allowed the production of very ornate glassware welcomed by the wealthy English upper class.

Despite all its advantages, the continental glassmakers did not immediately embrace this new production: they were producing white *cristallo* glass themselves thanks to the very pure sand found in the north of Europe and the knowledge learnt from the Venetians. Lead crystal would only cross the Channel around one century after its discovery.

Nevertheless, in time, English lead crystal, which lent itself so admirably to the production of high lustre and brilliancy when decorated by cutting, proved to have a greater attractiveness than the lime glass made in Venice. From this time the fate of the Italian industry was sealed, and as the 17th century drew to a close, Venetian glass import into England declined.

1.4.3 A New Player: Compagnie de Saint-Gobain with a New Process to Make Mirrors

The fame of Venetian glass was due not only to the cristallo glassware, but also to mirrors popular among all the aristocracy in Europe. In 1634, Louis XIII published the following edict:

> E. de Grammont and J.A. d'Anthonneuil travelled in foreign countries, and stayed there for several years, and searched secrets and rare and useful inventions, unknown in our realm, and concerning particularly the making of mirrors, their cutting and polishing; they are said to have succeeded so well that their work is beautiful, skill-rich and useful, the more so as the manufacturing of mirrors being not yet realized in France, is reserved to the Venetians who are the masters for this production and sell it at high prices in our realm, from where a lot of money escapes, which would not have happened if the manufacture was established in France [. . . We] allow them to establish in this city of Paris a manufacture making plate glass for mirrors . . . with special prerogative for a few years. [1.17]

It was only in 1665, during the reign of Louis XIV, that Colbert created the Manufacture Royale des Glaces with an impressive series of financial (the Manufacture was a privately owned company) and honorific (royal coat of arms on its gate, livery of the gate-keeper) privileges. In 1672, Colbert announced to his royal master: "Our mirrors are now more perfect than those of Venice." [1.17]

The manufacturing process relied on cylinders produced in Normandy (Tourlaville) with the silvering being made in Paris. The mirrors of the Galerie des Glaces in Versailles were made by this method in 1685.

Why did the French glassmakers have such difficulties in making this glass with the same method as was used to make window glass?

Mirror plate glass was made thicker than the window glass so that it could bear grinding, using sand, and polishing, using rouge (iron oxide), by which means an even, lustrous finish was imparted [1.11, p. 41]. While window glass was increasingly used during the 17th and 18th centuries, plate glass remained a luxury product.

Only the purest ingredients, the best soda and lime, and thoroughly washed white sand, went into the manufacture of this kind of glass, and the whole batch was very carefully prepared and fritted before being placed into the melting pots. Being thick glass, any discoloration was readily noticeable. Any spots in the glass itself or unevenness of the surface meant that these glasses, chiefly used for mirrors, would fetch much lower prices. The emphasis, therefore, was always upon high quality.

Although plate glass was made with much purer materials than window glass, the glassmaker manipulated his molten glass in much the same way when making both varieties. In both cases he blew the glass into a cylinder, which he slit along its length and then flattened out into a pane. This method had serious disadvantages, the main being the limit imposed upon the size: the cylinder could not be blown more than one meter long without a loss of thickness that would make grinding impossible. This disadvantage could however, be overcome if the glass, instead of being made into a pane via a cylinder, was cast straight on to a flat table, rolled out and allowed to cool. The resulting glass would not be transparent, but the usual finishing processes of grinding and polishing would remove these defects.

Bernard Perrot, in Orléans, was probably the inventor of the process. As a result of his work, several Frenchmen, acting through Abraham Thévart, were granted Letters Patent in December 1688 which gave them a monopoly of plate-glass manufacture by the casting process for the French home market and later for export as well. They went to Saint Gobain where wood was plentiful and cheap as the Société des Grandes Glaces. The new company competed with the Manufacture and eventually threatened its life as the new process was able to produce plate glass of much larger size.

In 1695, Louis XIV decided that the two companies were to merge: the new Company took the name of Manufacture des Glaces de France, which was to become much later Compagnie de Saint-Gobain. It kept using both methods of manufacturing plate glass until the 19th century when glass blowing was eventually abandoned.

Plate glass (Fig. 1.7) was made by pouring the molten glass onto a large iron casting-table, and rolling it by means of a heavy iron roller driven by two workmen. The thickness of the plate was defined by the use of two iron slips laid along the edges of the table on which the roller rested. Thus, by using slips of different depths, glass plates of varying thickness were obtained. To adjust the width of the plate and to prevent glass from flowing onto the sideslips, two guides of cast-iron were set upon the table at the required distance apart. These guides were shaped to fit the front of the roller and were driven forwards by the roller, so determining the width to which the glass spreads during the rolling process [1.20, p. 468].

After casting, the plate was cooled down in special kilns (carcaise) and polished. In this method, three distinct processes were carried out, grinding, smoothing, and the final polishing operation. The first two were identical in character, and consisted in rubbing down the surface of the glass with flat plates of iron, using sand as an abrasive. In grinding the main part of the excess glass was removed by the use of coarse sand, whilst finer sand grains employed in the smoothing process served to eliminate the larger defects left by the coarser particles preceding them. After grinding and smoothing, the glass surface had a dull grey appearance. Polishing consisted in rubbing tools shod with felt over the surface of the glass, iron oxide (rouge) being used as a polishing agent. While the first two operations removed large amounts of glass from the plate, the last actually took away nearly no material, but served to level the undulations, producing the smooth surface characteristic of plate glass [1.20, p. 475].

In theory, the casting process was far more straightforward than the complicated method of making a flat pane of glass by way of a cylinder. In practice, however, casting, grinding, and polishing required a large capital outlay. Instead of the small customary glasshouse, a large casting hall was needed, complete with an extensive melting furnace in the center, a number of sizeable annealing ovens around the walls (one for each plate made), a casting table upwards of 3 meters long and 2 meters wide, and cuvettes in which the molten glass could be transferred from the furnace to the casting table together with a crane to carry them. There was also the machinery required for grinding and polishing as well as the warehouse accommodation [1.11, p. 44]. It explains why Saint-Gobain did not have many competitors for a long time.

1.4.4 Innovation in Container Glass Linked with Champagne Wine Development

Champagne wine appeared during the reign of Louis XIV with Dom Perignon, a monk of the Abbey of Hautvillers near Epernay [1.21]. Its particularity is to be aged directly in the bottle, at least since 1759, which leads to the pressure rising inside the container because of the carbon dioxide emitted during fermentation. Around this time, nearly half of the bottles broke during the process, making champagne a very expensive wine. The champagne industry therefore demanded bottles with much more mechanical resistance.

Before the 19th century, the main quality of bottles was their strength. "As soon as they were of a neat

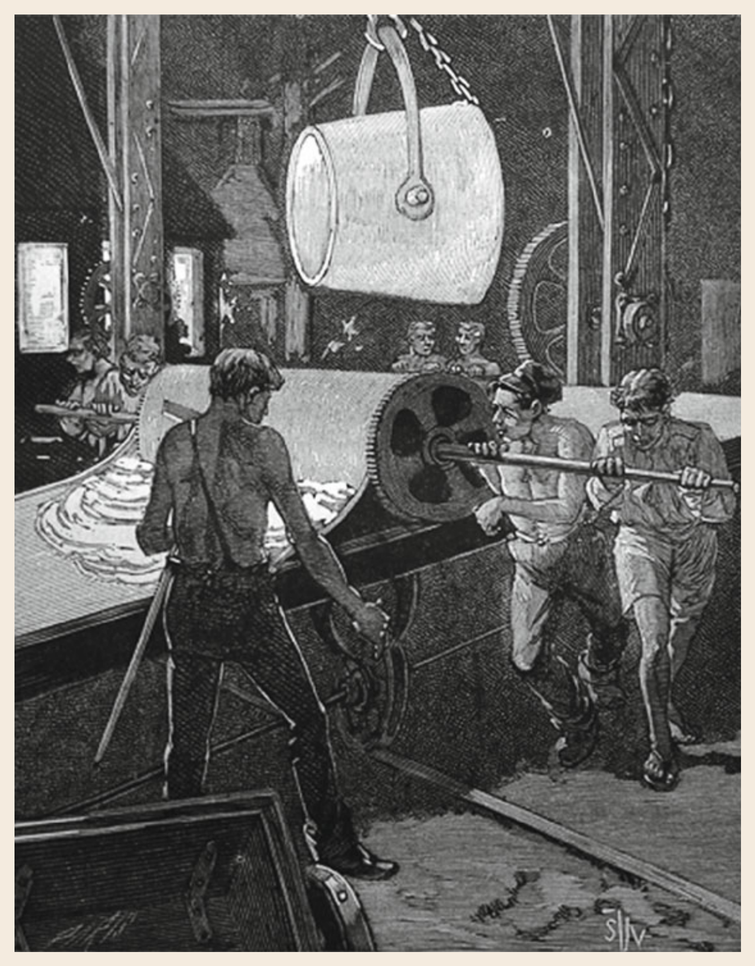

Fig. 1.7 Casting plate glass (A. Bitard, Les arts et métiers illustrés, around 1890)

brown or green color, not cloudy, and without too many bubbles, the color intensity did not really matter" [1.19]. This color depended largely upon the nature of the raw materials, which in turn depended on the situation of the glass factory. Thus, near big cities, new ashes were used as well as *charrées*, the product of the leaching of wood ashes by laundry women. The other materials were sand that could be yellow, more or less clay containing, and crude soda ash from seaweeds. When the sand was very siliceous, clay was added. When sand and clay contained only a small proportion of limestone, chalk was added. Finally, broken bottles and residues from the fabrication could be part of the mixture. Obviously bottle glass was not of the best quality compared to cristallo!

The improvement of the Champagne bottle initially came from the improved regularity of its thickness, which was better mastered by the glassmakers and resulted in better mechanical resistance. The improvements in the glass composition did not occur until the end of the 19th century.

No real evolution occurred as far as the container glass process is concerned until the beginning of the twentieth century and the beginning of mechanization: a semiautomatic process in 1895 and automation (feeder + machine) in 1915–1920.

1.5 19th Century, the Century of Technical Revolutions

The end of the 18th century saw many evolutions in the sciences and thus the 19th century brought many important innovations in glassmaking.

1.5.1 Raw Materials: From Natural Soda-Ash to Artificial Soda and Sodium Sulfate

Lavoisier died at the end of the 18th century but he had introduced the main laws of what we would now consider as real chemistry, beginning by weighing whatever entered a crucible, but also the results of the chemical process. More rational experimentation led to better controlled raw materials and glass.

Soda in the 18th Century, a Variable and Expensive Product

Before the French revolution, sodium carbonate or soda ash was prepared by means of the calcination of marine plants containing sodium as various salts, tartrate, oxalate, and chloride. The name *soda* comes from that of a family of plants, for instance *salsola soda*. The best soda ashes which came from Alicante (Spain) were called Barilla, because of the local name of the plant, barilla. The content in sodium carbonate was very variable in the ashes. Since chemical analysis was impossible at the time, the glassmakers usually had an empirical method to judge their quality: in addition to color, "he added the smell and the taste to determine their causticity which had to be frank and stinging without bitterness." A small piece was put on his tongue to judge if it did not smell of sulfides, the sign for a bad quality soda ash [1.19].

The usual impurities in this natural raw material were alkaline salts soluble in water like sulfate or chlorides, calcium or magnesium insoluble salts, or charcoal coming from the calcination. Charcoal was partly eliminated by the fritting step that contributed to a faster melting operation because decarbonation and dehydration took place during the first firing. It also extended the life of the furnace.

The drawbacks of natural soda inspired glassmakers and their suppliers to find a way to obtain a more stable flux. It began by the systematic purification of the natural soda ash and resulted in the invention of an industrial method to manufacture sodium carbonate from sodium sulfate. A third step was the discovery that sodium sulfate and even sodium chloride could be used as fluxes in glassmaking. The last step was the invention of Ernest Solvay, producing sodium carbonate directly from sodium chloride at the end of the nineteenth century (1865).

The Initial Improvement: Soda Ash Purification

Venetian glassmakers knew how to obtain purer soda ash by water extraction. Pierre Delaunay Deslandes, the new manager of Saint Gobain factory, for plate-glass manufacture, adopted this process in 1758. He obtained a much more stable and purer raw material, which considerably improved the quality of plate glass. In parallel, he observed that he had to compensate the CaO content in his glass brought by the unpurified soda ash by addition of limestone. He said in his memoirs:

> Lime was used in plate-glass fabrication without knowing; no attention was paid to the fact that natural soda ash contained more than half earth matters which, after having spent a considerable time in fritting furnaces had acquired the properties of lime. [1.22]

The experimental method used by Deslandes is interesting: "he took leached soda ash, fritted it to discolor it, made comparative mixture with this frit and with lime and observed that the result was the same." [1.23] The comparative test was most probably the workability of the glass, as the viscosity of glass is highly dependent on its composition.

> Then he tried the stone with which lime was made, the limestone and found no difference. He does not indicate why, at this point of his trials, he did not perseverate in this direction and definitely adopted limestone instead of lime. We have to imagine that, his furnaces being less efficient than the modern ones, they needed a already prepared element instead of a product which had to be decomposed.

However, slightly later on, Deslandes understood that the unfritted mixture melted just as well as the fritted composition and he stopped this operation. This text is quite interesting: it illustrates the experimental process by trials and comparisons used at that time when no analytical process was available, and also shows that Deslandes was familiar with the chemical knowledge then available: water solubility of alkaline salts, filiation between $CaCO_3$, CaO and $Ca(OH)_2$, even if he did not have any conceptual tool to explain the reactions.

It also brings to light the regularity problem related to the flux supply. Beside the supply security, the import of soda ashes from Spain was very expensive for French companies. In fact, the French Science Academy proposed a prize in 1775 for the solution to the transformation of marine salt (NaCl) into sodium carbonate without any success.

By the time of the French Revolution, the problem of the flux supply had been plaguing the French glass industry for many years, for both technical and economical reasons.

Invention of *Artificial* Soda Ash

According to *P. Flamm*,

> Chemistry had identified that marine salt, so widely spread on the earth, was a combination of two simple bodies, chlorine linked to soda. Hence it was natural that researches would deal with this so abundant salt, in order to find an economical process to isolate soda. [1.24]

This innovation was partly brought about for political reasons [1.19]. Until then, the price of natural soda alone had not been a sufficient incitement: the French science academy proposed a prize but

> France continued to give each year to Spain 20 to 30 millions of francs for the soda ash supply. The Revolution war having arisen, imports of soda ash and potash were hampered (by the continental blockade) and all the potash that France was producing was immediately consumed by saltpeter and powder manufactures. The 'Comité de Salut Public' in 1793, ordained that the most exact indications should be given about all the soda ash manufactures.

It was only then that the method to prepare soda ash advantageously from marine salt or rock salt was determined [1.12].

Nicolas Leblanc, supported by the Duke of Orléans, had invented a process to manufacture artificial soda ash in 1791 and the factory worked without interruption until November 1793 when the Duke of Orléans perished on the scaffold. His assets were sequestered, the factory was stopped, and the equipment sold. When the decree of the Comité de Salut Public was announced, Leblanc allowed the publication of his process, until then kept secret. The only reward he obtained was the restitution of the Saint Denis factory without any financing to make it work. Tired of his attempts to obtain justice, Leblanc committed suicide in January 1806 [1.9], but his invention remained.

> Artificial soda ash is obtained by calcination of a mixture of sodium sulfate, coal and chalk. … The exact mixture is introduced in an elliptical furnace at a temperature slightly higher than cherry red, the mixture is stirred every quarter of an hour. In time, the matter becomes thicker. Then it is worked with an iron rod and extracted. This matter is artificial soda ash. [1.24]

According to *Louis Figuier*:

> It would be nearly impossible to estimate exactly the immense gains that industry made thanks to the discovery of Nicolas Leblanc, who made possible to extract soda ash from sodium chloride contained in sea-water. Whence did Nicolas Leblanc draw the countless riches with which he blessed Europe? From the application of a chemical fact the announcement of which would not have needed four lines in a scientific publication of the period, the decomposition of marine salt by chalk at high temperature. [1.9]

The artificial soda ash, richer in sodium carbonate than the natural soda ashes, but containing inconvenient impurities like calcium sulfide was used initially for container and sheet glass, but not for plate glass. However, producers rapidly managed to purify it and, in 1868, they were able to make a product containing 95% to 97% of sodium carbonate.

In 1810, the soda ash manufacture was sufficient for all the needs of French industry: a decree of 11 July prohibited the import of foreign soda in France. At the same time, the Compagnie de Saint-Gobain, not being able to find a suitable supplier for its plate glass, decided to manufacture its own soda ash, on the site Charles-Fontaine bought for this purpose. In 1823 the soda factory was transferred to Chauny.

The Direct Use of Sodium Sulfate or Sodium Chloride as a Flux

One of the drawbacks of the Leblanc process is its cost. Glassmakers explored the use of the chemical precursor of sodium carbonate, sodium sulfate and even sodium chloride. In 1810, Clément Desormes from Saint-Gobain patented two processes, one of them using sodium sulfate and sodium chloride (sodium "muriate") and the second, simply sodium chloride, which gave no interesting result, but indicated a trend.

A fundamental chemical problem had to be overcome: in the beginning of the 19th century, sodium sulfate was not considered as a possible flux because unlike sodium carbonate, it does not easily combine with silica.

In 1813, the German chemist *Gehlen* determined how to successfully use sulfate directly in furnaces, mixing it with limestone and coal [1.25]:

> For 100 of silica. 33 to 40 of sodium sulfate are necessary, 20 to 40 of calcium carbonate or its

> equivalent quantity in lime, from 1.65 to 2 of ground anthracite or 2.30 to 2.80 of charcoal.

Despite the success of Gehlen's method, at first, manufacturers were not allowed, at least in France, to sell it because the government dreaded that sodium chloride, highly taxed, could be extracted from it. When it had been well-proved that sodium chloride produced from sodium sulfate would be much more expensive than marine salt, the government decided at last, in 1824, to allow the sale of sodium sulfate. It was first used to make sheet glass in Prémontré (Aisne). However, at first they fritted the mixture of sand, sulfate, chalk, and coal. Its use was very soon extended to other sheet glass manufacturers and even to half-white glass tableware fabrication.

The use of sulfate for plate glass met a huge problem: the resulting glass was slightly green. Theoretically, there was no reason why the glass would not be as clear as with sodium carbonate. Chemists imagined that the light color obtained could be attributed to a reaction of part of the coal on soda ash. Gay-Lussac himself, who for several years was president of the Board of Saint-Gobain, was sure that, for this reason, it would be impossible to substitute sulfate for carbonate in plate-glass manufacturing. It was Pelouze who corrected this error: in the 1850s, being convinced that the mixture of pure raw materials should yield a clear white glass, he determined that the color was due to a small quantity of iron oxide. As sand and lime used in Saint Gobain were free from iron, he looked more precisely at the sodium sulfate manufacturing process for a source of iron.

Firstly, he discovered that, sodium sulfate usually contained a slight excess of sulfuric acid which reacts with the iron-rich clay of the pot. Secondly, that iron oxide came mainly from the bottom of the furnace where marine salt was decomposed by sulfuric acid, and remained in the sodium sulfate in more or less large proportions.

Pelouze worked out the purification of sulfate and could entirely replace sodium carbonate by sodium sulfate in the plate-glass fabrication. This brought about large savings which allowed producers to drastically decrease the price of plate glass. (2.06 versus 4.63 $\mathrm{F/m^2}$ for the raw materials in 1868, the price of sodium carbonate being 5 times that of the sulfate)

The bottle glassmakers, looking at whatever savings they could make, used sodium chloride together with sodium sulfate as soon as the end of the eighteenth century during the French revolution when sea salt was no longer taxed. The process included a previous fritting of the whole or part of the mixture and it seems that the incorporated water was enough to help the reaction between silica and sodium chloride, which is difficult at high temperature.

> When sea salt was taxed again, container glass producers obtained from the government that a half decomposed salt would be processed for them, containing roughly half sulfate and half chloride, which is much cheaper than pure sulfate and could be advantageously used in bottle manufacturing. [1.19]

This product was used until the next generation of furnaces appeared, the Siemens regenerative tank furnaces, which were corroded too rapidly by chlorides.

A New and Last Evolution: The Solvay Process

The Leblanc process provided relatively expensive sodium carbonate, so that chemists persevered in their efforts to find a cheaper process. The ammoniac process was theoretically known since 1811, but devising an economical industrial process was difficult. E. Solvay, in Couillet, Belgium, used it for the first time in 1865. In this process sea salt is treated by ammonia, then by carbon dioxide, produced by limestone decarbonation, to yield sodium bicarbonate and ammonium chloride. When heated, bicarbonate yields carbonate. One of the advantages of this process is that ammonia can be recycled by reaction between ammonium chloride and limestone. Therefore, the process is economically more favorable and the sodium carbonate much cheaper.

In spite of the fact that the sodium carbonate produced with the Solvay method was much cheaper, the substitution of sulfate by carbonate took a long time: partial substitution trials after 1887, in Saint Gobain plants, did not give any positive results [1.23].

One of the particularities of the sulfate glasses is their chemical activity at high temperature which leads to the liberation of gas at high temperature, which is useful for homogenization. This degassing happens either when the temperature is increased by spontaneous reduction of sulfate into sulfite, or, at lower temperature, following stirring with a wood rod or a potato, both being reducing agents which produce the same result. It is called *maclage* or shearing. A healthy boiling is obtained, which improves the homogeneity and the refining of the glass, but which also presents problems with installations.

> Shearing is not used everywhere with the same intensity; some plants use it as a help without decreasing the heat in the furnace; others, and especially those which have less strong pots, reduce heat and use this process, the chemical reduction of

> sulfate inducing a sufficient degassing effect without the need to heat. [1.23]

A too violent foaming induces an accelerated wear of the pots, and glassmakers always tried to obtain the same effect without heating too much or even without foaming, despite the fact that some *work* from the glass seems to be essential for homogenization.

The economic advantage of Solvay carbonate did not allow the glassmakers to escape the question of replacing sulfate by carbonate in the beginning of the 20th century.

> In 1906, in the Montluçon plant of Saint Gobain, trials were conducted with carbonate and it was concluded that carbonate glass could not be refined at the usual temperature of furnaces, but that, if a small amount of sodium or calcium sulfate was added, it refined all right and that sulfuric acid seemed to have a real influence on the glass melting. [1.23]

In 1922 the Society of Glass Technology had discussions about the advantages and drawbacks of the use of sulfate and carbonate as raw materials in glass batches [1.26] "Should window glass made with soda-ash be inferior to window glass made with salt-cake (sodium sulfate)?" It would seem apparent that the use of soda-ash as a constituent of the batch is less corrosive on the tank-blocks.

Turner added:

> he hoped that someone might have referred to the difference in the working properties between glass produced from soda-ash and salt-sake containing batches? [1.26]

The viscosity is the same, but

> he understood the consensus of opinion among manufacturers of window glass was that the batch which contained at least a proportion of salt-cake was preferred, mainly because the glass, although being somewhat less fluid, had apparently a longer viscosity range. The salt-cake glass was often spoken of as being 'sweeter.' [1.26]

Hodkin added: "the salt-cake glass was a more readily worked material."

Rees mentioned: "the ordinary glass bottle-maker undoubtedly seemed to prefer glass which contains some salt-cake." Dr. Travers said that

> when the glass-makers were unanimous in making a statement, there must surely be something definite about it, and although their mode of expressing it might be somewhat puzzling to the man of science, the latter must make his business to try to find some explanation. [1.26]

Mr. Barker thought that "sweetness" in glass was closely associated with its homogeneity. It was possible to get a greater degree of homogeneity with a salt-cake batch than with soda ash. A thoroughly homogeneous glass could be blown out better, and because of this it was referred to as "sweeter."

Nevertheless, in 1927, *W.E.S. Turner* could say [1.27]:

> the weekly tonnage for some tanks has, since 1916, been increased six-fold. The four most important factors that have brought about this enormous advance are not directly associated with furnace design. They are: (1) the substitution of salt-cake by soda ash in glass batches, (2) the general reduction in the lime content employed and increase of the alkali content, (3) improved mixing of the batch, (4) the use of automatic machines.
>
> . . . Although in one or two instances the advantages of soda ash were recognized and employed before the war, the substitution of soda ash for salt-cake began to occur generally in this country about 1916/1917, and it would not be exaggerating, I think, to say that this change led to a speeding up of melting of quite 40 per cent.

This analysis did not escape the glassmakers, and the result was the usual glass batch with sodium carbonate, mixed with sodium sulfate to enhance its homogeneity, which they are still using today, one century later.

1.5.2 The Development of New Furnaces

C.W. Siemens had invented a new process, combining a gas producer and regenerators [1.28, 29], and the first patent was taken in England in 1857 [1.30]. The fundamental idea was to make use of the enormous amount of heat lost up the chimney to preheat the ingoing combustion air and the gas [1.19].

The Regenerative Furnace

A chamber full of bricks (Fig. 1.8) stacked to have as many interstices as possible between them is placed between the furnace and the chimney: the burnt gases release their heat in this chamber, the temperature decreasing towards the other end nearer to the chimney. After half an hour a valve is changed to close off the chimney and another one opened to allow the external air into the chamber: the air will be heated when flowing through the chamber previously heated and will reach the combustion chamber at high temperature.

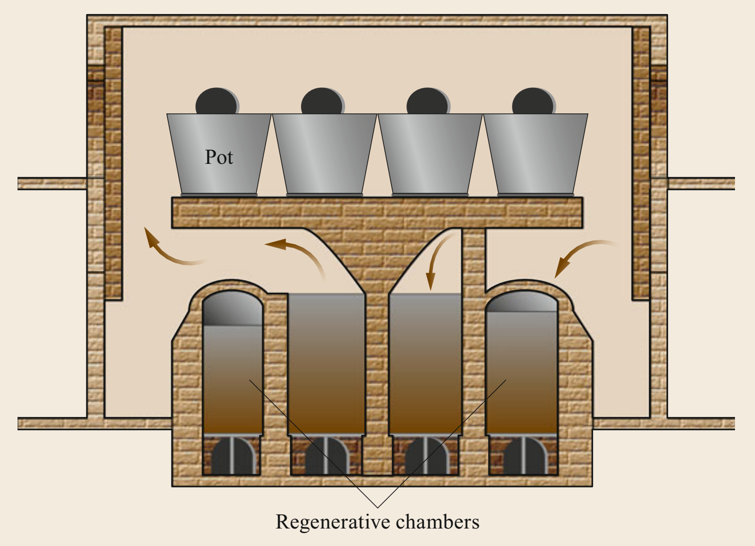

Fig. 1.8 The Siemens pot furnace with regenerative chambers. *Arrows* indicate the circulation of gases: on the *right*, hot combustion gasses from the furnace, heating the right side regenerator; on the left, air and gas are heated when circulating through the previously heated chamber (after [1.12])

Table 1.6 Number of Siemens regenerative pot-furnaces built or ordered in 1863 [1.31]

Great Britain	4 furnaces (Chance – Birmingham) 2 furnaces (British Plate Glass works – St. Helens) 1 furnace (Stevenson & Co – Glasgow)
Germany	2 furnaces (Siemens – Dresden) 2 furnaces (Broederson & Co – Hamburg)
France	2 furnaces (Montluçon) 5 furnaces ordered (Saint-Gobain)

At the same time other valves led the exhaust gases into a second set of chambers filled with bricks during another period of half an hour and the valve is reversed. This process saves a large part of the energy necessary to heat the fuel and the air up to the furnace temperature, and the furnace itself can more easily reach a higher temperature.

Gas Producer. Beside the regenerative furnace principle, the process used gases produced by the partial combustion or distillation of coal, realized by the admission of steam and of a quantity of air insufficient to produce perfect combustion in the gas producer (Fig. 1.9). The Siemens system thus consists in removing the coal or other solid fuel from the furnace by supplying the furnace with gas and air already heated to a high temperature.

Development of the Regenerative Furnaces. In England, a first regenerative glass furnace was built in Rotherham in 1860 to melt lead glass. In 1861, a new British patent was obtained (22 January) with special application to glass melting [1.28].

Chance Brothers in England were the first to decide to build a Siemens regenerative furnace to make window glass (cylinder method): the furnace, ready by the end of 1861, was quite successful. In 1862, they adopted the Siemens principle for three other sheet glass furnaces, and in 1863, for another two (Table 1.6).

At this time, *C.W. Siemens* also had an address in Paris and took charge of the realization of the drawings and plans of the ordered furnaces and supervised the operation [1.31]. The royalties, calculated so as to represent 12 to 14 per cent of the profits registered during the application of this process, were to be paid by annuities, or all at once by a reasonable compensation.

In 1862 (17 December), Saint-Gobain paid 200 000 francs for five plate-glass pot furnaces: three for Saint-Gobain, one for Cirey, and one for Mannheim. A first furnace was built in the Halle-Neuve in Saint-Gobain and blessed on May 21st 1863 by Mgr. Christophe, bishop of Soissons and Laon [1.23].

A Cost-Effective Process. The Saint-Gobain Glacerie of Cirey had its 16-pot gas regenerative furnace at the end of the next year (1864). This furnace consumed only 48 kg of coal per square meter of plate glass, representing 50% savings on fuel consumption compared to the previous furnaces without regeneration chambers, and produced 5793 m^2 of plate glass in 33 castings.

The application of the regenerative heating process, together with a gas producer brought substantial savings compared to direct coal-heating but moreover allowed the furnace to reach higher temperatures and consequently notably increased glass quality.

The Siemens regenerative pot furnace of the first generation kept many characteristics of the older tradi-

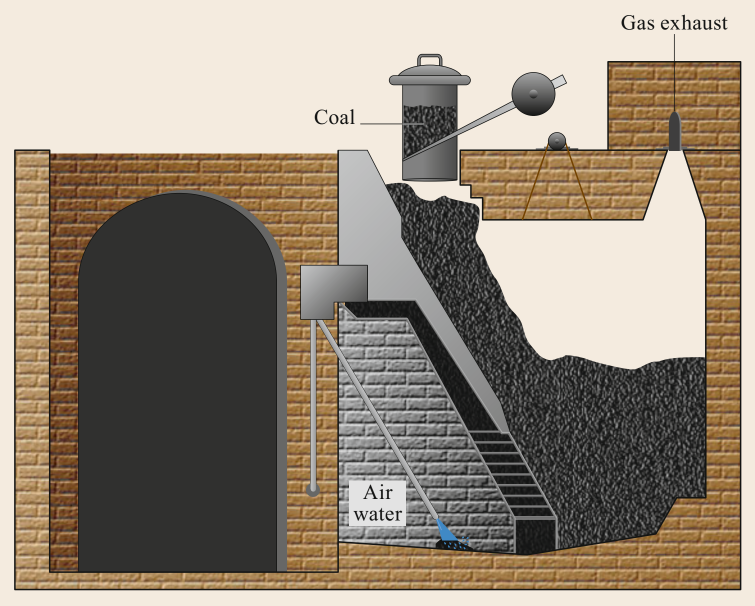

Fig. 1.9 Siemens gas producer (after [1.20])

tional furnaces (Fig. 1.8): the burners were set in the siege, where the grates were previously placed, i. e., at each end of the trench, one or two meters from the wall. Gas and air arrived vertically in the furnace. The first furnace of Saint-Gobain (Aisne) was for 20 pots, 9 on each side and one at the wall. Its laboratory was 8.37 m long, 3.5 m wide, and 1.85 m high. The regenerative chambers situated under the furnace were 3.5 m long, 1.1 m wide, and 2.3 m high. Those first furnaces were progressively modified, with the help of Siemens, until they achieved a satisfactory design. For instance, the distribution, as well as the geometry, of the burners along the axis or in the corners, was studied so as to increase the homogeneity of the heating to obtain the same advancement of the melting process in all the pots along the furnace. The bottom was cooled by air circulation. These furnaces lasted 16 to 18 months.

The success of the Siemens regenerative pot furnace was quite fast in England, France, and Belgium despite the fact reported by Bontemps that the operation of these furnaces was more difficult than that of the traditional furnaces. In the US, the first regenerative pot furnace was built in 1865 (O'Hara Glass Works, Pittsburgh, PA).

Heat Transmission: Radiation Furnaces

In 1884, *Frederic Siemens* published his paper about a new way to heat gas regenerative furnaces [1.31]:

> In all the types of furnaces designed until now, it was always considered that the first condition of success was to make the heating chamber as small as possible, so that the flame can be in very close contact with the inside walls of the furnace, and more especially with the matter being heated.
>
> Lately M. Frederic Siemens asked himself if this design was correct and, after long and serious experiments, he convinced himself that the furnaces have to be designed so that the flame only radiates its 'caloric' on the matter to be heated and does not come into close contact with them. Having the flames travel horizontally above the melt and relying largely on radiant transfer decreased batch carry over and volatilization from the melt. In the furnaces he is now constructing, the gas and air inlets, instead of being placed so that the flame impinges on the batch placed in the furnace, are situated at a small distance of the crown of the heating chamber, and also of the walls of this chamber, so that gas and air, after the inflammation, have a large space for their combustion and for the free development of the flame. When there are crucibles they must be set with enough space between them so that the radiating heat has free access all around them. In gas regenerative furnaces, the temperature of the flame is sufficient to heat by radiation: the matters absorb most of the heat thus produced, and, consequently, there is no reason not to increase the laboratory of those furnaces. Experience shows that large fuel savings can be made and in many cases, indirect savings also come from the increased yield and the increased quality of the

> metal produced without contact with the flame. Finally furnaces have a much longer life.

(Essentially due to less volatilization from the batch—Fig. 1.10; see the new position of the burners.)

New Design of the Furnace and Gas Producer System. The main characteristic of those furnaces is the position of the burners horizontally in the walls of the combustion chamber (Fig. 1.10). Two other changes were also proposed for the "Four Siemens Nouvelle disposition" [1.32]: to put the gas producer close to the furnace itself and have regenerators only for the air, the gas being directly injected in the furnace without being heated and burned in the regenerative chamber.

> The new furnace is much smaller, usually half the old one, meaning considerable savings on the building cost. The savings on fuel can be evaluated between 25 and 30% compared to the first furnaces.

Data about the yield in these furnaces can be found in a Saint-Gobain document of 1911, where Mr. Boudin, the manager of the Saint-Gobain factory had to justify his yield compared to that of other Saint-Gobain factories: it was 0.4 t/day m^2 in Saint-Gobain (Aisne), 0.48 t/day m^2 in Montluçon and 0.36 t/day m^2 in Pisa: this is not so far from what is done today!

In 1893, a comparison was made between the traditional furnaces with burners in the siege and the new ones with burners in the wall [1.23] (Table 1.7). From those results one can draw the conclusion that the glass was melted much better in radiation furnaces but that the crown was too low and thus was attacked, at least in the Saint-Gobain-type furnaces, which still had a very low crown height at this time. In 1896, the following conclusions were drawn:

- Furnace life: The burners in the walls are more advantageous. They are easily accessible, easier to maintain. Less deposits in the regenerative chambers: they last longer, the crown is less attacked.
- Pots are less violently attacked and the attack is more uniform among them.
- The refractories of the burners absorb a large quantity of heat and the beginning of the melting process is long and thus very regular.
- Glass quality: The old furnaces gave a good quality for a short period. Then the combustion was no longer optimal and the quality decreased. In a furnace with burners in the walls, the quality is more constant.

The fuel consumption is the same. Until the beginning of the twentieth century, the Saint-Gobain plate-glass pot furnaces like the tank furnaces still had a regenerator chamber for gas, though it was smaller than that for air.

A Revolution: Regenerative Tank Furnaces

As *Michael Cable* said, the regenerative tank furnace (Fig. 1.11) was the greatest advance in glass technology since Roman times [1.28]. Siemens's patent of 1870 reveals that the Siemens brothers were not sure of the possibility to use real *tanks* without pots. In the 1872

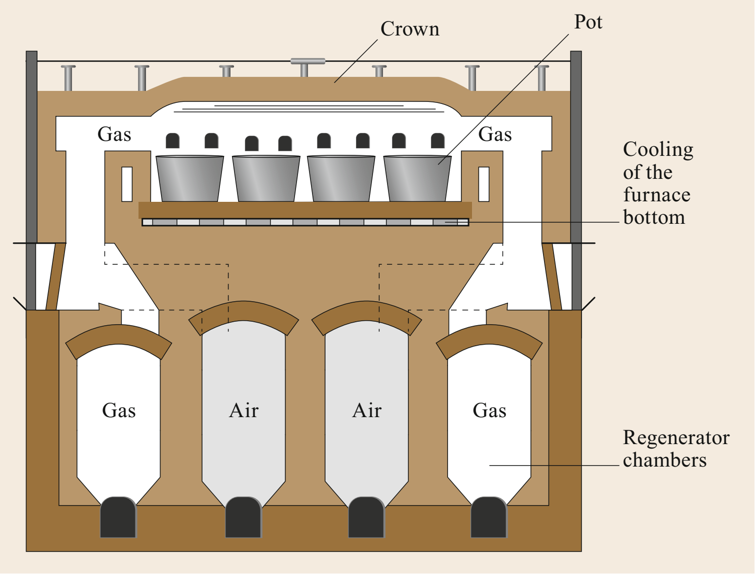

Fig. 1.10 Siemens radiation pot furnace: Air and gas arrive into the furnace through the ports, alternately from left to right and right to left as the currents are reversed. Note the position of the ports above the melts and parallel to the vault (compare with air and gas coming upwards in Fig. 1.8). (After [1.20])

Table 1.7 Quality data comparisons between traditional furnaces and the new ones. Defects in plate glass melted in furnaces with burners in the siege (traditional) and in the wall (radiation furnace) [1.23]

	Burners in the siege	Beaudoux burners in the wall
Number of plate-glass casting	2386	2432
Number of unmolten sand particles	2405	460
Number of crown stones	2772	5358
Number of sand stones per plate	1.01	0.19
Number of crown stones per plate	1.16	2.20

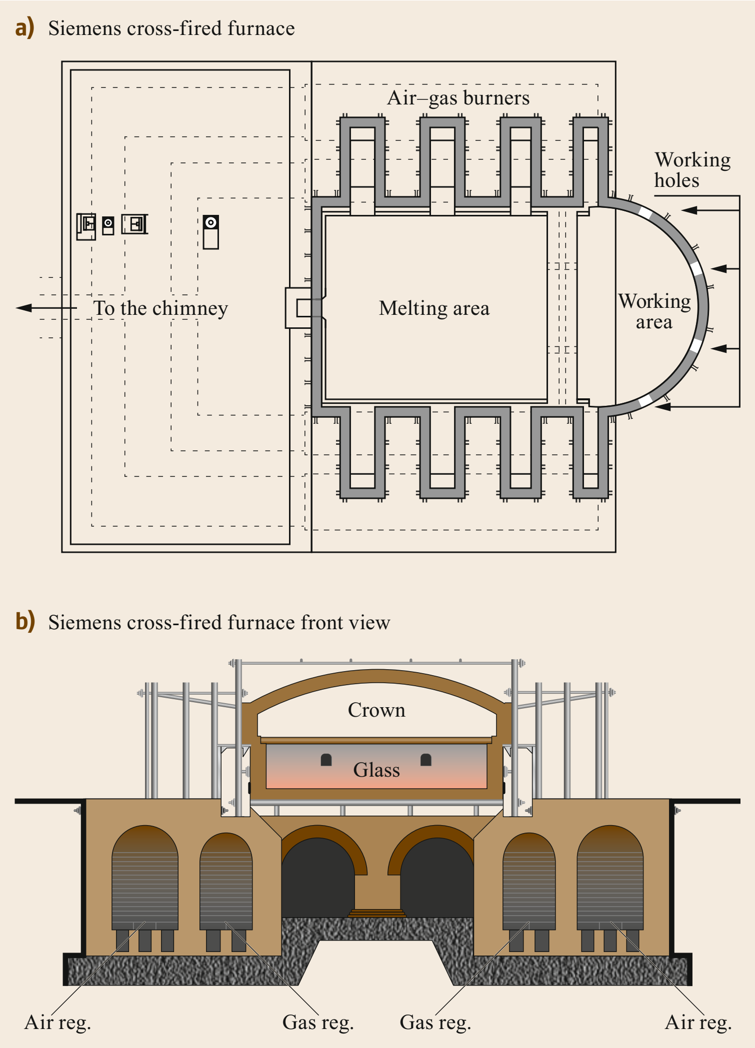

Fig. 1.11a,b Old Siemens crossfired (side-port) tank furnace (**(a)** cross section, **(b)** plan view) (after [1.20])

patents, however, the use of pots had been forgotten in favor of tanks. The Siemens Brothers now had to solve the various problems due to inadequate refractory blocks.

The first company to try the tank furnace was Pilkington Brothers. In May and July 1872, Windle Pilkington missed five successive Pilkington Board meetings. The minutes record that he was in Switzerland, but he had also gone to Germany [1.11].

> On his return, at a Board meeting held on July 10th, it was decided to put a continuous tank on the cylinder place upon the principles of the one that he has seen working at Dresden.

In April 1873, blowing of sheet glass began and an enthusiastic entry in the minutes on the 17th records that

> the metal at first was slightly seedy from the cullet but had continued to improve and at the present moment is beating any pot-furnace on the ground … Consider that we ought to seriously discuss the advisability of getting the patent secured to us by Siemens for our special use and will see Siemens if all be well next week

This exclamation was followed by 3 months silence, without a word about the tank or about negotiations with Siemens, until July 21st when the next reference occurs. Then, on August 14th the tank began to make glass "for the second time."

Obviously, soon after April 17th, something happened to the first attempt, which suddenly quenched the partner's initial enthusiasm. What went wrong at the first attempt? James Taylor, then a young man working in the laboratory later recalled that the tank

> only worked one week before the bottom was eaten through; the metal leaked and set the place on fire. Nothing further was heard of this experiment for several months … The first tank failing at the end of the first week, MM Pilkington decided to abandon, but after several Board meetings and Mr. Windle Pilkington stating that, if they would not make another attempt, he would secure a piece of ground himself and erect one on his own account, they then gave way and agreed to another trial where he succeeded [1.33].

In fact, at the second attempt, the tank ran nonstop for 97 days. In the original version the side walls and crown of the furnace had been built on top of the side-blocks holding the molten glass. When the furnace bottom wore out, the whole furnace collapsed. In the second attempt they were independently supported.

Having built one successful tank, Pilkington began to substitute tanks for pots at a rapid rate. A second tank was in use in February 1874. At the end of August 1876, there were nine tank furnaces in operation and the ground was being cleared for a tenth. Chance & Co. "anxious to find out every detail about their rival's progress," [1.33] kept a record of statements made by anyone who came to them from St Helens. Early in 1877, they had the information that Pilkington was

> at that time using tanks nine feet wide and 36 feet long whereas formerly their tanks had been 12 feet wide and rather shorter in length. These held 2′6″ of melted glass when the tank is new. When the sides are worn thin, less glass is put in lest the sides should burst. The sides require renewal every 3 or 4 months. If they last 4 months it is good working. The bottom of the tank needed renewing every 10 or 11 months. In each case these renewals took about three weeks.

In May 1877, 12 tanks were at work and more were being built. The number of furnaces was so large that the Siemens Brothers agreed to receive royalties at a lower rate than the four shillings per ton of finished glass that they usually charged, itself much lower than the five shillings royalty on their pot furnaces.

In the Compagnie de Saint-Gobain, the new tank technology was not perceived as being able to melt good quality plate glass. It was possibly the same at Chance & Co where rolled plate-glass production was fast increasing compared to the traditional window glass blowing.

The first tank furnace was finally built at Saint Gobain to produce thin rolled glass No. 4 (see below for the development of this new production) in Saint-Gobain (Aisne) in 1881, in Stolberg in 1884 and a second furnace in 1888 (end-fired furnace). Their characteristics were close to our present-day furnaces: the superstructures and the tank itself were separately supported, room was provided under the furnace in case the bottom wore out because of the molten glass.

Table 1.8 gives the characteristics of all the tank furnaces in use in 1913 in Saint-Gobain: New factories had been settled in Spain and Germany since the end of the nineteenth century [1.23].

1.5.3 Progresses in Pyrometry

In 1782 Wedgwood observed that ceramic products often have their beauty or value considerably depreciated by too much or not enough heat during the firing process [1.34]. What is more, with no determination of the conditions of firing, the artists could not use even their own experiments to improve their production. This problem was quite true as well for glassmaking where temperature is as important as in ceramics. One of the major innovations in the 19th century was the measurement of high temperatures.

Wedgwood created a very simple *pyrometer* which used clay retraction during firing. It consisted of refractory clay cylinders and could be used to indicate the reproducibility of the temperature from one experiment to another.

Instead of following the variations in dimension of a crystallized material like clay, the progressive melting of a partly vitreous body can be used to indicate temperature. Lauht and Vogt in the Manufacture de

Table 1.8 Tank furnaces working in Saint-Gobain in 1913 according to Document Saint-Gobain Archives

Furnace	Surface (m^2)	Depth (m)	Number of burners and distribution	Air chamber volume (m^3)	Gas chamber volume (m^3)
Saint-Gobain 1	61	1.2	1 at the doghouse 5 side port		
Saint-Gobain 2	37	1.4	3 side port	22	16
Montluçon 1	46	1.25	4 side port	47	23
Montluçon 2	49	1.6	4 side port	45	31
Stolberg 1	52		4 side port	20	17
Stolberg 2	34	1.25	3 side port		
Mannheim 1	42	1.2	5 side port		
Mannheim 2	24	1.33	2 side port	27	17
Pise 1	34	1.45	2 end port	35	16
Pise 2	46	1.65	5 end port	27	26
Arija	19	1.2	2 side port	21	14
Altwasser 2	30	1.35	4 side port	20	14
Altwasser 41	48	1.3	2 end port	26	18
Altwasser 42	30	1.35	2 side port 2 end port	27	16
Bilin	50	1.2	4 side port	30	24
Dux	84	1.2	6 side port	38	34

Sèvres developed this idea, before 1882. They established a series of small prisms constituted of various mixtures presenting variable *melting* points, adapted to the Sèvres porcelain manufacture. Seger, the manager of a ceramic research laboratory in Berlin published in 1886 a paper where he presented a series of *montres fusibles* covering the range between 600 and 1800 °C every 25 °C. In the continuous furnaces they could be introduced into the furnace during the firing.

A Scale for Temperature

Since Wedgwood, many scientists tried to measure high temperatures although not very successfully. Until the end of the 19th century the confusion was considerable. For instance, the estimated temperature of a steel furnace varied, following the operator and the system he used, between 1500–2000 °C, that of the sun between 1000–1 000 000 °C!

H. Le Châtelier explained the major difficulty of the problem: to measure a length or a weight is to count how many unit bodies have to be added to make an equivalent either of the length or of its weight of the studied body. This idea supposes two physical laws: equivalence and additivity. The first law is respected by temperature, but the second one is not. It is possible to identify the temperature by comparison with that of a chosen body but temperature is obviously not additive.

Consequently, temperature has to be determined by the measurement of a phenomenon varying with temperature; for instance, the expansion of mercury counted with reference to the temperature of ice melting, with a unit equal to 1/100 of the expansion between the melting temperature of ice and its boiling temperature at atmospheric pressure.

Four data have to be chosen to define temperature: the phenomenon, the body, the origin of the scale, and the unit. Consequently the number of thermometric scales is unlimited and very often the scientists chose their own as the best. For instance, a few thermometric scales are given in Table 1.9.

The enormous differences that could be found in the literature of this period were mainly due to the choice of a scale rather than to problems of measurement. In order to escape this confusion, a unique temperature scale

Table 1.9 Thermometric scales [1.34]

Authors	Underlying phenomenon	Material	Origin/zero point	Unit
Fahrenheit	Expansion	Mercury	Hard winter	1/180
Réaumur	Expansion	Mercury	Ice	1/80
Celsius	Expansion	Mercury	Ice	1/100
Wedgwood	Permanent contraction	Clay	Dehydration	1/2400
Pouillet	Expansion at constant pressure	Air	Ice	1/100
Thermodynamic scale	Reversible heat exchange	Any	Zero heat	
Siemens	Electrical resistance	Platinum	Ice	

Table 1.10 Fixed points used to establish the thermometric scale [1.34]

	Sn	Naphthalene	Zn	S	Sb	Al	Zn	Ag	Au	Pt
Melting	232		420		630	655		962	1065	1780
Boiling		218		445			930			

Table 1.11 Color of bodies versus temperature

Color	Temperature (°C)	Color	Temperature (°C)
Red beginning	525	Dark orange	1100
Dark red	700	Light orange	1200
Beginning cherry red	800	White	1300
Cherry red	900	Soldering white	1400
Light cherry red	1000	Blazing white	1500

had to be chosen: at the end of the 19th century, it was that of the gas thermometer. Their expansion was large enough to be very precisely measured.

A reference gas pyrometer using the measure of the pressure change of a gaseous mass maintained at constant volume was designed. (Pouillet, Becquerel, Saint-Claire-Deville). Its volume and fragility made it unsuitable for everyday measurements. It was only used to scale other pyrometers.

The reference thermometer chosen by the International Bureau of Weight and Measures (BIPM) to define the practical scale of temperatures was the hydrogen thermometer, at constant volume and loaded with gas at 1000 millimeters of mercury pressure at the temperature of melting ice. Practically, at high temperatures, nitrogen is easier and its expansion is quite close to that of hydrogen.

Any other pyrometer can be used as soon as it has been scaled with this thermometer. According to Le Châtelier, the fix points that could be used for the indirect scaling of a thermometric range were the ones shown in Table 1.10.

Invention of the Thermocouple

Becquerel, Barus, and Le Châtelier invented the *electrical pyrometer* at the end of the 19th century. It used the measurement of the emf (electromotive force) developed by the temperature difference between two similar thermoelectric soldering joints. This pyrometer was widely used in laboratories and factories. Becquerel used the discovery of Seebeck (1830) to derive this pyrometer, with a platinum/palladium couple. Le Châtelier restudied the problem to solve errors observed which were due to the lack of homogeneity of some metals and their oxidation at high temperature. The best couple he chose was Pt/Pt + 10% Rh, rhodium being possibly replaced by iridium. This pyrometer was not robust enough to be used in factories at this time [1.17] (contrary to what is done at present in modern installations).

Optical Pyrometer

The use of radiation emitted by glowing bodies to evaluate the temperature was not new at the end of the 19th century: in all periods, glassmakers driving their furnace took those emissions into account and their optical variations, intensities, color. For instance, Pouillet established a scale with reference to the air thermometer [1.34] (Table 1.11).

In 1859, Kirchhoff showed that an incandescent body emitted radiation, the intensity of which increases with temperature, and that the maximum of intensity goes from red to blue in the spectrum when temperature is increased. Estimation of the temperature can be done by measurements of the total intensity of the luminous radiation, the intensity of a radiation of a particular wavelength, or the relative intensity at different wavelengths. The problem is to have a device robust enough to be used in industrial situations.

The optical pyrometer designed by Le Châtelier uses the measurement of the intensity of a precise radiation emitted by the heated body by comparison with that of a known flame the image of which is projected on the image of the body to be measured with an optical device. Le Châtelier used this apparatus to measure the highest temperatures he could find in nature or industry. Those data are interesting because they are probably among the first exact available measurements (Table 1.12).

This measurement indicates that the furnaces of the end of the 19th century were probably heated one hundred degrees lower than the present-day furnaces. We

Table 1.12 Various industrial temperature measurements [1.34]

Siemens Martin Furnace (steel)	1490–1580 °C
Glass furnace	1375–1400 °C
Hard porcelain furnace	1370 °C
Incandescence lamp	1800 °C
Arc lamp	4100 °C
Sun	7600 °C

Table 1.13 Evolution of the maximum size and price of plate glass manufactured in Saint Gobain [1.17, p. 444]

Date	Surface area (m^2)	Length (m)	Width (m)	Price for 1 m^2 (F)
1806	4.25	2.50	1.70	226 (1805)
1839	8.73	3.80	2.30	127 (1835)
1844	11.66	4.30	2.70	
1855	18.40	5.40	3.40	61 (1856)
1867	21.80	5.90	3.70	47.75 (1862)
1878	26.50	6.40	4.10	40.30 (1884)
1889	34.20	8.10	4.20	30.23 (1889)

Table 1.14 Time necessary to make plate glass: evolution between 1765 and 1889 in hours [1.17, p. 447]

	1765	1862	1889
Preparation of the batch	3	3	3
Melting and casting	28	24	24
Annealing	96	84	72
Cutting	6	6	6
Grinding	36	28	28
Smoothing	5	5	22
Polishing	72	24	22
Total	246	174	127

shall see that this increase was made possible by a considerable change in the refractories (and the furnace design and insulation) during the 20th century.

1.5.4 Innovations in Flat Glassmaking Around the End of the 19th Century

Evolution of Plate Glass, the Most Expensive Product

At the end of the 19th century Saint-Gobain produced plate glass for mirrors by casting. In 1868, Bontemps thought that no "other factory has ever been the model for all others to the degree that had been achieved by Saint-Gobain." It has not only been the

> model for all others created in France or in foreign countries but hardly any other has been established without the cooperation of the directors of Saint-Gobain or workers coming from that company. [For instance] the first cast plate glass works in England was set up at Ravenhead only in the summer of 1773; this company had the assistance of a M. Delille from Saint-Gobain; it was the British Plate Glass Company. [1.19]

Heretofore, the practice used in making plate glass was to ladle the molten glass from its melting pot into a casting pot, according to the size of sheet to be made, and then to heat the casting pot for some hours, and pour the glass on to a table and roll it out. The ladling and heating of the intermediate pot were laborious and costly. Rough (unpolished) plate glass had come largely into use at railway stations and other buildings, made by this process of glassmaking. Thus, plate glass was beginning to have new uses in architecture, but it was too expensive to be used polished.

That being said, many improvements were made during the 19th century on plate-glass production. The tendency was to an increased demand towards the production of larger and larger sheets of polished plate glass [1.20, p. 469].

Along with the decrease of prices, the market was widening: in 1897, Henrivaux wrote that it had doubled in twenty years and that plate-glass manufacturing was no longer a luxury industry (Table 1.13).

In 1897, seven plate-glass factories worked in France, five in Belgium, six in Germany, six in England, one in Russia, one in Italy, and four in the US. In 1893, 2 400 000 m^2 of plate glass were manufactured in Europe. In 1897, the surface was 3 600 000 m^2. During this period, the US production increased from 500 000 m^2 in six factories to 1 200 000 m^2 made in 13 factories.

The time to make plate glass was diminished by a factor of two since 1765 (Table 1.14).

This evolution in price and volume was for a large part due to the introduction of new mechanical means of working to operate casting, grinding, and polishing [1.17, pp. 414–425]. The end of the 19th century saw the reign of mechanical engineers. One of them was Lucien Delloye, who, after having successfully dealt with grinding and polishing machines became the Plate-glass General Manager of Saint-Gobain and earned the consideration of all the European glassmaking community of this time through the creation of the International Plate Glass Convention [1.35].

Up to 1900, plate glass was always cooled in special kilns, but the following years saw the introduction of annealing lehrs. Movement along the lehr was obtained by means of mechanically worked rods.

Improvements in Window Glass Production

In 1872, sheet glass [1.11, p. 146] works benefited from two recent innovations: the first innovation, the Bievez lehr enabled sheets rapidly cooled by being raised successively on iron bars and so kept apart, to be annealed in twenty-five to thirty minutes as compared to seven or eight hours in the piling kilns. The other innovation was an appliance to assist glassmakers in blowing the heaviest of cylinders. It had been invented by Windle Pilkington and was patented in 1871. Four such machines were in use by the beginning of the following year [1.11, p. 446]

The major advance was the development of tank furnaces. To feed in raw materials at one end of a tank, melt them as they passed along, and then cool the molten glass to the correct consistency for working by the time it reached the other end, would allow window glass manufacture to become a continuous process. The twenty-four hour interval while the molten glass was prepared, inevitable with the existing pot furnaces, could be avoided and time, fuel, and labor saved. Therefore, sheet glassmakers were among the first (along with container glassmakers) to adopt the new Siemens tank furnace, as we saw above.

At Pilkington Brothers, the largest recorded weekly output of window glass before the introduction of tank furnaces was 350 000 ft [1.11]. The weekly average throughout the year 1877 was just over 500 000 feet (Note the expression of the surface in linear feet, making the data impossible to translate! The reader will consider only the increase in output) and throughout 1887, just over 900 000 ft. The 1 250 000 ft mark was passed in the early 1890s and, by the end of the century, production exceeded 1 600 000 ft per week.

A New Type of Glass: Hartley's Patent Rolled Plate Glass

Various molded glassware, lighthouse parts for instance, were also produced. In the Chauny factory, Saint-Gobain had been manufacturing thin plate glass by blowing, according to the *Nuremberg* process, since 1839. In 1852, the new Director, Hector Biver had previously worked in the British Plate Glass Company. He brought from England the idea of manufacturing this thin roofing glass by the new Hartley's patent rolled plate glass method instead of blowing. On October 28th 1854, the Board allowed the production of the "verre de toiture cannelé" [1.23].

The process, derived from the casting of plate glass (which has never been patented), was much simpler and cheaper than the cylinder window-glass process, giving the possibility of new applications. Besides, this production, being of a lesser quality than the plate glass, opened up the possibility of experimenting with new processes and among them new furnaces such as tank furnaces.

Hartley's invention [1.36] consisted of dispensing with the costly processes of receiving the melted *metal* into a crucible, instead ladling the *metal* directly from the pot on to the table and then rolling it out in the ordinary manner. He applied one, two, or more ladles full to make each sheet, and found that the several ladles did not need to be poured on at the same time, but may be added towards the end of the previous quantity. This was a way to produce long sheets of rough plate glass that were comparatively narrow, at a considerable saving of labor and cost; when made they were annealed by piling in the same manner as was practiced in annealing crown and sheet glass, which avoided the use of the costly furnaces employed to anneal plate glass [1.23].

The glass produced in this way was considerably thinner than standard size plate glass.

> Hartley's patent rough-plate glass has been recommended for conservatory and hothouse roofs. It was strongly recommended by Dr Lindley who said: 'this glass is prepared by rolling which destroys transparency without diminishing translucency. It is slightly rough on the surface, which has the important effect of dispersing the sun's rays instead of concentrating them. The roughness however, renders it less agreeable to the eye, and would make it objectionable for the perpendicular sides of glass houses' [1.37].

The thinness made the glass roofing much lighter.

> One of the main features of Hartley's Glass Works is the glass covering. It is glazed over its whole extent with Hartley's Patent Rough Plate, one-eighth of an inch-thick, the kind now almost universally used for conservatory and railway station roofs, and which was supplied by Mr. Hartley in the instance of the immense roof erected at the Great Western Railway Station at Paddington; the new baths at Buxton are also glazed with this same material. The size of the squares is 76 inches by 20. They amount to no less than 1560 in number (equal to 16 400 superficial feet), and yet to no more than fourteen tons in weight! — An extraordinary lightness, if we contrast it with the glass roofing of

> the Great Northern Railway Station in London, in which the plates are half an inch thick, and consequently, enormously heavier. In equal areas of roofing, the difference between the rough-plate of MM. Hartley would be that between fourteen tons and fifty-six! [1.38]

When the Crystal Palace was built for the Great Exhibition of 1851 Hartley offered to provide all the glass necessary of 1/8th inch (3.175 mm) thickness at £18 13s 4d/t. Glass of that thickness weighs 7.94 kg/m^2. The offer was not accepted because there was insufficient experience of that kind of glass: it was feared that this glass would be more fragile than blown glass and it was absolutely necessary to avoid accidents in covering with glass a building in which so many people and valuable objects were to be gathered together.

Siemens tanks furnaces were also used for making rolled plate glass and the output of rolled plate glass grew at a pace comparable with that of sheet glass, although the increase was not as regular because of an irregular market. In England there were three factories making rolled plate with Hartley's license (Pilkington's, Chance's, and Hartley's) and their combined annual production was certainly at least 2500–3000 t or 200 000–300 000 m^2. Hartley's process had also been adopted by Saint-Gobain who used the name "patterned glass" [1.19].

The Saint-Gobain Company made only one grade of this patterned glass, which was 5–6 mm thick and pieces below half a square meter sold at a net price of 6 F in half-white or 6.80 F in white glass. Sizes up to a square meter cost 6.80 F in half-white and 7.60 F in white glass. The prices fell considerably as its consumption increased.

Saint-Gobain sold patterned glass for the glasshouses in Jardin des plantes (1854), for the Halles de Paris (1855), 4500 m^2 for the Milan railway station in 1862, and 40 000 m^2 of roughly ground patterned glass for the glazing and roofing of the Palace of the permanent Exhibition in Auteuil (1862) [1.39].

Thus, by the end of the 19th century, in addition to molded glassware, two different types of plate glass were manufactured in Saint-Gobain: the usual thick plate glasses which were polished for making mirrors (two grades: No. 1, thick, and No. 3, half-thick), and the thin plate glass (No. 4) which was used without polishing for roofing (Table 1.15).

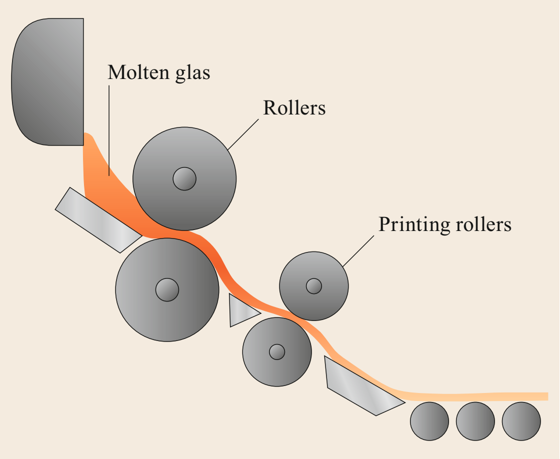

Fig. 1.12 Chance's rolled glass

Chance's Rolled Glass

In the late 1980s George and Edward Chance successfully developed a machine (Fig. 1.12), patented in 1884, whereby the molten glass was poured down an inclined plane and passed between a pair of iron rollers [1.11, p. 150]. In 1890, Edward Chance perfected the machine by adding a second pair of rollers, one of this second pair impressing a pattern when required. A further short inclined platform carried the still soft glass onto a horizontally moving table whence it was drawn at the rate at which it was pressed. The first cylinders were water-cooled, since they come into contact with the hot glass.

The manufacture of rolled plate glass became of primary importance to the Chances and the royalties from other companies, including Saint-Gobain operating under license, were considerable.

Wired Glass

One of the earliest machines [1.20] to make wired glass was due to Tenner, with Appert designing a later machine (Fig. 1.13). The casting table is mounted on a wagon running on rails and passing between two rollers upon the fixed frame. Above the first roller is a cylinder having a rough surface tapering somewhat from center to sides and provided with a brake arrangement. Above this cylinder and a little to the side of it is the roller for holding the wire net.

Before rolling is begun, wire is run over the rough surface cylinder and beneath the rollers, then finally

Table 1.15 Plate glass production in Saint Gobain (Aisne) before and after the arrival of Hector Biver

Production (m^2)	1851	1855	1856
Plate glass No. 1	25 568	98 324	88 095
Plate glass No. 3	6666	24 549	34 479
Thin glass No. 4	20 373 (hand-blown)	27 931 (thin plate)	40 579 (thin plate)

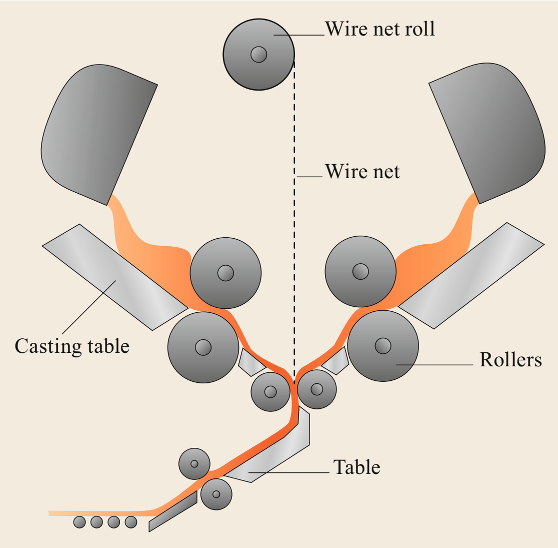

Fig. 1.13 Wired rolled glass

clamped to the end of the table at a height above the casting table equal to that at which it is desired it be embedded in the glass. Glass is now poured onto the table, which has been set beneath the roller. Then, after translation of the casting plate, a new charge of molten glass is poured upon the already rolled but still soft plate, in front of the second roller and this completes the plate by rolling out a glass layer above the wire. The two layers unite to form a single plate.

A later process was much simpler: the wire was clamped above the table at the correct height and glass poured on and rolled in the usual way. The roller forces the fluid glass through the meshes of the wire, to unite again beneath it, thus giving in one simple operation the required result.

State of Manufacturing of Flat Glass Products at the End of the 19th Century

The technical progress in processes during the second half of the nineteenth century brought about a considerable increase over the old production in plate glass but also a diversification which would allow new changes during the twentieth century. One of the most important ones was the revolution in furnaces, the transfer of at least a part of the production of flat glass to a potentially continuous process through the use of radiation-tank furnaces.

During those years, the plate glass world had completely changed. In 1878, the Duc de Broglie, in his report to the assemblée générale of Saint-Gobain, spoke about the complete transformation of the plate glass industry which has

> left behind its Gold Age of the 1860s: our company, that of Oignies and Floreffe in Belgium, that of Aniche in France, and the English companies, shared the world market and lived in good intelligence; they prudently harmonized their production means with the consumer needs and wisely developed. [1.39]

The reasons for this change were numerous: the new American plate-glass makers were making one third of the global production in 1870. Several new companies had appeared in Belgium: Auvelais (1876), Moustiers (1883), Saint-Roch (1889), and Charleroi (1890). The new plate glass factories created in Belgium and in the United States did not conform to the previous European agreements: the combination of larger and larger production with higher and higher importation taxes, strongly cut down the exportations to the US, causing a disorder which had proved fatal to the plate-glass makers in England, leaving only Pilkington Brothers among the previous plate-glass companies.

In France, new players had appeared beside Saint-Gobain: Aniche, Maubeuge (Pilkington 1891), and Boussois (Charleroi 1899). In Germany, the Glas und Spiegel Manufaktur (1872), Herzogenrath (1877), and Altwasser (1872) factories were created.

In 1870, the global production was 1 100 000 m^2 plate glass (26% in Saint-Gobain factories). In 1913, it was 13 500 000 m^2 (17% Saint-Gobain with 30% in France).

As a consequence of those major technical improvements but also of the increased competition on the market, the price of plate glass and other types of glasses had significantly decreased during this period: 54 $\mathrm{F/m}^2$ in 1855, 33 $\mathrm{F/m}^2$ in 1865, and 14 $\mathrm{F/m}^2$ in 1895.

1.5.5 Container Glass Making at the End of the 19th Century

At the end of the 19th century, bottles were still hand made but their fabrication had been largely improved since the early days.

Use of the Siemens Tank Furnace

One of the major improvements was the use of the Siemens end-port tank furnace (Fig. 1.14) that allowed continuous work and thus a much larger output than with the old pot furnaces. On the side of the furnace were the working holes, just above the glass level. A secondary wall situated on the outside of the furnace wall somewhat protected the workers from the heat radiated by the furnace thanks to the air space between it

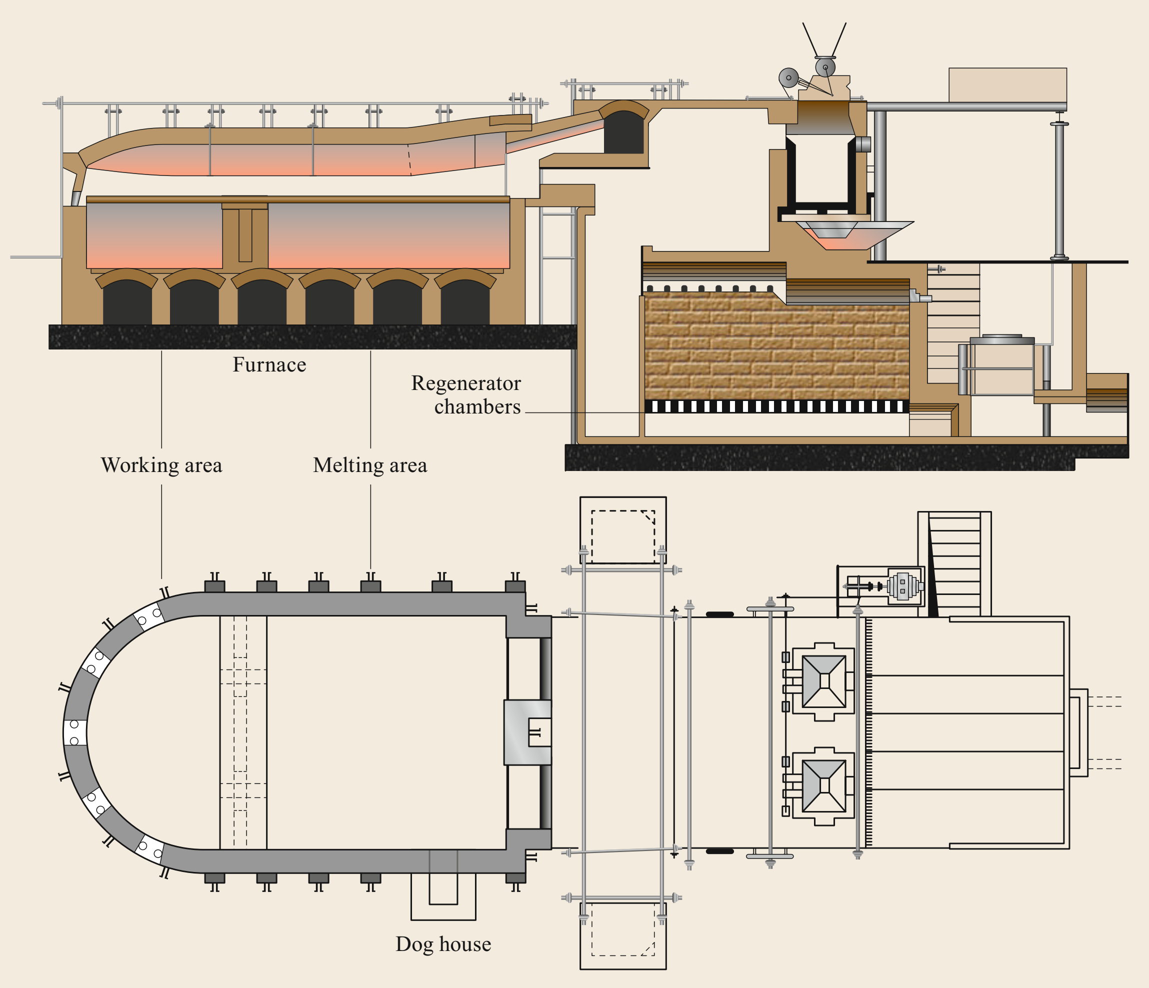

Fig. 1.14 End-port (horse-shoe) tank furnace, (*Top*) side view, (*bottom*) plan view (after [1.20])

and the furnace itself. An opening in this wall gave the men access to the molten glass.

Inside the furnace and immediately in front of the working hole was a ring, made of fire-clay, floating on the melt and preventing the gathering of surface scum.

The gatherer used his previously slightly heated blowpipe to collect the desired amount of glass from the tank and after examination for the presence of drops, blisters, or stones from the furnace, the blower took the pipe from the gatherer and proceeded to roll the glass upon the marver while rotating the pipe. Then he applied his lips to the end of the pipe and, by blowing, distended the gathering into a hollow globe known as the *parison*.

The bottom of the parison was flattened on a plate, its neck rolled to the desired diameter and the parison was adjusted by holding the pipe vertical and allowing the glass to lengthen by virtue of its own weight. The parison was then blown to shape in the mold.

After blowing had been continued for a sufficient length of time to allow the bottle to become set enough, the bottle was removed from the mold and separated from the pipe by a slight thermal shock. It was taken by means of the punty (in the form of a split cylinder of iron fixed upon the end of an iron rod) with the diameter of the cylinder being such as to allow it to gently grip the bottle.

Then, the finisher gathered a little glass on a small iron rod and ran it evenly around the rim of the bottle neck, and pressed it with tongs on the bottle neck rim while revolving the punty to mold the thread of glass to form a collar on the neck-ring of the bottle. The finished bottle was then taken to the lehr.

Bottle-Making by Machine

In 1886 Ashley, of Castleford in England, thought that much of the preliminary work in shaping parisons for mold-blown bottles might be mechanically performed.

He introduced a first mold, the parison mold, to replace the first blowing step. A further improvement was the use of compressed air for blowing up the bottle in the finishing or "blow" mold. Finally, the machine worked with three molds, the parison (or blank) mold, the mold for the neck-ring of the bottle, and finally the finishing or blow mold. The parison was made in three steps: the glass was introduced into a parison mold equipped with the neck-ring mold, upside down, the neck of the bottle being down. Air was introduced to press the glass inside the neck-ring mold. The system was then returned so that the neck-ring mold would be situated under the compressed air admittance, and another air injection pierced the neck and formed the hollow parison. Then the mold opened and the parison was transferred to the finishing mold to be blown into a bottle. This machine was soon adopted in England.

In France, in 1894, Claude Boucher also designed a manual compressed air machine, capable of replacing the glassblower in all of the operation except the gathering of the molten glass in the furnace [1.40]. The invention was improved until 1898, when it appeared that its use required a much simplified training for the glassworkers (a few months instead of 10 years) to be able to produce glass bottles with a much better output (2.5 times), even better than the Ashley machine (2 times) thanks to the presence of two alternating parison molds. While one was filled, the other one could shape the parison. As soon as the parison was finished in the second mold and transferred into the finishing mold, the system was inversed to blow the glass already injected in the first mold.

This machine was the cause for a strong disquiet among the glass blowers. Nevertheless, the first mechanically created bottles were made and sold in 1898. In 1906, 108 machines were currently working in most factories (except Champagne bottles makers!). Claude Boucher received a prize from the Académie des Sciences in 1902.

1.6 The Revolutions of the Twentieth Century

Rationalization, also as a result of the reduced available workforce after World War I, led to the development of new techniques and processes.

1.6.1 Mechanization Mainly After the First World War

The beginning of the 20th century was important for the development of mechanization of glass manufacturing in all branches of the activity, except for plate glass (which will come later, at the end of the 1920s). Industrial developments could not keep up with the rate technical progresses were made: not only did it mean a drastic change in factory organization, which did not please the very specialized glassworkers, but also because it needed rather heavy capital investments and the beginning of the century was not very bright from the economical point of view in Europe. This was for a large part due to the fast development of the glass industry in America. Because of the American glass industry, and because of the high taxes imposed by the American government on glass imports, the traditional export market of European companies evaporated within a few years, and the crisis lasted until they organized the market between them via two (at least) International conventions, one for special glass and one for plate glass [1.35]. They had considerably improved their results when the War was declared.

In 1918, when the war ended, the needs of the market for glass were huge and factories had to produce again as rapidly as possible. Thousands of glassworkers had disappeared during the war and many of the factories, especially the continental ones, had to a large part been destroyed. They were reconstructed with integration of mechanical processes that had mostly been designed before the war.

1.6.2 Window Glass

The increased demand for flat glass in buildings and the more economic processes to prepare it went hand in hand.

Drawn Cylinder Process, an Improvement but not a Breakthrough

The beginning of the 20th century was to see considerable changes in the fabrication of sheet/window glass. One of the most spectacular inventions was the drawn cylinder process, invented by John H. Lubbers in the early 1890s with financing from the American Window Glass Company. It began with the introduction of a mechanical, but not continuous process [1.11, p. 192]. A large pipe was dipped into molten glass in a specially constructed pot that was filled with sufficient glass to make a single cylinder. As it was slowly raised, it drew up the glass with it. Compressed air, passed through the blowpipe, was blown at such a rate as would maintain the diameter constant. This way a cylinder of 10 m in length and 0.70 m in diameter could be drawn. Afterward, the giant cylinders had to be cut into smaller lengths, flattened in the usual way, and annealed.

Around 1905, Windle Pilkington went to America to see the cylinder process and returned with the opinion that the glass produced was not yet of sufficient quality for the British market. In 1908, Pilkington Brothers decided to consider a proposition from American Window Glass Company and an agreement was signed in April 1909.

An experimental machine was set up at the end of the same year and commercial machines in May 1910 and April 1912. The quality was poor and could not replace the hand-blown glass process. "The machines make poor glass, but they make so much more glass that they can pick out a great deal of good glass and sort it very carefully." [1.11]

In 1910, Lucien Delloye, General Manager of Glass in Saint-Gobain decided to buy the process from American Window Glass and the first machine was set up in the Aniche factory between 1911 and 1912 with an 8-machine tank furnace. The second factory was established in Chalon-sur-Saône in 1914 for the market in the south of France, and two others in Bilin (Germany) in 1911, in Rome in 1911–1912, and in Spain. Except in Italy, the process could not compete with hand-made sheet glass blowing. The Aniche factory was destroyed during the First World War and in the end, sheet glass was made by the old hand-blowing process until the end of the 1920s [1.39, p. 426]. The process was exploited only in Chalon with poor economical results. It was the same for Pilkington's factory in Canada.

In Saint Gobain, and even in Italy, the hand-blowing process was replaced by another method (Fourcault process) around 1926–1927, which directly draws sheets of glass. Nevertheless, *Damour* reports in 1936 [1.41] that, in America, the Window Glass Company was still making sheet glass with this method and actually obtained sheets of quite a good quality.

Direct Drawing of Glass Sheets

The previous methods to make sheet glass are not only labor-intensive but also gave a product liable to have many defects, while the size of the sheets is also limited. Therefore, it was natural that the idea of producing glass by machinery in longer lengths than could be obtained by hand working should have been conceived. The initial idea was simple, and was patented in 1857 by William Clark of Pittsburgh [1.20, p. 458]: it was to dip a *bait* into the molten glass to which the glass would attach itself, and gradually withdraw this from the molten glass. The method had one major defect, which could not be overcome for half a century: when a sheet of glass is so drawn, the second stratum is somewhat shorter than the first, the third less still, and so on, so that, instead of a parallel-sided sheet, the two bounding edges approach each other and a triangular sheet is obtained. To solve the problem several workers tried the method of drawing the sheet downwards, allowing the glass to flow through a slit of suitable size. The same difficulty occurred: the sheet becoming heavier, the weight drew thinner the portion that was not yet set and rupture finally occurred.

Fourcault Method. E. Fourcault obtained the first success at the Dampremy glassworks in Belgium in 1903: his method consisted in drawing the sheets vertically from a tank of molten glass (Fig. 1.15). Overcoming of the surface tension of the sheet by gravitational pull caused a narrowing of the sheet of glass. If the liquid were given an upward velocity at the drawing point counteracting the gravitational tendency, the uniform width of the sheet would be maintained. To produce this upward movement, Fourcault used a *float*, a long trough of refractory material having, along its base, a slit parallel to the length of the trough. In the process, the trough was caused to sink somewhat in the glass at a definite depth of penetration. Molten glass was therefore forced through the slit at the desired rate. The glass was seized as it emerged from the opening by means of a bait and drawn off in sheet form, which remained uniformly of the same size as the slit. Two water-cooled tubes against the sides of the slit chilled the glass when it emerged.

Above the troughs were placed the drawing machines, sort of rectangular towers four meters high, through which passed a framework with a series of rollers set in pairs. Their rotation served to draw the sheet as it is formed. The rate of working was 30 m/h for glass that was 2 mm thick. Sheets of glass made by this method are 1—1.25 m wide. The slow, even, cooling with no contact with chilling materials gives a glass free from strain which can be cut without trouble.

Several machines could be placed around the end of a tank furnace. In 1912, the S.A. des Verreries de Dampremy began the production of sheet glass with eight machines. The production improved but the glassmakers adopted this process for sheet glass only, due to the numerous defects caused by contacts with the refractories of the trough. In France, in 1928–1929, sheet glass was produced mainly with this process; hand blowing had definitely been abandoned.

The process was still in use after the float glass process had revolutionized the production of flat glass, until the patent expired, especially in Eastern Europe.

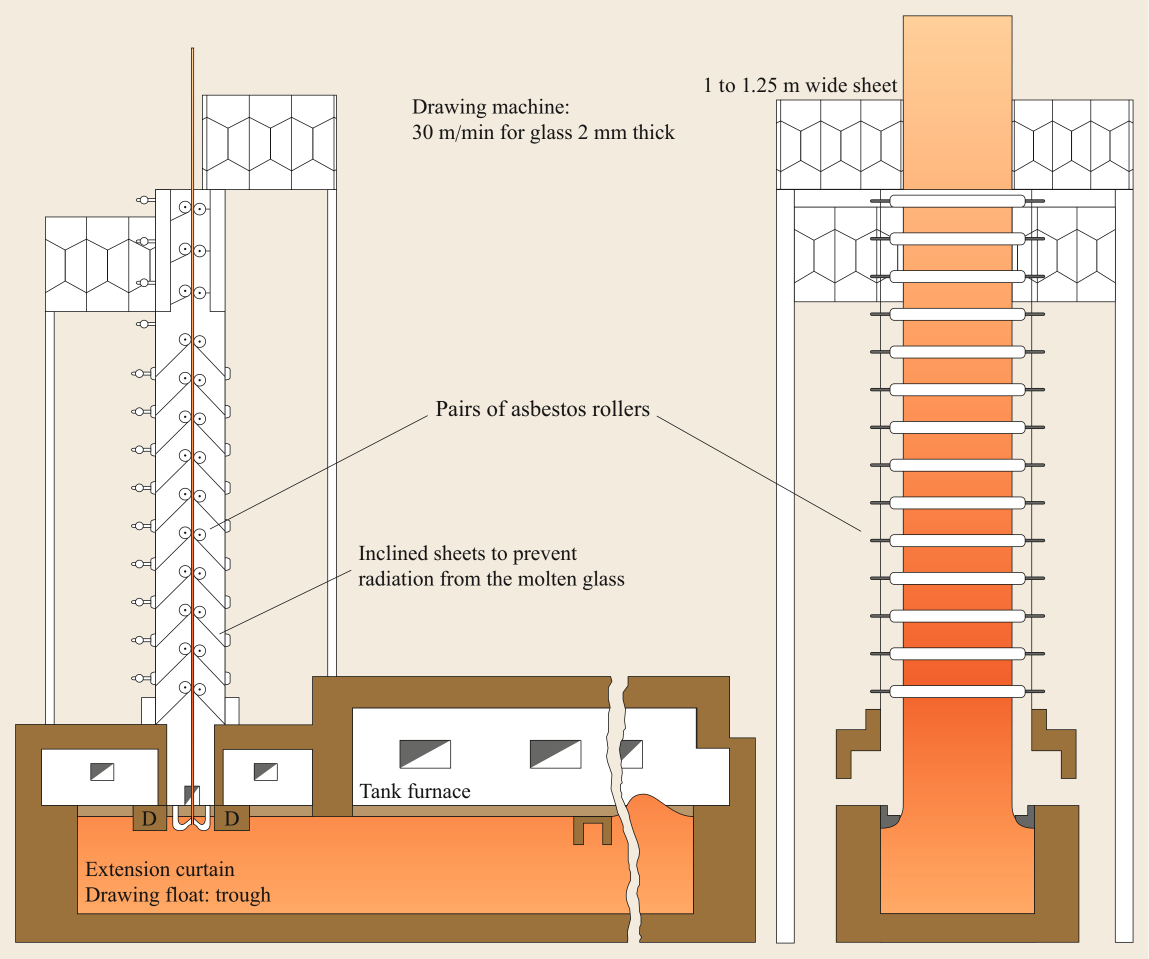

Fig. 1.15 Fourcault method (after [1.20])

Colburn Process. I.W. Colburn began his researches in 1900 but Libbey & Owens who acquired his patent rights developed his process and they perfected the machine at their works in Toledo (Fig. 1.16). Several improvements in the method of keeping the width of the glass sheet were tried and the last one was to set a pair of water-cooled, channeled rollers placed at each end of the sheet just above the level of the molten glass in the pot. These rollers gripped the edges of the sheet as it was drawn and so maintained the width.

When the sheet had risen vertically to a height of 1 m, it was softened by gas jets and turned over rollers until it lay horizontally, after which it passed through an annealing lehr.

The bending roller must be cooled as it came into contact with the glass, or else deterioration would have ensued. The marking of the glass by this bending roller constituted one of the difficulties of the method, but in 1915, a factory of the new Libbey Owens Sheet Glass Company was using this process. It was quite successful in Europe and competed with the Fourcault process, promoted by Saint-Gobain for sheet glass.

Pittsburgh Process. This process was developed [1.11, p. 207] during the 1920s by the Pittsburgh Plate Glass (PPG) Company, already the giant of the American plate glass industry before 1914, but not at that point particularly interested in sheet glass manufacture. The process differed from those of Fourcault and Colburn in an essential feature: the method of drawing the ribbon of glass from the tank. But it was like the Fourcault machine in that it had a vertical lehr, thus being economical in the use of ground space.

In this process, like in the Libbey–Owens (Colburn) process, the sheet of glass was drawn from the molten glass without any contact with another surface and it gave a sheet with a very bright fire-polished surface. In order to do that, the process

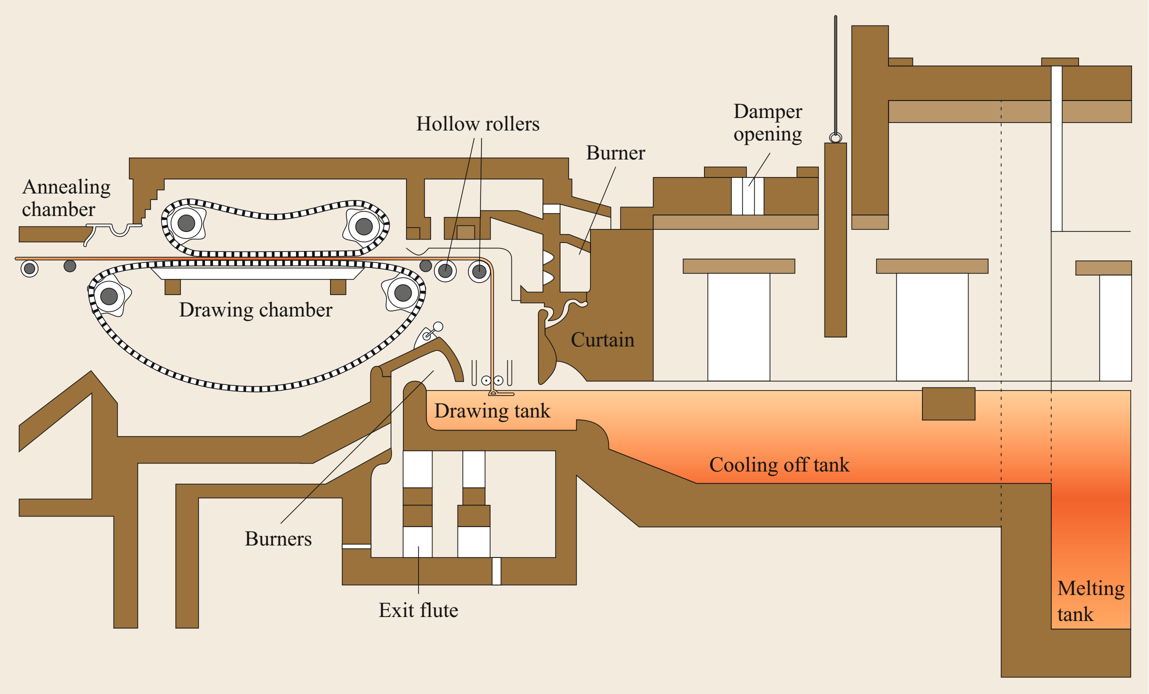

Fig. 1.16 Sheet-drawing: Libbey–Owens (Colburn) process (after [1.20])

used a refractory device immersed in the molten glass roughly 8 cm under the surface. It protected the drawn glass against radiation from the melt and kept its viscosity constant. The width of the glass ribbon was maintained by a pair of rollers placed on each end of the sheet similarly to the Libbey–Owens process. The sheet of glass then rose in the same kind of rectangular tower as in the Fourcault process and was progressively cooled down until it was cut.

This process was perceived as interesting but Saint-Gobain perfectly understood that its implementation was more complicated than that of the Fourcault process and needed a real team of engineers to ensure a smooth start of this process in plants [1.39, p. 430]. An agreement was signed with PPG in May 1929. A new company was created to deal with the patents, bringing together Saint-Gobain, PPG, Saint-Roch, and Boussois. An operational team of five engineers was commissioned from Saint-Gobain to make the connection between the European and American factories, and to install and improve the process. Even Pilkington Brothers used the services of this organization when they decided to use the PPG process in Britain. The first experimental attempts to draw glass at St. Helens were made in March 1930; and as early as April 1931 Austin Pilkington could describe the PPG machine as "really a winner" [1.33]. In the following November the first four machines went into commercial operation and the drawn cylinder process was then rapidly abandoned at Pilkington Brothers.

The Pittsburgh process turned out to be the most profitable window glass process for years, until the float glass process appeared in the 1960s.

1.6.3 Plate Glass

In 1919, most plate glass factories were equipped with the same installations as they had been at the end of the 19th century: melting of glass in pots containing around 2.5 t of glass in regenerative gas furnaces, casting and annealing in static furnaces (*carcaises*). In a few Saint-Gobain factories (Franière in Belgium or Pisa in Italy) a tunnel furnace had been introduced where plate glass passed through decreasing temperature zones, from 650–550 °C, the annealing being performed in space instead of time. Thence, the casting table (10 m × 5 m) could be fixed and reinforced, which was much more favorable in terms of product quality.

Bicheroux Process

Between 1910 and 1914, trials were made by Bicheroux, in Herzogenrath (Germany), a factory that Saint-Gobain had bought in 1905. This process (Fig. 1.17), derived from the Chance process, consisted in casting the molten glass contained in its pot after extraction

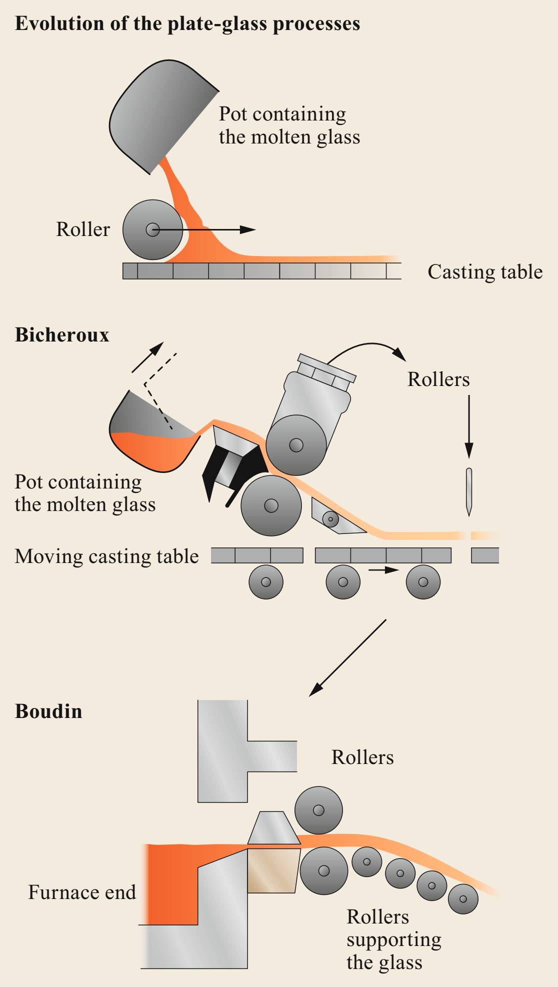

Fig. 1.17 Plate glass: Evolution of the process

from the furnace between two cast iron rollers on a moving table. This approach gave two nearly parallel sides so that less material had to be removed before polishing (less than 2 mm instead of 3.5 mm with the classical process). It was generalized in the 1920s in most plate-glass works in Saint-Gobain and in other companies. The license was sold to all European and American plate-glass makers in the framework of the Plate-glass International Convention, during the interwar years.

Boudin Process

This was derived from a combination of the Bicheroux process and the continuous tank furnace: hot glass was directly introduced into the machine from the end of the furnace (Fig. 1.17). The use of the tank furnace in plate-glass production came about 50 years after that of sheet glass because the refractories used in tank furnaces were very rapidly damaged and stones appeared in the glass sheet [1.39, p. 399]. It was easy to replace a pot (after 15–20 castings) but not the whole furnace. The tank furnace began to be used for plate glass after the development of new refractories in 1925–1930, the electrocast refractories. Saint-Gobain, Saint-Roch, and Corning wanted to manufacture electrocast refractories in Europe and created the Société Française de l'Electro-Réfractaire in 1928. The first factory was settled in Modane where Saint-Gobain already worked a hydroelectric plant and a chemical products factory.

In 1932, Boudin set his first machine in Chantereine (near Compiègne), the model plate glass works of Saint-Gobain. Despite the fact that, when the glass is still hot, it subsides between two rollers, the continuous sheet is at least as good as that obtained by the Bicheroux process. This process is still used at present to manufacture printed glass.

Continuous Grinding and Polishing of Plate Glass

At the Cowley Hill factory of Pilkington Brothers, a continuous grinding and polishing system was being developed [1.11, p. 204]. A continuous sequence of cast iron tables carried the rectangular plates of glass under a series of grinding heads with subsequent polishing under the same continuous line. One side of the glass was dealt with at a time. The first experimental model was running at the beginning of 1920, but much development lay ahead; it was not until May 1923 that this machine finally went into service. This gave Pilkington Brothers an international advantage in plate glass manufacture by the middle of the 1920s.

Lucien Delloye visited the installation in April 1923. An agreement (January 1924) was negotiated between the Plate Glass International Convention, Pilkington, and Heuze-Malevez-Simon, one of the developers of the technique together with Pilkington, the content of which was that the only licensees on the European continent would be the members of the Plate Glass International Convention. The first continental installation occurred in Herzogenrath, a Saint-Gobain factory in Germany, and improved in the years 1927–1929. Full-size machines were then settled in Franière (1932) and Chantereine (1935). Only three other factories outside of Saint-Gobain ever used this set up: Boussois, Auvelais, and Moustiers.

What was further needed was a machine that could grind and polish the ribbon of glass on both sides simultaneously as it emerged from the lehr and before it was cut into plates. Twin grinding was finally developed in the early 1930s and came into service in 1935 at the Doncaster works and in Cowley Hill in 1937.

The twin grinder first ran at 1 m/min but it was later improved until the ribbon of glass passed through it at the rate of 5 m/min. It came to be used by all the main manufacturers in the world for the greater part of their plate-glass production.

In 1937, Saint-Gobain and Pilkington negotiated directly and, from this date to 1950, the former was the only licensee for the twin grinder.

The polishing step was still performed as before until Saint-Gobain invented a complementary polishing machine, the Jusant at the end of the 1950s, which allowed working the glass ribbon emerging from the furnace in a continuous way: it came too late and was soon replaced by the float glass process.

Automotive Glass and Safety Glass

During the 1920s the growing motor industry provided a new market for glass. At first the few open cars required only a small amount of plate glass (never sheet glass which was not of a sufficient optical quality) for their windscreens. But, as the number of cars multiplied and the closed saloon became more popular, much larger quantities of glass were bought by the car manufacturers and eventually sales of plate glass to them exceeded those for building. Moreover, the car industry began to require safety glass, first laminated and then toughened. The fitting of safety glass in windscreens of British cars became compulsory from the beginning of 1932.

The research team in the Saint-Gobain laboratory searched for a process to improve the flatness and polish of the plate of glass. The idea was to homogeneously reheat the previously cut up plate hung in an electrical furnace at 680 °C (the softening point), and cool it down symmetrically with controlled compressed air streams. Together with Boussois for Securit glass, they took patents that were exploited in the whole world. In September–October 1930, Pilkington became a licensee. In the US, Saint-Gobain and Boussois created American Securit with Corning in 1933 (to bring an American-like air to the society) and important agreements were concluded with the two American plate-glass giants PPG and LOF (Libby–Owens–Ford).

Another type of safety glass was the Triplex glass, a sandwich of a plastic foil between two glass plates [1.39, p. 411]. The inventor, Edouard Benedictus, started in 1909 the Société du Verre Triplex and Delpech the English Triplex Company. This society was profitable thanks to war supplies, and developed during the 1920s. Pilkington bought shares in the society in 1925. After having tried to launch a new fabrication of Triplex glass in the Cirey factory, Saint-Gobain decided to enter the small Société du Verre Triplex, as well as Boussois, Aniche, and the Société Franco-Belge pour la Fabrication Mécanique du Verre (Libbey–Owens process), members of the association of various French plate glassmakers: this was in agreement with the general political principles of Saint-Gobain at that time.

The glassmaker's society was completely reorganized. A new factory was built in Longjumeau, near Paris, in order to be closer to the car manufacturers: for instance, in 1928, Citroën bought 600 m^2/day. Various modifications were made and new patents taken, which much improved the quality. It is interesting to note that, contrary to Securit glass, the Triplex plates could be cut according to any dimensions the customer wanted.

Pilkington Brothers, by failing to acquire the Triplex Safety Glass Company Ltd. when that processing company was still a small concern, lost an opportunity to control the supply of glass to their most promising market. Nevertheless, Triplex soon became Pilkington's largest customer and, in 1929, the two companies joined forces to create a subsidiary under the name of Triplex (Northern) Ltd. In 1955, Pilkington surrendered control of this subsidiary in return for a greater interest in Triplex itself.

1.6.4 Float Glass

A discontinuous process of casting-made plate glass, followed by grinding and finally polishing on the same discs. Glass manufacturers had long looked forward to the day when they could flow a ribbon of glass from a tank. Experiments at the Ford Motors Company in Detroit did not succeed in the 1920s because of the poor glass quality coming from the tank furnace. The problem began to attract the attention of a newcomer to the Pilkington Company, Alastair Pilkington, a member of a branch of the family that had not previously been connected with the glass industry [1.11, p. 208]. He joined Pilkington in 1947 after completing a Mechanical Science degree in Cambridge, and, in 1950, took charge of production at one of the plate-glass factories. In October 1952, he began to explore the possibility of using liquid metal as a means of supporting the uneven and rough ribbon of glass that emerged from the rollers. In his own words:

> the basic idea is a continuous ribbon of glass moving out of the melting furnace and floating along the surface of molten metal at a strictly controlled temperature. Because the glass has never touched anything while it is soft except a liquid, the surface is unspoiled, it is the natural surface which molten glass forms for itself when it is cooled from liquid to solid. Because the surface of the metal is dead flat, the glass is dead flat too. Natural forces

> of weight and surface tension bring it to an absolute thickness. [1.11, p. 208]

In March 1953, it was proved that the glass could be fire-finished by floating on liquid metal. Could a glass of good quality be produced? A new plant was built early in 1954 to produce a 40 cm ribbon but, although the surface was considerably better than that of the pilot run, it was still far from perfect. Nevertheless, in September 1954, it was agreed to design and build a plant capable of making a ribbon 80 cm wide, with promising results. In April 1955, the Pilkington Board decided to take the decisive step and build a full-scale production unit to make float glass 2.30 m wide. It was started up at Cowley Hill in April 1957, but difficulties of formidable proportion appeared, which needed more than a year of struggle to be solved, with the big continuous plant swallowing vast sums of money all the time.

Finally, the first good float glass was at last made in July 1958. This early output went to Triplex, Pilkington's largest single customer, who agreed to use it in the manufacture of their safety glass. Despite this success, in January 1959, Sir Harry Pilkington stressed that they had not seen the best float glass, nor the cheapest. Years of development still lay ahead before the full commercial advantages of the new product could be fully realized. Between 1952 and the end of 1958, Pilkington had spent over four million pounds on the development of the float process.

1.6.5 Container Glass

Until the end of the 19th century container glass was still mainly hand-made. Glass blowing was a source of illnesses for the workers, but also opposed evolution. The end of World War I—with many factories destroyed and a significantly reduced workforce—gave rise to the design of more rationalized and automatic manufacturing.

The First Automatic Machines

Several types of machines were used until the last evolution around the middle of the 20th century.

Press and Blow Machines. Press and blow machines were the first and the easiest machines to set up: molten glass was gathered and dropped into the parison mold, the neck-ring mold was placed on this mold and the plunger was entered into the molten glass forcing it into the shape of the mold and also up into the neck-ring mold where it was chilled and able to keep its shape [1.20, p. 412]. The plunger was removed and the neck-ring mold plus the parison (blank) lifted from the mold and transferred in one of the finishing molds. The blowing head was put into position and the bottle was blown to shape, removed from the molds, and annealed. Narrow-neck bottles could not be made by this method.

Narrow-Neck Bottle Machines. The general solution was to invert the parison mold, the neck-ring mold and the plunger being placed at the bottom. Glass was dropped in at the top as before, the requisite quantity being cut off with the shears, plugged to shape the neck-ring, given a preliminary blow to form the parison (blank), and then transferred to the blow mold.

Multiple-mold Machines. Desire for an increased rate of production led manufacturers to design machines with several sets of parison and blowing molds. Two turntables were generally used, one set with the parison molds, the second the blow molds and these were rotated mechanically. As each mold approached the gatherer it received its quota of glass, after which the blank was formed. Further rotation brought it into juxtaposition with one of the blow molds, when a boy seized the ring-mold, and the parison was rapidly transferred from one mold to the other. Rotation of the blow mold table brought the parison under a blowhead timed to descend at the correct moment and blow the bottle. On passing further stages in its journey, the mold was opened and the bottle removed. Three people, one to gather, one to transfer, and one to remove could keep a number of molds working without undue effort.

Machines with Automatic Transfer and Take-out Devices

A further improvement in bottle machines of the multiple mold type was a device for the transfer of the blank to the blow mold, and an apparatus for removing the finished bottle from the blow mold [1.20]. A number of these machines were invented, for instance, the Hartford-Fairmont, Lynch, and O'Neill machines to cite the best known among them. The Hartford-Fairmont was designed for wide-neck bottles and the parison molds were placed neck uppermost and did not invert. The other ones were designed for either narrow- or wide-mouth ware and glass was fed into an inverted parison mold. Those machines were designed to reinvert the parison mold between filling the glass and delivering the blank to the blow mold.

The O'Neill Machine. This machine was comprised of two circular tables, each equipped with six molds (Fig. 1.18). Glass gathered was dropped into the mold through a pouring ring. When sufficient glass had been run in, a trigger was touched and this set in operation

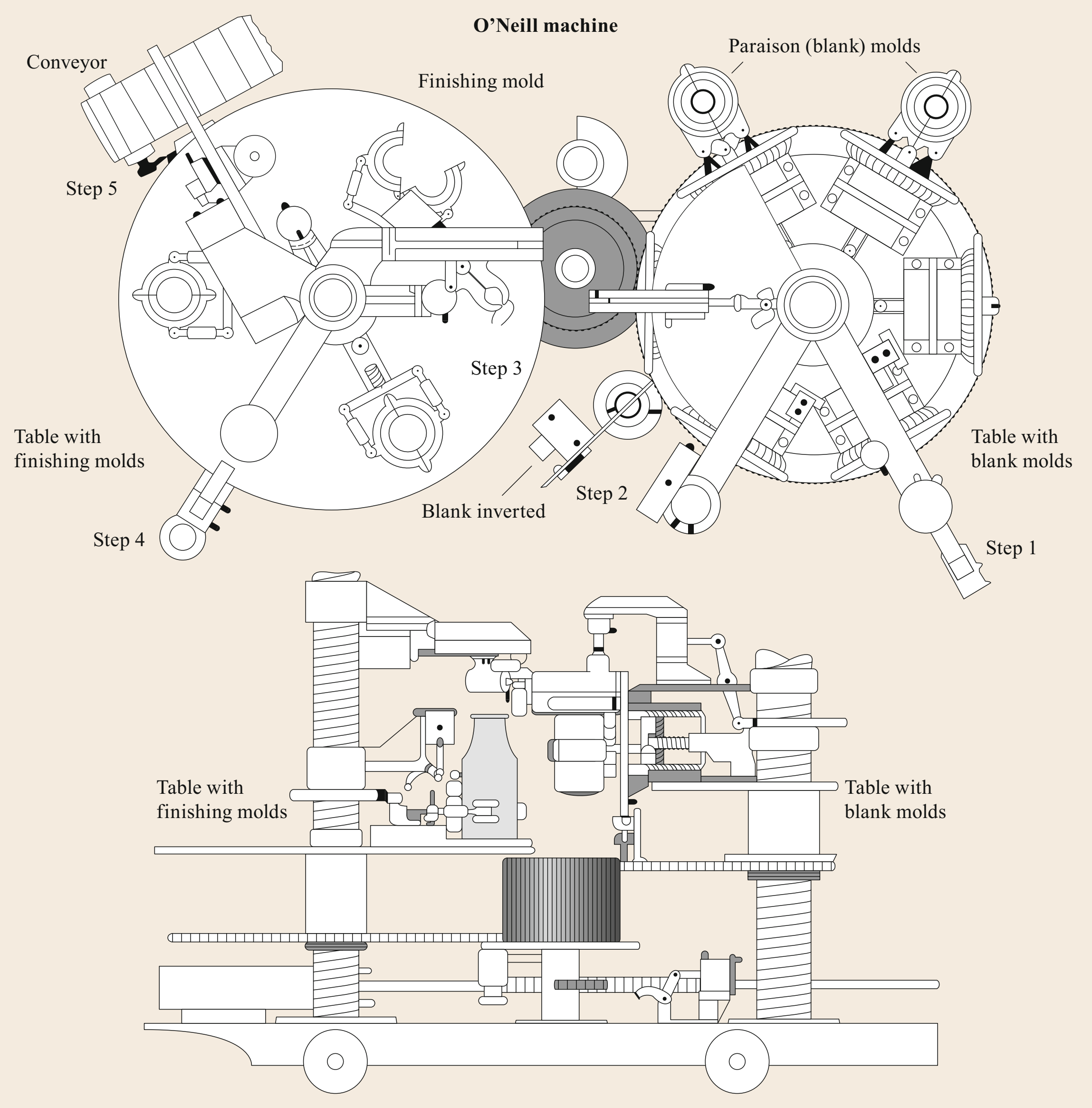

Fig. 1.18 O'Neill bottle machine

the shears that cut off the glass. The parison mold was in an inverted position and as shears opened, a head was forced down upon the pouring ring, a valve was opened and compressed air blew the glass down around the plunger situated below in the neck of the mold. The head rose and the plunger pulled out of the neck, when the mold advanced to the second position. At this point a solid head was pressed down upon the mold to close the opening and air was admitted from below, thus blowing the glass into the shape of the mold. The head rose and the mold advanced into position three, rotating as it moved, until the charge had been inverted. In this position the mold opened, leaving the blank suspended by the ring-mold: it moved across until it was in position over the corresponding blow mold set on the second rotating table. This blow mold closed over the blank and, as it did so, the ring mold opened and freed the glass entirely from contact with the first table.

In the next position of the blow mold, compressed air was released and the bottle was blown. At next-to-last position, the finishing mold was opened and a pair of automatic pincers seized the bottle at the same instant, carried it from the table, and placed it on a suitable conveyor, whence it was transferred to the lehr.

Lynch Machine. The Lynch machine was introduced in 1928 in Cognac. In this machine (Fig. 1.19), the ring-mold opened independently of the rest of the parison mold and served to sustain the blank during the transfer from the parison mold to the blow mold. Like in the O'Neill machine, the inversion of the parison took place during the process. The Lynch machine was, in the beginning, 1.5 times faster than the O'Neill. It received many improvements until it was *dethroned* by the Hartford IS (Individual Section) machine.

Completely Automatic Machines. Patents addressing this problem were numerous in the beginning of the 20th century. There were two *schools*, one thinking that it was easier to feed the molds with very hot glass, which had just to flow or be sucked from the furnace, and the other one estimating that it would be better to cool down the glass sufficiently to be able to form a kind of parison which could be sheared and introduced into the mold.

In both systems, a subsidiary compartment was then added to the working end of the furnace to stabilize the temperature of the glass corresponding to the subsequent process [1.20, p. 426].

Problems Due to the Chemical Composition of the Bottle Glass. At first it was easier and more economical to supply the molten glass to the machines by hand because the conditions for an automatic gathering were numerous and not at all met by the glass process.

The source of molten glass had to be constant and steady, with an invariable surface level and, more important, the glass must not devitrify under the condition of working. This last point was not at all fulfilled by the type of chemical composition used for bottle glass at the beginning of the 20th century.

We saw that container glassmakers obtained a mixture of sodium chloride and sodium sulfate as a flux to be mixed with the sand in the beginning of the 19th century. Except possibly in very few markets (Champagne for instance), glass bottles had to be cheap to be attractive to customers. Therefore the flux, which was the most expensive element of the batch, was limited as much as possible. This trend was enhanced by the development of Siemens regenerative tank furnaces, which presented an increased melting efficiency compared to the traditional furnaces.

At the end of the 19th century, the chemical compositions of container glasses were quite peculiar [1.17, 42] for French container glasses (Table 1.16).

The compositions were very rich in alkaline-earth oxide and were therefore quite easy to melt: the very fluid glass was easily homogenized. The problem was that devitrification (tendency to crystallize) occurs most readily in glasses containing the largest proportion of alkaline-earth oxides. Bontemps observed that:

> if ones examines the glass remaining in the bottom of pots used for bottle glass, when they have been removed from the furnace, it is seen that this glass is completely devitrified and very like coarse pottery ... All bottle glasses are to some degree subject to this defect and it can only be prevented by keeping the furnace at a sufficiently high temperature and completing working out as quickly as possible. [1.19, p. 149]

Therefore, this type of composition was not compatible with the use of tank furnaces and inclusion in an automatic process, where devitrified glass could not be eliminated from the installation, as was possible with the use of pots.

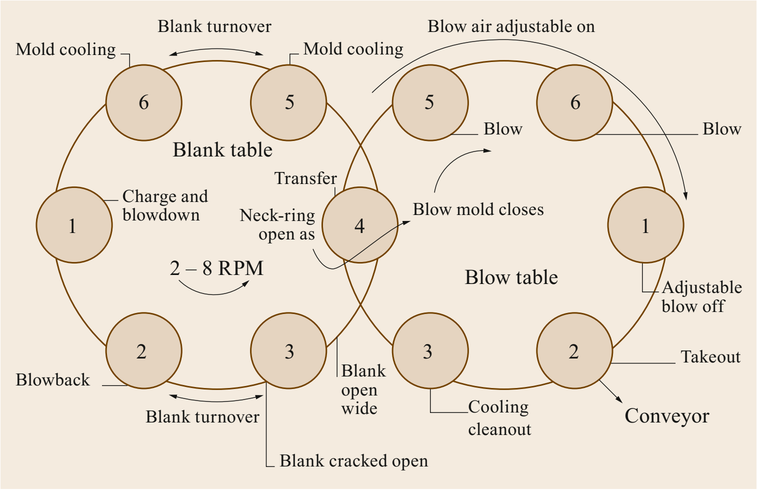

Fig. 1.19 Lynch bottle machine (plan)

Table 1.16 Chemical compositions of bottle glass at the end of the 19th century before and after mechanization

In (wt%)	*Clear* glass Cognac 1897	Champagne < 1897	Vauxrot < 1897	Fourmies < 1897	Cognac 1899	Lynch machine 1929 Damour 1929
Silica	62.5	61.9	59.7	62.5	69.5	70
Alumina	4.4	4.4	2.4	2.9	2	3
Iron oxide	1.3	1.8	2.2	2.2	1	2
Lime	20.5	18.0	21.4	21.3	16	13.5
Magnesia	5.4	6.4	8.0	4.0		
Sodium oxide	4.7	6.2	6.1	6.8	10.5	11.5
Potassium oxide	0.9	1.1	0	0.5		

Data from *Henrivaux*, in a later book (1904), shows that the composition had a much higher content in alkaline oxide than before (Table 14 in that book, later compositions): the ratio between alkaline-earth and alkaline oxides had been reduced and the behavior of the glass was certainly much improved and made compatible with the modern processes [1.43]. In fact, during the 20th century, the composition of bottle glass progressively got in line with the soda-lime silica glass used by tableware or flat glass productions.

Fluid Glass Feeding Devices. In the bottom of this compartment a hole was provided through which glass flowing from the tank could run in a stream into the parison molds, which passed below (on the rotating machines). One of the difficulties was to hold up the stream of glass during the period of substitution of a full mold to an empty one. Another problem came from the coiling of the stream of glass, giving charges not very suitable for entering the mold, and presenting a tendency for the formation of bubbles.

The Homer Brooke Feeder. The Homer Brooke feeder was of this very earliest type: a continuous stream of molten glass issues from the orifice below which is the table supporting the parison molds. A cup was introduced between the stream of glass and the molds to collect the glass and in time it turned over and delivered the molten glass into the parison mold.

A Suction Feeder, the Owens Bottle Machine (1903). This machine operated adjacent to an auxiliary furnace, and consisted of a revolving pot with a combustion chamber of 3 m in diameter and 20 cm deep, this being supplied continuously from the tank. A portion of the revolving pot projected beyond the walls of the combustion chamber, exposing a segment of the glass surface. The gathering molds of the machine dipped into this exposed molten glass consecutively as the machine rotated, and as each mold dipped into the glass a vacuum was automatically created in the mold, sucking the glass up to it and thereby forming the parison. As the mold rose up and moved away from the glass a knife automatically cut off the string of glass that remained attached, dropping that portion back into the furnace.

This machine was one of the first automatic machines after the Ashley and Boucher semiautomatic ones. It did not meet with great success in France, considering the cost of the installation and the difficulties linked with the suction: the quality of the glass was destroyed by the periodic suction step despite the rotation of the furnace. Even if it could widely increase the productivity, in most places glassmakers preferred to keep their Boucher machines while waiting for the probable development of the gravity feeder. In the beginning, another machine used this type of suction to feed the mold, the Roirant machine of 1923, which was not very successful either.

Cooled-down Glass.

The Hartford-Fairmont Gravity Feeder (1915). The particularity of this feeder is that it delivers glass at the working temperature at the end of a long chamber allowing it to cool down from the furnace temperature. Its first design was described as follows in 1925 [1.20, p. 429]: the feeder ends up in a lip beyond which is situated the extrusion orifice. Into the chamber dipped a paddle that drove successive waves of glass of uniform size over the lip by a regular vertical and horizontal back and forth motion. The successive waves of glass were forced through the orifice by a plunger (or needle) moving vertically (Fig. 1.20). The glass, being at working temperature, formed gobs of a size and shape very accurately determined by the length of the paddle stroke and its depth of immersion, the shape of the plunger, and the timing of the various motions. This feeder might be used to supply a single forming machine but it could serve three or four machines using a hinged receiving trough below the orifice. This trough moved in turn in step with water-sprayed, inclined, cast-iron troughs leading to the machines. The hot gob created a water-vapor cushion on which it rested as it slid down the trough, so tending to prevent deformation.

A major improvement in the Hartford-Fairmont feeder was the disappearance of the paddle, replaced by a cavity created by a rotating refractory cylinder (tube)

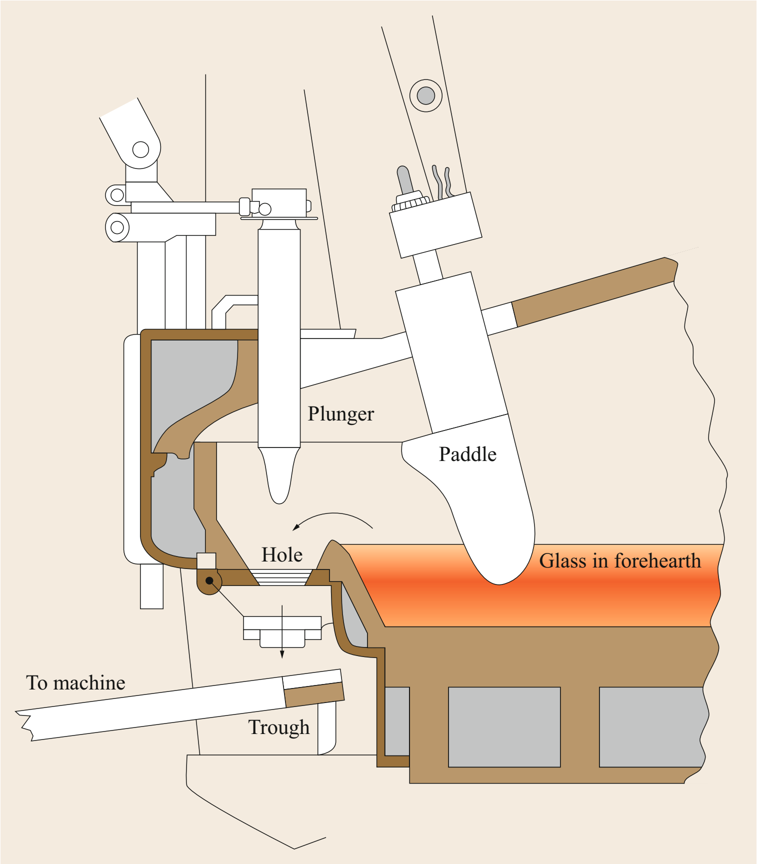

Fig. 1.20 Hartford-Fairmont feeder: first device with a paddle (after [1.20])

set over the orifice (Fig. 1.21): when the plunger rises in the tube, glass is drawn up in the tube above the hole; when the plunger goes down, a definite quantity of glass is expulsed through the hole forming the gob.

The appearance of the Hartford-Fairmont feeder turned out to be the encouragement necessary for the development of automatic machines: the gathering problem was finally solved.

The Lynch and O'Neill machines were adapted to the Hartford-Fairmont feeder gathering.

The Hartford Individual Section (IS) Machine. This machine (Fig. 1.22) was revolutionary insofar as there is no real limit to the number of molds that could be set on a single machine. It is no longer a machine with two rotating tables. The *sections* are arranged in line, each of them consisting of a parison mold above a neck-ring mold and of a finishing mold in front of the machine, all of them fixed. The transfer of the parison, processed neck down from the blank mold to the finishing mold is operated by a mobile arm, inverting the parison. The limitation of the movements allows this machine to be run at a very high rate. They can also make two or three bottles per section. The Hartford-Fairmont device ensured the delivery of the glass gob into the parison mold.

The machine was only 10% faster than the Lynch machine but its flexibility determined its success. It was installed for the first time in 1952 in Lagnieu (Saint-Gobain Company).

Saint-Gobain Invests in Container Glass Making

In the 1920s, Saint-Gobain finally decided to invest in bottle glass making, after a technical journey of the General Manager Eugène Gentil, sent by Lucien Delloye to the US in order to perform a large review of the situation of glass making in that country (not only sheet or plate glass). He was impressed by the technical quality of American plants using automatic machines, thus reducing handwork. Eugène Gentil went back there in 1921 and came back with a good opinion of the Lynch machine, using the Hartford-Fairmont feeder. In 1924–1925, the Company decided to undertake manufacturing of the Lynch machines, the feeders, and the annealing lehr in order to centralize their conceptions and more easily generalize the best innovations in all the factories.

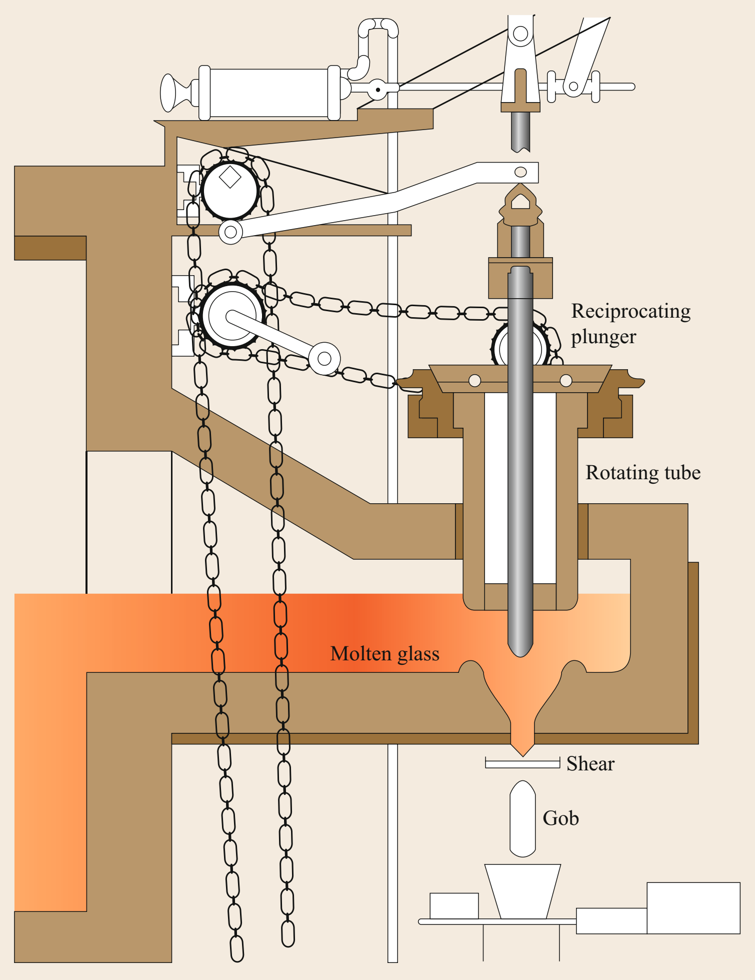

Fig. 1.21 Hartford-Fairmont feeder: new device with a rotating tube and a plunger

In 1927, the production of the first Lynch machine equipped with a Hartford feeder was of 60 million bottles in the Verreries à Bouteilles du Nord in which Saint-Gobain had a 15% share in the 1920s and eventually became a majority shareholder a few years later. At the end of the same decade, Saint-Gobain had 70% of the shares in the Etablissements Boucher and they convinced them to use the Lynch machine with the Hartford feeder instead of developing their own process. The other French participations of Saint-Gobain were in Verreries du Saumurois (1924), Verreries mécaniques de l'Anjou (1927), the Verrerie d'Hirson (1928), the Verreries de Carmaux, the Verreries of the group Paul-Laurent (Saint-Romain-le Puy, Saint-Yorre, Pont-St-Esprit) from 1925 to 1930, the Verreries Aupècle (1936), and the Etablissements Deviolaine (1937 with Vauxrot).

A new plant was built in 1925 (Société d'Exploitation Verrière du Bugey) in Lagnieu (Ain) to make glass pots and various containers for perfumery, pharmacy, and food. This society, in which Saint-Gobain had a 56% share, built a new plant in Sucy-en-Brie (1926), also equipped with the Lynch machine.

In 1930, a new plant was built in La Chapelle-Saint-Mesmin, near Orléans by a company, which would in time sell it to Saint-Gobain (1936). The production of bottles taking place in this plant was transferred and La Chapelle would produce tableware in pressed glass. Toughening was adapted to this kind of glass in 1936–1937 in the Central Laboratory of Saint-Gobain and it was the beginning of a famous product, Duralex.

At the same time, other glassworks allied with the Souchon Company but they mainly bought the O'Neill machine.

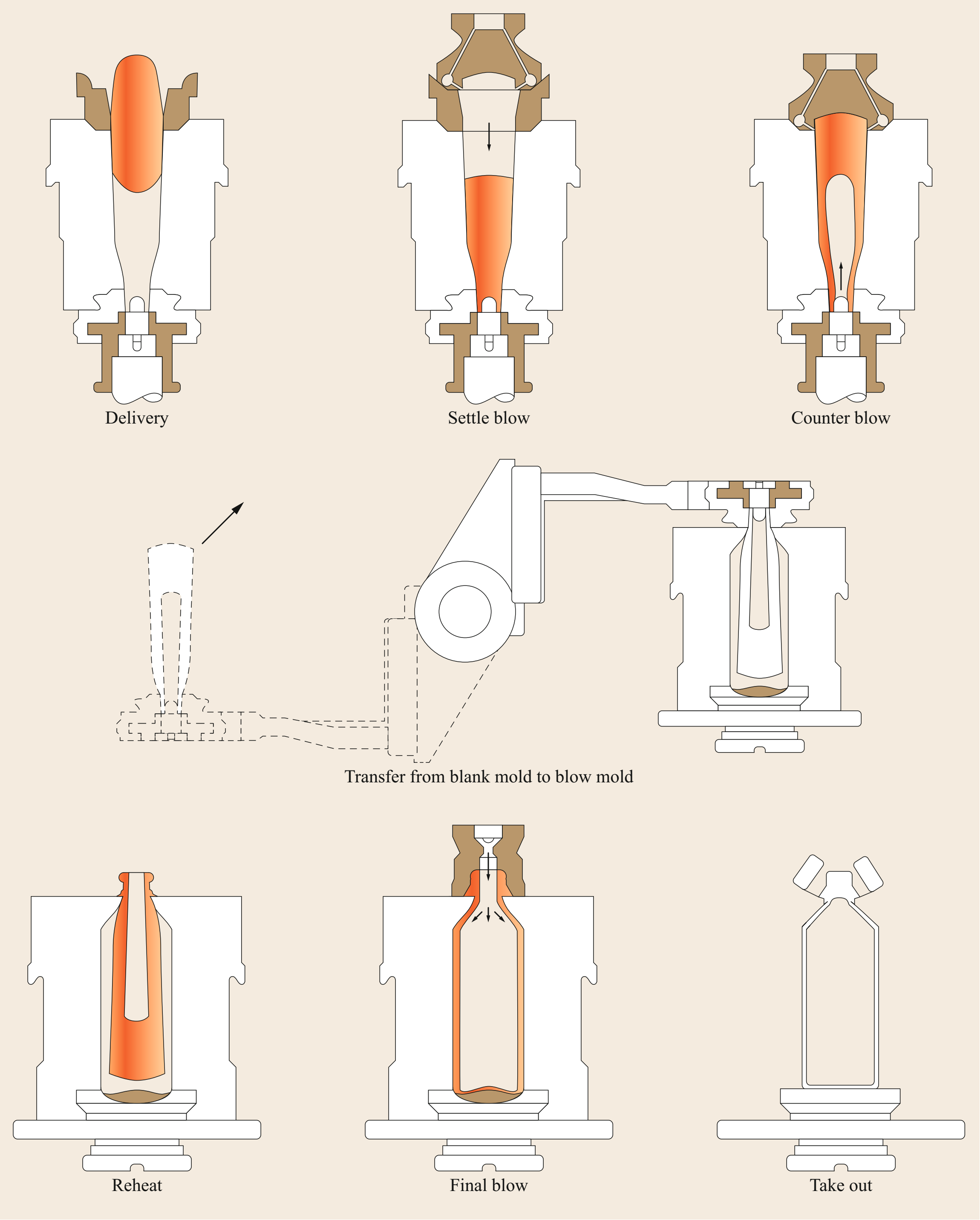

Fig. 1.22 IS machine process

1.6.6 Textile Fiber Glass

The 20th century saw the emergence of numerous technical glass products: all of them will not be described in this part, simply because they will be dealt with in other chapters. Two of them, at least, have had a sufficiently long history, textile fiber glass and insulating fiber glass, to be briefly described here. The reader will find more precise details in the corresponding chapters.

At the end of the 19th century, E.D. Libbey produced fibers by softening glass rods with a burner and winding them [1.44]. They were occasionally used to make materials but it did not really work. From 1938, the company Owens-Corning-Fiber Glass began to draw glass fibers from molten glass, with a device pierced with holes of 1–2.5 mm diameter: filaments are extruded because of the hydrostatic pressure in the crucible, and they are wound on a drum, with the speed (10–50 m/s) determining the size of the filaments, between 5–25 μm. Then the filaments are brought together to form a thread. Those threads of glass were at first used to realize printed circuits and to reinforce plastics.

The initial need for these fibers was for printed circuits, and more generally for electrical uses. This process makes use of a different type of glass without sodium oxide, the electrically conductive element in the soda-lime silica glass, E-glass. It is therefore a much more complicated and very technical glass to manufacture because no flux is introduced in the batch. Instead of any alkaline oxide, boron oxide, an oxide with a very low viscosity and a very low melting point (300 °C) was used to help the melting process, in addition to using silica of very small grain size, calcium borate, and alumina. Nevertheless, the melting temperature of this glass is quite high.

Containing a few percent of boron oxide, it has never been made with the regenerative furnaces, the regeneration chambers of which would have been destroyed too fast by the low melting boron oxide fumes, but with another type of furnace, the recuperator furnace, equipped with a metallic heat exchanger in the exhaust gas flow, thus heating the air or oxygen supplied for the combustion.

1.6.7 Insulation Glass

Insulation wool was most probably produced accidentally in small quantities before any industrial process had been studied, just with a powerful stream of very warm air or gas on a stream of molten glass. Many different processes were later developed to produce these types of products.

Two of these processes are gas processes, either with a flame or with vapor. The first was the Ohio Insulation Company process (1935), which attacked a stream of molten glass with a high-pressure vapor stream oriented in the same direction. The result is an unwoven material, which can be used to reinforce asphalt shingles for roofing.

The second process was invented at the end of the Second World War in Owens-Corning-Fiber Glass: the Aerocor process consists in producing rods of glass 1 mm thick and pushing them into a stream of hot gases emerging from a burner. The glass is then stretched and forms filaments of a fine glass-wool on which is deposited a binder to make a sort of porous and insulating blanket which was used at first for plane insulation.

The third process is purely mechanical: it was invented in 1955 at the Johns Manville Company. Molten glass falls on a very fast horizontally rotating wheel. The glass drops ejected by the first wheel arrive on a second one turning in the opposite direction and on a third one turning in the same direction as the first one. The projections issuing from the last wheel are a mixture of drops and filaments and are then processed as in the previously described system, giving what is usually called Rock wool because the batch was initially made with basalt rocks having a very low viscosity adapted to this process when melted at high temperature. The furnace used mostly for this production is an unusual one in the glass industry: a cupola, a device more frequent in metallurgy, where the compacted batch is introduced into alternate layers together with coke as a fuel.

In 1931, Hager invented an original process using centrifugal force to stretch molten glass falling on a circular refractory device having radial slots. Streams of glass are ejected by the centrifugal force through the slots and stretching is produced by friction between the high-speed streams of molten glass and the surrounding air.

In 1957, Saint-Gobain (Isover) achieved the development of the process: the molten glass is supplied to the fiberizing machine, it flows into the spinner, where it is ejected by centrifugal force through the band of this spinner in refractory steel drilled with a multiplicity of holes of about 1 mm diameter each, creating the fibers.

A strong annular burner situated outside and above the spinner completes the stretching of the filaments down to a very small size around 1 μm in diameter and projects them into the reception zone. In between they are sprayed with a binder, arrive on the conveyor and are shaped into a blanket. Then the glass fiber blanket passes through a curing oven and can be compressed to achieve its final thickness.

1.7 Conclusion

Despite all the misadventures which could have occurred within five thousand years, glass has survived and developed to be an essential material in our lives today. I would like to recall a few words from *Georges Bontemps* at the beginning of his famous book, the Guide du Verrier, in 1868 [1.19]:

> Among the numerous and varied products that attest to the industrial genius of mankind, few others have as many uses as glass or possess such marvellous properties. No other material could replace glass in its most important applications; only iron could dispute the pre-eminence of this diaphanous substance that, above all, while protecting us from the intemperance of our climates, allows us to enjoy the clarity of daylight. If our most fastidious habitations are ornamented with mirrors and chandeliers, the facets of which prismatically refract and reflect the light with such brilliance, it is also true that few humble thatched cottages are without some window panes, a small mirror and a few drinking glasses. Not being subject to decomposition by acids (other than fluorhydric) glass is eminently suitable for the storage without alteration of liquids of all kinds and, by its transparency, allows us to appreciate their condition. Glass has also prolonged the active career of many a man, who without it would be condemned to predictable old age: how many of our statesmen, scientists, artists, and industrialists would not be reduced to regrettable inaction without the indispensable aid of their spectacles.
>
> However, these are not the only important results of the admirable properties of this material. It is to glass that the natural sciences owe their most notable discoveries; by its use they have been increased, clarified and placed on solid principles. It is by means of glass that man has able to investigate the two limits of infinity (microscopy and telescope).
>
> Glass allows us to decompose light, to analyze and weigh the atmosphere, measure heat, study electricity and all aerial fluids, the invisible agents that influence so powerfully the great phenomena of Nature and by which man passes over the seas against the winds, shrink distances by locomotion, rises into the skies, and communicates instantaneously with all corners of the world.
>
> The multiplicity and importance of these advantages, exclusively due to glass, ensure a legitimate interest in researches into its invention. One should be curious about who first made it, how it was improved and the uses to which it has been put.

This is what was tried in this chapter, even if many properties or applications have not been treated, such as optical properties and optical glass for instance, which would be part of other chapters in the book.

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Marie-Hélène Chopinet

Saint Gobain Research
Aubervilliers, France
chopinet.marie-helene@orange.fr

Marie-Hélène Chopinet received her PhD in 1978 from the University of Paris VI. She worked as a Research Engineer for Saint Gobain for over 35 years (until her retirement). Her main scientific activities included the development of glass formulations, the melting process, and the improvement of glass durability and color.