Evolution of the alkaline raw materials in glass batches since the XVIIIth century

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The evolution of the alkaline raw materials used in glass-making follows very closely the evolution of industrial chemistry since the end of the XVIIIth century. After the necessary purification of natural soda ash due to market requirements for a whiter glass, the French revolution and the following events accelerated the transition towards synthetic sodium carbonate produced by the Leblanc-process during the XIXth century. The cost of this industrial raw material induced glassmakers producing non-white glasses like bottle-glass to use either the old impure materials or mixtures of sodium chloride and sodium sulphate, precursor of sodium carbonate in the Leblanc process. Sodium sulphate itself was widely used in plate-glass factories when it was understood that the coloration it produced in glass was due to iron impurities and could be removed by a chemical process and, more important, that its reaction with silica was possible when carbon was added to the batch. The discovery of the Solvay-process at the end of the century provided a cheaper industrial sodium carbonate and the change from all the previous forms of alkaline raw material to the new one was completed before the end of the first half of the XXth century.

Introduction

"Until the beginning of this century (the XIXth), the manufacturing techniques were limited to a very small number of elements; wood was the only fuel; wood ashes, potash, lead oxide and silica were almost alone introduced into the glass batch.

But, since the day when science took hold of this industry, and that distinguished scientists of our time were able to determine precise vitrification rules, it made such progresses that its products reached a very high level of completion.

From one side, development of heat theory gave glass manufacturers many kinds of fuels and various heating systems; from another part, chemistry created new raw materials, ones more profitable than the others and helped the glassmakers to discover them." wrote Pierre Flamm in 1862[1].

Among the new raw materials created by industrial chemistry during the XIXth century are alkalis, essential to the glassmakers as "glass is a potash, soda or lead based silicate and silica alone is impossible to melt at the highest temperature of our furnaces. Nevertheless it becomes fusible when mixed with substances, which have a great affinity with it at high temperature; its molecules open and enter a combination with them, forming silicates.

The substances mostly used in glass-making are potash, soda ash and lead; because of the property they show to melt silica, they are called 'fluxes" by the glass-makers"

Before industrial chemistry

The oldest flux is natron, the natural sodium carbonate found in the Middle-East salt-lakes. It was used all around the Mediterranean Sea, the bulk glass being eventually melted in Syria, Egypt or Lebanon and imported as a raw material by craftsmen in western Europe. Quite early in history glassmakers understood that ashes could be used as fluxes as they were for washing. The type of plants which were burnt, depended on the location of the glass factory: ground plants or sea plants, giving respectively potash and soda ash.

Potash

"Ashes coming from the combustion of wood or other plants are sometimes directly used as fluxes in a few glass factories located in places where wood is cheap. Those ashes are more or less rich in potash, depending on the plants they come from, the soil they grow on and the time of the year they were cut." [2] "The youngest parts of a tree give more potash than old ones; stems more than branches and herbaceous plants more than ligneous ones. The barks yield more ashes than wood, but those ashes are poorer in potash.[…] 100 kilograms of oak, beech, hornbeam or aspen wood (trunks and branches) yield roughly ½ of ashes, from which are extracted 150 to 200 grams of potash saline. Elder tree, laburnum, mulberry tree, hazel tree give 2 to 4 kilograms of ashes and 400 to 500 grams of saline. Potato, buckwheat, rape, poppy, nettle or thistle stalks yield 5 to 10 kilograms of ashes."
Ashes used in the same amount would not achieve the same result, as they do not contain the same amount of salts whatever the plants :

Maize stalks	19.8 %	Sunflower	34.9 %	Vine shoots	16.2 %
Willow	7.8 %	Elm tree	10.2 %	Oak	11.1 %
Aspen	6.1 %	Beech tree	21.9 %	Fern (in august)	11.6 %

Table 1 – Salt content in various plants or trees

The chemical composition of the salts themselves are very different from one another. An analysis of ashes made is given by Fontenelle[3] for corn straw :

Potash	12.5	Potassium sulphate	2	Silica	61.5
Potassium phosphate	5	Alkaline-earth phosphates	6.2	Metal oxides	1
Potassium chloride	3	Alkaline earth carbonates	1	Losses	7.8

Table 2 – Chemical composition of corn straw ashes

Ashes from ground plants have a quite high content in alkaline earth phosphates and carbonates. It explains the high Ca and P contents of the old glasses though those elements were rarely intentionally introduced into the batch in those days. But the alkali carbonate (the really efficient flux) content is sometimes very low.

In fact, very often the glassmaker uses his own ashes when using wood as fuel in the furnace. In this case, his aim is to burn his wood so as to get the highest temperature with the smallest quantity of wood and not to obtain as good ashes as he can.

If he is a bottle glassmaker, he can use the crude ashes in his batch after having strongly and for a long time calcinated them to eliminate the residual charcoal. Afterwards they are sieved to separate small stones, and even charcoal which would not have been burnt. Then he still has to frit the batch prepared with those ashes. In the neighbourhood of large cities, bottle glassmakers use "charrées", i.e. ashes used by laundrymen for washing. Naturally those "charrées" are not very rich in alkalis but they still help the vitrification.

If one wanted to make white glass, the ashes had to be purified : after complete calcination, leaching of the ashes yields the water soluble salts which were known as saline and were mainly potassium carbonate, the insoluble salts being precipitated.

Soda ashes

Before the French revolution, soda ash was the result of the calcination of seaweeds and other marine plants containing NaCl. In Europe, the best soda ashes came from Spain. They were prepared from plants called *Soda*. As a rule the Mediterranean soda ashes had a better reputation than those coming from the Atlantic Ocean coasts which were made with seaweeds, like *kelp* in England. An analysis of kelp ash is given in G. Bontemps 's book:

Sodium carbonate	4	Calcium sulphate	3	Potassium sulphate	14
Charcoal	2	Calcium carbonate	23	Water	13
Silica	1	Sodium chloride	38		

Table 3 - Chemical composition of English kelp

The amount of sodium carbonate was usually very fluctuating in those raw materials. The analysis being obviously impossible, the glassmaker usually had a recipe to judge the soda ash quality "As a rule, the best [soda ashes] are dark grey and do not contain too much charcoal. To those means of judging soda ashes by their aspect, one can add the use of one's nose and tongue: put on one's tongue, [they have to present] a clear and pungent causticity without any bitterness. At last, some saliva is put on a piece of soda ash and if an hepatic smell develops, it indicates the presence of sulphides, sign of a lesser quality soda ash."

When glassmakers wanted to prepare white glasses they had to leach the mixture of salts to obtain, as in the case of potash, the sodium salts alone. The best Spanish soda ash, after leaching, gave around 40 % of sodium salts, a mixture of 55 to 60 % of sodium carbonate, around 30 to 35 % of sodium sulphate, 10 % sodium chloride and 3 to 4 % water.

Acceleration towards industrial chemistry due to History ?

"The impurity and the low titre of crude soda ashes required very expensive treatments; nothing else existing, the glassmaker yielded to necessity. During the continental blockade [Bonaparte and the French Directory], deliveries of foreign soda ashes suddenly stopped. Most of the factories using soda [like glass- and, most important, soap-manufacturers] were threatened by unemployment. The Directory stimulated scientists to do research in order to replace this salt by others products, or to produce it with the raw materials which could be found in the country. Science that had been previously the «infant of empiricism» largely repaid its debts. Chemistry had identified that common salt, so widespread on earth, was made of two simples bodies, chlorine combined with soda; therefore, it was natural that research was done about this salt in order to find an economical process to isolate soda." After many trials, the Leblanc process was discovered and successfully applied.

Sodium sulphate was produced without it being known, when manufacturing hydrochloric acid by reaction and distillation of common salt with sulfuric acid; but it was not identified in the residue of this operation and it was thrown away until Glauber recognized it.

Artificial soda ashes are obtained by calcination of a mixture of sodium sulphate, charcoal and chalk; it is thrown into a furnace at a temperature slightly higher than cherry-red, the mixture is stirred every quarter of an hour and thickens. After mixing, it is heated again. The end product is artificial soda ash.". It is the Leblanc process.

The crude artificial soda ash, richer in sodium carbonate than the various and changing "natural" soda ashes, was at first used only in bottle glass and plate glass manufacturing. The producers rapidly began to purify it and obtained a product containing at first 70 to 75 % of sodium carbonate and up to 95 to 97 % in 1868.

"The common salt decomposition processes discovered and applied at the end of the last century [XVIII^th^ century] which had so many important consequences for so many chemical products, also transformed the glass art." wrote G. Bontemps in 1868.

Why not Sodium Sulphate or even Sodium Chloride ?

One of the drawbacks of the Leblanc process was its cost: consequently the use of artificial soda ash was restricted by the glassmakers to very special productions, the plate glass used to make mirrors, for instance. Other glasses were made as previously but glassmakers thought about the use of the sodium carbonate precursors in the Leblanc process: sodium sulphate or even sodium chloride.

But sulphate was known as not good for vitrification. "It does not combine with silica [contrary to carbonate], floats on the molten glass in the pots and has to be taken away, either with iron glass pockets if there is too much of it, or by volatilization, which is time consuming." So, at the beginning of the XIX^th^ century, the way to make glass directly with sulphate was not known and, anyway, the artificial soda ash manufacturers were not allowed to sell sodium sulphate, at least in France : the government was afraid that people would re-produce common salt without it being taxed.

In 1813, the German chemist Gehlen understood how to use sulphate directly in the furnaces, by using a mixture of sulphate, limestone and carbon with sand: "For 100 of silica, add 33 to 40 of sodium sulphate, 20 to 40 of calcium carbonate or lime, 1.65 to 2 of powdered anthracite or 2.3 to 2.8 of wood charcoal". Around 1824, the French government became convinced that common salt produced from sulphate would be much more expensive than even the highly taxed natural sea salt and let the sulphate producers sell it to glassmakers. From this time on, it was used first in window glass and lately for plate glass manufacturing: M. Pelouze in Saint-Gobain, showed that the blue colour it gave to the glass, was due to iron impurities and not intrinsic to the raw material. After the purification method was worked out, it was entirely substituted to the much more expensive sodium carbonate (5 times more) and allowed a significant decrease of the price of mirrors during the XIX^th^ century (2.06 F vs. 4.63 F/m^2 for the raw materials – 1868).

During the French revolution, when sodium chloride was no more taxed, bottle glass makers, always looking for cheaper batches[4], used some of it together with sodium sulphate. The process included a preliminary heating of all or part of the batch and it seems that the water incorporated was enough to ensure the reaction of sodium chloride with silica which is very difficult at high temperature. When common salt was again taxed, they obtained a mixture of sodium sulphate and chloride which was cheaper than the end-product, sulphate. That was used until the new generation of furnaces, the Siemens tank furnaces which were quickly corroded by chloride batches. So, around 1870, they had to move to sulphate too.

A new evolution : the Solvay process

The Leblanc process yielded expensive sodium carbonate. So, chemists went on working in order to find a cheaper new process. The ammonia-soda process[5] was theoretically known since 1811 but a suitable and economical means of large-scale production had evaded industrial chemists. The Solvay process was devised and first put into commercial use by E. Solvay who built a plant in 1865 in Couillet, Belgium. In the process, common salt is treated with ammonia and then CO_2 produced by decarbonation of lime to form sodium bicarbonate and ammonium chloride. When heated the bicarbonate yields sodium carbonate. One of the advantages of this process compared to the previous one is the recycling of ammonia produced by reaction of ammonium chloride with lime.

Though this new process provided soda ash more cheaper than the old Leblanc process, the substitution of salt-cake by soda ash was very slow in glassmaking : it began around 1917 but in 1922 there were very hard discussions among glassmakers concerning "the advantages and disadvantages attending the use of salt-cake or soda ash as a constituent of glass batches"[6]: "Should window glass made with soda-ash be inferior to window glass made with salt-cake or less workable in glass gathering ?." " The batch which contained at least a proportion of salt-cake was preferred, simply because the glass, although being somewhat less fluid, had apparently a slightly longer viscosity range." One of the members said very accurately that "he 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 that it was said to be sweeter". In 1927, W.E.S. Turner[7] could say that the tanks tonnage increase (threefold for some of them since 1916) was partly due to the substitution of salt-cake by soda ash with a speeding up of melting of 40 %. This was not missed by the glassmakers.

The result was the soda-ash batch with some salt-cake added to it to enhance the homogenization: it is still the batch used in present days for many glass products.

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[1] P. Flamm, in *Le verrier du XIXème siècle* (Paris, 1862).

[2] G. Bontemps, in *Guide du verrier* (Librairie du dictionnaire des arts et manufactures, Paris, 1868).

[3] J. de Fontenelle, in *Nouveau manuel complet du verrier* (1829 - refondu en 1900 par H. Bertran).

[4] MH Chopinet, Verre **6[5]**, p. 63 (2000).

[5] Encyclopaedia britannica, Ammonia-soda process and Solvay, Ernest

[6] General discussion of the Society of Glass Technology, Journal of the Society of Glass Technology **5**, p. 151 (1922).

[7] W.E.S.Turner, Journal of the Society of glass technology **11**, p. 313 (1927).