

PROCESS FOR PREPARING BATCH MATERIALS FOR THE
MANUFACTURE OF GLASS

5 The invention relates to a process for preparing certain materials that can be used for manufacturing glass.

10 In the context of the present invention, "batch materials" should be understood to mean all materials, vitrifiable materials, natural ores or synthesized products, materials coming from recycling of the cullet type, etc. which can be used in the composition for feeding a glass furnace. Likewise, "glass" should be understood to mean glass in the widest sense, that is to say any glassy-matrix, glass-ceramic or ceramic
15 material. The term "manufacture" should be understood to mean the indispensable step of melting the batch materials and possibly all the subsequent/complementary steps aimed at refining/conditioning the molten glass for the purpose of giving it a final shape, especially
20 in the form of flat glass (glazing), hollowware (flasks and bottles), glass in the form of mineral wool, (glass wool or rock wool) used for its thermal or acoustic insulation properties, or possibly even glass in the form of so-called textile yarns used in reinforcement.

25 The invention relates most particularly to the batch materials needed for manufacturing glass having a significant content of alkali metals, especially sodium, for example glasses of the silica-soda-lime type used for the manufacture of flat glass. The batch
30 material most frequently used at the present time for providing sodium is sodium carbonate Na_2CO_3 , a choice which is not without drawbacks. This is because, on the one hand, this compound provides only sodium as constituent element of the glass, all the carbon-
35 containing part decomposing and being given off in the form of CO_2 during melting. On the other hand, it is an expensive batch material compared with others since it is a synthetic product obtained by the Solvay process from sodium chloride and lime, which process involves a

number of manufacturing steps and is not very energy-saving.

This is the reason why various solutions have already been proposed for using, as a sodium source, not a carbonate but a silicate, possibly in the form of a mixed silicate of alkali metals (Na) and alkaline-earth metals (Ca) which is prepared beforehand. The use of this type of intermediate product has the advantage of providing jointly several of the constituents of the glass and of eliminating the decarbonization phase. It also makes it possible to speed up the melting of the batch materials as a whole and to favour their homogenization during melting, as indicated, for example, in Patents FR-1,211,098 and FR-1,469,109. However, this approach poses the problem of manufacturing this silicate and does not propose a completely satisfactory method of synthesis.

The object of the invention is therefore to develop a novel process for manufacturing this type of silicate, which is especially suitable for providing industrial production with a reliability, an efficiency and a cost which are all acceptable.

The subject of the invention is firstly a process for manufacturing compounds based on silicates of alkali metals such as Na, K and/or based on alkaline-earth metals such as Mg or Ca and/or based on rare earths such as cerium Ce, optionally in the form of mixed silicates which combine at least two elements among alkali metals, alkaline-earth metals and rare earths, especially silicates which combine alkali metals with alkaline-earth metals and/or rare earths. This process consists in synthesizing these compounds by the conversion of silica and of one or more halides, especially one or more chlorides, of the said alkali metals and/or the said alkaline-earth metals and/or the said rare earths, of the NaCl, KCl or CeCl₃ type, (and optionally halides, especially alkaline-earth metal chlorides, in the case of silicates containing them),

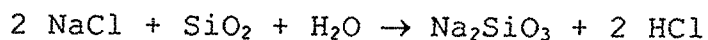
the heat needed for this conversion being supplied, at least partly, by one or more submerged burners.

Still within the framework of the invention, all or some of the halides may be substituted as source
5 of alkali metals/alkaline-earth metals/rare earths by sulphates or even by nitrates. It may thus be sodium sulphate Na_2SO_4 . Within the context of the invention, these various starting products (halides, nitrates, sulphates) are therefore to be considered as
10 equivalents and as being interchangeable.

The term "silica" should be understood here to mean any compound containing mostly silica (silicon oxide) SiO_2 , even if it may also contain other elements or other minor compounds, this being most particularly
15 the case when natural materials of the sand type are used.

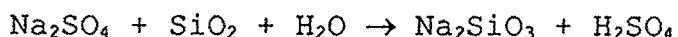
The expression "submerged burners" should be understood here to mean burners configured so that the "flames" that they generate or the combustion gases
20 resulting from these flames develop within the reactor where the conversion takes place, within the actual mass of the materials undergoing conversion. Generally, they are placed so as to be flush with or project slightly from the side walls or from the sole of the
25 reactor used (we refer here to flames, even if they are not strictly speaking the same "flames" as those produced by overhead burners, for greater simplicity).

The invention thus results in a particularly judicious technological solution in order to be able to
30 exploit on an industrial scale a chemical transformation already proposed by Gay-Lussac and Thénard, namely the direct conversion of NaCl into soda, involving the reaction of NaCl with silica at high temperature in the presence of water according to
35 the following reaction:



the principle consisting in extracting the soda by forming the silicate, the equilibrium being always shifted in the direction of NaCl decomposition because the two phases are immiscible.

- 5 (if sodium sulphate is used instead of sodium chloride, the reaction is as follows:



- 10 In fact, SO_3 is firstly formed, which is transformed into sulphuric acid due to the effect of the temperature and of the water of combustion of the submerged burner).

- Hitherto, this reaction has caused considerable
15 processing problems associated with difficulties in producing an intimate mixture of the reactants and in ensuring that these are replenished during manufacture, also associated with difficulties in discharging HCl (or H_2SO_4) without it reacting again with the silicate
20 formed, in extracting the silicate and in being able to supply sufficient thermal energy.

The use of submerged burners for supplying this thermal energy solves at the same time most of these difficulties.

- 25 In fact, it has already been proposed to use heating by submerged burners for melting vitrifiable materials for making glass. For example, reference may be made to Patents US-3,627,504, US-3,260,587 or US-4,539,034. However, the use of such burners in the
30 specific context of the invention, namely the synthesis of silicates from salts, is extremely advantageous:

- this is because this mode of combustion generates water, which water, as was seen above, is indispensable in the desired conversion. By virtue of submerged
35 burners, it is thus possible to manufacture *in situ* the water needed for the conversion, at least partly (even if, in some cases, it may be necessary to supply additional water). It is also certain that the water is introduced within the other starting substances, namely

the silica and the salt(s) (for the sake of brevity, the term "salts" will be used to mean the chloride-type halides of alkali metals, rare earths and, optionally, alkaline-earth metals, used as the starting reactants),
5 this being, of course, propitious to promoting the reaction;

→ moreover, the combustion of [sic] submerged burners causes, within the materials undergoing the reaction, strong turbulence and strong convection movements
10 around each "flame" or "flames" and/or each of the jets of gas coming from each of the burners. Consequently, it will therefore ensure, at least partly, vigorous stirring between the reactants, which stirring is needed in order to guarantee intimate mixing between
15 the various reactants, most particularly those introduced in solid (pulverulent) form such as the silica and the salt(s);

→ submerged burners are also particularly advantageous from the strictly thermal standpoint, since they supply
20 heat directly to the point where it is needed, namely in the mass of the products undergoing the reaction, therefore minimizing any loss of energy, and because they are sufficiently powerful and effective for the reactants to be able to reach the relatively high
25 temperatures needed for their melting/conversion, namely temperatures of at least 1000°C, especially about 1200°C;

→ furthermore, they are a mode of heating that is particularly environmentally friendly, by especially
30 reducing as far as possible any emission of NO_x-type gases.

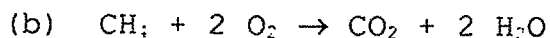
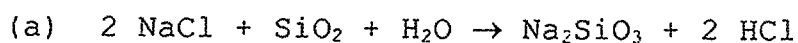
It may therefore be concluded that the effectiveness of these burners at every level (quality of the mix, excellent heat transfer and one of the
35 reactants being generated *in situ*) means that the conversion is highly favoured, this being so without there necessarily being a requirement to achieve extremely high temperatures.

The oxidizer chosen for feeding the submerged burner(s) may simply be air. However, an oxidizer in the form of oxygen-enriched air, and even substantially in the form of oxygen alone, is preferred. A high oxygen concentration is advantageous for various reasons: the volume of flue gases is reduced, this being favourable from an energy standpoint and avoids any risk of excessive fluidization of the materials undergoing the reaction that might cause them to be projected against the superstructures or the roof of the reactor where the conversion takes place. Furthermore, the "flames" obtained are shorter and of higher emissivity, thereby allowing more rapid transfer of their energy to the materials undergoing melting/conversion.

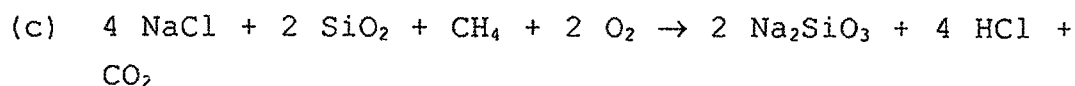
With regard to the choice of fuel for the submerged burner(s), two approaches are possible, which are alternatives or can be combined:

- it is possible to choose a liquid fuel, of the fuel oil type, or a gaseous fuel, of the natural gas type (mostly methane), propane or hydrogen;
- it is also possible to use a fuel in solid form, containing carbon, for example coal, or any material containing hydrocarbon, optionally chlorinated, polymers.

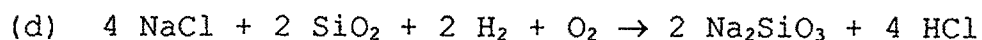
The choice of oxidizer and the choice of fuel for the submerged burners influence the nature of the products obtained, apart from the silicates. Thus, when the burners are fed with oxygen and with natural gas, schematically the following two reactions occur: (starting from the simplest situation in which it is desired to make the Na silicate from NaCl, but it is possible to transpose it to all other cases, whether of making K silicate, Ce silicate or silicates containing Ca or Mg, etc.):



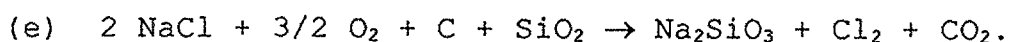
These two reactions may be combined into a single reaction:



5 When a hydrogen fuel is used rather than natural gas, there is no longer any emission of CO_2 and the overall reaction may be written as:



10 When a carbon-containing solid-type fuel is used, always with an oxygen-type oxidizer, the following reaction may be written:



15 This time, what is produced is therefore no longer HCl but chlorine Cl_2 as by-products of the conversion.

 It is therefore clear from these various reactions-balances that the conversion envisaged by the invention also generates halogen-containing derivatives most particularly utilizable chlorine-containing derivatives such as HCl or Cl_2 , which are found in the flue gases. Two ways of operation are possible:

25 → one consists in re-treating them as effluents. Thus, it is possible to neutralize HCl with calcium carbonate CaCO_2 , which amounts to manufacturing CaCl_2 , which is possibly utilizable (for example, for removing snow from roads);

30 → the other way consists in considering the conversion according to the invention as a means of manufacturing HCl or Cl_2 (or H_2SO_4) an industrial scale, these being base chemicals widely used in the chemical industry. (It is possible, especially, for the chlorine obtained electrolytically, which is necessary for the manufacture of chlorinated polymers of the PVC or polyvinyl chloride type to be substituted with the HCl or the Cl_2 manufactured according to the invention). In
35 this case, it would then be necessary to extract them from the flue gases and thus establish an industrial production line for HCl or Cl_2 , for example by incorporating the apparatus for carrying out the

process according to the invention directly in a chemical industry site needing these types of chlorinated product. Thus, utilizing the chlorinated derivatives formed makes it possible to further lower
5 the cost of the batch materials containing alkali metals necessary for the manufacture of glass.

A first outlet for the silicates manufactured according to the invention relates to the glassmaking industry: they may replace, at least partly, the
10 conventional batch materials which provide alkali metals or rare earths, most particularly with regard to sodium by at least partially substituting CaCO_3 with Na_2SiO_3 . The silicates of the invention may therefore be used to feed a glass furnace, this being done
15 especially in two different ways:

→ the first way consists in treating the silicates formed in order to make them compatible with use as vitrifiable batch materials for glass furnaces: this therefore involves extracting them from the reactor and
20 generally converting them "cold" into a pulverulent solid phase, especially through a granulation step using techniques known in the glassmaking industry. There is therefore a complete separation between the silicate manufacturing process and the glass
25 manufacturing process, with suitable forming, and possible storage/transportation, of the silicate formed, before it is fed into the glass furnace;

→ the second way consists in using the silicate(s) formed according to the invention "hot", that is to say
30 in using a glass manufacturing process which incorporates a prior step of manufacturing the silicate which is to be fed, while still molten, into the glass furnace. Thus, the silicate can be manufactured in a reactor connected to the glass furnace, constituting
35 one of its "upstream" compartments, as opposed to its possible "downstream" compartments intended for the refining/conditioning of the glass once melted.

In both these situations, the glass furnace may be of conventional design (for example, an electric

melting furnace using submerged electrodes, a crown-fired furnace operating with lateral regenerators, an end-fired furnace, or any type of furnace known in the glassmaking industry, thus including furnaces with
5 submerged burners), optionally with a design and a mode of operation which are slightly modified so as to be suitable for a melting process involving no carbonate or with less carbonate than in the case of standard melting processes.

10 It should be noted that certain silicates other than sodium silicate are also highly advantageous to manufacture according to the invention. Thus, the invention makes it possible to manufacture potassium
15 silicate from KCl, this being, at least economically, highly advantageous as a batch material containing Si and K for manufacturing glasses called "mixed alkali" glasses, that is to say those containing both Na and K. These glasses are especially used for making touch
20 screens, glasses for television screens, and glasses for plasma display panels.

Likewise, the invention allows more economical manufacture of special glasses containing additives for which chlorides are less expensive than oxides. This is the case of rare earths such as cerium, the presence of
25 cerium oxide giving the glasses UV screening properties, and rare earths of this type are also included in the composition of special glasses having a high elastic modulus for hard disks. The invention thus makes it possible to have a batch material containing
30 Si and Ce - cerium silicate -, for a moderate cost.

Another additional advantage of the invention is that the silica introduced at the start undergoes, during conversion into silicate, a certain de-ironing, since iron chloride is volatile: the glass produced
35 from this silicate, by using at least a certain amount of this silicate, will therefore tend to be clearer than a glass using none of this type of silicate at all. This is advantageous from an aesthetic standpoint

and tends to increase the solar factor of the glass (in a "flat glass" application).

5 A second outlet for the silicates manufactured according to the invention, (apart from those used as batch materials for glass furnaces), more particularly sodium silicate, is in the detergents industry, sodium silicate Na_2SiO_3 frequently being used in the washing powder/detergent compositions.

10 A third outlet for the silicates (and optionally the chlorinated derivatives) formed according to the invention is in the preparation of special silicas, commonly called "precipitated silicas" used, for example, in the composition of concretes. The silicates formed according to the invention may in fact
15 be subjected to acid attack, advantageously by hydrochloric acid HCl which has also been formed by the conversion according to the invention, so as to precipitate silica in the form of particles having a particular particle size: the intended particle size is
20 generally of the order of a nanometre (1 to 100 nm, for example).

The sodium chloride also formed during the precipitation of the silica may advantageously be recycled, again serving most particularly as raw
25 material for the silicate manufacture according to the invention. This is an extension of the invention in which, starting from a particulate silica of "coarse" particle size (of about 1 micron or coarser, for example), a particulate silica is again obtained, but
30 the particle size is much less, this control and this particular size opening the way to a very wide variety of uses in materials used in industry.

More particularly for this third outlet, it is advantageous to choose rather an alkali metal sulphate
35 than a chloride: not HCl but H_2SO_4 is recovered, which serves for the acid attack of the sodium silicate thus formed. It is this type of acid which is normally used in the chemical industry to prepare precipitated silicas. It is more advantageous than HCl in this

particular case since it avoids any risk of forming residual chlorides in the precipitated silica, these being potential sources of corrosion in certain applications of the silica.

5 One process for manufacturing precipitated silica according to the invention may thus entail, schematically:

→ a reaction in a furnace fitted with submerged burners (especially oxygas or oxyhydrogen burners) between a
10 silica sand of suitable purity and sodium sulphate, with an amount of water to be added in a controlled manner as a complement to that generated by the combustion, sodium silicate is formed according to the abovementioned reaction, it is removed continuously,
15 the SO_3 generated is converted into H_2SO_4 which is recovered, for example, in the flue provided as a consequence;

→ the sodium silicate produced with the suitable $\text{SiO}_2/\text{Na}_2\text{O}$ module is then attacked under appropriate
20 conditions (especially in terms of pH) by the sulphuric acid recovered, the silica is thus precipitated and then treated for the purpose of giving it the desired properties for the envisaged applications (for example as a filler for rubber, for tyres, etc.);

25 → during this reaction, sodium sulphate re-forms, and this in turn may be concentrated and recycled in the furnace fitted with submerged burners as sodium source.

It may be seen that this process may operate continuously, in a closed loop, as regards the acid and
30 the sodium source. It behaves as a "silica sieve" without any consumption other than that of sand and energy. It is also possible to recover the heat from the flue gases and the heat of condensation of SO_3 in a suitable exchanger in order to produce, for example,
35 the vapour needed for concentrating the aqueous solutions.

This type of process is applied in a quite similar manner if an alkali metal other than sodium (or a derivative other than a sulphate) is used or any

other element is used if its sulphate is at all thermally unstable and liable to result in the same type of reaction.

Another advantageous application of the process
5 relates to the treatment (inerting by vitrification most particularly) of chlorine-containing waste, most particularly chlorine-containing and carbon-containing waste such as chlorinated polymers (PVC, etc.); the melting by submerged burners, according to the
10 invention, can pyrolyse this waste with, as ultimate combustion products, CO_2 , H_2O and HCl , the HCl (or even H_2SO_4) possibly being, as seen previously, neutralized or utilized as it is. It may also be noted that such waste can therefore also serve as carbon-containing
15 solid fuel, which in fact can allow the amount of fuel to be injected into the burners to be decreased. (Other types of waste, such as foundry sand, may be involved). The pyrolysis of these various types of waste is here again advantageous from an economic standpoint since
20 their cost of treatment, which is moreover necessary, is deducted from the cost of producing the silicates according to the invention. Rather than actually pyrolysing the waste, it may also be vitrified.

Given below are a few details about the
25 inerting of such organochlorine-containing waste: it is therefore possible to add, to the sand and to the chloride or equivalent, solid or liquid waste of the organochlorine-containing type. It is also possible to add various additives, such as lime, alumina (in the
30 form of clay, a less expensive raw material for example) or other oxides. Thus, a true vitrification is performed, the vitrified material obtained being capable of coating and of stabilizing possible mineral fillers contained in the waste in question. This
35 vitrified material may then be discharged. The acid produced may be recovered in an absorption tower filtering the flue gases and may be recycled. This process is economically highly advantageous: first, the main flux used is provided by the salt and at least

some of the energy necessary for the vitrification is provided by the waste itself. Secondly, it provides the possibility of recycling the acid formed, especially HCl. Of course, it is possible to combine several types
5 of combustible waste. For this application, it is preferable to manufacture an alkaline-earth-rich silicate, or consisting only of an alkaline-earth silicate: since what is involved is the inerting of the waste, and not the manufacture of a high-quality glass,
10 it is advantageous essentially to use alkaline-earth silicates, since the raw material providing the alkaline-earth metals in question is less expensive than that providing alkali metals.

The subject of the invention is also the
15 apparatus for carrying out the process according to the invention, which apparatus preferably comprises a reactor equipped with one or more submerged burners and with at least one means for introducing silica and/or halides (or equivalents of the sulphate or nitrate
20 type) below the level of the molten materials, especially in the form of one or more feed-screw batch chargers. The same is true, preferably, for the solid-type or liquid-type fuels which may be used, such as the organochlorine-containing waste mentioned above. It
25 is thus possible to introduce directly into the mass of products undergoing melting/reaction at least those of the starting reactants capable of vapourizing before having the time to react: one thinks here most particularly of sodium chloride NaCl, and a residence
30 time sufficient for liquid or solid fuels to complete their combustion is guaranteed.

Preferably, the walls of the reactor, especially those intended for being in contact with the various reactants/reaction products involved in the
35 conversion, are provided with refractory materials lined with a metal lining. The metal must be able to withstand the various types of corrosive attack, especially here that caused by HCl. Titanium, a metal from the same family, or an alloy containing titanium,

or else zirconium or an alloy containing zirconium are preferred. Advantageously, provision may be made for all the elements inside the reactor, emerging in the latter, to be based on this type of metal or to be
5 protected on the surface by a coating of this metal (the batch chargers and submerged burners). It is preferable for the walls of the reactor, and also especially all the metal parts inside the latter, to be associated with a fluid-circulation cooling system of
10 the water-box type. The walls may also be entirely made of metal, with no or very few standard refractories used for the construction of glass furnaces.

The walls of the reactor define, for example, an approximately cubic, parallelepipedal or cylindrical
15 cavity (having a square, rectangular or round base). Advantageously, several points of introducing the starting reactants may be provided, for example distributed in a regular manner in the side walls of the reactor, especially in the form of a certain number
20 of batch chargers. This multiplicity of supply points allows the amount of reactants in each of them to be limited and a more homogeneous mixture in the reactor to be obtained.

The reactor according to the invention may also
25 be equipped with various means for treating the chlorinated effluents, especially for recovering or neutralizing effluents of the Cl_2 , HCl or H_2SO_4 type, and/or with means for separating the solid particles, especially those based on metal chlorides, from the
30 gaseous effluents. These means are advantageously placed in the flue(s) which extract the flue gases from the reactor.

Finally, the subject of the invention is also a process for producing glass containing silica and
35 alkali-metal oxides of the Na_2O or K_2O type and/or alkaline-earth metal oxides of the MgO or CaO type and/or rare-earth oxides of the CeO_2 type, by melting vitrifiable materials in which the heat needed for the said melting comes at least partly from submerged

burners. In this case, the invention resides in the fact that the batch materials containing alkali metals of the Na or K type, or alkaline-earth metals or rare earths of the Ce type, are at least partly in the form of halides, especially chlorides, of the said elements, such as NaCl, KCl or CeCl₃, or sulphates or nitrates. This is the second major aspect of the invention in which, as it were, everything takes place as if the silicate, described previously as "in situ", were manufactured during the actual process of melting the vitrifiable materials in order to produce glass. The economic advantage of replacing all or part, especially, of the sodium carbonate with NaCl is clear. In this case, there are the same advantages as those mentioned above, relating to silicate manufacture independently of glass manufacture, namely especially the lesser iron content in the glass, possible utilization of the chlorinated (halogenated) derivatives produced, pyrolysis or vitrification of waste, the latter being, moreover, possibly suitable to act as solid fuel, etc.

The invention will be explained in detail with the aid of an embodiment illustrated by the following figure:

□ **Figure 1:** a schematic plant for manufacturing sodium silicate according to the invention.

This figure is not necessarily to scale and has been extremely simplified for the sake of clarity.

It shows a reactor 1 comprising a sole 2 of rectangular shape which is pierced regularly so as to be equipped with rows of burners 3 which pass through it and penetrate slightly into the reactor. The burners are preferably covered with titanium and are cooled with water. The side walls are also cooled with water and comprise a coating of electrocast refractories 5 or are made entirely of titanium-based metal. The level 5 of materials undergoing reaction/melting is such that the feed-screw batch chargers 6 introduce the reactants through the side wall below this level.

The sole comprising the burners may have a greater thickness of electrocast refractories than the side walls. It is also pierced with a tap hole 10 for extracting the silicate.

5 The roof 8 may be a suspended flat roof made of refractory materials of the mullite or zirconia-mullite or AZS (aluminium-zirconia-silica) type or of any ceramic material resistant to HCl and/or NaCl. It is designed to be impermeable to the flue gases containing
10 HCl: a non-limiting solution for guaranteeing this impermeability consists in using a honeycomb ceramic structure consisting of hollow hexagonal pieces in which an insulation is placed. Impermeability is therefore achieved between the pieces on the back
15 surface by an HCl-resistant low-temperature mastic. It thus protects the metal supporting structure. The flue 9 is also constructed from HCl- and NaCl-resistant materials (oxide refractories, silicon carbide, graphite). It is provided with a system for separating
20 the solid particles which are liable to condense (metal chlorides) and with an HCl recovery tower, these not being illustrated.

Once the silicate has been extracted from the reactor via the tap hole 10, it is conveyed to a
25 granulator (not illustrated) of the type used in the glassmaking industry or in the sodium silicate detergents industry.

The object of the process is to manufacture a silicate which is highly concentrated in terms of sodium, this being quantified in a known manner by a
30 molar ratio of Na_2O with respect to the total ($\text{SiO}_2 + \text{Na}_2\text{O}$) in the region of 50%, by introducing into the reactor, via the batch chargers, a mixture of sand (silica) and NaCl. These two reactants may also be
35 introduced separately and may have been optionally preheated before they are introduced into the reactor.

Preferably, the burners 3 are fed with oxygen and with natural gas or hydrogen.

The viscosity of the batch during melting/reaction and the high reaction rate obtained by virtue of submerged-burner technology make it possible to achieve high specific draws - to give an order of
5 magnitude of, for example, at least 10 tonnes/day.

In conclusion, the process of the invention opens up a new way of manufacturing silicates, most particularly sodium, potassium and cerium silicates (or else alkaline-earth metal silicates), for a moderate
10 cost. It also falls within the context of the present invention of using *mutadis mutandi* the same process for manufacturing no longer silicates but titanates, zirconates and aluminates of these elements (optionally mixed with silicates).

Thus, a metal may at least partially substitute for silicon, especially a metal belonging to the transition metals and more particularly to those of column IVB of the Periodic Table, such as Ti or Zr, or to the metals of column IIIA of the Periodic Table,
20 such as Al. The advantage of such a substitution is that the product obtained is soluble in water. The selection [sic] attack of these products in aqueous solution, especially by using hydrochloric acid formed during the conversion, results in the precipitation of
25 particles no longer of silica, as mentioned earlier in the text, but of corresponding metal oxide particles such as TiO_2 , ZrO_2 and Al_2O_3 , which particles are generally nanometric in size, as when starting with silica, and which may have numerous applications in
30 industry. It is thus possible to use them as fillers in polymers and concretes, and to incorporate them into ceramic or glass-ceramic materials. It is also possible to exploit their photocatalytic properties: particularly intended are TiO_2 particles (which may be
35 incorporated into photocatalytic coatings having antisoiling properties for any architectural material, glazing, etc.).

In order to manufacture these titanates, zirconates, or aluminates according to the invention,

the process described earlier for obtaining silicates is transposed, starting from halides of the NaCl type and from metal oxides of the metals involved (TiO_2 , ZrO_2 , Al_2O_3 , etc.).

5 Alternatively, it is possible to use directly, as metal-containing starting product for the conversion, the halide of the said metal and no longer its oxide. This may especially be a chloride, such as TiCl_4 , ZrCl_4 or AlCl_3 (it is also possible to choose as
10 metal-containing starting products a mixture of an oxide and a chloride of the said metal). In this case, the material containing alkali metals may be the same NaCl-type halide used for making silicate, this salt possibly being supplemented with or replaced by soda
15 when it is sodium alkali metal which is involved.

 Just as in the case of "precipitated silica", this extension of the process according to the invention may thus be seen as a means of modifying, especially reducing, the size of the particles of a
20 metal oxide so as to provide it with other applications in industrial materials.

 It should be noted that the invention makes it possible to recycle various types of waste. In particular, this may mean cleaning/treating polluted
25 sand, especially resulting from oil slicks: the contaminated sand may thus be collected as a starting product for silica. This has two major advantages:

→ first, the sand is already impregnated with fuel (fuel oil or the hydrocarbon compounds which
30 contaminate it);

→ secondly, this is a simple method for stripping coasts and beaches of their polluted sand, when any other means for cleaning the sand is too lengthy or too expensive. The method of the invention therefore makes
35 it possible to completely remove the fuel oil. It is advantageous, for this type of application, to manufacture silicates of alkaline-earth metals or mostly based on these elements: just as for the abovementioned application to the inerting of

organochlorine-containing waste, it is economically more advantageous to use raw materials based on alkaline-earth metals than raw materials based on alkali metals.

CLAIMS

1. Process for manufacturing compounds based on one or more silicates of alkali metals such as Na, K
5 and/or alkaline-earth metals such as Ca, Mg and/or rare earths such as Ce, optionally in the form of mixed silicates which combine at least two of these elements, by the conversion of silica and of halides, especially of one or more chlorides, or of sulphates or nitrates,
10 of the said alkali metals and/or of the said rare earth and/or of the said alkaline-earth metals, such as NaCl, KCl or CeCl₄, *characterized in that* the heat necessary for this conversion is supplied, at least partly, by one or more submerged burners.
- 15 2. Process according to Claim 1, *characterized in that* the submerged burner(s) is(are) fed with an oxidizer in the form of air, oxygen-enriched air or oxygen.
- 20 3. Process according to either of the preceding claims, *characterized in that* the submerged burner(s) is(are) fed with a fuel in the form of natural gas, fuel oil or hydrogen and/or in that solid-type or liquid-type fuel, especially fuel containing carbon materials based on polymers, possibly chlorinated
25 polymers, or based on coal, is supplied near the said burner(s).
4. Process according to one of the preceding claims, *characterized in that* the combustion created by the submerged burner(s) at least partly ensures
30 stirring of the silica and of the halide(s).
5. Process according to one of the preceding claims, *characterized in that* the combustion created by the submerged burner(s) at least partly generates the water needed for the conversion.
- 35 6. Process according to one of the preceding claims, *characterized in that* the conversion also generates halogenated derivatives, especially utilizable chlorinated derivatives such as HCl or Cl₂, or H₂SO₄.

7. Process according to one of the preceding claims, *characterized in that* the silicate(s) formed is(are) treated in order to make it(them) compatible with use as one or more vitrifiable batch materials for
5 a glass furnace, the treatment comprising, in particular, a granulation step.

8. Process according to one of Claims 1 to 6, *characterized in that* the silicate(s) formed is(are) fed hot into a glass furnace.

10 9. Apparatus for carrying out the process according to one of the preceding claims, *characterized in that* it comprises at least one reactor (1) equipped with one or more submerged burners (3) and at least one means for introducing silica and/or the halide(s),
15 sulphates or nitrates and optionally the solid or liquid fuels, below the level of the materials undergoing melting, especially in the form of one or more feed-screw batch chargers (6).

10. Apparatus according to Claim 9, *characterized in that* the walls (2, 4) of the reactor (1), especially those intended to be in contact with the various reactants/reaction products involved in the conversion, are provided with refractory materials, for example of the electrocast type or with refractory materials lined
25 with a metal lining of the titanium or zirconium type or are based on these types of metal, and are preferably combined, at least in the case of the side walls (4), with a cooling system using the circulation of fluid of the water type.

30 11. Apparatus according to Claim 9 or Claim 10, *characterized in that* the walls of the reactor (1) define an approximately cubic, parallelepipedal or cylindrical cavity.

12. Apparatus according to one of Claims 9 to 11, *characterized in that* the reactor (1) is equipped with means for treating the chlorinated effluents, especially means for recovering HCl or Cl₂ or H₂SO₄ or for neutralizing HCl and/or means for separating solid

particles, for example those based on a metal chloride, from the gaseous effluents.

13. Use of the process according to one of Claims 1 to 8 or of the apparatus according to one of Claims 9 to 12 for preparing vitrifiable batch materials for the manufacture of glass.

14. Use of the process according to one of Claims 1 to 8 or of the apparatus according to one of Claims 9 to 12 for preparing raw materials, especially sodium silicate Na_2SiO_3 , for the manufacture of detergents.

15. Use of the process according to one of Claims 1 to 8 or of the apparatus according to one of Claims 9 to 12 for preparing raw materials, especially sodium silicate Na_2SiO_3 , for the manufacture of precipitated silica, more particularly from silica and sodium sulphate.

16. Use of the process according to one of Claims 1 to 8 or of the apparatus according to one of Claims 9 to 12 for vitrifying/inerting waste of the organochlorine-containing-type waste, preferably by the conversion of silica and of alkaline-earth-containing raw material at least.

17. Use of the process according to one of Claims 1 to 8 or of the apparatus according to one of Claims 9 to 12 for re-treating sand polluted by fuel oil or other hydrocarbon compounds, preferably by the conversion of silica and of alkaline-earth-containing raw material at least.

18. Process for obtaining glass containing silica and alkali-metal oxides, of the Na_2O or K_2O type and/or alkaline-earth metal oxides of the CaO or MgO type and/or rare-earth oxides of the CeO_2 type, by melting vitrifiable materials in which the heat needed for the said melting comes at least partly from the submerged burner(s), *characterized in that* the vitrifiable materials containing alkali metals, of the Na or K type, or rare earths, of the Ce type, or alkaline-earth metals, are at least partly in the form of halides,

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especially chlorides or sulphates or nitrates, of the said elements, such as NaCl, KCl, CeCl₄ or Na₂SO₄.

