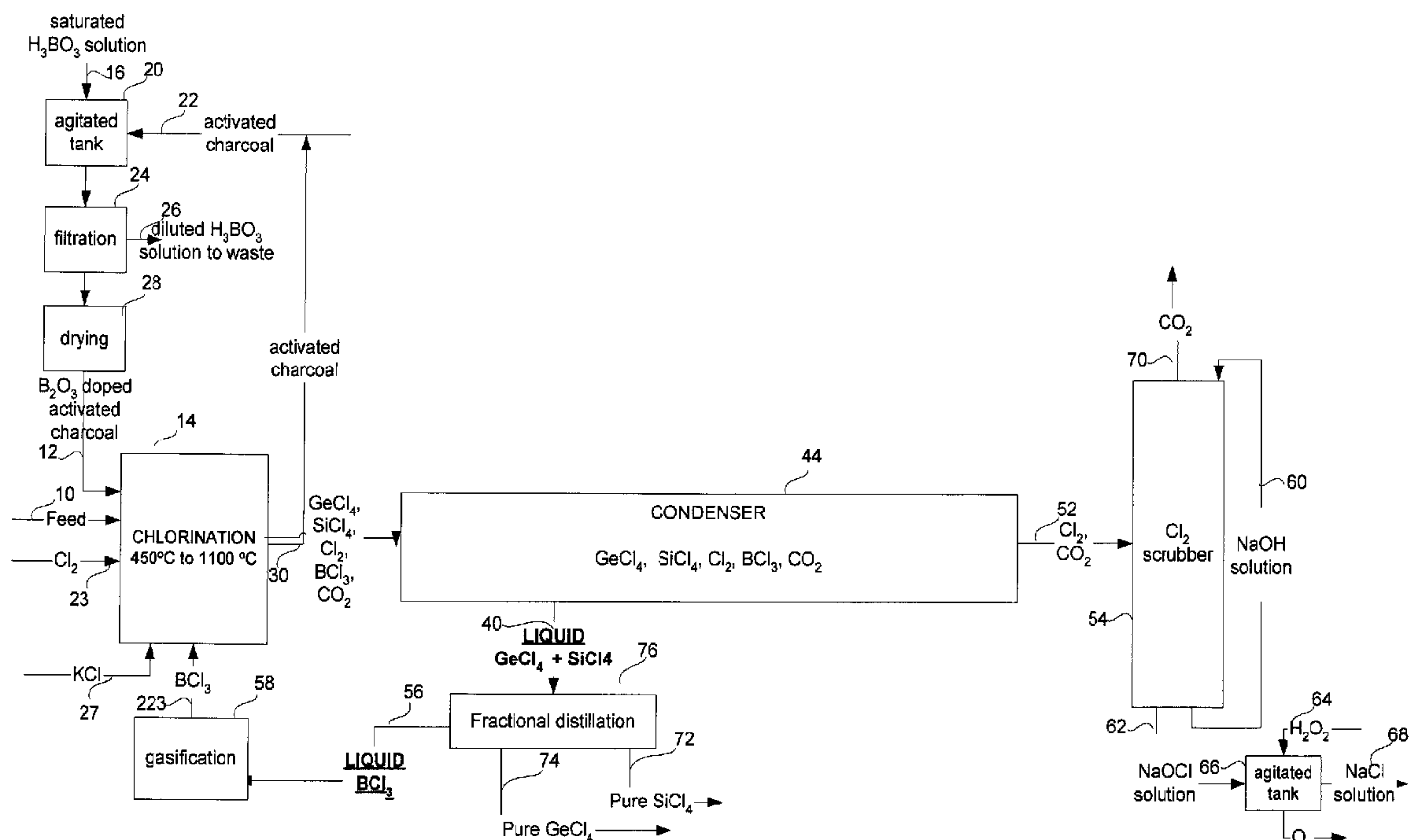




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(54) Titre : PROCEDE DE RECUPERATION DE GeCl_4 ET/OU SiCl_4 A PARTIR DE FIBRES OPTIQUES OU DE
RESIDUS DE VERRE ET PROCEDE POUR PRODUIRE DU SiCl_4 A PARTIR DE MATIERES RICHES EN SiCl_2
(54) Title: GeCl_4 AND/OR SiCl_4 RECOVERY PROCESS FROM OPTICAL FIBERS OR GLASSY RESIDUES AND
PROCESS FOR PRODUCING SiCl_4 FROM SiO_2 RICH MATERIALS



(57) Abrégé/Abstract:

A method is provided for producing GeCl_4 with or without SiCl_4 from optical fibers, the method comprises the steps of: reacting comminuted optical fibers including germanium and optionally silicon oxides with a reagent including a solid carbonaceous



(57) Abrégé(suite)/Abstract(continued):

reducing agent, chlorine and a boron compound to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 in accordance with the reactions: $2\text{BCl}_3(\text{g}) + 1.5\text{GeO}_2 = 1.5\text{GeCl}_4(\text{g}) + \text{B}_2\text{O}_3$; $2\text{BCl}_3(\text{g}) + 1.5\text{SiO}_2 = 1.5\text{SiCl}_4(\text{g}) + \text{B}_2\text{O}_3$; $\text{B}_2\text{O}_3 + 1.5\text{C} + 3\text{Cl}_2 = 2\text{BCl}_3(\text{g}) + 1.5\text{CO}_2$; and then condensing the gaseous GeCl_4 , BCl_3 and optionally SiCl_4 into liquid GeCl_4 , BCl_3 and optionally SiCl_4 . The invention further provides a method for producing SiCl_4 (and optionally GeCl_4) from glassy residues obtained from optical fiber manufacturing and wasted optical cables. The method includes the steps of: reacting comminuted glassy residues with a reagent including a solid carbonaceous reducing agent, a salt, a boron compound to obtain a gaseous product including SiCl_4 , BCl_3 , and optionally GeCl_4 ; and then condensing the gaseous SiCl_4 , BCl_3 (with or without GeCl_4) into liquid SiCl_4 , BCl_3 and GeCl_4 . There is also provided a method for producing SiCl_4 from a SiO_2 containing material.

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(54) Title: **GECL₄ AND/OR SICL₄ RECOVERY PROCESS FROM OPTICAL FIBERS OR GLASSY RESIDUES AND PROCESS FOR PRODUCING SICL₄ FROM SIO₂ RICH MATERIALS**

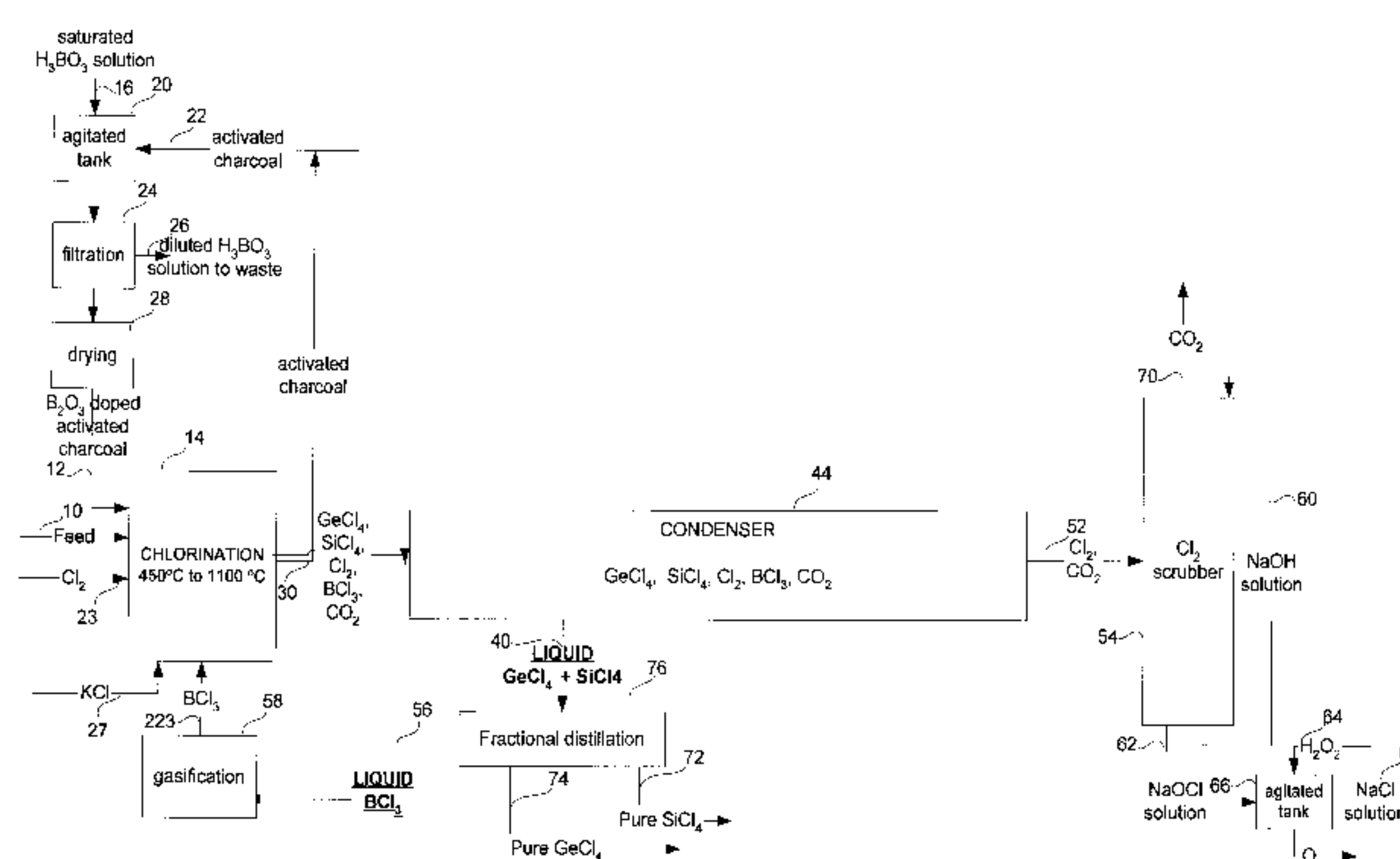


Figure 6

(57) Abstract: A method is provided for producing GeCl₄ with or without SiCl₄ from optical fibers, the method comprises the steps of: reacting comminuted optical fibers including germanium and optionally silicon oxides with a reagent including a solid carbonaceous reducing agent, chlorine and a boron compound to obtain a gaseous product including gaseous GeCl₄, gaseous SiCl₄, and gaseous BCl₃ in accordance with the reactions: 2BCl₃(g) + 1.5GeO₂ = 1.5GeCl₄(g) + B₂O₃; 2BCl₃(g) + 1.5SiO₂ = 1.5SiCl₄(g) + B₂O₃; B₂O₃ + 1.5C + 3Cl₂ = 2BCl₃(g) + 1.5CO₂; and then condensing the gaseous GeCl₄, BCl₃ and optionally SiCl₄ into liquid GeCl₄, BCl₃ and optionally SiCl₄. The invention further provides a method for producing SiCl₄ (and optionally GeCl₄) from glassy residues obtained from optical fiber manufacturing and wasted optical cables. The method includes the steps of: reacting comminuted glassy residues with a reagent including a solid carbonaceous reducing agent, a salt, a boron compound to obtain a gaseous product including SiCl₄, BCl₃, and optionally GeCl₄; and then condensing the gaseous SiCl₄, BCl₃ (with or without GeCl₄) into liquid SiCl₄, BCl₃ and GeCl₄. There is also provided a method for producing SiCl₄ from a SiO₂ containing material.

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GeCl₄ AND/OR SiCl₄ RECOVERY PROCESS FROM OPTICAL FIBERS OR
GLASSY RESIDUES AND PROCESS FOR PRODUCING SiCl₄ FROM SiO₂
RICH MATERIALS

FIELD OF THE INVENTION

5 [0001] The invention relates to a process for recovering germanium and silicon from optical fibers and, more particularly, it relates to a process for recovering germanium and silicon chlorides from optical fibers containing germanium and silicon oxides. The invention relates to a process for producing SiCl₄ from silicon oxides such as SiO₂ and to a process for concurrently producing SiCl₄ and GeCl₄ from glassy residues such as optical fibers.

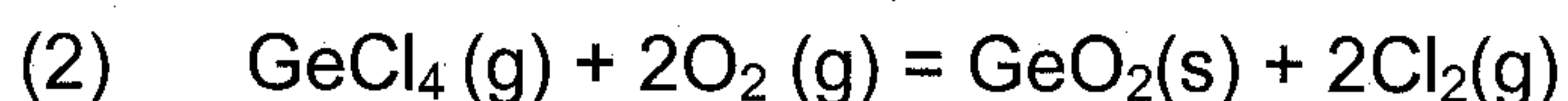
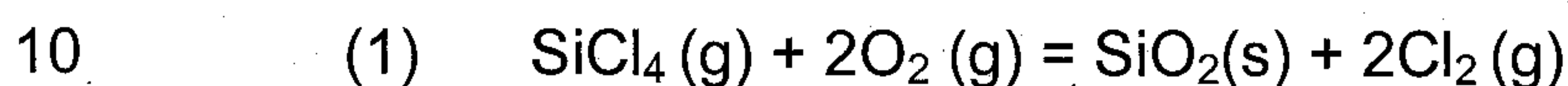
DESCRIPTION OF THE PRIOR ART

[0002] Processes for manufacturing optical cables including optical fibers, as active components for light signal transmission, are typically separated in three major steps: a) preform manufacturing, b) optical fiber drawing, and c) optical fiber cabling (Williams, 2000, The case of high purity silicon and its application in IT and renewable energy, UNU/IAS, 145 p.). Optical fibers have a core presenting a high refractive index surrounded by a cladding showing a lower refractive index (Alwayn, 2004, Optical network design and implementation, Cisco Press, 840 p.). Often, the core is made of fused silica containing germanium oxide, used as a doping agent, to increase the refractive index of silica. The cladding is habitually made of pure silica.

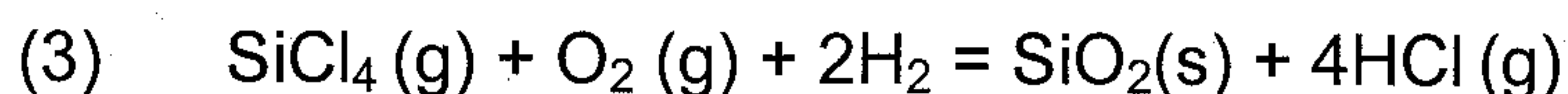
[0003] The manufacturing of optical fibers is based on dechlorination reactions where chlorides are transformed into oxides in a chemical reactor heated at around 1000 °C. The oxides are deposited on a solid support made of silica. Three main deposition systems exist (Williams, 2000). First, in a modified chemical vapor deposition (MCVD) process, the oxides are deposited inside a high purity silica tube, the dechlorination reactions are conducted until the tube is filled. The resulting glass rod is sintered into a preform and the obtained preform is ready for the drawing step. Second, an outside deposition system (ODS) uses

a glass rod as a support where the oxide particles built up, the dechlorination reactions are conducted until the desired rod diameter is reached. The rod is then sintered into a preform. Finally, the axial vapor deposition (AVD) process is somewhat similar to the ODS system, except that the building up of the oxide material is conducted from a point as opposed to the entire rod length. The resulting soot is sintered into a preform.

[0004] The dechlorination reactions which occur in the MCVD process for manufacturing optical fibers made of SiO₂ and GeO₂ are (Tandon, 2005, Int. J. Appl. Ceram. Technol., 2, 6, 504-513):



[0005] For the ODS and AVD processes, the dechlorination reactions are (Williams, 2000):



[0006] SiCl₄ and GeCl₄ are the starting chemical components for these three processes.

[0007] By carefully choosing the adequate reagent mixture, preforms consisting of a core enriched in a given high refractive index oxide, surrounded by a cladding of pure silica are obtained from these processes. The preforms are placed on a vertical shaft. A small furnace melts the basal tip of the blank preform. The melted material is pulled as an optical fiber which is coated and rolled up onto a spool (Yin and Jaluria, 1998, Trans. ASME, 120, 916-930).

[0008] The industry of optical fibers used extremely pure starting chlorides quoted as optical grade specification (99.999999 wt%, 6 decimal nines) in order to produce optical fibers made of pure oxides. Such purity is necessary to assure no distortion of the optical signals transmitted (Alwayn, 2004). Because

of the purity required, the chlorides used in the dechlorination reactions are very expensive. This is specifically true for germanium tetrachloride, germanium being a scarce element in the earth crust (Höll, R, Kling, M, Schroll, E: Metallogenesis of germanium - a review. Ore Geology Reviews 30 (2007), 145-180).

- 5 [0009] Manufacturing optical fibers produce important losses. An amount of high purity glasses substantially equal to the amount of optical fiber produced is defective or lost during the fabrication (Ma, Ogura, Kobayashi and Takahashi, Solar Energy Materials and Solar Cells, 2004, 81, 477-483).

- 10 [0010] The optical fibers, often called the glassy components, contained in end-of-life cables are presently considered as a zero value component. When optical cable recycling is performed, the glassy components are disposed in cement production furnaces or as raw material for civil engineering work (NTT Group, Environmental protection activity annual report, 2004).

- 15 [0011] An efficient process is thus needed in order to recycle defective optical fibers, losses of high purity glasses occurring during manufacturing of optical fibers, and optical fibers presents in end-of-life optical cables.

[0012] Japanese publication No. 2004-243264 by Takahashi reports the use of a novel thermal plasma system by which high purity SiO_2 from optical fiber residues are converted to solar grade silicon (SOG-Si) used for the production of solar panels.

- 20 [0013] South Korean publication No. 2005-0077446 by Jin, Kang and Lee instructs on the recovery of non deposited SiO_2 during the preform filling. The non deposited glassy particles are recovered on a glass particles collector. These particles are manufactured into a new preform using a special injection equipment.

[0014] Other patents listed below concern methods for dismantling optical cables into their basic components and therefore they are not related to the recovery of high-purity components from optical fibers.

5 [0015] Japanese publication No. 2005-104128 by Nakane teaches on the recycling of plastics and rubbers from wasted optical cables for the recovery of high-purity polyethylene and aluminum.

10 [0016] Japanese publication No. 2006-182863 by Ito, Usami and Masura, relates to the separation of organic clad from optical fiber residues obtained by segregation of optical cables. The process involves solvent extraction and screening to obtain a clean quartz-glass material recycled as cement component and coated resins recycled as a solid fuel.

[0017] Japanese publication No. 2006-187764 by Ito, Usami and Masura, reports on the recycling of optical cables by crushing and sieving into usable materials.

15 [0018] These three previous documents demonstrate that technologies are available to isolate the glassy components from optical cables. All of those approaches are based on low cost technologies such as crushing, sieving, and solvent extraction in order to isolate the glassy components from the other optical cable components.

20 [0019] Two publications, concerning the recycling of glassy residues, originating from the production of optical fibers or from end-of-life optical cables, as high-purity products, have been located. These two publications are derived from the Japanese Publication No. 2004-243264 by Takahashi on the recycling of high-purity glassy materials by a thermal plasma system. The first one by Ma, et al., (2004) presents the previously described technology. The second one by Ogura, Astuti, Yoshikawa, Morita and Takahashi (2004, Ind. Eng. Chem. Res., 43, 1890-1893) describes a process using an arc-plasma furnace by which a mixture of silicon carbide and silicon is obtained from a feed of wasted optical fibers. 25 When the silicon carbide product is recycled in the process furnace, the yield of high-purity silicon production increased. This process is run at very high

temperature and produce silicon as a feedstock for the fabrication of solar panels.

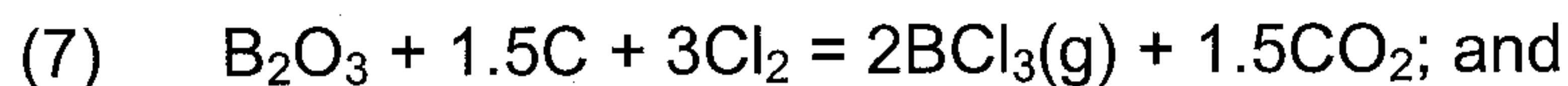
[0020] In addition, Bohrer, Amelse, Narasimham, Tariyal, Turnipseed, Gill, Moebuis and Bodeker (1985, Journal of Light Wave Technology, LT-3, 3, 699-705) have developed a process for the recovery of the unused GeCl_4 in reactions (2) and (4) exiting the deposition system and present in the process effluents. GeCl_4 is trapped into the gas scrubber as soluble germanate ions. After, a certain recirculation time to build up the concentration, the germanate ions react with magnesium sulfate to precipitate magnesium germanate which is filtered, dried, bagged and sold to a manufacturer.

[0021] US Patent no. 4,490,344 discloses BCl_3 as a chlorination agent for the formation of SiCl_4 from SiO_2 .

BRIEF SUMMARY OF THE INVENTION

[0022] It is therefore an aim of the present invention to address the above mentioned issues.

[0023] According to a general aspect, there is provided a method for producing GeCl_4 from optical fibers; the method comprising the steps of: reacting comminuted optical fibers including germanium oxides with a reagent including a solid carbonaceous reducing agent, chlorine and a boron compound to obtain a gaseous product including gaseous GeCl_4 , and gaseous BCl_3 in accordance with the reactions:



condensing the gaseous GeCl_4 and BCl_3 into liquid GeCl_4 and BCl_3 .

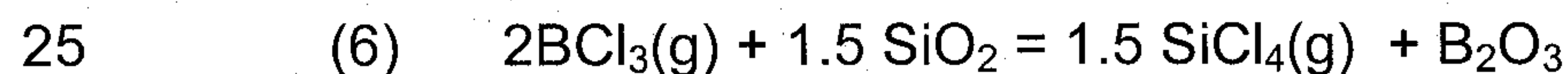
[0024] According to another general aspect, there is provided a method for producing GeCl_4 as starting components for optical fiber manufacturing. The method comprises the steps of: reacting comminuted optical fiber glassy

residues including germanium and silicon oxides with a reagent including a solid carbonaceous reducing agent, chlorine and a boron compound to obtain a gaseous product including gaseous GeCl_4 , and gaseous BCl_3 ; condensing the gaseous GeCl_4 and BCl_3 into liquid GeCl_4 and BCl_3 .

- 5 [0025] According to a further general aspect, there is provided a method for chlorinating GeO_2 encapsulated into glasses. The method comprises the steps of: reacting comminuted glasses with a reagent including a solid carbonaceous reducing agent, chlorine and a boron compound to obtain a gaseous product including gaseous GeCl_4 , and gaseous BCl_3 ; and condensing the gaseous GeCl_4 and BCl_3 into liquid GeCl_4 and BCl_3 .

- [0026] According to still another general aspect, there is provided a method for producing GeCl_4 from optical fibers. The method comprising the steps of: reacting optical fibers including germanium oxides with a reagent including a reducing agent and BCl_3 to obtain a gaseous product including gaseous GeCl_4 , and gaseous BCl_3 ; and condensing the gaseous GeCl_4 and BCl_3 into liquid GeCl_4 and BCl_3 .

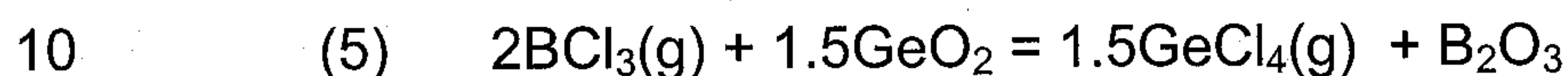
- [0027] According to another aspect, there is provided the methods for producing GeCl_4 from optical fibers, optical fibers glassy residues or any other GeO_2 containing residues as defined above, wherein the residues also contain SiO_2 , the method comprising the steps of: reacting residues including germanium and silicon oxides with a reagent including a solid carbonaceous reducing agent, chlorine and a boron compound to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 in accordance with the reactions:



condensing the gaseous GeCl_4 , SiCl_4 and BCl_3 into liquid GeCl_4 , SiCl_4 and BCl_3 .

[0028] According to a further aspect of the invention, the is provided the methods as defined above wherein the liquid GeCl_4 and/or liquid SiCl_4 and/or liquid BCl_3 are separated by fractional distillation.

[0029] According to a general aspect, there is provided a method for producing GeCl_4 and SiCl_4 from optical fibers, the method comprising the steps of: reacting comminuted optical fibers including germanium and silicon oxides with a reagent including a solid carbonaceous reducing agent, chlorine and a boron compound to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 in accordance with the reactions:



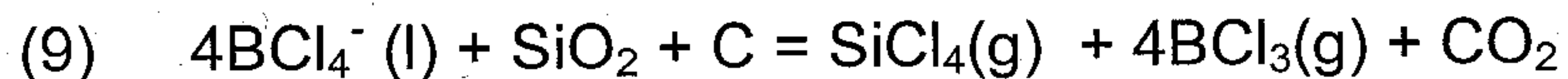
firstly condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature; and secondly condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing temperature and above BCl_3 condensing temperature.

[0030] According to another general aspect, there is provided a method for producing GeCl_4 and SiCl_4 as starting components for optical fiber manufacturing. The method comprises the steps of: reacting comminuted optical fiber glassy residues including germanium and silicon oxides with a reagent including a solid carbonaceous reducing agent, chlorine and a boron compound to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 ; firstly condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature; and secondly condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing temperature and above BCl_3 condensing temperature.

[0031] According to a further general aspect, there is provided a method for chlorinating GeO_2 encapsulated into SiO_2 glasses. The method comprises the steps of: reacting comminuted SiO_2 glasses with a reagent including a solid carbonaceous reducing agent, chlorine and a boron compound to obtain a
 5 gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 ; and condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature.

[0032] According to still another general aspect, there is provided a method for
 10 producing GeCl_4 and SiCl_4 from optical fibers. The method comprising the steps of: reacting optical fibers including germanium and silicon oxides with a reagent including a reducing agent and BCl_3 to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 ; and condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering the gaseous product temperature below
 15 GeCl_4 condensing temperature and above SiCl_4 condensing temperature.

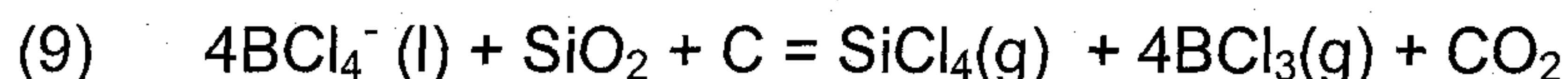
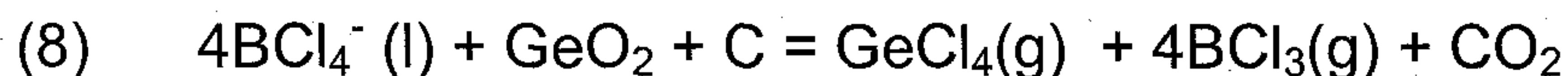
[0033] According to a further general aspect, there is provided a method for producing SiCl_4 from optical fiber glassy residues, the method comprising the steps of: reacting comminuted optical fiber glassy residues with a reagent including a solid carbonaceous reducing agent, a salt selected from the group
 20 consisting of KCl , CsCl , and RbCl , and a boron compound to obtain a gaseous product including gaseous SiCl_4 in accordance with the reactions:



[0034] and condensing the gaseous SiCl_4 and BCl_3 into liquid SiCl_4 and BCl_3 . Optionally, chlorine gas can be added as reagent.

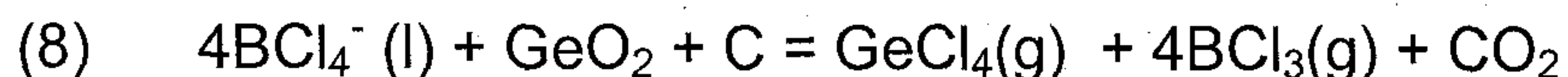
25 [0035] Still, according to a further general aspect, there is provided a method for producing SiCl_4 , and optionally GeCl_4 from optical fiber glassy residues, the method comprising the steps of: reacting comminuted optical fiber glassy residues with a reagent including a solid carbonaceous reducing agent, a salt selected from the group consisting of: KCl , CsCl and RbCl , a boron compound

and, optionally chlorine to obtain a gaseous product including gaseous SiCl_4 and optionally GeCl_4 in accordance with the reactions:



- 5 and condensing the gaseous SiCl_4 , GeCl_4 if present, and BCl_3 into liquid SiCl_4 , GeCl_4 and BCl_3 .

[0036] According to a further general aspect, there is provided a method for producing SiCl_4 and GeCl_4 from optical fiber glassy residues, the method comprising the steps of: reacting comminuted optical fiber glassy residues with a
10 reagent including a solid carbonaceous reducing agent, a salt selected from the group consisting of KCl , CsCl , and RbCl , chlorine and a boron compound to obtain a gaseous product including gaseous GeCl_4 and gaseous SiCl_4 in accordance with the reactions:



firstly condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature; and secondly condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing
20 temperature and above BCl_3 condensing temperature.

[0037] According to another general aspect, there is provided a method for producing GeCl_4 and SiCl_4 as starting components for optical fiber manufacturing. The method comprises the steps of: reacting comminuted optical fiber glassy residues with a reagent including a solid carbonaceous reducing
25 agent, a salt selected from the group consisting of KCl , CsCl , and RbCl , chlorine and a boron compound to obtain a gaseous product including gaseous GeCl_4 and gaseous SiCl_4 ; firstly condensing the gaseous GeCl_4 into liquid GeCl_4 by

lowering gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature; and secondly condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing temperature and above BCl_3 condensing temperature.

- 5 [0038] According to a further general aspect, there is provided a method for producing SiCl_4 from a SiO_2 containing material. The method comprises the steps of: reacting a comminuted SiO_2 containing material with a reagent including a solid carbonaceous reducing agent, a salt selected from the group consisting of KCl , CsCl , and RbCl , chlorine and a boron compound to obtain a
10 gaseous product including gaseous SiCl_4 ; and condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing temperature and above BCl_3 condensing temperature.

- [0039] According to still another general aspect, there is provided a method for producing SiCl_4 from glassy residues. The method comprising the steps of:
15 reacting glassy residues with a solid carbonaceous reducing agent, a salt selected from the group consisting of KCl , CsCl , and RbCl , chlorine and a boron compound to obtain a gaseous product including gaseous SiCl_4 ; and condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering the gaseous product temperature below SiCl_4 condensing temperature.

20 **BRIEF DESCRIPTION OF THE DRAWINGS**

[0040] Fig. 1 is a flow diagram of the process in accordance with an embodiment, with a reagent including B_2O_3 doped activated charcoal;

[0041] Fig. 2 is a flow diagram of the process in accordance with another embodiment, with a reagent including gaseous BCl_3 ;

- 25 [0042] Fig. 3 is a flow diagram of a SiO_2 and GeO_2 chlorination process in accordance with an embodiment, with a reagent including B_2O_3 doped activated charcoal;

[0043] Fig. 4 is a flow diagram of the SiO_2 and GeO_2 chlorination process in accordance with another embodiment, with a reagent including activated charcoal;

5 [0044] Fig. 5 is a flow diagram of the SiO_2 chlorination process in accordance with still another embodiment, with a SiO_2 rich feed material;

[0045] Fig. 6 is a flow diagram of the SiO_2 chlorination process in accordance with still another embodiment, with a SiO_2 rich feed material;

[0046] Fig. 7 is a schematic perspective view of an experimental set up in accordance with an embodiment; and

10 [0047] Fig. 8 is a schematic perspective view of the experimental set up shown in Fig. 7, showing the position of a sample beaker.

[0048] It will be noted that throughout the appended drawings, like features are identified by like reference numerals.

DETAILED DESCRIPTION

15 [0049] Referring to the drawings and, more particularly, referring to Figs. 1 and 2, processes for producing concurrently germanium tetrachloride and silicon tetrachloride from optical fibers are described. In the processes, germanium and silicon oxides (GeO_2 and SiO_2) present in optical fibers are converted into germanium and silicon chlorides (GeCl_4 and SiCl_4). The produced chlorides are
20 identical to those commonly employed in the manufacture of optical fibers.

[0050] For instance, the optical fibers, as feed material 10, can be glassy residues originating from optical fiber production, i.e. glassy residues originating from optical fiber production facilities or oxides particles carry over in a scrubber unit of optic fiber production facilities, or glassy residues originating from end-of-
25 life optical fibers, i.e. optical fibers originating from the dismantling of used optical cables.

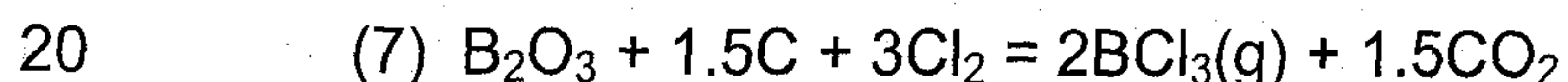
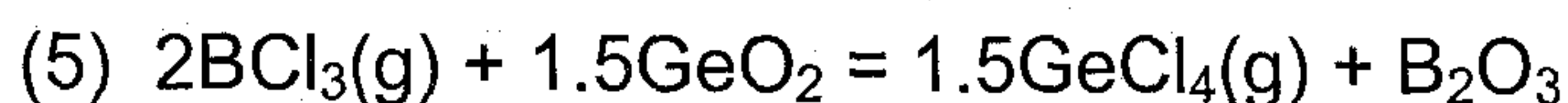
[0051] The glassy residues, as feed material 10, are first dried and comminuted before being introduced in a chlorination reactor 14. The glassy residues can be either crushed or shredded to particles having an average size ranging between micrometers to millimeters. For instance, the particle average size can range
5 between 10 and 250 μm . In an embodiment, the particles have a substantially uniform size.

[0052] These glassy residues can have a resin coating. This resin coating does not negatively interfere in the GeCl_4 and SiCl_4 manufacturing process. On the opposite, the resin coating can have a positive effect on the process as the
10 organic coating can be used as a reducer during the carbochlorination process.

CHLORINATION AND PRIOR PREPARING STEPS

[0053] As mentioned above, for manufacturing optical fibers, the dechlorination reactions (1) to (4) are carried out. To recover silicon and germanium contained in the glassy residues as oxides, these reactions are reversed.

15 [0054] According to another aspect of the invention, boron trichloride is used as the effective chlorination agent for GeO_2 and SiO_2 . More particularly, the following reactions take place:



[0055] The action of BCl_3 on SiO_2 to produce SiCl_4 and B_2O_3 is recognized at a temperature around 350 °C (Kroll, Metal Industry, 1952, 81, (13), 243-6; Savel'ev et al., Neorganicheskie Materialy, 1973, 9, (2), 325-6). Moreover, B_2O_3 can be chlorinated (or regenerated) as BCl_3 by the action of Cl_2 and a reducing agent
25 such as coke or activated charcoal (Alam et al., 2004, Kirk-Othmer Encyclopedia of chemical technology, 138-168).

[0056] To recover silicon and germanium contained in the glassy residues as oxides, BCl_3 is now used as effective chlorination agent in a relatively low temperature process. More particularly, BCl_3 is a chlorinating agent for GeO_2 encapsulated into SiO_2 glasses. Therefore, the above-mentioned reactions can
5 be used to simultaneously produce GeCl_4 and SiCl_4 from optical fiber glassy residues containing silicon and germanium oxides.

[0057] As it will be described in more details below, BCl_3 can be added as a gas or can be generated *in situ* through reaction (7).

[0058] For carrying out the chlorination reactions, a reagent mixture including a
10 reducing agent 22, 122, chlorine (Cl_2) 23, 123 and boron 16, 116 is provided in addition to the glassy residue feed material 10 (Figs. 1 & 2).

[0059] The reducing agent can be a solid carbonaceous reducing agent such as metallurgical coke or activated carbon, for instance.

[0060] Referring to **Fig. 1**, there is shown that, in an embodiment, the reducing
15 agent and boron of the reagent mixture are provided as a reducing agent doped with a boron compound 12. More particularly, a boron compound is adsorbed on a solid reducer prior to the chlorination step 14. In the embodiment shown, the solid reducer 22 is activated charcoal. As it will be described in more details below, high conversion rates for GeO_2 and SiO_2 were obtained when the reagent
20 mixture included the reducing agent with the adsorbed boron compound.

[0061] The reducing agent with the adsorbed boron compound 12 is obtained from a solution saturated with a boron compound 16, such as H_3BO_3 , for instance. In an agitated tank 20, the saturated solution is mixed with the solid reducing agent 22, such as activated charcoal, for instance. The solid
25 carbonaceous reducer containing the adsorbed boron compound is separated by filtration 24, for instance, from the solution 26 and can be dried 28 at a temperature of 500°C for three hours. In an alternate embodiment, the solid carbonaceous reducer containing the adsorbed boron compound can be dried at a temperature ranging between 450 and 550°C for 30 minutes to three hours.

The drying step 28 can be carried out in an inert atmosphere such as with nitrogen, for instance. The drying step 28 removes any form of water which could be detrimental to the chlorination process.

5 [0062] The adsorption, filtration and drying steps 20, 24, 28 are usually carried outside the chlorination reactor.

[0063] Referring now to **Fig. 2**, there is shown that, in an alternate embodiment, the reducing agent 122, such as activated charcoal for instance, and boron 116 are distinctly provided. Instead of being adsorbed on the reducing agent 122, boron is provided separately as gaseous BCl_3 116.

10 [0064] Now referring simultaneously to **Figs. 1 and 2**, there is shown that the chlorination reaction is carried out in a chlorination reactor 14, 114 at a temperature ranging between 450 and 1100 °C. In an embodiment, the reactor 14, 114 is made from a material resisting to the corrosive nature of gases contained therein.

15 [0065] In the chlorination reactor 14, 114, a gaseous product 30 is obtained. The gaseous product 30 includes, amongst other, gaseous GeCl_4 and SiCl_4 . A continuous chlorine flow (Cl_2) is maintained in the chlorination reactor and GeCl_4 and SiCl_4 leave the chlorination reactor 14, 114 as vapor phases and are carried out by the gaseous product flow toward the condensation sections 32, 34, 36.
20 The gaseous product 30 leaving the carbochlorination reactor 14 is essentially composed of GeCl_4 , SiCl_4 , Cl_2 , BCl_3 , and CO_2 .

[0066] At the exit of the carbochlorination reactor 14, 114, the gaseous product 30 and the solid reducer 222 are separated via a filtration system (not shown). The solid reducer 222 is collected in a receiving bin and is reused in the
25 chlorination process as reducing agent.

[0067] The gaseous product 30 is collected in a pipe system connecting the chlorination reactor 14, 114 to a first condensing unit 32. The pipe system is thermostated, i.e. the gas temperature inside the pipe system is controlled. Thus,

the temperature can be maintained over the boiling temperature of GeCl_4 (84°C), one gaseous product component. The boiling points of the other gaseous product components exiting the carbochlorination reactor 14, 114 are lower than GeCl_4 boiling point. Thus, all gaseous product components remain in gaseous phase in the pipe system extending between the chlorination reactor 14, 114 and the first condensing unit 32.

FIRST CONDENSING UNIT: GeCl_4

[0068] The first condensing unit 32 condenses selectively $\text{GeCl}_4(\text{g})$ from the other gaseous product components and, more particularly, $\text{SiCl}_4(\text{g})$, $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{CO}_2(\text{g})$.

[0069] To perform this selective condensation of GeCl_4 , the temperature inside the condenser 32 is set to a set-point slightly below GeCl_4 boiling point and slightly above SiCl_4 boiling point ($57,6^\circ\text{C}$). The gaseous product 30 is cooled and washed with liquid GeCl_4 38.

[0070] The condenser 32 is filled with perforated spheres made of a resistant material. A recycling loop of liquid GeCl_4 connected to a shower nozzle, placed at the top of the unit, assures adequate percolation and contacts between the liquid phase 38 and the gaseous product 30. The condensed liquid GeCl_4 40 is collected in a reservoir placed at the base of the condensing unit 32. The gaseous product 42 exiting the condenser 32 is essentially composed of $\text{SiCl}_4(\text{g})$, $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, and $\text{CO}_2(\text{g})$. It is directed via a second pipe system to a second condensing unit 34 where gaseous SiCl_4 is condensed, as it will be described in more details below.

[0071] As for the first pipe system extending between the chlorination reactor 14, 114 to the first condensing unit 32, the second pipe system is thermostated. Thus, the temperature can be maintained over SiCl_4 boiling temperature ($57,6^\circ\text{C}$) and below GeCl_4 boiling point (84°C). Thus, all gaseous product components remain in gaseous phase in the second pipe system extending between the first and the second condensing units 32, 34.

SECOND CONDENSING UNIT: SiCl_4

[0072] This second condensing unit 34 is similar to the first condensing unit 32, except that the temperature inside the condenser 34 is set to a point slightly below SiCl_4 condensation point and that the gaseous product 42 entering the
5 condenser 34 is washed with SiCl_4 in liquid phase 44. These operating conditions allow the selective condensation of SiCl_4 46 which is collected in a reservoir located at the base of the condensing equipment 34. Hence, the gaseous product 48 exiting the second condenser 34 essentially includes $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{CO}_2(\text{g})$. It is directed towards a third condensing unit 36 where
10 the condensation of BCl_3 is carried out through a third pipe system.

[0073] As for the previous pipe systems, the third pipe system is thermostated and its temperature is maintained over BCl_3 boiling temperature ($12,5^\circ\text{C}$) and below SiCl_4 boiling point ($57,6^\circ\text{C}$). Thus, $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{CO}_2(\text{g})$, the gaseous product components, remain in gaseous phase in the third pipe system
15 extending between the second and the third condensing units 34, 36.

THIRD CONDENSING UNIT: BCl_3

[0074] In the third condensing unit 36, gaseous BCl_3 is condensed. The temperature inside the condenser 36 is adjusted to a set-point slightly below the condensation point of BCl_3 and the gas entering the condenser 36 is washed
20 with liquid BCl_3 50 allowing its selective condensation. The gaseous product 52 exiting the condenser 36 includes $\text{Cl}_2(\text{g})$ and $\text{CO}_2(\text{g})$ and it is directed towards a scrubbing and a neutralization systems 54.

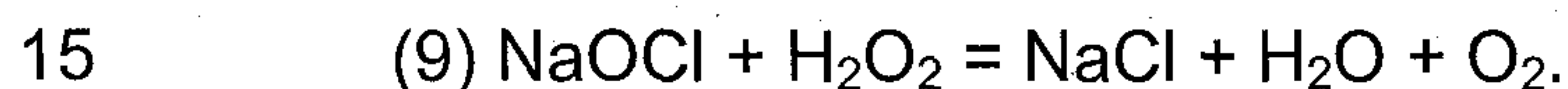
[0075] Liquid BCl_3 56 obtained at this condensation step can be recycled as a reagent 223 to the chlorination reactor 14 after a gasification step 58. The
25 quantity of recycled BCl_3 223 used to chlorinate the optical fiber feed 10 is balanced with additional input of BCl_3 116 or solid boron compound 16, if necessary.

SCRUBBING AND NEUTRALIZATION

[0076] Chlorine (Cl_2) is removed from the gaseous product 52 in a scrubber 54. This scrubbing unit 54 includes a vertical cylinder containing perforated plastic spheres. The scrubber 54 is filled to a certain extent with a solution of NaOH 60. A system, including a pump linked to a recycling loop and a spray nozzle located at the top of the scrubber 54, allows the gaseous product 52 to be washed and contacted with the NaOH solution 60. The following reaction occurs between chlorine contained in the gaseous product 52 and the NaOH solution 60:



[0077] The pH of the solution is controlled by an exterior supply of concentrated NaOH. The NaOCl solution 62 resulting from the scrubbing procedure is subsequently treated with H_2O_2 64, in an agitated tank 66, in order to obtain a sodium chloride solution 68 by the reaction



[0078] The gas exiting at the top of the scrubber contains essentially CO_2 70. If necessary, the CO_2 70 exiting the process can be trapped or neutralized by an existing complementary technology aiming at CO_2 emanation recovery.

 Cl_2 COMPRESSOR

20 [0079] In an alternate embodiment, the chlorine scrubber unit 54 can be replaced by a chlorine compressor which allows compression of gaseous chlorine into a liquid chlorine and therefore its separation from gaseous CO_2 . The compressed chlorine can be stored in gas cylinders for future uses such as one of the chlorination process reactant.

25 LIQUID GeCl_4 AND LIQUID SiCl_4

[0080] The process described above transforms optical fibers glassy residues in chloride forms which can be directly used as feed material for manufacturing optical fibers. The liquid chlorides selectively separated during the process and

collected at the base of the GeCl_4 condenser and the SiCl_4 condenser are of relatively high purity.

[0081] If necessary, additional purification steps can be performed on the separated chlorides obtained from the process. These additional purification
5 steps can include one or several methods such as distillation, fractional distillation, solvent extraction and resin purification.

Alternative embodiment

[0082] Referring to the drawings and, more particularly, referring to **Figs. 3 to 5**, processes for producing chlorides from oxide containing feed materials are
10 described. More particularly, in **Figs. 3 and 4**, processes for producing concurrently germanium tetrachloride and silicon tetrachloride from optical fiber glassy residues are described. In the processes, germanium and silicon oxides (GeO_2 and SiO_2) present in optical fibers or other glassy residues are converted into germanium and silicon tetrachlorides (GeCl_4 and SiCl_4). The produced
15 tetrachlorides are identical to those commonly employed in the fabrication of optical fibers. In **Fig. 5**, a process for producing silicon tetrachloride from a SiO_2 -rich material is described. The silicon oxide (SiO_2) presents in the SiO_2 -rich material is converted into silicon tetrachloride (SiCl_4).

[0083] For instance, the optical fibers, as feed material 10, can be glassy
20 residues originating from optical fiber production, i.e. glassy residues originating from optical fiber production facilities or oxide particles carry over in a scrubber unit of optic fiber production facilities, glassy residues originating from end-of-life optical fibers, i.e. optical fibers originating from the dismantling of used optical cables, or glassy residues isolated from wasted optical cables.

25 [0084] These glassy residues, as feed material, can have a resin coating. This resin coating does not negatively interfere in the GeCl_4 and SiCl_4 manufacturing process. On the opposite, the resin coating can have a positive effect on the process as the organic coating can be used as a reducer during the carbochlorination process.

[0085] In an alternate embodiment, the feed material 110 (see Fig. 5) can include a SiO_2 -rich material which is substantially free of GeO_2 , such as quartz, and which will be converted into SiCl_4 in a chlorination reactor 14. In an embodiment, the SiO_2 -rich material includes more than 90 wt% of SiO_2 . For SiO_2 rich feed substantially free of GeO_2 , the fractional distillation step is simplified since no GeCl_4 is present in the mixture. If necessary a primary condensing unit can be added at the exit of the reactor to remove unwanted high boiling points chloride impurities.

Prior preparing steps

[0086] The feed material 10, 110, either the glassy residues or the SiO_2 -rich material, are first dried and comminuted before being introduced in a chlorination reactor 14. The feed material 110 can be either crushed, grinded, or shredded to particles having an average size ranging between micrometers to millimeters. For instance, the particle average size can range between 10 and 250 μm . In an embodiment, the particles have a substantially uniform size.

[0087] In an alternate embodiment, the grinded feed material 10, 110 is introduced in the reactor 14 without being previously dried. The drying step can be carried out within the reactor 14 or the process can be drying step free. The feed material 10, 110 can be dried at a temperature ranging between 400 and 600 $^{\circ}\text{C}$ for 0.5 hour to 3 hours, for instance. Moreover, the reagent mixture or only a portion thereof can be introduced in the reactor 14 while carrying the drying step, as it will be described in more details below. The drying step can be carried out in an inert atmosphere such as under nitrogen, for instance. The drying step removes any form of water which could be detrimental to the chlorination process.

Chlorination

[0088] As mentioned above, for manufacturing optical fibers, the dechlorination reactions (1) to (4) are carried out. To recover silicon and germanium contained in the glassy residues as oxides, these reactions are reversed in a chlorination procedure.

[0089] For carrying out the chlorination reactions, a reagent mixture including a reducing agent 12, 22, a salt 27 such as KCl, RbCl, and CsCl, chlorine (Cl_2) 23 and a boron compound, either B_2O_3 (**Fig. 3**) or boron trichloride (BCl_3) 29 (**Figs. 4 and 5**), is provided in addition to the feed material 10, 110, either the glassy residues or the SiO_2 -rich material. In **Figs. 3 to 5**, the salt of the reagent mixture is KCl. The salt mass represents 3 to 15 wt% of the total solid feed mass, i.e. the feed material mass, the reducing agent mass, and the salt mass. Particularly, KCl is used. More particularly, when KCl is used, chlorine gas (Cl_2) may be omitted with still excellent results.

10 [0090] The reducing agent 12, 22 can be a solid carbonaceous reducing agent such as metallurgical coke or activated carbon/charcoal, for instance. The ratio between the reducing agent mass and the feed material mass varies between 0.3 and 1.

[0091] In an embodiment, a portion of the reagent mixture is added to the
15 comminuted feed material 10, 110 before carrying out the drying step. For instance and without being limitative, the reducing agent 12, 22 and the salt 27, i.e. the solid components of the reagent mixture, can be added to the comminuted feed material 10, 110 before carrying out the drying step. As mentioned above, the drying step can be carried out at a temperature ranging
20 between 400 and 600 °C for 0.5 hour to 3 hours, for instance. Once the drying step is terminated, the other components (Cl_2 and BCl_3) of the reagent mixture are added to the dried solid components.

[0092] Referring now to **Fig. 3**, there is shown that, in an embodiment, the reducing agent 12 is provided as a reducing agent doped with a boron
25 compound and the feed material 10 includes glassy residues. More particularly, the boron compound is adsorbed on a solid reducer prior to the chlorination step 14. In the embodiment shown, the solid reducer 22 is activated charcoal.

[0093] The reducing agent with the adsorbed boron compound 12 is obtained from a solution saturated with a boron compound 16, such as H_3BO_3 , for

instance. In an agitated tank 20, the saturated solution is mixed with the solid reducing agent 22, such as activated charcoal, for instance. The solid carbonaceous reducer containing the adsorbed boron compound is separated by filtration 24, for instance, from the solution 26 and can be dried 28 at a temperature of 500 °C for three hours. In an alternate embodiment, the solid carbonaceous reducer containing the adsorbed boron compound can be dried at a temperature ranging between 450 and 550 °C for 30 minutes to three hours. The drying step 28 can be carried out in an inert atmosphere such as with nitrogen, for instance. The drying step 28 removes any form of water which could be detrimental to the chlorination process.

[0094] The adsorption, filtration and drying steps 20, 24, 28 are usually carried outside the chlorination reactor 14. In this embodiment, the reagent does not compulsorily include a fresh BCl_3 supply 29 (see **Figs. 4 and 5**). However, as it will be described in more details below, recycled BCl_3 can be added to the reagent.

[0095] Referring now to **Fig. 4**, there is shown that, in an alternate embodiment, the reducing agent 22, such as activated charcoal for instance, is distinctly provided from boron. In this case, a fresh BCl_3 supply 29 is added to the reagent. As for the embodiment described above in reference to **Fig. 3**, the feed material includes glassy residues.

[0096] Referring now to **Fig. 5**, there is shown that, in an another alternate embodiment, the feed material 110 includes a SiO_2 -rich material and the reducing agent 22, such as activated charcoal for instance, is distinctly provided from boron. In the embodiment shown in **Fig. 5** and described below, the reagent includes a fresh BCl_3 supply 29. It is appreciated that, in an alternate embodiment, a reducing agent doped with a boron compound can also be used with a SiO_2 -rich feed material.

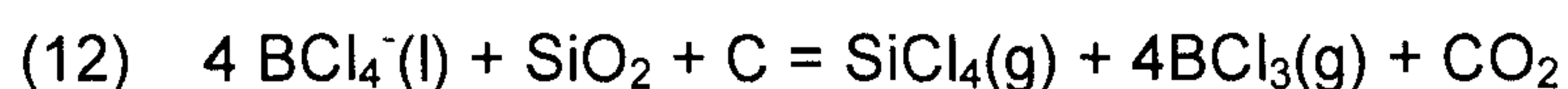
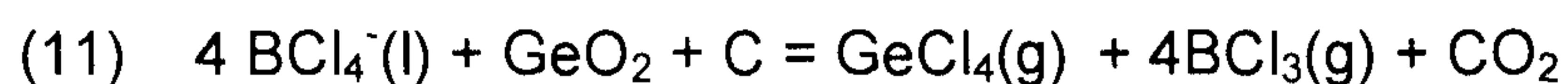
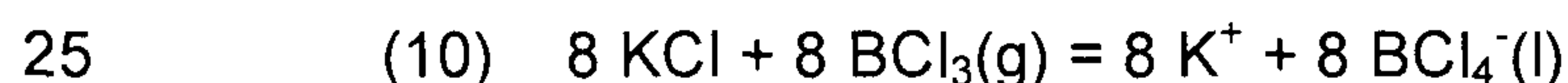
[0097] Now referring simultaneously to **Figs. 3 to 5**, there is shown that the chlorination reaction is carried out in a chlorination reactor 14 at a temperature

ranging between 450 and 1100 °C and, in an alternate embodiment, the temperature is ranging between 750 and 950 °C. In an embodiment, the reactor 14 is made from a material resisting to the corrosive nature of gases contained therein.

[0098] In the chlorination reactor 14, a gaseous product 30 is obtained. The gaseous product 30 includes, amongst other, gaseous GeCl_4 and SiCl_4 if the feed material 10 includes glassy residues (**Figs. 3 and 4**) or gaseous SiCl_4 if the feed material 110 includes a SiO_2 -rich material (**Fig. 5**). A continuous chlorine flow (Cl_2) 23 is maintained in the chlorination reactor and the gaseous product 30, including gaseous SiCl_4 and GeCl_4 , if any, leaves the chlorination reactor 14 as vapor phase and is carried out toward the condensation sections 32, 34, 36, 132, as it will be described in more details below. The gaseous product 30 leaving the carbochlorination reactor 14 is essentially composed of GeCl_4 , SiCl_4 , Cl_2 , BCl_3 , and CO_2 if the feed material includes glassy residues (**Figs. 3 and 4**) and SiCl_4 , Cl_2 , BCl_3 , CO_2 , and possibly other chloride impurities, if the feed material includes a SiO_2 -rich material (**Fig. 5**).

[0099] Muettertides (Journal of the American Chemical Society, 1957, vol., 79, 6563-6564) have demonstrated that tetrachloroborate salts of the type KBCl_4 , RbBCl_4 and CsBCl_4 can be prepared by reacting at high temperature an appropriate salt such as KCl with gaseous BCl_3 .

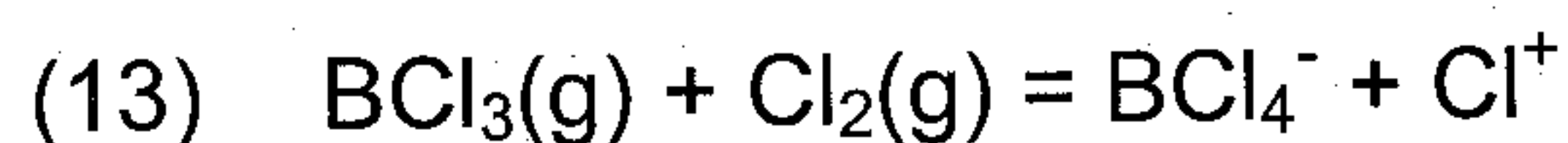
[00100] In the chlorination reactions of the process, BCl_4^- is used as the effective chlorinating agent for SiO_2 glasses and GeO_2 glasses contained in optical fibers and for SiO_2 contained in SiO_2 -rich material. More particularly, the following reactions take place to simultaneously produce GeCl_4 and SiCl_4 from glassy residues:



[00101] If the feed material is substantially free of GeO_2 , the same reactions take place, except reaction (11).

[00102] The reactions are carried out at a temperature ranging between 450 and 1100 °C, in an alternate embodiment, at a temperature ranging between 800 and 900 °C, and, in still an alternate embodiment, at a temperature ranging between 825 and 875 °C.

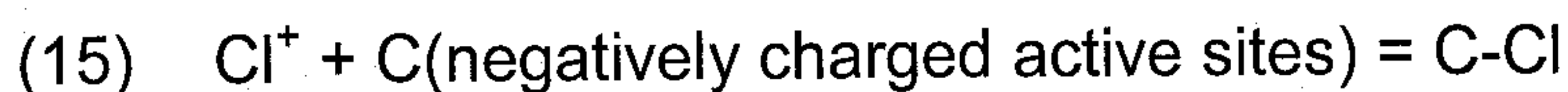
[00103] At a temperature proximate to 850 °C, KBCl_4 is in liquid phase since this temperature is above the melting point of KCl (776 °C). The oxide and carbon particles are probably partially surrounded by a liquid bath containing K^+ and BCl_4^- ions. The BCl_4^- ion being the chlorinating agent, Cl^- is transferred to the oxide surface via the reactions (11) and (12) which lead to the production of a gaseous phase including BCl_3 , SiCl_4 , GeCl_4 , if any, and CO_2 , which escapes the KBCl_4 liquid bath. Then, gaseous BCl_3 enters the reactor gaseous atmosphere in which a flow of BCl_3 and Cl_2 is maintained. BCl_3 is a strong Lewis acid (Alam et al., 2004, Kirk-Othmer Encyclopedia of chemical technology, 138-168) and therefore a portion of BCl_3 reacts with Cl_2 to give:



[00104] The ion BCl_4^- can then reenter the liquid bath by, using ion K^+ , from reaction (10):



[00105] The ion Cl^+ produced at reaction (13) is probably reacting with the exposed surfaces of a carbonaceous reducing agent (metallurgical coke, graphite or activated charcoal) at active sites where a high density of unpaired electrons are present (Bandosz and Ania, in: Activated carbon surfaces in environmental remediation, Elsevier 2006, p. 159-229), as illustrated by:

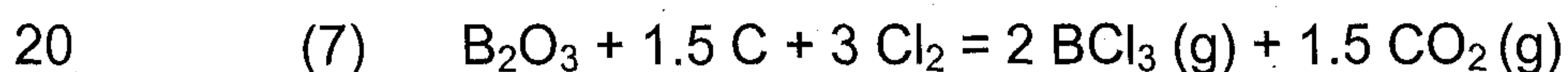


[00106] In the reactor 14 where reactions are conducted, GeCl_4 , if any, and SiCl_4 are present as gases. Since a continuous flow of Cl_2 23 is maintained in the system, GeCl_4 , if any, and SiCl_4 leave the reactor as vapor phases and are carried out by the gas flow toward the condensation sections of the process, which will be described in more details below. The gases leaving the carbochlorination reactor 14 include GeCl_4 , if any, SiCl_4 , Cl_2 , BCl_3 , and CO_2 .

[00107] The gaseous product 30 and the solid reducer 22 are separated via a gas/solid separator (not shown). The solid reducer 22 is collected in a receiving bin and is reused in the chlorination process as reducing agent.

10 [00108] To recover silicon and germanium contained in the glassy residues as oxides, BCl_4^- is used as effective chlorination agent in a relatively low temperature process. More particularly, BCl_4^- is a chlorinating agent for GeO_2 encapsulated into SiO_2 glasses. Therefore, the above-mentioned reactions can be used to simultaneously produce GeCl_4 and SiCl_4 from optical fiber glassy residues containing silicium and germanium oxides. BCl_4^- is also a chlorination agent for SiO_2 in SiO_2 -rich feed material to produce SiCl_4 .

[00109] As was described above and will be described in more details below, BCl_3 can be added as a gas (**Figs. 4 and 5**) or can be generated *in situ* (**Fig. 3**) through reaction



[00110] The gaseous product 30 is collected in a pipe system connecting the chlorination reactor 14 to a first condensing unit 32 (**Figs. 3 and 4**) or a primary condenser 132 (**Fig. 5**). The pipe system is thermostated, i.e. the gas temperature inside the pipe does not allow the condensation of the gas before it reaches the condenser unit. Thus, the temperature can be maintained over the boiling/condensing temperature of GeCl_4 (84 °C) if the system includes a first condensing unit 32 (**Figs. 3 and 4**) and above the boiling/condensing temperature of SiCl_4 (57,6 °C) if the system includes a primary condenser 132 (**Fig. 5**). For a glassy residue feed material, the boiling points of the other

gaseous product components exiting the carbochlorination reactor 14 are lower than GeCl_4 boiling point. Thus, all gaseous product components remain in gaseous phase in the pipe system extending between the chlorination reactor 14 and the first condensing unit 32 or the primary condenser 132.

5 First condensing unit: GeCl_4 (Figs. 3 and 4)

[00111] If the feed material 10 includes glassy residues and thus the gaseous product 30 includes gaseous GeCl_4 , the first condensing unit 32 condenses selectively $\text{GeCl}_4(\text{g})$ from the other gaseous product components and, more particularly, $\text{SiCl}_4(\text{g})$, $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{CO}_2(\text{g})$ as shown in Figs. 1 and 10 2.

[00112] To perform this selective condensation of GeCl_4 , the temperature inside the condenser 32 is set to a set-point slightly below GeCl_4 boiling point and slightly above SiCl_4 boiling point (57,6 °C). The gaseous product 30 is cooled and washed with liquid GeCl_4 38.

15 [00113] The condenser 32 is filled with perforated spheres made of a resistant material. A recycling loop of liquid GeCl_4 connected to a shower nozzle, placed at the top of the unit, assures adequate percolation and contacts between the liquid phase 38 and the gaseous product 30. The condensed liquid GeCl_4 40 is collected in a reservoir placed at the base of the condensing unit 32.
20 The gaseous product 42 exiting the condenser 32 is essentially composed of $\text{SiCl}_4(\text{g})$, $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, and $\text{CO}_2(\text{g})$. It is directed via a second pipe system to a second condensing unit 34 where gaseous SiCl_4 is condensed, as it will be described in more details below.

[00114] As for the first pipe system extending between the chlorination
25 reactor 14 to the first condensing unit 32, the second pipe system is thermostated. Thus, the temperature can be maintained over SiCl_4 boiling temperature (57,6 °C) and below GeCl_4 boiling point (84 °C). Thus, all gaseous product components remain in gaseous phase in the second pipe system extending between the first and the second condensing units 32, 34.

Primary condenser (Fig. 5)

[00115] If the feed material 110 includes a SiO_2 -rich material which is substantially free of GeO_2 , the first condensing unit 32 can be replaced by a primary condenser 132 as shown in Fig. 5 since the gaseous product 30 is also substantially free of gaseous GeCl_4 . It is appreciated that the first condensing unit 32 can be either by-passed or removed.

[00116] This primary condensing step is carried out for SiO_2 -rich feed material containing a substantial amount of other oxides than GeO_2 . These oxides as well as SiO_2 are transformed in chlorides and are transported outside the chlorination reactor 14 as gases. These chlorides (MCl_x) have to be condensed separately from SiCl_4 to avoid contamination in the subsequent process steps. Thus, the primary condenser 132 condenses chloride impurities, as a mixture, from the other gaseous product components and, more particularly, $\text{SiCl}_4(\text{g})$, $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, and $\text{CO}_2(\text{g})$.

[00117] To perform this selective condensation, the primary condenser 132 is in fluid communication with the chlorination reactor 14 and contains large surface deflectors to collect these chloride impurities.

[00118] The temperature inside the primary condenser 132 is adjusted to be slightly above the boiling/condensing temperature of SiCl_4 (57.6°C), in order to assure maximal removal of unwanted chlorides and to allow SiCl_4 to exit the primary condenser 132 as a gas 42.

[00119] The condensed chlorides 140 are collected in a reservoir placed at the base of the primary condenser 132. The gaseous product 42 exiting the condenser 132 is essentially composed of $\text{SiCl}_4(\text{g})$, $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, and $\text{CO}_2(\text{g})$. It is directed via a second pipe system to a second condensing unit 34 where gaseous SiCl_4 is condensed, as it will be described in more details below.

[00120] As for the first pipe system extending between the chlorination reactor 14 to the primary condenser, the second pipe system is thermostated. Thus, the temperature can be maintained above SiCl_4 boiling temperature

(57.6°C). Thus, all gaseous product components remain in gaseous phase in the second pipe system extending between the primary condenser 132 and the second condensing unit 34.

Second condensing unit: SiCl_4

5 [00121] This second condensing unit 34 is similar to the first condensing unit 32, except that the temperature inside the condenser 34 is set to a point slightly below SiCl_4 condensation point and above BCl_3 condensation point and that the gaseous product 42 entering the condenser 34 is washed with SiCl_4 in liquid phase 44. In an embodiment, the temperature inside the condenser 34
10 ranges between 15 and 25 °C. These operating conditions allow the selective condensation of SiCl_4 46 which is collected in a reservoir located at the base of the condensing equipment 34. Hence, the gaseous product 48 exiting the second condenser 34 essentially includes $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{CO}_2(\text{g})$. It is directed towards a third condensing unit 36 where the condensation of BCl_3 is carried out
15 through a third pipe system.

[00122] As for the previous pipe systems, the third pipe system is thermostated and its temperature is maintained over BCl_3 boiling temperature (12.5 °C) and below SiCl_4 boiling point (57.6 °C). Thus, $\text{BCl}_3(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{CO}_2(\text{g})$, the gaseous product components, remain in gaseous phase in the third pipe
20 system extending between the second and the third condensing units 34, 36.

Third condensing unit: BCl_3

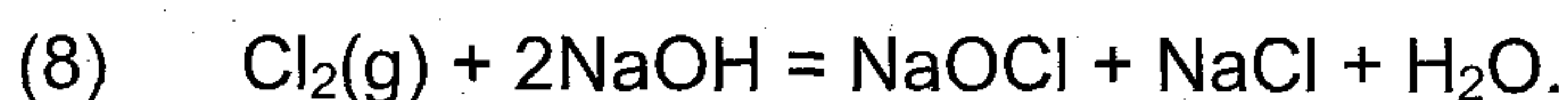
[00123] In the third condensing unit 36, gaseous BCl_3 is condensed. The temperature inside the condenser 36 is adjusted to a set-point slightly below the condensation point of BCl_3 and the gas entering the condenser 36 is washed
25 with liquid BCl_3 50 allowing its selective condensation. In an embodiment, the temperature inside the condenser 36 ranges between 0 and 10 °C. The gaseous product 52 exiting the condenser 36 includes $\text{Cl}_2(\text{g})$ and $\text{CO}_2(\text{g})$ and it is directed towards a scrubbing and a neutralization systems.

[00124] Liquid BCl_3 56 obtained at this condensation step can be recycled
30 as a reagent 223 to the chlorination reactor 14 after a gasification step 58. The

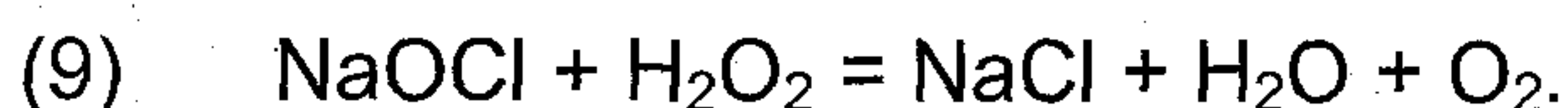
quantity of recycled BCl_3 223 used to chlorinate the optical fiber feed 10 and SiO_2 rich feed 110 are balanced with additional input of BCl_3 29 or solid boron compound 16, if necessary.

Scrubbing and neutralization

5 [00125] Chlorine (Cl_2) is removed from the gaseous product 52 in a scrubber 54. This scrubbing unit 54 includes a vertical cylinder containing perforated plastic spheres. The scrubber 54 is filled to a certain extend with a solution of NaOH 60. A system, including a pump linked to a recycling loop and a spray nozzle located at the top of the scrubber 54, allows the gaseous product
10 52 to be washed and contacted with the NaOH solution 60. The following reaction occurs between chlorine contained in the gaseous product 52 and the NaOH solution 60:



[00126] The pH of the solution is controlled by an exterior supply of
15 concentrated NaOH . The NaOCl solution 62 resulting from the scrubbing procedure is subsequently treated with H_2O_2 64, in an agitated tank 66, in order to obtain a sodium chloride solution 68 by the reaction



[00127] The gas exiting at the top of the scrubber contains essentially CO_2
20 70. If necessary, the CO_2 70 exiting the process can be trapped or neutralized by an existing complementary technology aiming at CO_2 emanation recovery.

Cl_2 compressor

[00128] In an alternate embodiment, the chlorine scrubber unit 54 can be replaced by a chlorine compressor which allows compression of gaseous
25 chlorine into a liquid chlorine and therefore its separation from gaseous CO_2 . The compressed chlorine can be stored in gas cylinders for future uses such as one of the chlorination process reactant.

Liquid GeCl_4 and liquid SiCl_4

[00129] The process described above transforms optical fibers glassy residues or any materials rich in SiO_2 in chloride forms which can be directly or indirectly used as feed material for manufacturing optical fibers, various
5 electronic components or solar panels. The liquid tetrachlorides selectively separated during the process and collected at the base of the GeCl_4 condenser and the SiCl_4 condenser are of relatively high purity.

[00130] If necessary, additional purification steps can be performed on the separated tetrachlorides obtained from the process. These additional purification
10 steps can include one or several methods such as distillation, fractional distillation, solvent extraction, resin purification or by a common ion effect.

Alternative embodiment (Fig. 6)

[00131] Alternatively, the gas leaving the reactor 14 and containing SiCl_4 and GeCl_4 is condensed in a single condenser unit 44. After this condensation
15 step, the components of liquid mixture obtained are separated by fractional distillation 76 providing a means to obtain pure SiCl_4 72 and GeCl_4 74.

[00132] Condensing the gaseous phase exiting the reactor into a suitable condenser as a liquid is achieved at a temperature whereas the gas vapor pressure is sufficiently low for obtaining a liquid containing Cl_2 , BCl_3 , SiCl_4 and
20 GeCl_4 . The obtained liquid is then transferred to a fractional distillation column.

[00133] If necessary, the gaseous phase exiting the condenser is neutralized into a scrubber 54 whereas Cl_2 is transformed to NaOCl 62, and residual BCl_3 , SiCl_4 and GeCl_4 to their corresponding oxides and/or hydroxides.

[00134] The fractional distillation column is operated in such a way that
25 firstly Cl_2 is condensed from the top of the column. When Cl_2 is completely removed from the mixture, the operational parameters are modified to obtain BCl_3 56 at the top of the column which is also condensed independently. After the complete removal of BCl_3 from the mix, the parameters are adjusted to obtain pure SiCl_4 72 at the top of the column which is collected separately. At

the end of the distillation step for SiCl_4 , the bottom flask contains only GeCl_4 74. Such a distillation procedure allows the recovery of four independent liquid compounds Cl_2 , BCl_3 , SiCl_4 and GeCl_4 .

[00135] Liquid Cl_2 can then be recycled as a reacting agent for the process after a suitable gasification step. Liquid BCl_3 can also be recycled as a reacting agent for the process after a suitable gasification step.

Experimental set up (Figs. 7 and 8)

[00136] Referring to **Figs. 7 and 8**, there is shown an experimental set up for carrying out the processes described above. The experiments were performed into a cylindrical horizontal reactor 310 including a quartz tube having an inert lining and heated by an electrical furnace 312, as reaction tube. Cylinders of Cl_2 , BCl_3 and N_2 gases 314 were connected to the reaction tube 310. Pressure regulators and mass flow controllers 316 were used to obtain a quantitative distribution of gases into the reaction tube 310 (**Fig. 7**). Gases leaving the reactor 310 were scrubbed in a scrubber 318 by a NaOH solution, which was periodically changed. $\text{CO}_{(g)}$ and $\text{CO}_{2(g)}$, were not neutralized by the scrubber 318 and were evacuated by the laboratory fume hood (not shown).

[00137] A small number of experiments were conducted using CO as a reducing agent. In these cases, a fourth gas bottle and a corresponding mass flowcontroller were added to the experimental set-up.

[00138] In a typical experiment, the following steps were carried out. A given type of an optical preform residue was grinded to minus 20 μm . This grinded material was placed in a beaker 320 (**Fig. 8**), if necessary, as it will be described in more details below in reference to equations 10 and 11, a solid reducer was added as well as H_3BO_3 (directly or adsorbed on the solid reducer). Alternatively, the grinded material was placed in beaker 320, and if necessary, a solid reducer was added with or without KCl , as salt for the reagent mixture.

[00139] The beaker 320 was positioned in the center of the reaction tube 310 (**Fig. 8**). N_2 flowed in the system and the solid was dried for a period of one

hour at a temperature of 500 °C. At the end of the drying step, the furnace temperature was set between 450 °C and 1100 °C. When the reaction temperature was reached, the flow of N₂ was stopped and Cl₂ flowed into the system at a total flowrate varying from 0.1 to 0.4 liter per minute with or without
5 CO or BCl₃ as required. When CO was used the flowrate ratio Cl₂/CO was set to one for most experiments. When BCl₃ was used the flowrate was set to 0.1 liter per minute. After a given period of time, GeCl₄(g) and SiCl₄(g) were produced, exited the furnace 312 and were scrubbed.

[00140] The conversion rates of GeO₂ and SiO₂ for a given experiment
10 were calculated from the mass variations in GeO₂ and SiO₂ between the masses initially present and those observed at the end of the experiment in the solid residue left in the beaker 320. The mass variations were attributed to the transformations of GeO₂ and SiO₂ into their respective tetrachlorides (GeCl₄ and SiCl₄). These tetrachlorides, being volatile in the temperature range
15 investigated, were carried outside the beaker 320 containing the preform sample and were scrubbed by the NaOH solution. The mass variations were calculated from the weight of the sample and the solid residue combined to the respective concentrations of GeO₂ and SiO₂. The analyses were realized by fusion with lithium metaborate followed by dissolution in HNO₃ and HCl, the resulting liquids
20 were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Table 1. Experimental parameters and results.

# Experiment	Beaker type	Time (min)	Stirring	Temperature (°C)	Boron compound		Type solid Reducer		Mass solid reducer (g)	Gaseous reducer	Flowrate gaseous Reducer (L/min)	Flowrate O_2 (L/min)	Conversion rate SiO_2 (%)	Conversion rate GeO_2 (%)
					Mass preform (g)	Quantity Boron compound (g)	Type solid Reducer	Mass solid reducer (g)						
1	Fused Quartz	30	700	0.2502	H_3BO_3	0.2502	Ø	Ø	CO	Ø	0.4	24	Ø	24
2	Fused Quartz	60	700	0.2502	No	Ø	Metallurgical Coke	0.5004	Ø	Ø	0.4	3	Ø	3
3	Fused Quartz	90	700	0.2645	H_3BO_3	0.2645	Metallurgical Coke	0.5290	CO	0.4	0.4	24	0.4	24
4	Fused Quartz	90	850	0.2536	Non	Ø	Ø	Ø	CO	0.4	0.4	1	0.4	1
5	Fused Quartz	30	850	0.2576	H_3BO_3	0.2576	Metallurgical Coke	0.5152	Ø	Ø	0.4	29	0.4	29
6	Fused Quartz	60	850	0.2657	H_3BO_3	0.2657	Metallurgical Coke	0.5314	CO	0.4	0.4	25	0.4	25
7	Fused Quartz	60	1000	0.2542	H_3BO_3	0.2542	Ø	Ø	CO	0.4	0.4	7	0.4	7
8	Fused Quartz	13	1000	0.2534	H_3BO_3	0.2533	Metallurgical Coke	0.5064	Ø	Ø	0.4	30	0.4	30
9	Fused Quartz	90	1000	0.2672	H_3BO_3	0.2672	Metallurgical Coke	0.5343	Ø	Ø	0.4	30	0.4	30
10	Fused Quartz	30	1000	0.2603	No	Ø	Metallurgical Coke	0.5207	CO	0.4	0.4	6	0.4	6
11	Graphite	20	850	0.2514	B_2O_3 on activated charcoal	0.2664	Activated charcoal	1.7360	Ø	Ø	0.4	67	0.4	79
12	Ceramic	60	850	0.2530	B_2O_3 on activated charcoal	0.2665	Activated charcoal	1.7361	Ø	Ø	0.4	65	0.4	76
13	Graphite	20 + 20 + 20	850	0.2512	B_2O_3 on activated charcoal	0.2664	Activated charcoal	1.7355	Ø	Ø	0.4	72	0.4	84

Table 2. Experimental parameters and results.

Sample number		Time (min)		Partial mixing		Temperature (°C)		Sample type		Mass SiO ₂ (g)		Type of Boron addition		KCl % ⁻¹		Type of reducing agent		Mass of Reducing agent (g)		Addition of CO		CO Flow (L/min)		Cl ₂ Flow (L/min)		Sample weight before reaction (g)		sample weight after reaction (g)		Weight loss (%)		Conversion rate SiO ₂ (%)		Conversion rate GeO ₂ (%)	
1	30	Ø	850	Preform	0.2503	BCl ₃	0.1 L/min	23	Darco 20X40	0.8642	Ø	Ø	Ø	0.4	1.4489	0.7637	47.29	98	96																
2	30	Ø	850	Preform	0.5000	BCl ₃	0.1 L/min	13	Darco 20X40	0.9000	Ø	Ø	Ø	0.4	1.6105	0.5589	65.30	98	99																
3	30	Ø	850	Preform	0.2501	BCl ₃	0.1 L/min	23	Darco 20X40	0.8643	Ø	Ø	Ø	0.4	1.4491	0.6818	52.95	98	97																
4	30	Ø	850	Preform	0.9006	BCl ₃	0.1 L/min	13	Darco 20X40	0.9002	Ø	Ø	Ø	0.4	2.0711	0.4779	76.93	97	99																
5	30	Ø	850	Preform	0.2502	BCl ₃	0.1 L/min	14	Darco 20X40	1.7288	Ø	Ø	Ø	0.4	2.3135	1.5271	33.99	96	96																
6	60	Ø	850	Preform	0.2502	BCl ₃	0.1 L/min	14	Darco 20X40	1.7285	Ø	Ø	Ø	0.4	2.3133	1.4153	38.82	95	97																
7	30	Ø	850	Preform	0.9006	BCl ₃	0.1 L/min	13	Darco 20X40	0.4506	Ø	Ø	Ø	0.4	1.5537	0.1424	90.83	94	95																
8	30	Ø	850	Preform	0.2504	BCl ₃	0.1 L/min	12	Darco 20X40	1.7285	Ø	Ø	Ø	0.4	2.2491	1.6148	28.20	88	96																
9	30	Ø	850	Preform	0.2501	BCl ₃	0.1 L/min	7	Darco 20X40	1.7285	Ø	Ø	Ø	0.4	2.1171	1.5011	29.10	85	95																
10	30	Ø	700	Preform	0.2505	BCl ₃	0.1 L/min	14	Darco 20X40	1.7288	Ø	Ø	Ø	0.4	2.3138	1.9136	17.30	72	72																
11	30	Ø	850	Preform	0.2505	BCl ₃	0.1 L/min	4	Darco 20X40	1.7377	Ø	Ø	Ø	0.4	2.067	1.6094	22.14	71	78																
12	30	Ø	850	Preform	0.2501	BCl ₃	0.1 L/min	Ø	Darco 20X40	1.7289	Ø	Ø	Ø	0.4	1.979	1.6235	17.96	61	68																
13	30	Ø	850	Preform	0.2501	BCl ₃	0.1 L/min	Ø	Ø	0.0000	CO	0.4	CO	0.4	0.2501	0.1370	45.22	51	49																
14	30	Ø	850	Preform	0.2500	B ₂ O ₃ AC	0.5000	12	Darco 20X40	1.7285	Ø	Ø	Ø	0.4	2.8128	1.4274	49.25	79	78																
15	30	Ø	850	Preform	0.2505	B ₂ O ₃ AC	0.4998	Ø	Darco 20X40	1.7281	Ø	Ø	Ø	0.4	2.4784	1.448	41.58	60	64																
16	30	Ø	1000	Preform	0.2503	Ø	Ø	Ø	Metallurgical Coke	0.5207	CO	0.4	CO	0.4	0.781	0.7107	9.00	6	NA																
17	60	Ø	700	Preform	0.2502	Ø	Ø	Ø	Metallurgical Coke	0.5004	Ø	Ø	Ø	0.4	0.7507	0.7143	4.85	3	NA																
18	90	Ø	850	Preform	0.2536	Ø	Ø	Ø	Ø	Ø	CO	0.4	CO	0.4	0.2536	0.2487	1.93	1	NA																

-1: (mass of KCl/total mass of the sample) X 100

5 NA: not analyzed

B₂O₃ AC: B₂O₃ adsorbed on activated charcoal

Darco 20x40 : Darco® 20x40

Examples

[00141] For all experiments, the experimental parameters used and the conversion rates obtained are reported in **Tables 1 and 2**. The experiments of **Tables 1 and 2** were conducted with an optical fiber preform containing 99 wt% SiO₂ and 1 wt% GeO₂. The specific examples described below contain additional experimental details.

[00142] To evaluate the effect of the reducer nature, another chlorination process, referred here as the high temperature process, was carried out. This high temperature process uses chlorine gas or HCl gas in combination with a CO gas reducing agent to transform oxides phases in chlorides and, more particularly, to transform the components of optical fibers in their chloride precursors, GeCl₄ and SiCl₄. The reactions occurring at the carbochlorination step being:



15 and



[00143] The experiments were conducted at 1200 °C showed that less than 5 % of SiO₂, one of the two main chemical targets, was converted to a chloride form. Thus, this high temperature process was considered relatively non efficient.

Example 1. Identification of the main parameters influencing the simultaneous conversion of GeO₂ and SiO₂ into GeCl₄ and SiCl₄.

[00144] In order to minimize the number of experiments to identify the main parameters controlling the conversion of GeO₂ and SiO₂ into GeCl₄ and SiCl₄ an orthogonal matrix of the Taguchi type was constructed using four parameters: a) reaction time, b) reaction temperature, c) addition of boron, d) type of reducer. The reaction time was varied from 20 to 90 minutes. The temperature was

varied from 700 °C to 1200 °C. The solid reducers tested were metallurgical coke and gaseous CO. Boron was added directly as H_3BO_3 . The parameters tested and the conversion rates obtained, according to the pre-defined orthogonal matrix, are reported at **Table 1** under experiments No. 1-10. For these experiments only the conversion factor for SiO_2 was considered has being of significance for the variance analysis since the analytical errors on GeO_2 conversion rates were superior to those for SiO_2 and were introducing additional errors for the determination of the influent parameters. High conversion rates for SiO_2 tend to favor higher conversion rates for GeO_2 because of the physical nature of GeO_2 - SiO_2 glasses. More particularly, the main component, SiO_2 , is effectively removed as a gas and therefore it exposes GeO_2 to the chemical reactants present in the reactor. The conversion rates for SiO_2 varied from 1 to 30 % depending on the experimental conditions. The variance analysis for the parameters tested was calculated using the Optimum software distributed by TDC software.

[00145] Three important observations resulted from the analysis carried. First, the addition of boron as H_3BO_3 was always linked to the highest SiO_2 conversion rates. This parameter alone accounted for 66 % of the variance between all results. This observation is consistent with experimental data available from the scientific literature, as described above in the chlorination section. Second, metallurgical coke as a reducer was more efficient than CO alone or combined with metallurgical coke. Third, the reaction time within the selected matrix range, i.e. from 30 to 90 minutes, appeared to have little influence on the SiO_2 conversion rates.

[00146] The second and the third observations are related. Solid carbonaceous reducing agents, such as metallurgical coke, tend to accelerate chlorination reactions. This is attributed to the formation of atomic chlorine or activated chlorine species at their surfaces followed by desorption. These species then react with the surface of the compound targeted for chlorination (Korshunov, 1992, Metallurgical Review of MMIJ, 8, (2), pp. 1-33). The distance between a given carbonaceous solid reducer and an oxide surface is important.

If this distance increases to a certain level, the atomic chlorine or activated chlorine liberated in the gas phase can recombine, as the result of particle collisions, and become deactivated. During the chlorination reactions, the carbonaceous reducer surfaces in contact or near the oxides are consumed and therefore the distances separating the solid reducers and the oxides are constantly increasing and eventually reach a point where the concentrations of atomic chlorine or activated chlorine species are low due to recombination reactions. The reaction speeds are then lowered and proceed via a mechanism involving molecular chlorine (Barin and Schuler, 1980, Metallurgical Transactions B, 11B, pp. 199-207). For a given chlorination reaction conducted in a static reactor involving carbon as a solid reducer, two kinetic zones are thus recognizable. An initially rapid one characterized by fast reaction kinetics driven by atomic chlorine or activated chlorine species. A later slow one characterized by slow reaction kinetics conducted via molecular chlorine. It is probable that the selected reaction times were such that the chlorination reactions had already reached the slow kinetic zone showing only minor gains in the conversion rate of SiO_2 with time.

[00147] These observations were used to design experiments in order to increase the conversion rates of GeO_2 and SiO_2 . Equations 5 to 7 shows that only equation 7 requires the use of chlorine in the presence of a carbonaceous solid reducer. Once that BCl_3 is formed it is assumed that the reactions with GeO_2 and SiO_2 will occur rapidly and will not proceed through a diffusion mechanism implying atomic chlorine or activated chlorine species. BCl_3 is a very strong Lewis acid (Alam et al., 2004) and should react very rapidly with the two free electron pairs on each oxygen atom of GeO_2 and SiO_2 . Kinetic optimization of reaction 9, assuming BCl_3 formation is the slow step, should increase the entire kinetic of the chemical system. The next example illustrates the effects of the optimization of BCl_3 formation on the conversion rates of GeO_2 and SiO_2 .

Example 2. OPTIMIZATION OF BCl_3 FORMATION AND ITS EFFECTS ON THE CONVERSION RATES OF GeO_2 AND SiO_2

[00148] In order to maximize contact between a given boron compound and the carbonaceous solid reducer, a solution saturated with boric acid was placed in a beaker with activated charcoal. The pulp was then agitated and filtered. The solid residue obtained was dried over night in an oven at 150 °C. The resulting activated charcoal doped with boron was used for the experiments.

[00149] It is known that BCl_3 react vigorously with water, in fact with any compounds containing oxygen as explained above. To minimize side reactions of BCl_3 with water an addition to the experimental procedure already described was effected. The reagent, placed in the furnace, was dried at 500 °C for 3 hours under a nitrogen atmosphere before being exposed to the chlorine gas. The experimental parameters and the results for these experiments are reported in **Table 1** under experiments No. 11 and 12. For these two experiments, the conversion rates for GeO_2 are high, 79 % and 76% respectively for experiments 11 and 12. Similarly the conversion rates for SiO_2 are also high, 67 % and 65 % respectively for experiments 11 and 12. As expected, there is a direct relationship between GeO_2 and SiO_2 conversion rates. Comparatively to experiment 11, the reaction time was increased from 20 to 60 minutes in experiment 12. No important conversion rate improvement was observed; the conversion rates obtained for experiment 12 were within analytical errors of those of experiment 11.

Example 3. EFFECT OF A «SIMULATED PARTIAL MIXING» ON THE CONVERSION RATES OF GeO_2 AND SiO_2

[00150] Experiments 1 to 12 were carried inside a static horizontal reactor. It was not possible to revise Fig. 7 experimental set up into a dynamic arrangement without introducing major modifications to the system. However, in experiment 13, the experimental procedure was adapted in order to simulate one or several partial mixing episodes.

[00151] After a given reaction time, the chlorine flow was turned off and N₂ was flowed into the quartz reaction tube. The furnace temperature was lowered from the predetermined experimental temperature to 350 °C. The beaker containing the powder was withdrawn from the furnace still hot using a glass rod.

5 The powder was then mixed with a glass spoon for few minutes under a fume hood. The beaker containing the powder was then replaced in the furnace, the temperature was adjusted to the predetermined experimental temperature and a current of N₂ was maintained into the reaction tube. When the predetermined experimental temperature was reached, N₂ was turned off and Cl₂ flowed in the

10 system.

[00152] Experiment 13 of **Table 1** presents the experimental parameters and the conversion rates obtained. In this specific experiment, two partial mixing episodes were realized, each after a 20 minutes period of reaction time. The total reaction time under chlorine atmosphere was 60 minutes. The conversion

15 rates obtained for GeO₂ and SiO₂ were respectively 84 % and 72 %. Those results are directly comparable to experiment 12 for which all experimental parameters are equivalent to experiment 13 except that no partial mixing was involved. This comparison indicates that the simulated partial mixing resulted into an 8 % increase in the conversion rate of GeO₂, from 76 to 84 %, and into a

20 7 % increase in the conversion rate for SiO₂, from 65 to 72 %. Clearly mixing has a positive impact on the conversion rates.

[00153] As previously discussed in Example 1, any chemical methods, such as adsorption, or physical methods, such as mixing, increasing contacts between oxides particles and carbonaceous solid reducer particles appear to

25 enhance the global efficiency of the chlorination procedure.

[00154] The technology describes above allows the production of high purity chlorides from glassy residues originating from optical fibers manufacturing or isolated from wasted optical cables.

[00155] It allows to produce directly GeCl_4 and SiCl_4 from the customary components of optical fibers glassy residues, GeO_2 and SiO_2 , without the formation of intermediate components such as silicon and elemental germanium. Also, GeCl_4 and SiCl_4 obtained are isolated from one another and can be used
5 as primary reactants in the dechlorination reactions for such processes as MCVD, ODS, AVD and other related methods.

[00156] GeO_2 and SiO_2 , contained in glassy residues of optical fibers, are concurrently extracted from glassy residues of optical fibers as GeCl_4 and SiCl_4 respectively. Moreover, they are extracted as gaseous GeCl_4 and SiCl_4 which
10 leave the reaction reactor as gases.

[00157] The gaseous GeCl_4 and SiCl_4 leaving the reactor are condensed separately, as liquids, in the appropriate condensers placed at the exit of the chlorination reactor. The first condenser extracts and condenses mainly GeCl_4 whereas the second condenser extracts and condenses mainly SiCl_4 .

15 [00158] GeCl_4 and SiCl_4 obtained can be directly used as high purity chemicals for the production of optical fibers or others processes requiring high purity chemicals. Alternatively, GeCl_4 and SiCl_4 obtained can be submitted to an already existing purification procedure, such as fractional distillation, in order to reach the purity level needed.

20 [00159] Procedures are also available for the neutralization and/or the recycling of the chemicals needed in the process.

Example 4. BCl_3 as chlorination agent

[00160] Although chlorination reactions can be conducted in numerous ways, it is recognized that carbonaceous solid reducing agents such as
25 metallurgical coke and activated charcoal tend to accelerate chlorination reactions. This is attributed to the formation of atomic chlorine, activated chlorine species or ionic chlorine (Cl^- and/or Cl^+) at their surfaces followed by desorption. These species, herein referred to as active chlorine, then react with

the surface of the compound targeted for chlorination (Korshunov, 1992, Metallurgical Review of MMIJ, 8, (2), pp. 1-33).

[00161] The distance between a given carbonaceous solid reducer and an oxide surface is also relatively important. If this distance increases above a certain threshold, the active chlorine liberated in the gas phase can recombine and deactivate. During chlorination reactions, the carbonaceous reducer surfaces in contact or near the oxides are consumed and therefore the distance separating the solid reducer and the oxides is constantly increasing during the chlorination reaction process and eventually reaches a point where the active chlorine concentrations are low due to recombination reactions. The reaction speed thus slows down and the reaction proceeds via a mechanism involving molecular chlorine (Barin and Schuler, 1980, Metallurgical Transactions B, 11B, pp. 199-207).

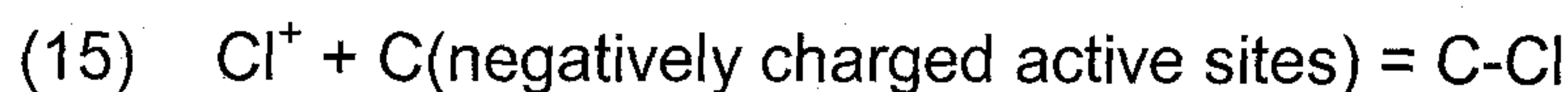
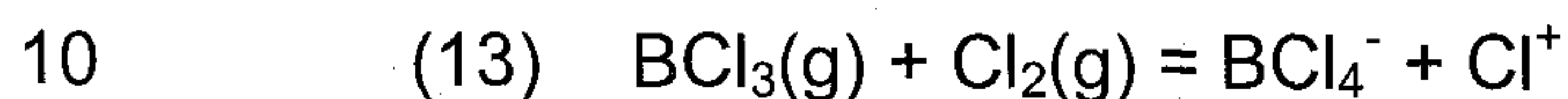
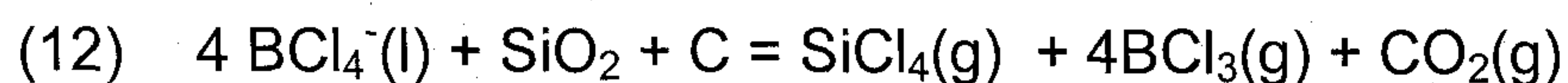
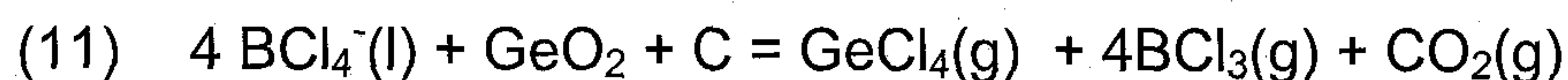
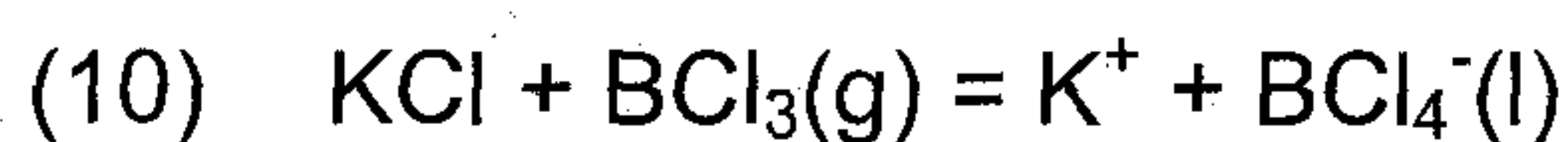
[00162] Thus for chlorination reactions, a rapid kinetic is first associated to the formation of active chlorine and second to the stability over time of active chlorine. The experiment designs were based on these two observations to obtain high conversion rates for SiO_2 and GeO_2 .

[00163] The action of BCl_3 on SiO_2 to produce SiCl_4 and B_2O_3 was recognized at a temperature around 350°C (See for instance Kroll, Metal Industry, 1952, 81, (13), 243-6; Savel'ev et al., Neorganicheskie Materialy, 1973, 9, (2), 325-6). B_2O_3 can be chlorinated (or regenerated) as BCl_3 by the action of Cl_2 and a reducing agent such as coke or activated charcoal (Alam et al., 2004, Kirk-Othmer Encyclopedia of chemical technology, 138-168). US Patent no. 4,490,344 discloses a combination of BCl_3 , Cl_2 and coke to produce SiCl_4 from SiO_2 in accordance with the following reactions:



[00164] These reactions are not carried out with active chlorine such as ionic chlorine (Cl^- and or Cl^+). Moreover, the stability of active chlorine is not considered in reactions 6, 7, 14 and 15.

[00165] In order to produce active chlorine and ion BCl_4^- , BCl_3 was reacted with KCl to produce the molten salt KBCl_4 . The following chemical system was used to chlorinate SiO_2 and GeO_2 :



[00166] To evaluate the chlorination reaction efficiency using BCl_4^- , a series of experiments was carried out. The results are reported in **Table 2** with sample numbers 1 to 11. The highest conversion rates were obtained for samples 1 to 7. More particularly, the conversion rates for both SiO_2 and GeO_2 in respectively SiCl_4 and GeCl_4 were equal to or higher than 94 wt%. The reaction temperature was maintained at 850 °C and the KCl content in the reagent mixture was varied from 13 to 23 wt%. The reaction duration was varied between 30 to 60 minutes and the ratio (oxide mass) / (activated charcoal mass) was varied between 0.14 to 1. For sample number 7, the ratio (oxide mass) / (activated charcoal mass) was adjusted to 2. For this specific sample, the conversion rates for SiO_2 and GeO_2 were respectively 94 wt% and 95 wt%.

[00167] Results from samples 8, 9, and 11 indicated that a decrease in the KCl addition resulted in lower conversion rates for SiO_2 and GeO_2 . Higher SiO_2 and GeO_2 conversion rates were obtained for KCl addition ranging between 12 and 15 wt% and, in an embodiment, proximate to 13 wt%.

[00168] In sample 10, lowering the reaction temperature from 850 °C to 700 °C reduced the conversion rates to 72 wt% for both SiO₂ and GeO₂.

[00169] One experiment was stopped after 10 minutes and the SiO₂-GeO₂ glasses were analyzed with a microprobe in order to search for the presence of B₂O₃. B₂O₃ was not detected in the analyzed sample. This was interpreted as an indication that the chlorination reactions were occurring in accordance with reactions 10 to 15 without the intermediate formation of B₂O₃.

[00170] These results show that the chlorination of SiO₂ and GeO₂ is efficiently conducted with a reagent mixture including BCl₃, KCl, Cl₂ and activated charcoal, a chemical system promoting the formation of BCl₄⁻ as chlorination agent. Conversion rates equal to or higher than 94 wt% for both SiO₂ and GeO₂ into their tetrachlorides SiCl₄ and GeCl₄ were obtained at temperatures around 850 °C and for a reaction time of approximately 30 minutes.

15 **Example 5. BCl₃ as chlorination agent**

[00171] To demonstrate that the chemical system using BCl₄⁻ described in the previous example is more efficient than one using BCl₃ as the chlorination agent (for example US Patent no. 4,490,344), experiments using a reagent mixture including BCl₃ but substantially free of KCl were conducted. Results are presented in **Table 2** with sample numbers 12 and 13.

[00172] Sample 12 was chlorinated under experimental conditions identical to sample 5 with exception that KCl was not added to the reagent mixture. For sample 12, the conversion rates for SiO₂ and GeO₂ were respectively 61 wt% and 68 wt%. For sample 5 having a reagent mixture including 14 wt% KCl, the conversion rates were 96 wt% for both SiO₂ and GeO₂.

[00173] These data clearly show the effect of the KCl addition in the reagent mixture. Addition of KCl in the reagent mixture leads to a 57 % increase in the SiO₂ conversion rate and a 41 % increase in the GeO₂ conversion rate.

For sample number 13, the activated carbon in the reagent mixture was replaced by CO. As for sample 12, the reagent mixture was substantially free of KCl. The conversion rates obtained were 51 wt% for SiO₂ and 49 wt% for GeO₂. Higher conversion rates for both SiO₂ and GeO₂ were obtained with activated carbon as
5 solid reducer in the reagent mixture rather than CO.

Example 6. Chlorination with B₂O₃ as a starting chemical component

[00174] BCl₃ can be produced by chlorination from B₂O₃ (Alam et al., 2004). In certain circumstances, it could be advantageous to prepare BCl₃ from B₂O₃ by chlorination, the produced BCl₃ being used as chlorination agent.
10 Experiments were conducted to investigate the effect of KCl addition in such cases.

[00175] As shown in **Fig. 3** to prepare the solid reducer, a solution saturated with boric acid was placed in a beaker with activated charcoal. The pulp was then agitated and filtered. The solid residue obtained was dried over
15 night in an oven at 150 °C. The resulting activated charcoal doped with boron was used for the chlorination experiments. It is known that BCl₃ react vigorously with water. To minimize side reactions of BCl₃ with water, an additional step was carried out in the experimental procedure. More particularly, the charge was dried in the furnace at 500 °C for 3 hours under a nitrogen atmosphere before
20 being exposed to the reagent mixture including gaseous chlorine.

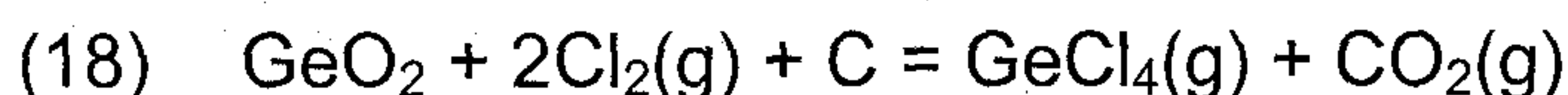
[00176] The experimental parameters and results for these experiments are reported in **Table 2** with sample numbers 14 and 15. For sample 14 wherein the reagent mixture includes 13 wt% KCl, the conversion rates obtained for SiO₂ and GeO₂ were respectively 79 wt% and 78 wt%. With a reagent mixture
25 substantially free of KCl and for the same experimental conditions, the conversion rates dropped to 60 wt% for SiO₂ and to 64 wt% for GeO₂ in sample 15. Adding KCl in the reagent mixture lead to an increase in the SiO₂ and GeO₂ conversion rates.

Example 7. Effect of using only Cl₂ and a reducer

[00177] Experiments were also conducted using Cl₂ as the only chlorination agent in the presence of a reducer. Reducers tested were gaseous CO and metallurgical coke. When CO is used, the reactions occurring in the
5 carbochlorination step are:



When CO is replaced by metallurgical coke, the reactions are:



[00178] Results reported in **Table 2** under sample numbers 16 to 18 indicated that the conversion rates for SiO₂ are smaller than or equal to 6 wt%. It is probable that the experimental conditions for samples 16 to 18 do not facilitate the formation of a high active chlorine concentration. Therefore the
15 efficiency of the chlorination is reduced when compare to experimental conditions using a reagent mixture including KCl and BCl₃ for similar reaction temperatures (850 °C and 1000 °C) and reaction time.

[00179] The technology described above allows the production of high purity tetrachlorides from glassy residues originating from optical fibers
20 manufacturing or isolated from wasted optical cables. The technology also describes a method for the production of SiCl₄ from material rich in SiO₂ and substantially free of GeO₂.

[00180] It allows to produce directly and concurrently GeCl₄ and SiCl₄ from the customary components of optical fibers glassy residues, GeO₂ and SiO₂,
25 without the formation of intermediate components such as silicon and elemental germanium. Also, GeCl₄ and SiCl₄ obtained are isolated from one another and can be used as primary reactants in the dechlorination reactions for such

processes as MCVD, ODS, AVD and other related methods since they are identical to those commonly employed in the fabrication of optical fibers.

[00181] GeO_2 and SiO_2 , contained in glassy residues of optical fibers, are concurrently extracted from glassy residues of optical fibers as GeCl_4 and SiCl_4 respectively. Moreover, they are extracted as gaseous GeCl_4 and SiCl_4 which leave the reaction reactor as gases.

[00182] In an alternate embodiment, SiO_2 contained in a SiO_2 -rich material rich can be transformed mainly in gaseous SiCl_4 which is subsequently condensed at the exit of the chlorination reactor.

[00183] The gaseous GeCl_4 and SiCl_4 leaving the reactor are condensed separately, as liquids, in the appropriate condensers placed at the exit of the chlorination reactor. The first condenser extracts and condenses mainly GeCl_4 whereas the second condenser extracts and condenses mainly SiCl_4 .

[00184] GeCl_4 and SiCl_4 obtained can be directly used as high purity chemicals for the production of optical fibers or others processes requiring high purity chemicals. Alternatively, GeCl_4 and SiCl_4 obtained can be submitted to an already existing purification procedure, such as fractional distillation, in order to reach the purity level needed.

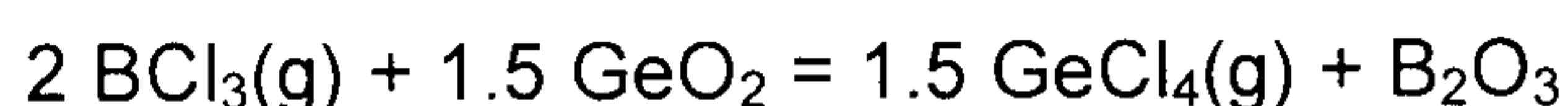
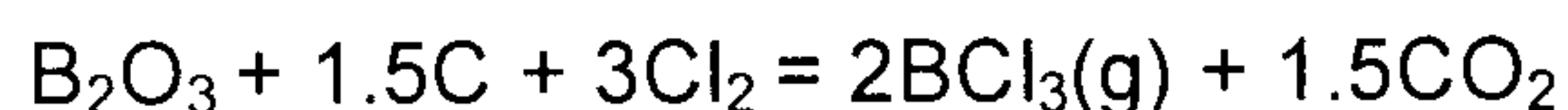
[00185] Procedures are also available for the neutralization and/or the recycling of the chemicals needed in the process.

[00186] The embodiments of the invention described above are intended to be exemplary only. For example, it is appreciated that any means for routing, transporting and transferring, solid, gas, liquid and pulp between the various process units can be used. The scope of the invention is therefore intended to be limited solely by the scope of the appended claims.

CLAIMS:

1. A method for producing GeCl_4 from GeO_2 -containing material, the method comprising the steps of:

- reacting comminuted residues of material containing germanium oxide with a reagent including a solid carbonaceous reducing agent doped with a boron compound and chlorine to obtain a gaseous product including gaseous GeCl_4 and gaseous BCl_3 in accordance with the following reactions:

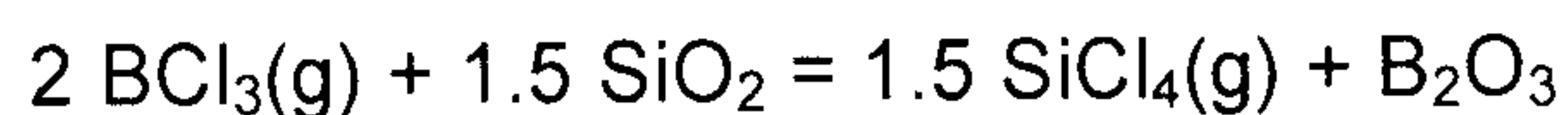
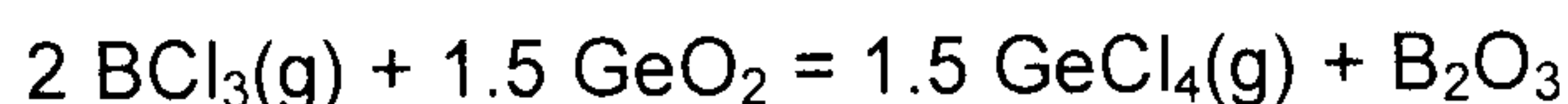


- condensing the gaseous GeCl_4 and BCl_3 into a mixture of liquid GeCl_4 and liquid BCl_3 by lowering gaseous product temperature below GeCl_4 , SiCl_4 and BCl_3 condensing temperatures.

2. The method as claimed in claim 1, further comprising separating the mixture of liquid GeCl_4 and liquid BCl_3 by fractional distillation.

3. The method according to claim 1, wherein the GeO_2 -containing material further contains silicon oxide, said method comprising the steps of:

- reacting comminuted residues of a material including germanium oxide and silicon oxide with the reagent to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 and gaseous BCl_3 in accordance with the reactions:



- condensing the gaseous GeCl_4 , SiCl_4 and BCl_3 into liquid GeCl_4 , SiCl_4 and BCl_3 by lowering gaseous product temperature below GeCl_4 , SiCl_4 and BCl_3 condensing temperatures.

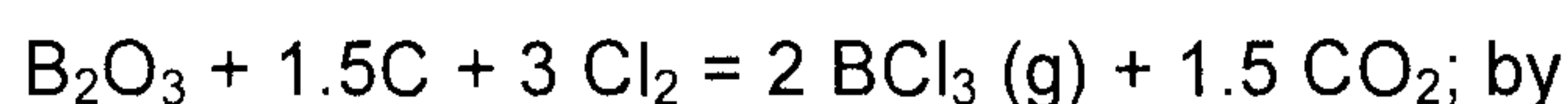
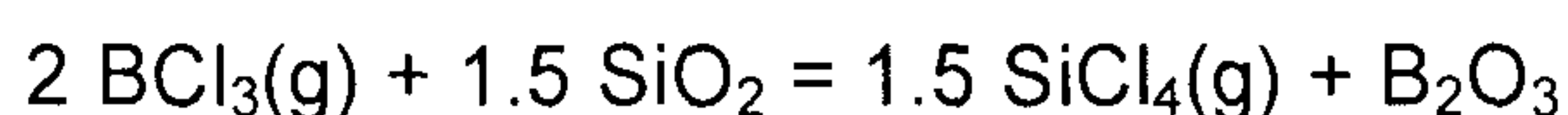
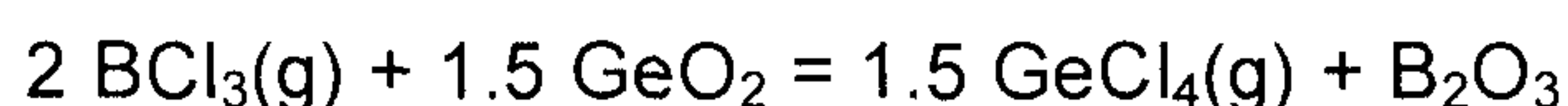
4. The method according to claim 3, further comprising using at least one of the resulting GeCl_4 and SiCl_4 for the production of starting components for optical fiber manufacturing.

5. A method for chlorinating GeO_2 encapsulated into SiO_2 glasses, the method comprising the steps of:

- reacting comminuted SiO_2 glasses with a reagent including a solid carbonaceous reducing agent doped with a boron compound and chlorine to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 ; and
- condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering gaseous product temperature below GeCl_4 , SiCl_4 and BCl_3 condensing temperatures.

6. A method for producing GeCl_4 and SiCl_4 from optical fibers containing GeO_2 and SiO_2 , the method comprising the steps of:

- reacting comminuted optical fibers including germanium and silicon oxides with a reagent including a solid carbonaceous reducing agent doped with a boron compound and chlorine to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 in accordance with the reactions:



- firstly condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature; and
 - secondly condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing temperature and above BCl_3 condensing temperature.
7. The method as claimed in any one of claims 1 to 6, further comprising
- adsorbing, in an agitated tank, the boron compound on the solid carbonaceous reducing agent, from a solution including the boron compound, to obtain the solid carbonaceous reducing agent doped with the boron compound;
 - separating by filtration the solid carbonaceous reducing agent doped with the adsorbed boron compound from the solution; and
 - drying the solid carbonaceous reducing agent doped with the adsorbed boron compound before carrying the reacting step.
8. The method as claimed in claim 7, wherein the boron compound is H_3BO_3 .
9. The method as claimed in claim 7, wherein the solution is saturated with the boron compound.
10. The method as claimed in claim 7, wherein the drying step is carried out at a temperature ranging between 450 and 550 °C.
11. The method as claimed in any one of claims 1 to 6, wherein the solid carbonaceous reducing agent is one of metallurgical coke and activated carbon.
12. The method as claimed in any one of claims 1 to 6, wherein the reagent further comprises gaseous BCl_3 .

13. The method as claimed in any one of claims 1 to 6, wherein the reacting step is carried out at a temperature ranging between 450 °C and 1100 °C in a corrosion-resistant reactor.
14. The method as claimed in any one of claims 1 to 6, further comprising recycling the solid carbonaceous reducing agent following the reacting step for reuse into the reagent of the reacting step.
15. The method as claimed in any one of claims 1 to 6, wherein the gaseous products further include Cl_2 and CO_2 , the method further comprising carrying the gaseous product containing gaseous Cl_2 and CO_2 towards at least one of a neutralization system and a recycling system.
16. The method as claimed in claim 15, further comprising neutralizing gaseous Cl_2 in a scrubber where gaseous Cl_2 is reacted with NaOH to produce NaOCl .
17. The method as claimed in one of claims 15 and 16, further comprising compressing gaseous Cl_2 in cylinders for reuse into the reagent of the reacting step.
18. The method as claimed in any one of claims 1 to 6, further comprising recycling liquid BCl_3 for reuse into the reagent of the reacting step.
19. The method as claimed in claim 18, wherein said recycling step further comprises gasifying the liquid BCl_3 .
20. The method as claimed in any one of claims 3 to 6, further comprising purifying at least one of liquid GeCl_4 and liquid SiCl_4 .
21. The method as claimed in claim 20, wherein the purifying step is carried out by at least fractional distillation.

22. The method as claimed in claim 6, further comprising grinding the optical fibers to obtain the comminuted optical fibers having a particle size ranging between 10 and 250 μm .

23. The method as claimed in claim 6, wherein the optical fibers originate from at least one of optical fiber manufacturing residues and wasted optical fibers.

24. A method for producing GeCl_4 and SiCl_4 as starting components for optical fiber manufacturing, the method comprising the steps of:

- reacting comminuted optical fiber glassy residues including germanium and silicon oxides with a reagent including a solid carbonaceous reducing agent doped with a boron compound and chlorine to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 ; by

firstly condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature; and

secondly condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing temperature and above BCl_3 condensing temperature of SiCl_4 .

25. A method for chlorinating GeO_2 encapsulated into SiO_2 glasses, the method comprising the steps of:

- reacting comminuted SiO_2 glasses with a reagent including a solid carbonaceous reducing agent doped with a boron compound and chlorine to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 ; and
- condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature.

26. The method as claimed in claim 25, secondly condensing the gaseous SiCl_4 in liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing temperature and above BCl_3 condensing temperature.

27. The method as claimed in claim 25, wherein the solid carbonaceous reducing agent is one of metallurgical coke and activated carbon.

28. The method as claimed in claim 25, wherein the reagent further comprises gaseous BCl_3 .

29. The method as claimed in claim 25, wherein the reacting step is carried out at a temperature ranging between $450\text{ }^\circ\text{C}$ and $1100\text{ }^\circ\text{C}$ in a corrosion-resistant reactor.

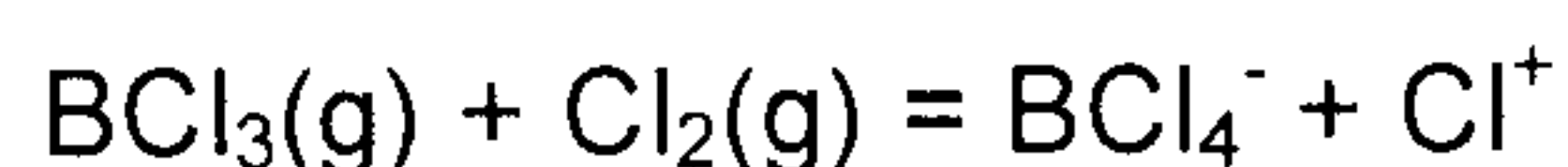
30. A method for producing GeCl_4 and SiCl_4 from optical fibers, the method comprising the steps of:

- reacting optical fibers including germanium and silicon oxides with a reagent including a carbonaceous reducing agent, a salt selected from the group consisting of: KCl , CsCl and RbCl , and BCl_3 to obtain a gaseous product including gaseous GeCl_4 , gaseous SiCl_4 , and gaseous BCl_3 ; and
- condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering the gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature.

31. A method for producing SiCl_4 from SiO_2 -containing material, the method comprising the steps of:

reacting comminuted SiO_2 -containing material with a reagent including a solid carbonaceous reducing agent, a salt selected from the group consisting of: KCl , CsCl and RbCl , and a boron compound to obtain a gaseous product including gaseous SiCl_4 in accordance with the reactions:

$XCl + BCl_3(g) = X^+ + BCl_4^-(l)$, where X is at least one of K, Cs, and Rb corresponding to the salt



condensing the gaseous $SiCl_4$ into liquid $SiCl_4$ by lowering gaseous product temperature below $SiCl_4$ condensing temperature;

wherein the ratio of salt mass and the sum of SiO_2 -containing material mass, solid carbonaceous reducing agent mass, and salt mass ranges between 0.03 and 0.15.

32. The method according to claim 31, wherein the comminuted SiO_2 -containing material is comminuted glassy residues.

33. The method according to claim 31, wherein the comminuted SiO_2 -containing material further contain GeO_2 and the reaction also produces $GeCl_4$ according to the reaction:



further comprising condensing the gaseous $SiCl_4$ and $GeCl_4$ into liquid $SiCl_4$ and $GeCl_4$ by lowering gaseous product temperature below $SiCl_4$ and $GeCl_4$ condensing temperatures.

34. The method according to claim 31, wherein BCl_3 is condensed along with condensing $SiCl_4$ by lowering gaseous product temperature below $SiCl_4$ and BCl_3 condensing temperatures.

35. The method according to claim 33, further comprising using the produced $GeCl_4$ and $SiCl_4$ as starting components for optical fiber manufacturing.

36. The method according to claim 31, wherein the reagent further comprises chlorine (Cl_2).

37. The method according to any one of claims 31 to 36, the comminuted SiO₂-containing material comprises comminuted optical fiber glassy residues containing GeO₂ and SiO₂.

38. A method for producing SiCl₄ and GeCl₄ from optical fiber glassy residues containing GeO₂ and SiO₂, the method comprising the steps of:

reacting comminuted optical fiber glassy residues with a reagent including a solid carbonaceous reducing agent, a salt selected from the group consisting of KCl, CsCl and RbCl, chlorine and a boron compound to obtain a gaseous product including gaseous GeCl₄ and gaseous SiCl₄ in accordance with the reactions:

$XCl + BCl_3(g) = X^+ + BCl_4^-(l)$, where X is at least one of K, Cs, and Rb corresponding to the salt



firstly condensing the gaseous GeCl₄ into liquid GeCl₄ by lowering gaseous product temperature below GeCl₄ condensing temperature and above SiCl₄ condensing temperature; and

secondly condensing the gaseous SiCl₄ into liquid SiCl₄ by lowering gaseous product temperature below SiCl₄ condensing temperature and above BCl₃ condensing temperature,

wherein the ratio of salt mass and the sum of optical fiber glassy residue mass, solid carbonaceous reducing agent mass, and salt mass ranges between 0.03 and 0.15.

39. The method as claimed in one of claims 37 and 38, wherein the ratio of solid carbonaceous reducing agent mass and glassy residue mass ranges between 0.3 and 1.

40. The method as claimed in any one of claims 31 to 37, further comprising drying the comminuted SiO_2 -containing material at a temperature ranging between 400 and 600 °C prior to carrying the reacting step.

41. The method as claimed in any one of claims 31 to 37, wherein the solid carbonaceous reducing agent is one of metallurgical coke, graphite and activated carbon.

42. The method as claimed in any one of claims 31 to 37, wherein the reacting step is carried out at a temperature ranging between 450 °C and 1100 °C in a corrosion-resistant reactor.

43. The method as claimed in any one of claims 31 to 37, further comprising recycling the solid carbonaceous reducing agent following the reacting step for reuse into the reagent of the reacting step.

44. The method as claimed in any one of claims 31 to 37, wherein the gaseous product further include Cl_2 and CO_2 , the method further comprising carrying the gaseous product containing gaseous Cl_2 and CO_2 towards at least one of a neutralization system and a recycling system.

45. The method as claimed in claim 44, further comprising neutralizing gaseous Cl_2 in a scrubber where gaseous Cl_2 is reacted with NaOH to produce NaOCl .

46. The method as claimed in claim 44, further comprising compressing gaseous Cl_2 in cylinders for reuse into the reagent of the reacting step.

47. The method as claimed in claim 44, further comprising condensing the BCl_3 into liquid BCl_3 by lowering gaseous product temperature below BCl_3 condensing temperature and recycling liquid BCl_3 for reuse into the reagent of the reacting step.

48. The method as claimed in claim 47, wherein said recycling step further comprises gasifying the liquid BCl_3 .

49. The method as claimed in claim 33, further comprising purifying at least one of liquid GeCl_4 and liquid SiCl_4 .

50. The method as claimed in claim 49, wherein the purifying step is carried out by fractional distillation.

51. The method as claimed in one of claims 37 and 38, further comprising grinding the glassy residues to obtain the comminuted glassy residues having a particle size ranging between 10 and 250 μm .

52. The method as claimed in claim 38, wherein the optical fiber glassy residues originate from at least one of optical fiber manufacturing residues and wasted optical fibers.

53. A method for producing GeCl_4 and SiCl_4 as starting components for optical fiber manufacturing, the method comprising the steps of:

reacting comminuted optical fiber glassy residues with a reagent including a solid carbonaceous reducing agent, a salt selected from the group consisting of KCl , CsCl and RbCl , chlorine and a boron compound in a ratio of salt mass and the sum of optical fiber glassy residues mass, solid carbonaceous reducing agent mass, and salt mass ranges between 0.03 and 0.15 to obtain a gaseous product including gaseous GeCl_4 and gaseous SiCl_4 ;

firstly condensing the gaseous GeCl_4 into liquid GeCl_4 by lowering gaseous product temperature below GeCl_4 condensing temperature and above SiCl_4 condensing temperature; and

secondly condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing temperature and above BCl_3 condensing temperature.

54. The method as claimed in claim 53, wherein the ratio of a mass of the solid carbonaceous reducing agent and a mass of the optical fiber glassy residues ranges between 0.3 and 1.

55. A method for producing SiCl_4 from a SiO_2 containing material, the method comprising the steps of:

reacting a comminuted SiO_2 containing material with a reagent including a solid carbonaceous reducing agent, a salt selected from the group consisting of KCl, CsCl and RbCl, chlorine and a boron compound in a ratio of salt mass and the sum of SiO_2 containing material mass, solid carbonaceous reducing agent mass, and salt mass ranges between 0.03 and 0.15 to obtain a gaseous product including gaseous SiCl_4 ; and

condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering gaseous product temperature below SiCl_4 condensing temperature and above BCl_3 condensing temperature.

56. The method as claimed in claim 55, condensing chloride impurities by lowering gaseous product temperature above SiCl_4 condensing temperature prior to carrying the SiCl_4 condensing step.

57. The method as claimed in claim 55, wherein the solid carbonaceous reducing agent is one of metallurgical coke and activated carbon.

58. The method as claimed in claim 55, wherein the boron compound comprises gaseous BCl_3 .

59. The method as claimed in claim 55, wherein the reacting step is carried out at a temperature ranging between 450 °C and 1100 °C in a corrosion-resistant reactor.

60. The method as claimed in any one of claims 55 to 59, wherein the ratio of a mass of the solid carbonaceous reducing agent and a mass of the SiO_2 containing material ranges between 0.3 and 1.

61. A method for producing SiCl_4 from glassy residues containing silicon oxide, the method comprising the steps of:

reacting the glassy residues with a reagent including a solid carbonaceous reducing agent, a salt selected from the group consisting of KCl, RbCl, and CsCl, chlorine and a boron compound in a ratio of salt mass and the sum of glassy residues mass, solid carbonaceous reducing agent mass, and salt mass ranges between 0.03 and 0.15 to obtain a gaseous product including gaseous SiCl_4 ; and

condensing the gaseous SiCl_4 into liquid SiCl_4 by lowering the gaseous product temperature below SiCl_4 condensing temperature.

62. The method as claimed in claim 61, wherein the ratio of a mass of the solid carbonaceous reducing agent and a mass of the glassy residues ranges between 0.3 and 1.

63. The method according to any one of claims 31 to 62, wherein the salt is KCl.

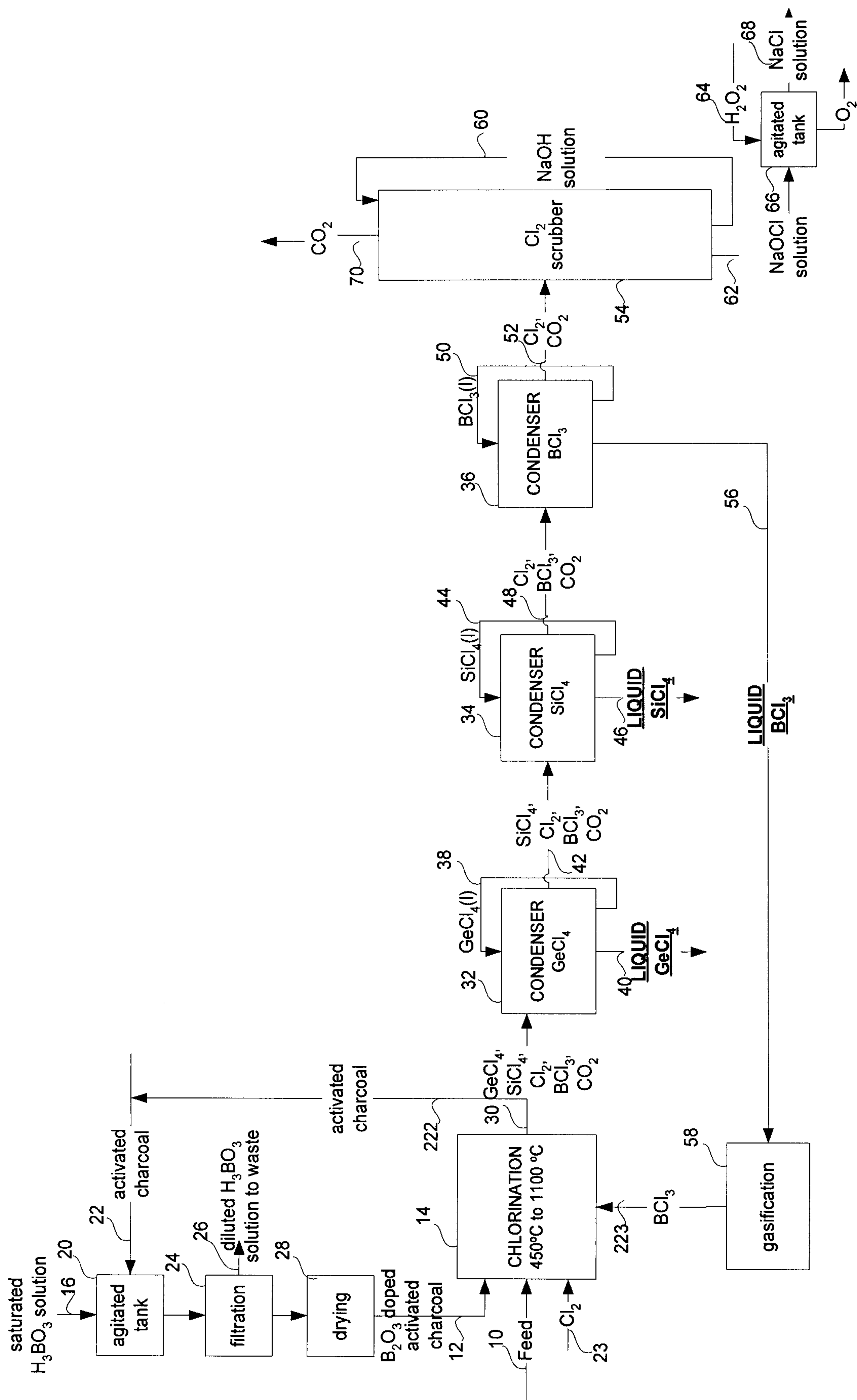


Figure 1

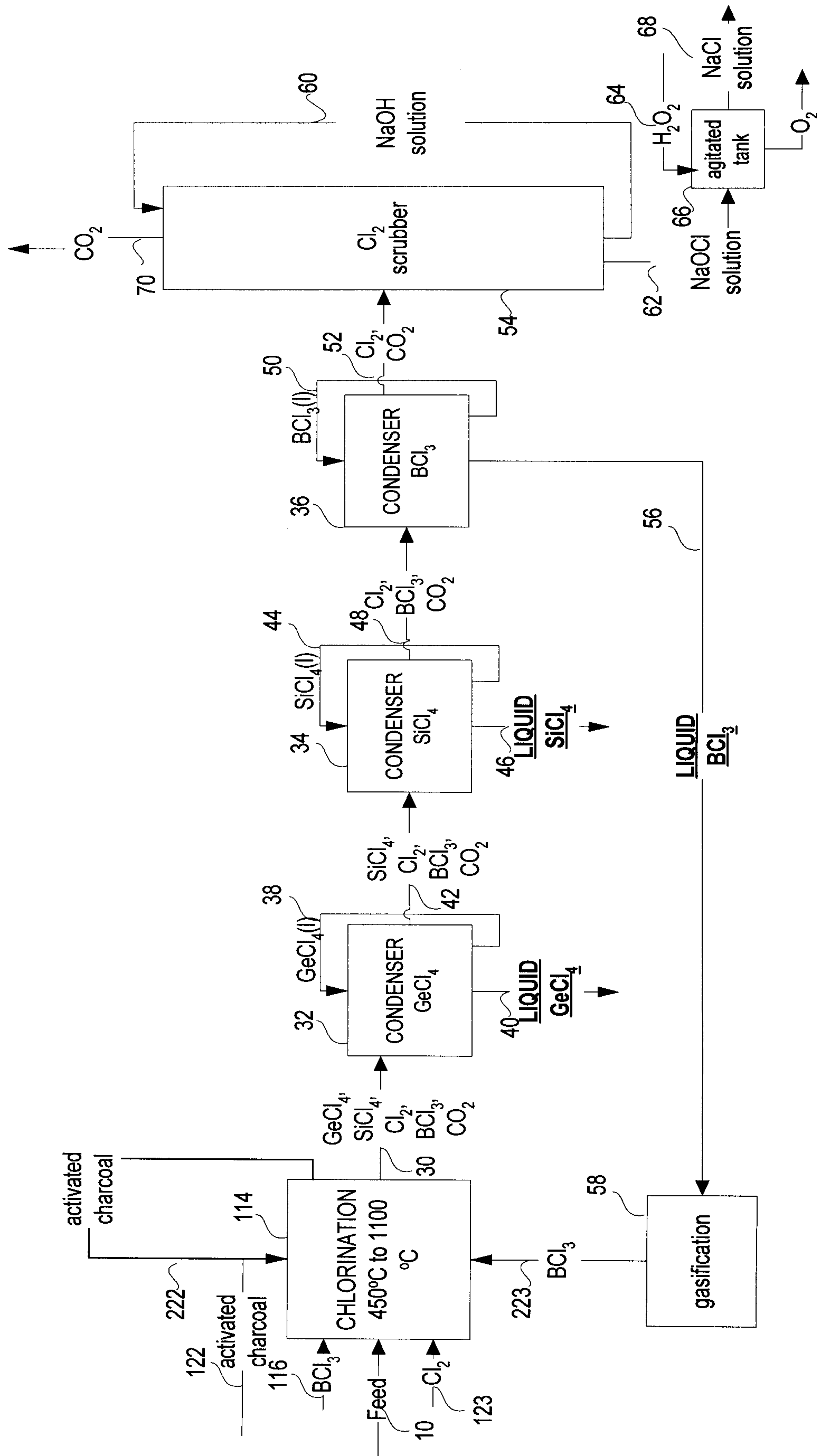


Figure 2

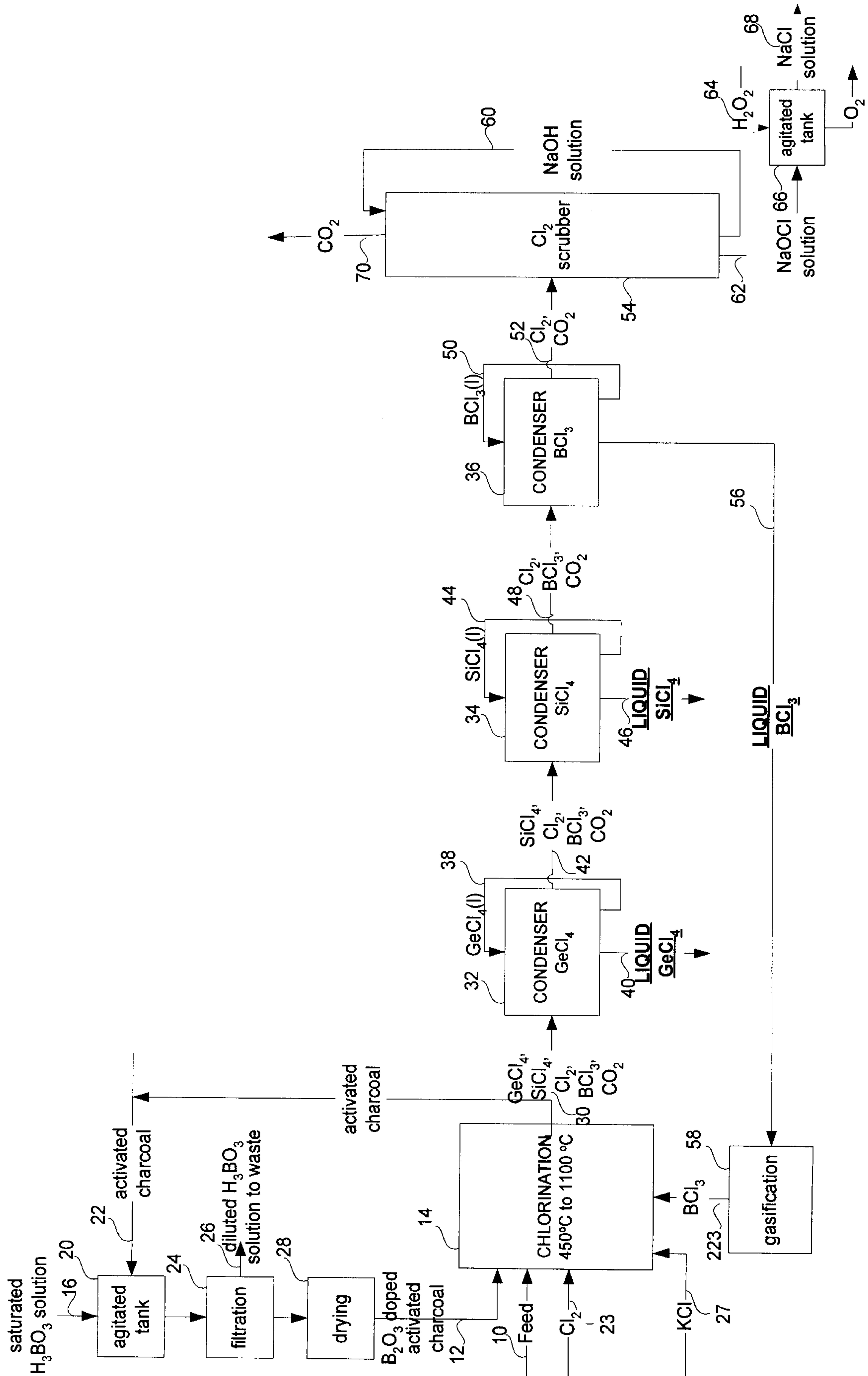


Figure 3

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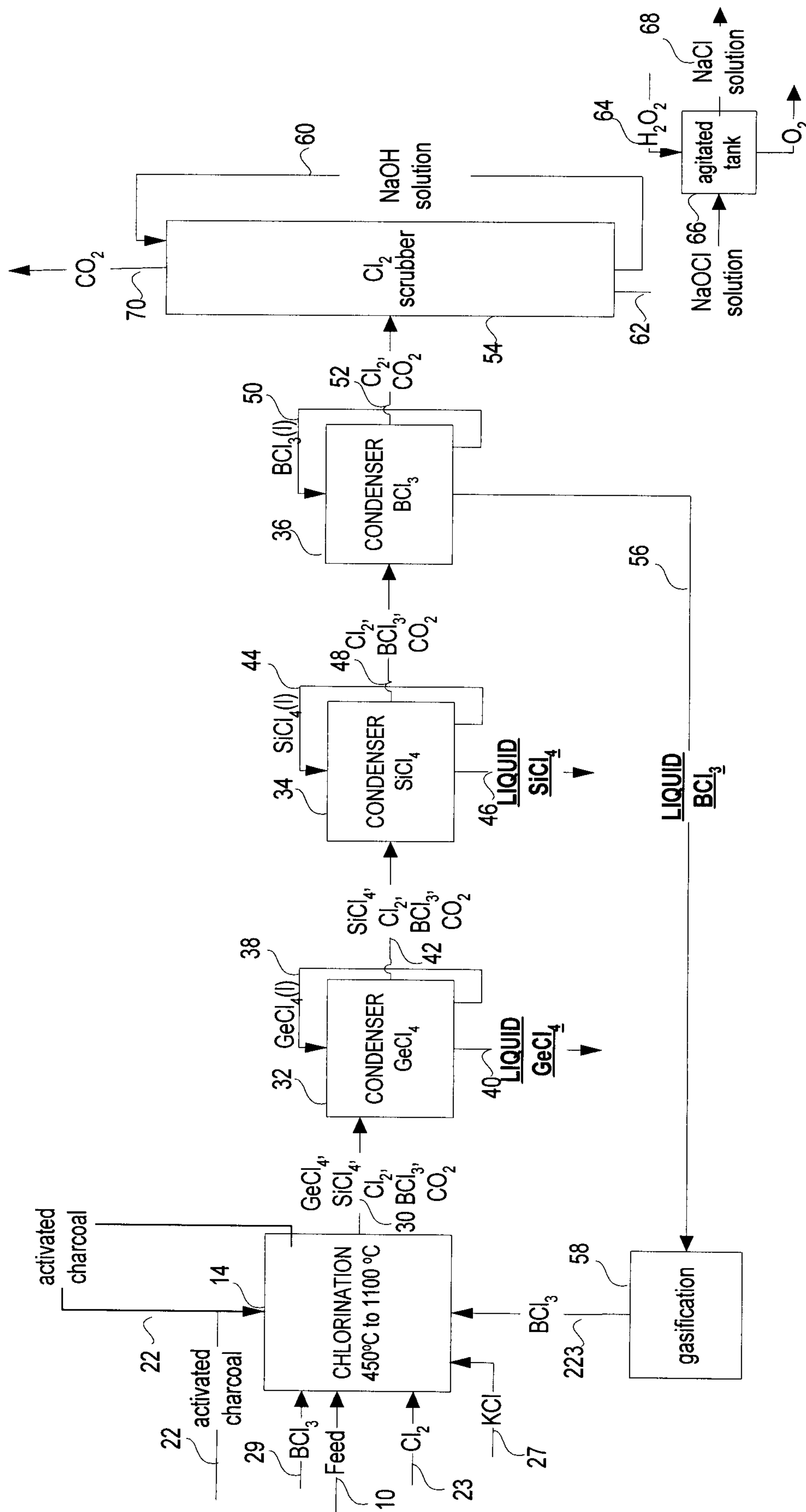


Figure 4

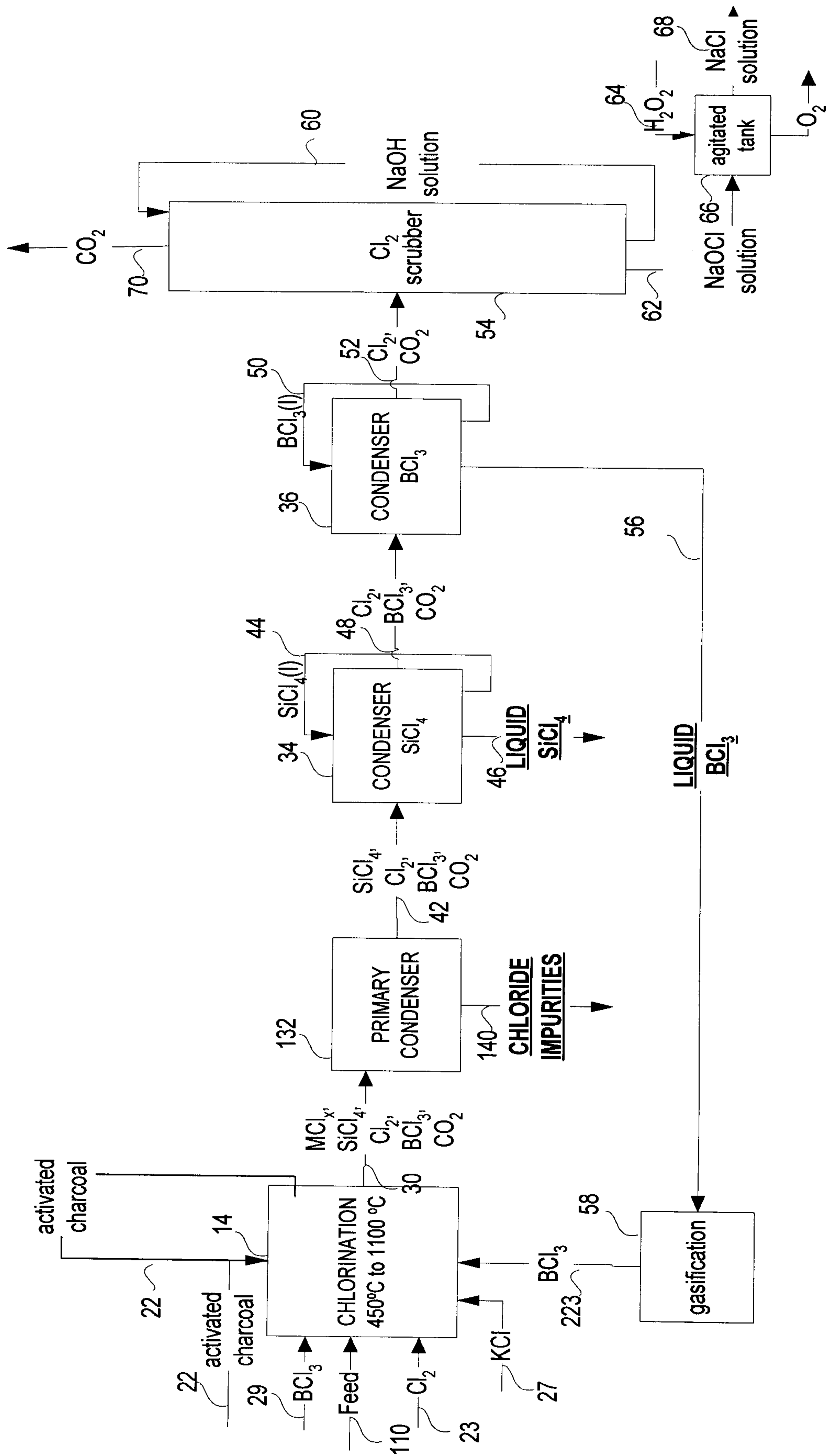


Figure 5

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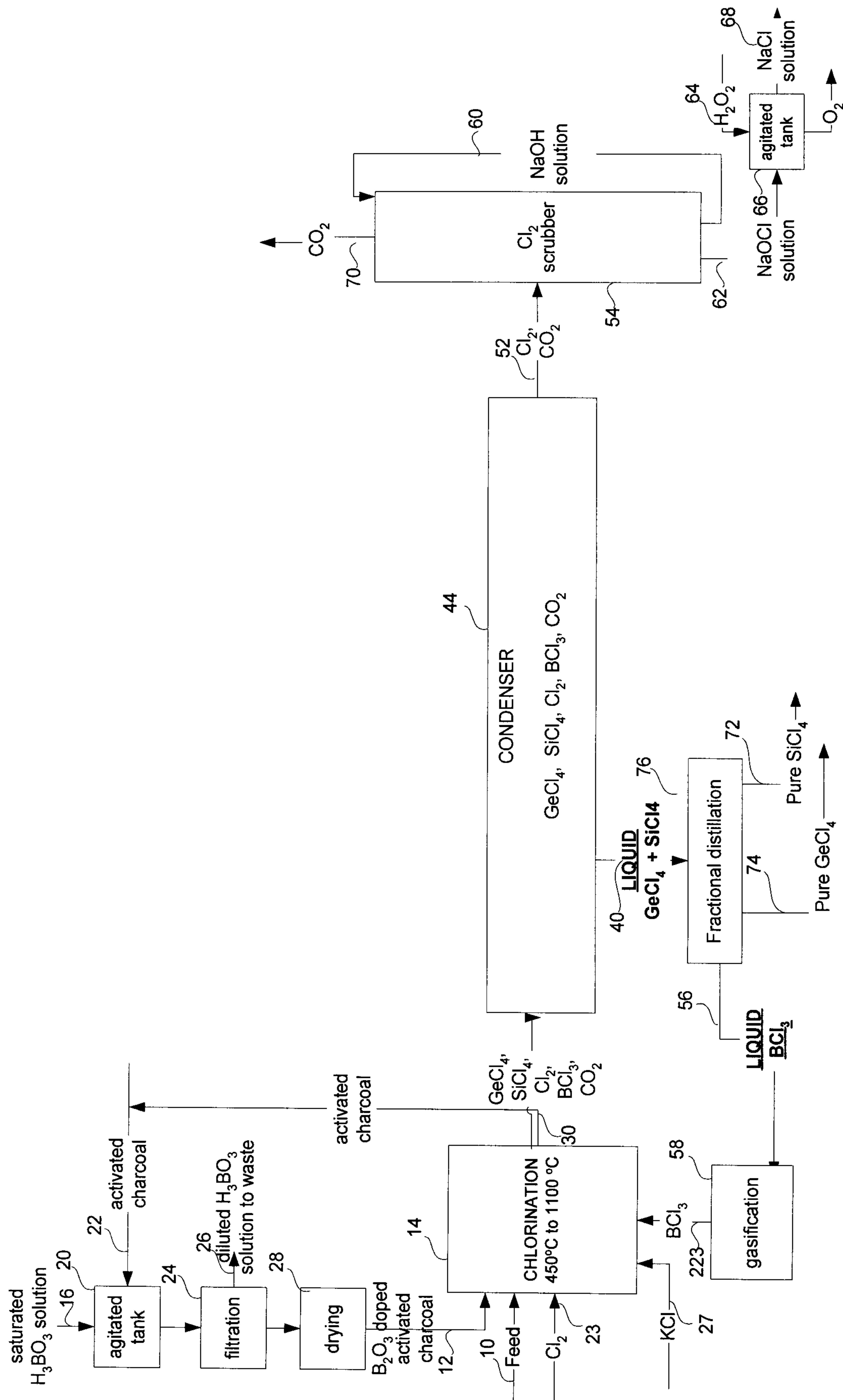


Figure 6

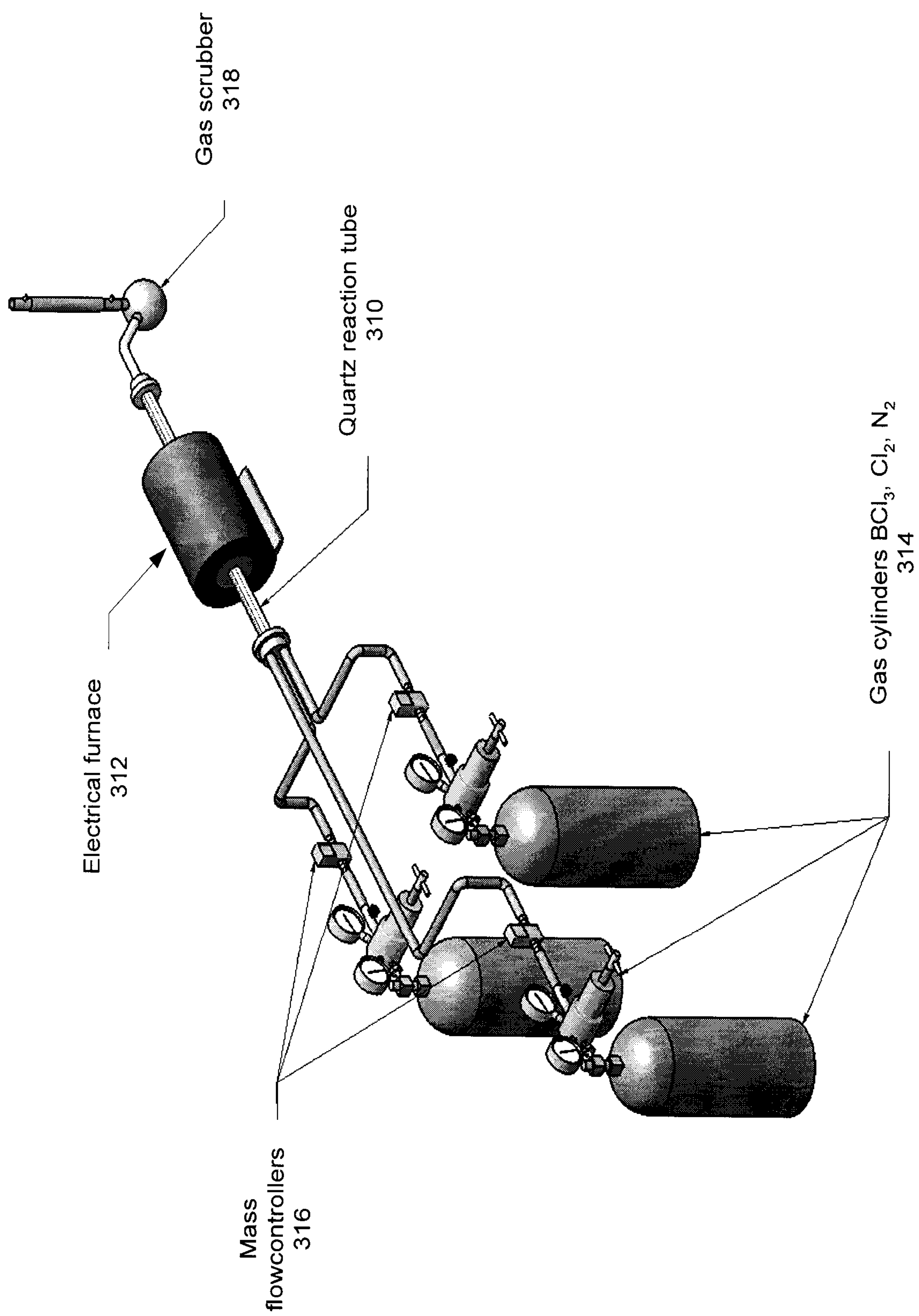


Figure 7

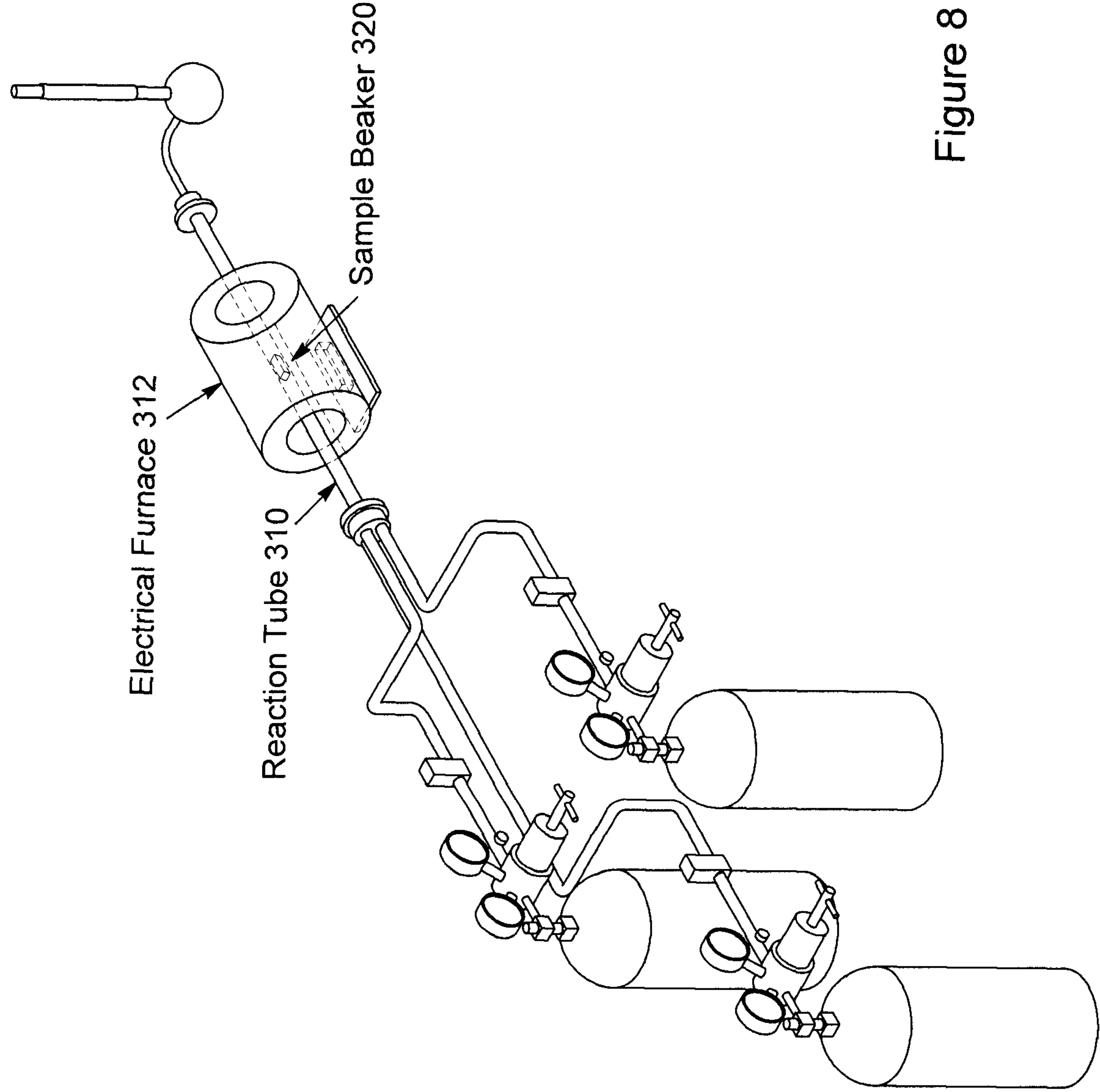


Figure 8

