A pyrometallurgical process and apparatus for converting spent potliners from aluminium manufacturing or other hazardous materials into an amorphous sodium and calcium fluoroalumino-silicate glass frit and a high carbon material. Spent potliners, silica or
siliceous material, and a calcium oxide source are fed into the non-burner end of a counter-current rotating kiln. The material is heated to destroy cyanides, convert fluoride salts to calcium fluoride and form a homogeneous liquid material. Carbon is then physically separated from the material. The material is then vitrified to produce a valuable glass frit and a high carbon material.
ABSTRACT

A pyrometallurgical process and apparatus for converting spent potliners from aluminium manufacturing or other hazardous materials into an amorphous sodium and calcium fluroaluminosilicate glass frit and a high carbon material. Spent potliners, silica or siliceous material, and a calcium oxide source are fed into the non-burner end of a counter-current rotating kiln. The material is heated to destroy cyanides, convert fluoride salts to calcium fluoride and form a homogeneous liquid material. Carbon is then physically separated from the material. The material is then vitrified to produce a valuable glass frit and a high carbon material.
PROCESS AND APPARATUS FOR CONVERTING SPENT POTLINERS INTO A GLASS FRIT, AND RESULTING PRODUCTS

FIELD OF THE INVENTION

The present invention relates generally to processing spent potliners from aluminium manufacturing or other hazardous materials. In particular, the invention relates to a pyrometallurgical process and apparatus for converting potliners into a glass frit, and to products obtained by the process.

BACKGROUND OF THE INVENTION

In the process of aluminum production, alumina is dissolved in cryolite in electrolytic cells, or pots, which are steel shells protected by refractory material and lined with carbon. A number of pots, usually more than 100, are arranged in series to form a potline. The pots contain a molten electrolyte consisting primarily of cryolite (Na$_3$AlF$_6$) and operate at approximately 930° to 1000°C. Other materials are added to the electrolyte to improve the efficiency of the operation or to reduce power consumption, such as alumina, aluminium fluoride, sodium fluoride, soda ash, calcium fluoride, lithium carbonate and magnesium oxide.

The hearth or lining of the cell is composed of carbon, which is backed by insulation and contained within a steel container called a potshell. The carbon portion of the lining serves as the cathode and contains the molten electrolyte. The carbon lining is composed of prefabricated carbon blocks joined together by a carbon paste, which is hydraulically rammed in the seams between the carbon blocks. The sidewalls of the lining are typically formed with carbon paste, but may contain prefabricated carbon blocks.

Over the life of the cathode and its cell lining, the carbon and insulating materials become impregnated with fluoride-containing salts. Failure can occur by cracking or excessive heaving of the lining. When these failures occur, the cell is taken off-line and the cathode lining material is removed from the potshell by mechanized digging equipment. This spent cathodic material is referred to as spent potliner (SPL).

In addition to containing fluoride salts, as mentioned above, SPL contains cyanides that are formed by the ingress of air through openings in the potshell and subsequent reaction of nitrogen with the carbon lining.
Spent potliner was listed by the Environmental Protection Agency (EPA) on Sep. 13, 1988 (53 Fed. Reg. 35412) as a hazardous waste (K088) under 40 C.F.R., Part 261, Subpart D because it may contain significant amounts of iron cyanide complexes and free cyanide. Thus there is a need in the aluminium industry for an economical process for detoxifying spent potliner such that the treated residue is not a hazardous waste. This is important because of the need for alternatives to land disposal of hazardous waste, established as national policy in the RCRA Hazardous and Solid Waste Amendments (HSWA) of 1984, and the anticipated lack of hazardous waste treatment capacity.

The composition of SPL is highly variable. One range of analyses is given in Table 1. A process for the treatment of SPL should be versatile enough to treat SPL generated while using different cell designs, electrolyte compositions, and insulation packages, and any residues generated should meet anticipated EPA-defined limits for all constituents of concern (e.g., cyanide, fluoride, organics and metals). The components of SPL of greatest concern environmentally are cyanide and soluble fluoride salts. Of environmental and safety concern is the presence of water reactive materials (carbides) created during the pot life and resulting in explosive gases (hydrogen, methane and ammonia) upon exposure to water or even moisture of the air.

Table 1. Chemical Composition of Spent Potliners

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Al</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>Si</th>
<th>F</th>
<th>Fe</th>
<th>CN</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>10-50</td>
<td>5-22</td>
<td>1-8</td>
<td>0.2-1</td>
<td>7-20</td>
<td>1-20</td>
<td>10-19</td>
<td>0.3-5</td>
<td>0.2-0.5</td>
<td>0.01-0.3</td>
</tr>
</tbody>
</table>

The aluminum industry has long recognized the environmental liability of SPL and has pursued many options for treatment and/or disposal. These options include landfills, recycling as a feedstock in other industries, such as the steel, cement, aluminum, or mineral wool industries, fluidized bed combustion, cryolite recovery, pyrohydrolysis, pyrosulfolyis, and others. Landfilling is an option that is presently available but will become increasingly expensive, and eventually may be prohibited, since hazardous waste landfills are required.

Certain existing treatment processes are described below, and are grouped into two categories based on the amount of carbon combusted in the described process. The first
three processes operate under conditions in which little, if any, carbon is combusted. In these three processes, the carbon remains in the final product.

U.S. Patent No. 5,164,174 (Reynolds Metals Company) describes a method for detoxifying SPL by thermal treatment in a counter-current rotary kiln. Limestone and metal silicates are added to destroy cyanides by oxidation, and convert the soluble fluoride salts to relatively insoluble calcium fluoride and fluoride-bearing minerals. Air emissions contain very little fluorine and cyanide because of the low kiln operating temperature (600° to 870°C). Ash and particulate matter is removed and recycled or land-filled. The discharge material is air cooled and contains the carbon. However, because of the relatively low processing temperatures, the conversion of NaF to CaF₂ is inefficient.

U.S. Patent No. 4,497,464 (Ogden Environmental Services) describes a process for the treatment of ground SPL to reduce cyanide content to environmentally non-hazardous levels. Ground SPL is roasted in a stream of air or nitrogen at a temperature between about 260° and 760°C (500° and 1400°F). Cyanide levels are reduced without combustion of a major portion of carbonaceous material, resulting in an end product rich in carbon and fluorine. Because no calcium oxide source is added the following chemical reactions do not occur:

\[
\begin{align*}
\text{CaCO}_3 \rightarrow & \text{CaO} + \text{CO}_2, \\
2\text{NaF} + \text{CaO} \rightarrow & \text{CaF}_2 + \text{Na}_2\text{O}; \text{ and} \\
2\text{AlF}_3 + 3\text{CaO} \rightarrow & 3\text{CaF}_2 + \text{Al}_2\text{O}_3. 
\end{align*}
\]

Therefore, the fluoride salts are not converted to a stable, calcium fluoride. The Ogden discharge is essentially a landfill material.

U.S. Patent No. 4,993,323 (Tabery et al.) describes a method for thermal destruction of SPL by Fluidized Bed Combustion (FBC) in a mixture of lignite and limestone. Fluoride salts are converted to calcium fluoride. Significant carbon would remain in the final product.

The following processes for processing SPL result in the combustion of large amounts of carbon.

U.S. Patent No. 4,763,585 (Ogden Environmental Services) describes a process for the combustion of ground SPL using about 1 to about 20 weight percent of a powdered inert anti-agglomeration additive. The SPL is burned at between 1400°F to about 2200°F (760° to 1204°C). The contaminated components are bound or encapsulated into a solid glassy slag,
described as a glassy sodium metal (Al) silicate matrix encapsulating fluorine residues. Silica is added to the feed. Conditions are adjusted to produce hydrogen fluoride, which is scrubbed with water to produce a hydrogen fluoride solution. The high combustion temperatures cause much of the carbon to be combusted. Since no calcium oxide source is added, the following chemical reactions do not occur:

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2; \\
2\text{NaF} + \text{CaO} & \rightarrow \text{CaF}_2 + \text{Na}_2\text{O}; \quad \text{and} \\
2\text{AlF}_3 + 3\text{CaO} & \rightarrow 3\text{CaF}_2 + \text{Al}_2\text{O}_3.
\end{align*}
\]

In fact, aluminium fluoride and hydrogen fluoride are produced. Also, this process is not able to convert substantially all of the fluorides salts to calcium fluoride. In fact, much sodium fluoride would be evaporated, and fluorine merely encapsulated as a calcium salt.

U.S. Patent No. 5,711,018 (Alcoa) describes an industrial waste management facility (IWMF) for disposing of SPL using a co-current gas-fired rotary kiln. The IWMF recovers and recycles fluorides from discharge gases to the molten bath and collects and withdraws glass frit residue. The operating temperature is between 1150°C and 1250°C, and cannot exceed 1250°C to avoid generating fluoride gas. A solid oxygenating and gasifying agent (e.g. limestone) is added to form CO₂ which reacts with C to form CO. The CO is burned above the molten bath. Siliceous material is added to the bath. Fluorides are fixed in the frit. Carbon is burnt, as it is not desired in the frit because of its deleterious effect on porosity and leachability. Silicon oxide is added to help convert the fluorides to a stable form. Due to poor kinetics, conversion of the fluorides salts to calcium fluoride is poor.

U.S. Patent No. 5,286,274 (El kem Technology) describes a method for treatment of SPL for use as a filler, or as a raw material. Crushed SPL is supplied optionally with an SiO₂ source, to a closed electrothermic smelting furnace. The SPL is melted at a temperature between 1300°C and 1750°C. An oxidation agent is supplied to the furnace to oxidize carbon and other oxidizable components, such as metals, carbides and nitrides. Further, a source of calcium oxide is supplied to the smelting furnace in an amount necessary to react with all fluoride present to form CaF₂ and to form a calcium aluminate or calcium aluminate silicate slag containing CaF₂. The slag is liquid at the bath temperature in the furnace, and it, and optionally a metal phase, are tapped from the furnace and cooled to blocks or granules. Cyanide is combusted, and the conversion of the fluoride salts to calcium fluoride is poor.
U.S. Patent No. 5,245,115 (Aluminium Pechiney) describes a thermal shock treatment of ground SPL mixed with a mineral additive (selected from the group consisting of anhydrous CaSO₄, CaO and mixtures thereof). The mineral additive combines, with or without melting or fusion, with fluorine-containing compounds to form CaF₂, binary, ternary or quaternary compounds of NaF, CaF₂, SiO₂, Al₂O₃, CaSO₄, Na₂SO₄, of the nephelite, hauynite or similar type. The conversion of the fluorides salts to calcium fluoride is poor.

U.S. Patent No. 4,113,832 (Kaiser Aluminum & Chemical Corporation) describes a treatment process for waste materials, such as SPL, channel and trench cleanings, floor sweepings and spent alumina from offgas purifying dry scrubbers. The waste material is pyrohydrolyzed at elevated temperature. Fluorides, such as NaF and HF can be recovered from the offgas generated by pyrohydrolysis, while alumina and Na₂O, or if desired, sodium aluminate, can be reclaimed from the solid residue of pyrohydrolysis. Na⁺ and fluorine are volatized in this process.

U.S. Patent No. 4,735,784 (Morrison-Knudsen Company, Inc.) describes a process for treating solid substantially non-volatile waste contaminated with a heat sensitive contaminant. At least a portion of the contaminating components (i.e. fluorine) are either decomposed or evolve from the melt as a gas. The slag is cooled and any remaining contaminating compounds are bound or encapsulated into a solid glassy slag. The residue from the slagging reaction is a glassy solid sodium metal silicate matrix. Substantially all of the fluorine is volatized and captured as HF.

U.S. Patent No. 6,074,623 (Vick et al.) describes a process of converting SPL by gasification technology to produce an inert vitreous frit and useful gases including hydrogen fluoride, hydrogen and carbon monoxide. Substantially all of the fluorine is volatized and captured.

The first processes, described in U.S. Patents Nos. 5,164,174 (Reynolds); 4,497,464 (Ogden) and 4,993,323 (No Assignee), relate to processes in which little, if any, carbon is combusted. In all instances, the carbon remains in the final product. Therefore, the described processes fail to provide a process where the carbon is removed. Likewise, these processes fail to provide a product from which carbon has been removed.

The next processes, described in U.S. Patents Nos. 4,763,585 (Ogden); 5,711,018 (Alcoa); 5,286,274 (Elkem) and 5,245,115 (Aluminum Pechiney); and 4,113,832 (Kaiser), relate to processes in which a large portion of the carbon is combusted and an attempt is
made to capture fluorine in the final product. These processes do not permit recycling of carbon and have poor conversion of the fluoride salts to calcium fluoride.

The final three processes, described in U.S. Patents Nos. 4,113,832 (Kaiser); 4,735,784 (Morrison-Knudson) and 6,074,623 (No Assignee), describe processes in which a large amount of fluorine is volatized and a large amount of carbon is combusted. These patents fail to provide processes in which fluorine is efficiently captured in the frit and carbon is separated by physical means.

It is, therefore, desirable to provide a process for converting SPL into a glass frit which obviates or mitigates at least one of the disadvantages of the prior art.

SUMMARY OF THE INVENTION

It is an object of the present invention to obviate or mitigate at least one disadvantage of previous processes, apparatuses and products.

In a first aspect, the present invention provides a process comprising the steps of: combining and heating spent potliner, a calcium oxide source and a silica source to destroy cyanides, convert fluoride salts to calcium fluoride and form a generally homogeneous amorphous liquid material; physically separating carbon from the material; and vitrifying the material.

In one embodiment, about 9 to about 19% of a total feed is aluminium. In one embodiment, the heating is effected in counter-current fashion. In one embodiment, the process further comprises, after the combining and heating step, a glass finishing step in which the material is held at a temperature sufficient to enhance matrix formation and to facilitate separation of carbon from the material. In one embodiment, the spent potliner is crushed to less than 6mm. In one embodiment, vitrifying the material is effected by quenching. In one embodiment, a sufficient amount of calcium oxide is used to result in a complete conversion of: CaCO₃ and NaF to CaF₂, Na₂O and CO₂, according to: CaCO₃ + 2 NaF → CaF₂ + Na₂O + CO₂. In one embodiment, an amount of calcium oxide is added to achieve a CaO to vitrified material ratio of between about 0.04 and 0.10. In one embodiment, an amount of silica is added to achieve a Na₂O/Si₂O₃ ratio in the vitrified material of between about 0.21 and about 0.36. In one embodiment, the material is heated to between about 800 and about 1200°C. In one embodiment, the heating is at a temperature which retains fluorine and carbon in the material. In one embodiment, glass is added to a molten portion of
the material to increase production and to improve cementitious properties of the vitrified material. In one embodiment, the material, after vitrification, is ground to between about 4000 and 8000 m³/kg.

In further aspect, the present invention provides an apparatus comprising: (a) a first vessel for heating a mixture of spent potliner, silica source and a calcium oxide source to destroy cyanides, convert fluoride salts to calcium fluoride and form a homogeneous liquid material, (b) a second vessel for physically separating carbon from the material; and (c) a third vessel for vitrifying the material. In one embodiment, the first vessel is a rotary kiln for heating in a counter-current fashion. In one embodiment, the second vessel is a glass finishing furnace for holding the material at a temperature sufficient to enhance matrix formation and to facilitate separation of carbon from the material. In one embodiment, the third vessel is a quench basin.

In a further aspect, the present invention provides a vitrified material made by the above-described process.

In a further aspect, the present invention provides a generally amorphous solid matrix of calcium and sodium fluoro-alumino-silicate with a carbon content of less than 1 weight percent and a calcium fluoride content of between about 5 and about 25 weight percent having cementitious properties when finely ground that is produced from spent potliners. In further embodiments, the solid is at least about 95%, at least about 99% amorphous, or at least about 99.8% amorphous. In one embodiment, the solid is in granular form. In one embodiment, the solid has a Blaine value of from about 2000 to 8000 cm²/g. In one embodiment, the solid has the following composition by weight: CaF₂ of about 5-35%, SiO₂ of about 30-60%, Na₂O of about 5-25%, Al₂O₃ of about 10-25% and less than about 1% carbon. In one embodiment, the solid has the following composition by weight: CaF₂ of about 10-25%, SiO₂ of about 35-45%, Na₂O of about 10-15%, Al₂O₃ of about 18-23% and less than about 1% carbon.

In a further aspect, the present invention provides a use of the generally amorphous solid described above together with an alkaline activator as a binder for the manufacture of concrete.

In a further aspect, the present invention provides a composition comprising Portland cement, the generally amorphous solid described above, silica fume, and slag. In one
embodiment, the composition comprises about 30-40% Portland cement, about 5-35% of the
generally amorphous solid, about 2-8% silica fume, and about 20-30% slag.

In a further aspect, the present invention provides a use of between about 20 to 30% by weight of the generally amorphous solid described above as a Portland cement substitute.

In a further aspect, the present invention provides a use of more than about 90% of the generally amorphous solid described above in cement.

In a further aspect, the present invention provides a use of the generally amorphous solid described above as a hydraulic binder.

Other aspects and features of the present invention will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present invention will now be described, by way of example only, with reference to the attached Figures, wherein:

Fig. 1 is a schematic of an apparatus according to an embodiment of the present invention;

Fig. 2 is a block diagram of a process according to an embodiment of the present invention;

Fig. 3 is a flow chart illustrating a process according to an embodiment of the present invention;

Fig. 4 is a schematic of a gas circuit of a process according to an embodiment of the present invention;

Fig. 5 is a schematic of a solid circuit of a process according to an embodiment of the present invention;

Fig. 6 is a schematic of a water circuit of a process according to an embodiment of the present invention;

Fig. 7 is a diffractogram of a product according to an embodiment of the present invention.
Fig. 8 is a graph showing chloride ion-permeability of blended concretes, some of which contain a product according to an embodiment of the present invention; and

Fig. 9 is a graph showing the expansion obtained on concretes, some of which contain a product according to an embodiment of the present invention.

DETAILED DESCRIPTION

Generally, the present invention provides a pyrometallurgical process and apparatus for converting spent potliners (SPL) from aluminium manufacturing, or other hazardous materials, into commercially saleable amorphous calcium and sodium fluoroaluminosilicate glass frit (an example of which currently carries the trade mark CAISiFrit®) and a high carbon material (an example of which currently carries the trade mark CAISiCoke®). Spent potliners, a calcium oxide source, and a silicate source are fed into a non-burner end of a counter-current rotary kiln. The material is heated to destroy cyanides, convert fluoride salts to calcium fluoride and form a homogeneous liquid material. Carbon is then physically separated from the material in a fixed-bed furnace in series with the rotary kiln and the material is then vitrified. Both the rotary kiln and the fixed-bed furnace are linked to a flue gas treatment system.

The term “spent potliners” is known in the art. The word “spent” is not intended to limit the expression “spent potliners” to potliners which are completely spent as manufacturers may determine when a potliner should be replaced according to different criteria. Potliners are replaced well before their useful life ends in certain instances, according to plant operations. Other hazardous materials, especially those containing aluminium, calcium, or silicon can be treated according to the present process, such as catalysts from petroleum refineries, polycyclic aromatic hydrocarbons, a contaminated refractories, water purifying muds, and carbon anodes from aluminium smelters.

The apparatus according to the present invention will now be described with reference to Figure 1. SPL, energy and additives are fed into a long body rotary kiln (101) at a non-burner end thereof (i.e. at the right hand side in Figure 1). The material passes through the kiln to a glass finishing furnace (103) and to a quench basin (105). Gas and water treatment systems are integrated with the apparatus as detailed below.
Referring to Figure 2 for a general description of the process, SPL (201), energy (203), and additives (205) are added to the long body rotary kiln (207) where heating occurs. Gases are treated by a gas treatment system (208) and are partially re-circulated into the kiln (207) and treated gases are discharged through a chimney (211). At the exit of the kiln, the material falls into glass finishing furnace (209) where the high carbon material (217) is separated and the remaining material passes to a quench basin (213) where it is vitrified into a glass frit (218). A portion of the water from the quench basin (213) is fed to the gas treatment system (208) and the balance is fed to the cooling circuit (214) and water treatment system (215), where it is cooled and returned to the quench basin (213). Since the process consumes water, make-up water (216) is added.

A process flow chart is provided in Figure 3. The feed comprising SPL and additives is combined and heated (301) to form a liquid material. Carbon is physically separated from the material (303). The material is vitrified to produce a glass frit (305). Between steps (301) and (303) the material may be held at a high temperature to enhance matrix formation (302). The process is described in greater detail below.

A) Crushing and preparation of the mixture (i) The SPL is crushed to a dimension of, on average, 6 mm and continuously sampled during stockpiling. In an integrated system, sampling takes place during silo filling so that a computer has the information at all times of which material corresponds to which analysis. As an example, eight silos can simultaneously be used to correctly homogenize the SPL destined to feed the furnace. Stockpiling inside specially a designed silo comprising air intake and filtering ventilation is preferred over large reclaiming stockpiles due to the reactivity of the material with moisture in the air. (ii) The crushed SPL is quarantined awaiting analysis. (iii) After receipt of the chemical composition data of the SPL, additives and reagents are added during its feeding accordingly to the analysis. The quantities of additives and reagents are determined by a software program to provide a consistent feedstock. Alumina bearing material such as recycled material is added to the SPL to present a total Al content of about 9 to 19% of the total feed, preferably 13.5%. Alternatively, SPL is crushed after been mixed to form the recipe. Enough calcium (such as CaCO₃, limestone, calcium oxide (or quicklime) hydrated lime, possibly dolomite, and calcium containing waste) is added to complete the following simplified reaction:

\[ \text{CaCO}_3 + 2 \text{NaF} \rightarrow \text{CaF}_2 + \text{Na}_2\text{O} + \text{CO}_2 \]

- 10 -
Additional calcium is added over the above stochiometric reaction amount for a ratio CaO/glass frit of between about 0.02 to 0.12, preferably about 0.07. Sufficient silica is added according to the sodium of the SPL to offer a final Na₂O/Si₂O₃ ratio of about 0.16 to 0.36, preferably about of 0.26 in the glass frit.

B) The furnace is fed. The furnace is preferably a long body rotary furnace (LBRF) or kiln. The material progresses from upstream to downstream passing through different thermal and physical phases. The feedstock is fed to the furnace by rate controlled conveyors and/or a chute.

C) Operation of the long body rotating furnace (LBRF). (i) The LBRF has a diameter of 3 m and a length of 40 m. It should be understood that while specific dimensions or shapes may be described or shown throughout this description, this is intended to be illustrative and not limiting. Infrared temperature detectors are disposed along its entire length to measure the exterior temperature of the furnace and, consequently, the temperature variations in the furnace. Once control is established it may be sufficient to monitor the cold end temperature of the process gases and the temperature of the exiting material. (ii) The material is progressively heated, starting from ambient, as it moves within the furnace. The heat source is downstream, making the process counter-current. Figure 1 shows the various phases through which the material passes. Zone 1 (1001) is the cold zone where material enters the kiln. Zone 2 (1002) is where the material is heated to between 800 and 1200°C and chemical reactions occur. In Zone 3 (1003), solid material slowly melts while continuing to undergo chemical reactions. In Zone 4 (1004), material is liquid and final chemical liaison are taking place. Zone 5 (1005) represents the secondary glass finishing furnace where separation of carbon takes place. The secondary glass finishing furnace should afford effectively separate carbon from the matrix. Zone 6 (1006) represents the quench basin. (iii) Increasing temperature favours the breaking of certain existing chemical bonds, and the creation of the bonds which define new compositions. This causes the destruction of cyanides by oxidation, and the capture of fluorides which pass from a sodium bond to a calcium bond. The primary reactions are as follows:

\[2\text{CN} + 2\text{O}_2 \rightarrow 2\text{CO}_2 + \text{N}_2\]
\[\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2\]
\[2\text{NaF} + \text{CaO} \rightarrow \text{CaF}_2 + \text{Na}_2\text{O}\]
2AlF₃ + 3CaO -> 3CaF₂ + Al₂O₃

(iv) The material, which at the entrance of the LBRF was composed heterogeneously of solid materials, gradually becomes a homogeneous liquid composition. In Zone 4 (1004), the matrix is formed and the following two reactions occur:

\[ \text{CaF}_2 + \text{SiO}_2 \rightarrow \text{Na}_2\text{O} + \text{Al}_2\text{O}_3 \]
\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]

D) Vitrification of siliceous matrix. (i) At the exit of the LBRF, the material, now in an amorphous state, falls into a secondary non-rotating furnace, or a glass finishing furnace (GFF), to prolong the time of retention at high temperature, thereby ensuring the complete formation of a complex matrix of fluroaluminosilicate of sodium and calcium. The GFF also permits the gravitational separation of carbon, and, by raking it or blowing it out, the production of a matrix with very little carbon. The carbon floating on the matrix is recovered instead of being burnt. Analysis of this high carbon material gives a carbon content as high as most metallurgical coke found on the market. Chemically, it consists of a pyrometallurgical coke containing greater than 80 percent carbon. In the less than 20 percent of ashes, 2 to 4 percent is calcium fluoride, a level which presents a marked advantage with respect to the fluidization and the lowering of eutectic points of clinkers and of metallurgical slags. The recovery of residual carbon in this process increases the global co-efficient of recycling of the spent potliners and reduces as much the greenhouse gas effect by tonne of spent potliners used. (iii) The glass liquid thus extracted is quickly immersed in water to rapidly reduce the temperature and to conserve its amorphous character, one of its essential qualities. (iv) The resulting glass frit, is dried and ground. The glass frit is preferably ground to a Blaine value of from about 2000 to 8000 cm²/g and more preferably about 4000 to 6000 cm²/g. The glass frit in matrix form is composed of (CaF₂ 5-35% or preferably 10-25%), SiO₂ (30-60% or preferably 35-45%), Na₂O (5-2 or preferably 10-15%) and Al₂O₃ (10-25%). Smaller amounts of CaO (3-12%) and Fe₂O₃ (1-3%) are also present. Less than 1% carbon is present. The ratio of glass frit to SPL is about 1.4 or 1.55.

E) Treatment of gases. Figure 4 illustrates the gas circuit. (i) In order to capture all the gases generated during the production of the glass frit the LBRF (403) and the GFF (401) are connected by a mobile head of high temperature type. The LBRF burner is shown as (402) while the burner of the GFF is shown as (412). This assures a sealed system, which,
under negative pressure, directs all the gases of combustion and gases of production (decomposition of carbonates and ferrocyanides, etc.) to an after-burner and purging system (404), before their emission to the chimney (410). (ii) A first purging takes place in the relaxation chamber (403a) of the furnace, through the vertical exit of gases to a high temperature cyclone (not shown). This avoids massive entrainment of dust downstream. The cyclone is not necessary. Once separated from the flux gas, the dust is re-fed to the LBRF via a solid feed circuit (discussed below with respect to Figure 5). (iii) The temperature in the after-burner system is raised to about 775-950°C, preferably 875°C to combust CO, and eliminate hazardous air pollutants such as polycyclic aromatic hydrocarbons. (iv) The gases are then cooled to a temperature compatible with the filter bags (407). This also neutralizes acid gases to be further polished in a dry reactor (406). (v) The dry reactor (406) eliminates, by injection of calcium hydroxide, HF and other acids, which may be found in the gas stemming from the after-burner (411). If the detection system signals the presence of fluorine gases to the chimney, the dry reactor (406) automatically increases the injection of calcium hydroxide in order to assure the quality of the emissions into the atmosphere. (vi) The filter bags (407) capture the solid dust coming from the dry reactor (406). The presence of an adequate cake on the filtrating sleeves helps to assure that the acidic molecules are absorbed by the Ca(OH)₂ and, therefore, plays a role similar of that of the dry reactor (406).

A further burner (412) is present for the GFF (401). Combustion of natural gas and/or other combustibles occurs at (413). Continuous natural gas measurement occurs at (414). Other combustibles, liquid or solid, can be used with the kiln burner. Natural gas is preferred at the after-burner to ensure complete burning of all elements which is the purpose of the after-burner.

F) Verification of atmospheric emissions. Figure 4 illustrates the gas circuit. (i) After filtering, the gases are directed to the chimney (410). Continuous measurement of the atmospheric emissions: HF, CO, CO₂, O₂, SO₂, NOₓ and opacity, are performed in the analysis and sampling atmospheric station (409).

G) Treatment of dust and returns. Figure 5 illustrates the solid circuit. (i) All dust coming from the gas treatment is returned into the solid feed and re-injected into the furnace. Feed debris, quench-water treatment mud and the like such as spent kiln refractories are also recycled back into the process. The SPL comes from SPL container (501) via a hopper (502) and conveyor (503) although conveyors are not necessary. Alternatively and more
preferred is to crush the SPL and homogenize it into the bank of silos. Additive silos (504) hold the additives. Recipe hopper (505) and furnace hopper (506) are used for feeding. Feed debris (507), post combustion and conditioning recycles (508), and recycles from filter bags (509) are re-fed into the furnace hopper (406). Also shown are the LBRF (510), LBRF burner (511), GFF (512), high carbon material container (513), glass frit quench basin (514), automatic glass frit sampler (515), and the glass frit (516).

H) Water treatment. Figure 5 illustrates the water circuit. (i) Lime is added to the treatment water to prevent its acidification. The water is then cooled before being recycled back to the quench basin. (ii) A portion of the water feeds the conditioning tower of the after-burner. Water cooling is done through evaporation. Overall, the process consumes water and, therefore, there is no waste water expelled. Referring to Figure 6, glass frit (609) is shown coming from quench basin (601). Water from quench basin (601) flows through holding basin (603) and pump basin (604) and therefore a portion is added to the conditioning and post-combustion tower (605) and the balance is fed to cold water treatment basin (608) from which water evaporates (606). Additional water (607) is added to the water basin (608). Waste water is collected in catch basin (602) and using collection basin pump (610) is pumped to holding basin (603). Water basin pump (611) is used to pump water to the quench basin (601).

Temperature profile in the kiln

The material temperature at the feed end is approximately ambient and at the exit end is 950-1250 °C and preferably 1050-1125 °C. Using the state of the material and the liquidus material temperature, the temperature at ten to twelve meters from the burner end of the furnace has been calculated to be 860 °C. At one meter from the burner, the temperature has been measured to be 1125-1150 °C. This temperature can be controlled by increasing or decreasing the amount of fuel used by the front burner. Additional correction involving the varying of the flame type from axial to radial is done after observing the location and state of the annulus at approximately ten to twelve meters from the burner end.

The gas temperature at the burner end of the kiln (exit of the kiln) is 1450 °C and the gas temperature and flow rate at the feed end of the kiln is measured. In relation to the feed rate, these measures indicate whether the profile is being raised or cooled. This is confirmed by the shell temperatures being measured continuously at some 20 sections, which trends
will indicate in which direction the process is proceeding. These shell readings are affected by the external temperature, wind, rain etc. and therefore are useful in a relative way to indicate a trend not absolute values. The shell temperature readings are also affected by the thickness and state of the refractory lining augmented by the thickness of present accretions. As discussed above, measurement along the shell can help but it not necessary.

If the profile is not controlled, the accretions inside the kiln will get rapidly to a point where you cannot feed more material. To remove these accretions, the operation is stopped to enter the kiln to physically break away the accretion with jack-hammers. Radial CO\textsubscript{2} blasting, axial gun shooting and superheating have proved themselves quite ineffective ways to remove/control the accretions.

Kinetics

Counter current kiln favors preheating of feed material and cooling of gas. The temperature inside the kiln is controlled by adjusting the ventilator (408) (see in Figure 4) situated before the escape chimney and the energy input by the primary burner.

The use of a LBRF (long body rotary kiln) in a counter-current set-up permits operators to properly, dynamically and relatively slowly raise the temperature of the material as it moves down the kiln towards the hot zone. The rotation of the kiln ensures an intimate contact between the different materials. The rotation also promotes rubbing of the different compositions one against the other in an eroding action. The necessary reactions can then take place in a catalytic and successive manner.

The use of a LBRF in a counter-current set-up ensures that most of the involuntarily release of volatized NaF and produced Na\textsubscript{2}O and HF will condense inside the LBRF with its cool gas exit and be brought back into the process stream due to the rubbing action of the feed material onto the walls.

Thermodynamic simulations have shown the necessity to minimize the amount of H\textsubscript{2}O vapor inside the kiln to prevent the reaction

\[ 2 \text{NaF} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{O} + 2 \text{HF} \]

The simulations also showed the necessity to finalize the process at less than 1200°C to reduce the vapor pressure of NaF and therefore the creation of HF due to the water vapor created by the combustion of natural gas.

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]
The process of the present invention employs these thermodynamic features. The process of the present invention thus differs from the others which heat rapidly the SPL and provoke the creation of HF.

An exemplary time for the material to pass through the LBRF is 1.5 to 2.5 hours.

**Auxiliary Feed Material**

In one embodiment, an auxiliary feed material is used to increase the production of the kiln and to improve cement properties. The counter-current LBRF has its cold zone at the feed section (upper section). Material is added in the hot zone right into the molten basin in the lower section of the kiln. This material is injected into the kiln at 60 feet/sec to reach 4 to 6 meters into the kiln. The added material then has time to melt and partially or totally mix with the glass matrix. Up to about 7 tons per hour is expected to be able to be added in this manner therefore greatly increasing the kiln output.

The injection into the hot zone of the kiln is also done because the material being injected is broken glass (cullet) which would negatively affect the melting (and chemical reactions) of the recipe if it was fed into the kiln in the cold upper zone. Cullet is presently preferred but others materials could be used.

These additions modify the structural liaison between the different components of the glass matrix which in turn affect the reactivity of the amorphous produced glass and thus, its cementitious properties. Lowering the ratios of Ca and Al/glass frit reduces its susceptibility to sulfate and carbonate attacks rendering the concretes made out of the glass frit more durable. These additions result in a product offering some of the properties actually brought to concretes by silica fumes.

The glass frit can make concretes at high temperatures without reactions creating deleterious ettringite. High temperature reduces strengthening time required by concretes therefore increasing the turn-over capability of pre-fab plants. An activator is used to turn the glass frit into a high performance binder for the manufacture of resistant and durable cements (an example of which currently carries the trade mark CA1SiBinderHP®).
Mass Balance

A study of the mass balance of this process during the recycling of 1000 metric tonnes of spent potliners revealed the following: a fluorine mass balance of 99.26% (the loss of fluorine by atmospheric emission represents only 0.003% of the total mass of fluorine fed in the form of potliner, a CO₂ mass balance of 99.02% (or 100% taking into account the admissible tolerance of the various instruments of measurement), a solid mass balance of 99.8% (or 100% taking into account the admissible tolerance of the various instruments of measurement). The fluorine mass balance confirms that fluorine is not lost somewhere in the process. The quantity of carbon feed as potliner was measured as 324.99 ± 2.03 metric tonnes and the carbon found in the glass frit and high carbon material respectively was 126.30 ± 0.51 and 102.12 ± 8.17 metric tonnes indicating that the quantity of carbon consumed during the process in the kiln and found as carbon dioxide gas in the chimney is 96.57± 8.43 metric tonnes. Only 0.84 tonnes of CO₂ are produced per tonne of potliner which favourably compares to 1.19 tonnes in another known process.

The Glass Frit

The glass frit is an amorphous siliceous material forming a calcium and sodium fluoroaluminosilicate matrix. This homogenous solid substance possesses a high reactivity potential and shows superior cementitious properties when finely ground. The glass frit once quenched is finely ground into a powder, of, for instance 410 m²/kg. Figure 7 is an X-ray diffraction analysis of the glass frit shows that the amorphous character of character of the glass frit. Although a 95% amorphous character is desired, at least 98%, is preferred, and at least 99% more preferred. Table 3 shows a chemical composition of the glass frit using one specific measurement. The values shown under the "normal" heading are the limits over which the material is declared a "Hazardous Material". TCLP is the standard practice defining the method to analyse lixiviation using an acidic medium.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Normal</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al, %</td>
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<td>12.0</td>
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<td>Ca, %</td>
<td></td>
<td>12.1</td>
</tr>
<tr>
<td>Mg, %</td>
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<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
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<tr>
<td>--------</td>
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<td>-------</td>
</tr>
<tr>
<td>Si, %</td>
<td>15.4</td>
<td></td>
</tr>
<tr>
<td>Fe, %</td>
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<td></td>
</tr>
<tr>
<td>K, %</td>
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<tr>
<td>F total, %</td>
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<td></td>
</tr>
<tr>
<td>Na, %</td>
<td>10.2</td>
<td></td>
</tr>
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</table>

**Lixiviation TCLP**

<p>| | | |</p>
<table>
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<tr>
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<tbody>
<tr>
<td>As</td>
<td>&lt; 5 mg/l</td>
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<tr>
<td>Ba</td>
<td>&lt; 100 mg/l</td>
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<tr>
<td>B</td>
<td>&lt; 500 mg/l</td>
<td>0.09</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 0.5 mg/l</td>
<td>0.34</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt; 5.0 mg/l</td>
<td>0.02</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt; 0.1 mg/l</td>
<td>&lt; 0.0004</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt; 5.0 mg/l</td>
<td>3.3</td>
</tr>
<tr>
<td>Se</td>
<td>&lt; 1.0 mg/l</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>U</td>
<td>&lt; 2.0 mg/l</td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>Nitrates+Nitrites</td>
<td>&lt; 1000 mg/l</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>Fluorides</td>
<td>&lt; 150 mg/l</td>
<td>11.9</td>
</tr>
<tr>
<td>Nitrites</td>
<td>&lt; 100 mg/l</td>
<td>&lt; 0.02</td>
</tr>
</tbody>
</table>

The glass frit is useful as a cementitious addition and hydraulic binder. When used as a cement enhancer, it has been demonstrated by a report prepared by the University of Sherbrooke that the glass frit improves the flowability of the blended concretes. This rheology allows for a reduction of the water to binder (W/B) ratio. Besides reducing the chemical admixture dosage requirements (especially in water reducer and superplasticizers), this improved rheology permits a reduction of the binder content without sacrificing either the workability or the physical properties of the concretes. The glass frit is a chloride-ion permeability reducer that enhances the durability of concrete. Figure 8 shows the results of chloride ion permeability tests carried out after 91 days of curing in 100% RH and at a temperature of 23±2°C, water to binder ratio (W/B) of 0.35, according to ASTM C1202 standard. The cements of Figure 8 are defined as follows: Control is 100% Portland cement. Binary is 75% Portland cement and 25% blast furnace slag. Binary CF is 75% Portland
cement and 25% glass frit. Ternary is 75% Portland cement, 20% of the glass frit, and 5% silica fume. Quat/FA is 50% Portland cement, 25% of the glass frit, 5% silica fume, and 20% flyash. Quat/slag is 40% Portland cement, 25% of the glass frit, 5% silica fume, and 30% slag.

Figure 8 shows that the permeability of concrete to chloride-ion decreases by more than 50% when using 25% of the glass frit as a Portland cement substitute. 20%-30% is presently preferred. Figure 8 shows that using the glass frit is a quaternary mixture resulted in a permeability reduction to 1/15th the level of a control concrete using a cement made of 100% Portland Type 10. Concrete's resistance to chlorine-ion attack is one of the most important factors to consider when determining its durability. This is precisely where the glass frit excels as an additive. Due to its discontinuous pore network, it ensures better resistance to salt, acid and water attack.

Figure 9 shows the expansion obtained on concrete prisms of 75 x 75 x 300 mm cured for longer than two years in 100% RH and at a temperature of 38°C, according to CSA A23.2-14A standard. Replacing 25% of the cement with the glass frit reduced expansion. Following standardized curing for 853 days, the expansion noted in concrete using 100% Portland cement was 0.23%; while it was 0.13% with cement containing 25% of the glass frit. To evaluate a material's effectiveness in controlling alkali-aggregate reaction, article 6 of CSA standard A23.2-28A stipulates a limit to the expansion of concrete containing additives to 0.04% after two years of curing. The analysis of the graph allows us to conclude that although the glass frit did not meet the standard, its expansion is still far less than that caused by commercial Portland Type 10 cement. However, even though the glass frit has a significant alkali content, when used in concentrations above 90%, it meets CAS norm A23, 2-28A article 6.

The glass frit being more than 99.8% amorphous, boasts strong binding potential as a cement. When ground to 4000 Blaine and when combined with an alkaline activator at hydration, it becomes an effective hydraulic binder enabling its use in RPC-type concretes. As shown by American laboratory F.L. Smidth, pulverization of the glass frit to 4000 Blaine required less energy than that of clinker or slag.

Resistance and other mechanical characteristics of concrete are improved when the glass frit is used. All tests performed to date by the University of Sherbrooke and St. Lawrence Cement corroborate this. More specifically, compressive, tensile and flexile
strengths of blended concrete are improved, as is durability. By substituting, as the principle durability agent, 20% The glass frit to the Portland cement used in the preparation of general use concretes, not only are the tensile, flexile and compressive strengths increased their permeability is also greatly reduced. Their workability is improved while smaller quantities of rheology enhancing agents are needed.

The paleness of finely ground Glass frit is another quality. This is especially true when the aesthetics of a finished product is perceived as a component of its quality and durability. The glass frit also shows potential as an element in the formulation of reactive powder concrete.

The glass frit allows for the reduction of greenhouse gas emissions (GHG). When used as a substitute of clinker in the manufacture of cement, it generates a credit equivalent to 450 kgs/mt of replaced Portland. This GHG credit reaches 650 kgs/mt of substituted Portland when cullet is added to the silica matrix. Thus is a more environmentally friendly and valuable material within a sustainable development framework. On an environmental and sustainable development level, the addition of The glass frit to cement is particularly beneficial. It eliminates an environmental risk for the aluminium smelters by transforming a hazardous waste into a commercially viable product. There will no longer be a need to landfill spent pot-liners, thus the major environmental benefit of this process. There are major socio-ecological benefits in the reclamation of residual hazardous materials into commercial products by the use of a clean, residue-less recycling process.

The high carbon material

Another product of the glass frit process is a high carbon material or coke (an example of which currently carries the trade mark CAISiCoke®). The high carbon material has a carbon content as high as most pyrometallurgical cokes found on the market. Minor metal oxides contained give the material additional metallurgical properties sought by cement and metallurgical industries. Primary users of the high carbon material may be cement and steel makers, who require coke to supply energy, or as a means of reducing oxides and recarbonising steel.
Table 4 shows the chemical composition of the high carbon material.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
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</tr>
<tr>
<td>Sulphur</td>
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<td>&lt; 0.1</td>
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<tr>
<td>Ca total</td>
<td>%</td>
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</tr>
<tr>
<td>Cd total</td>
<td>%</td>
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<tr>
<td>P total</td>
<td>mg/kg</td>
<td>290</td>
</tr>
<tr>
<td>CN total</td>
<td>mg/kg</td>
<td>1.3</td>
</tr>
<tr>
<td>Fluorine total</td>
<td>%</td>
<td>2.9</td>
</tr>
<tr>
<td>Pb total</td>
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<td>0.01</td>
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<td>Mg total</td>
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<tr>
<td>Na total</td>
<td>%</td>
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</tr>
<tr>
<td>Si total</td>
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</tr>
<tr>
<td>Al total</td>
<td>%</td>
<td>3.3</td>
</tr>
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</table>

**LIXIVIATION TCLP**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
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<tr>
<td>B</td>
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</tr>
<tr>
<td>Se</td>
<td>mg/l</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

The above-described embodiments of the present invention are intended to be examples only. Alterations, modifications and variations may be effected to the particular embodiments by those of skill in the art without departing from the scope of the invention, which is defined solely by the claims appended hereto.
CLAIMS:

1. A process comprising the steps of: combining and heating spent potliner, a calcium oxide source and a silica source to destroy cyanides, convert fluoride salts to calcium fluoride and form a generally homogeneous amorphous liquid material; physically separating carbon from the material; and vitrifying the material.

2. The process according to claim 1, wherein about 9 to about 19% of a total feed is aluminium.

3. The process according to claim 1, wherein the heating is effected in counter-current fashion.

4. The process according to claim 1, further comprising, after the combining and heating step, a glass finishing step in which the material is held at a temperature sufficient to enhance matrix formation and to facilitate separation of carbon from the material.

5. The process according to claim 1, wherein the spent potliner is crushed to less than 6mm.

6. The process according to claim 1, wherein vitrifying the material is effected by quenching.

7. The process according to claim 1, wherein a sufficient amount of calcium oxide is used to result in a complete conversion of: CaCO₃ and NaF to CaF₂, Na₂O and CO₂, according to:

   \[ \text{CaCO}_3 + 2 \text{NaF} \rightarrow \text{CaF}_2 + \text{Na}_2\text{O} + \text{CO}_2 \]

8. The process according to claim 1, wherein an amount of calcium oxide is added to achieve a CaO to vitrified material ratio of between about 0.04 and about 0.10.
9. The process according to claim 1, wherein an amount of silica is added to achieve a Na$_2$O/Si$_2$O$_3$ ratio in the vitrified material of between about 0.21 and about 0.36.

10. The process according to claim 1, wherein the material is heated to between about 800 and about 1200°C.

11. The process according to claim 1, wherein the heating is at a temperature which retains fluorine and carbon in the material.

12. The process according to claim 1, wherein glass is added to a molten portion of the material to increase production and to improve cementitious properties of the vitrified material.

13. The process according to claim 1, wherein the material, after vitrification is ground to between about 4000 and about 8000 m$^3$/kg.

14. An apparatus comprising: (a) a first vessel for heating a mixture of spent potliner, silica source and a calcium oxide source to destroy cyanides, convert fluoride salts to calcium fluoride and form a homogeneous liquid material, (b) a second vessel for physically separating carbon from the material; and (c) a third vessel for vitrifying the material.

15. The apparatus according to claim 14, wherein the first vessel is a rotary kiln for heating in a counter-current fashion.

16. The apparatus according to claim 14, wherein the second vessel is a glass finishing furnace for holding the material at a temperature sufficient to enhance matrix formation and to facilitate separation of carbon from the material.

17. The apparatus according to claim 14, wherein the third vessel is a quench basin.

18. A vitrified material made by the process according to claim 1.
19. A generally amorphous solid matrix of calcium and sodium fluoro-aluminosilicate with a carbon content of less than about 1 weight percent and a calcium fluoride content of between about 5 and about 25 weight percent having cementitious properties when finely ground that is produced from spent potliners.

20. The generally amorphous solid according to claim 19, wherein the solid is at least about 95% amorphous.

21. The generally amorphous solid according to claim 19, wherein the solid is at least about 99% amorphous.

22. The generally amorphous solid according to claim 19, wherein the solid is at least about 99.8% amorphous.

23. The generally amorphous solid according to claim 19, wherein the solid is in granular form.

24. The generally amorphous solid according to claim 19, wherein the solid has a Blaine value of from about 2000 to 8000cm²/g.

25. The generally amorphous solid according to claim 19, having the following composition by weight: CaF₂ of about 5-35%, SiO₂ of about 30-60%, Na₂O of about 5-25%, Al₂O₃ of about 10-25% and less than about 1% carbon.

26. The generally amorphous solid according to claim 19, having the following composition by weight: CaF₂ of about 10-25%, SiO₂ of about 35-45%, Na₂O of about 10-15%, Al₂O₃ of about 18-23% and less than about 1% carbon.

27. A use of the generally amorphous solid according to claim 19, together with an alkaline activator as a binder for the manufacture of concrete.
28. A composition comprising Portland cement, the generally amorphous solid according to claim 19, silica fume, and slag.

29. The composition according to claim 28, comprising about 30-40% Portland cement, about 15-35% of the generally amorphous solid, about 2-8% silica fume, and about 20-30% slag.

30. Use of between about 20 and about 30% by weight of the generally amorphous solid according to claim 19 as a Portland cement substitute.

31. Use of more than about 90% of the generally amorphous solid according to claim 19 in cement.

32. Use of the generally amorphous solid according to claim 19 as a hydraulic binder.
FIG. 2

Borden Ladner Gervais LLP / s.r.l.
Combining & Heating Feed

Retaining material at high temperature to enhance matrix formation

Physically separating Carbon from material

Quenching material to vitrify into a glass frit

FIG. 3
FIG. 7

FIG. 8

FIG. 9