Abstract: A method of extraction of a metal from an ore or ore concentrate, including the steps of melting a target metal-containing mixture in a heated process vessel at a minimum temperature to form a homogeneous melt in the presence of an appropriate flux material to lower the melting temperature of the target metal-containing mixture, to produce a molten ionic matrix which is largely amorphous and hygroscopic and cooling the matrix.
Removal of Metals from Complex Ores

Field of the Invention.

This invention relates to a method and device for the removal of metals from their naturally occurring ores and mineral concentrates preferably using vitrification processes.

Background Art.

The extraction and subsequent processing of metals from their naturally occurring ores is well known. Such processes include high temperature reduction smelting, chemical reduction, acid leach, gravity separation, hydro metallurgy, pyrometallurgy, pyro/hydrometallurgy, flotation, hydrolysis, and electrowinning.

For example, high temperature and pressure concentrated sulphuric acid leach processes are currently used to extract nickel and cobalt from nickel laterite ores. The high cost of corrosive chemicals, their logistics and safety, can sometimes lead to marginal profitability and questionable environmental acceptability. Such processes have also required the design and utilisation of equipment that is relatively new to the scale and utility demanded by the mining industry. Very high capital costs of the required high pressure autoclave support equipment and also long lead times of existing commercial extraction systems which are also prone to inefficiencies and substantial maintenance costs, make them less commercially preferred.

By way of background information and as outlined in United States Patent 6,261,527 Arroyo, et al. July 17, 2001, known reserves of nickel and cobalt in laterites comprising limonite and saprolite ore, are far greater than the rapidly depleting reserves in sulphide ores. However, processing laterite ores is difficult by conventional techniques. A number of new hydrometallurgical processes are being developed for the extraction of nickel and cobalt from nickeliferous laterite ores. Many of these processes require the dissolution of the ore matrix with sulphuric acid at high temperature (245°C-270°C.) and pressure (525-785psig), followed by solid-liquid separation and neutralization of residual free acid present at ambient pressure. This is known as the "Moa Bay Process".

In this process, the nickeliferous ore is first made into a pulp having a solids content of about 40% before leaching at high temperature and pressure. During pressure leaching most metals dissolve and iron and aluminium are rejected by
hydrolysis to hematite and alunite, respectively. After leaching, the pulp is cooled and washed by counter current decantation and the solids are directed to tailing treatment. Excess acid is neutralized and the remaining iron and aluminium are precipitated as hydroxides with the addition of coral mud. Nickel and cobalt are subsequently recovered via sulphide precipitation.

Variations of the aforementioned high-pressure acid leach (HPAL) are exemplified in U.S. Pat. No. 4,044,096.

U.S. Pat. No. 3,804,613 teaches a method of high-pressure acid leaching of saprolite ore at relatively low acid/ore ratios by preconditioning the saprolite with recycled leach liquor from the high-pressure step. This HPAL process is suitable for the treatment of high iron ores containing 40wt % iron or higher. Lateritic ores with an iron content less than 40 wt % contain a higher proportion of magnesium, which consumes higher acid volumes, and are therefore not economically suitable for direct high pressure leaching.

U.S. Pat. No. 3,991,159 teaches the use of saprolite ore to neutralize acid resulting from the high-pressure acid leach of limonite ore. Leaching of the saprolite fraction is carried out at high temperature (150°C -250°C) and pressure for effective iron and aluminium rejection, but with relatively low nickel extraction from the saprolite ore.

In another process, U.S. Pat. No. 4,097,575 teaches saprolite ore roasting at 500°C-750°C under oxidizing conditions to increase its acid neutralization capacity before contact with HPAL liquors.

While prior art HPAL methods obtain a high extraction of nickel and cobalt, they require the use of expensive equipment and sophisticated construction materials to withstand the use of concentrated acid at the high temperatures needed (200°C - 300°C), and particularly the high pressure. Furthermore, part of the rejected iron and aluminium are in the form of hydroxides, which are difficult to deal with. For example, U.S. Pat. No. 4,062,924 describes a method for leaching limonite ores in acidic media at temperatures up to 700°C and in the presence of hydrogen sulphide gas to precipitate dissolved nickel and cobalt. Most dissolved iron is also reduced to the divalent oxidation state in this process, consuming very high amounts of the reducing gas in addition to high acid consumption. U.S. Pat. No. 4,065,542 teaches a similar method. In this process, ferrous iron produced by the method described above is used
to leach metal values from manganiferous sea nodules.

U.S. Pat. No. 4,51 1,540 illustrates a way to recover nickel and cobalt from ores with a manganiferous matrix by leaching with sulphuric acid in the presence of sulphur dioxide gas at temperatures below the boiling point of the liquid solution.

U.S. Pat. No. 3,793,432 describes a limonite ore leached with sulphuric acid at a pH below 1.5, while simultaneously adding alkaline iron-precipitating agents. The process is carried out at atmospheric pressures, but requires leaching times in excess of 40 hours and usually from 60 to 100 hours for efficient nickel extraction and iron precipitation.

U.S. Pat. No. 4,410,498 teaches a method to leach saprolite ore with sulphuric acid at atmospheric pressure, while adding a reducing agent to maintain the redox potential between 400 and 600 mV.

In another process, described in U.S. Pat. No. 5,571,308, nickel and cobalt are leached from saprolite ore by contact with a mineral acid at room temperature or in the temperature range of 60°C-80°C.

To anyone skilled in the art it should be obvious from the above process descriptions that using current nickel laterite acid leach techniques, metal recovery efficiencies are still below both commercial and theoretical expectations. The complicated chemistry and mechanisms of unlocking metals or their ions from ore matrices using acid leach techniques, is at the core of recovery difficulties.

It will be clearly understood that, if a prior art publication is referred to herein, this reference does not constitute an admission that the publication forms part of the common general knowledge in the art in Australia or in any other country.

**Summary of the Invention.**

The present invention is directed to a method for the removal of metals from complex ores, which may at least partially overcome at least one of the abovementioned disadvantages or provide the consumer with a useful or commercial choice.

With the foregoing in view, the present invention in one form, resides broadly in a method of removal of a metal from an ore, including the steps of:

1. melting a target metal-containing mixture in a heated process vessel at a minimum temperature to form a homogeneous melt,
in the presence of an appropriate flux material to lower the melting temperature of the
target metal-containing mixture to produce a molten ionic matrix and

2. cooling the matrix.

The matrix will typically be cooled rapidly to preserve the target properties of the matrix being both hygroscopic and amorphous. This rapid cooling process can be achieved by air cooling or fluid quenching using water, saline solution or a supersaline ground water as examples.

According to an alternative embodiment, the invention resides in a method of removal of a target metal from a target metal-containing mixture, including the steps of

1. melting a target metal-containing mixture in a heated process vessel at a minimum temperature to form a homogeneous molten ionic matrix containing at least the target metal,
in the presence of an appropriate flux material to produce a molten ionic matrix and

2. cooling the matrix.

It is preferred that silica, normally present as silicate will be present in the molten ionic matrix in the order of approximately 30% of the total by mass. If not present due to the composition of the target metal-containing mixture of appropriate flux material, silica may be added through the addition of silica sand for example.

The invention as described in the above statements particularly and this specification generally has the distinct advantage of being able to treat the full mineralogical range of nickel laterites, which conventional processes such as the Caron and HPAL processes cannot.

According to a further alternative embodiment, the invention resides in an apparatus for the removal of a target metal from a target metal-containing mixture by formation of a molten ionic matrix, the apparatus including a heated process vessel without pressure to melt a target metal-containing mixture at a minimum temperature in the presence of an appropriate flux material including a glass-forming silica to lower the melting temperature of the target metal-containing mixture, to form a homogeneous molten ionic matrix containing at least the target metal and an associated cooling assembly adapted to cool the molten ionic matrix.

According to a particularly preferred embodiment of invention, process raw materials, including said naturally occurring ore bodies containing at least one
target metal or metal compound, are combined with fluxing agents to promote melting to form a fluid 'glass' body. Said molten 'glass' is further heated and/or given sufficient residence time to substantially assimilate said target metal compounds and to degrade or destroy existing mineralogical bonds. Ionic and/or colloidal forms of the target metals will then effectively be in solution within said molten glass body. Further components within the novel 'glass' formulations will control the role of any one or more of metal or other ions introduced from the naturally occurring ore bodies. Such further components encourage specific metal ions to be available either as network extenders or network modifiers.

Typically the cooling process "locks" the form of the ionic matrix in which the target metal has been liberated from less desirable materials. By controlling such matrix positioning as part of the fluxing/fusing/residence process, specific target metal ions may be subsequently retrieved from the 'glass' or solidified body by downstream processes, including by solvent and/or electrolytic treatments. Other downstream processes may include ion exchange process steps.

The objective is to produce a homogeneous melt with the silica of the ore and the added flux, typically NaOH or Na₂CO₃, combining to produce a soluble water glass according to the equation:

\[ 2\text{NaOH} + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \] (or as shown in some literature, \( \text{Na}_2\text{O-SiO}_2 \))

This water glass is a most aggressive agent which completely dissolves the target-metal containing material in the furnace, converting the target metal when molten, to an amorphous soluble admixture or glass. The quenched product remains amorphous but importantly is hygroscopic. This material preferably quickly breaks down in a water quench to become a formless sludge

Typically the flux will be added to a process vessel and then heated to form a molten flux pool with the target metal-containing mixture gradually added to the molten flux pool.

Silica, boron, arsenic and phosphorous exemplify the primary characteristics of glass network formers. For example, with a silica-based network each oxygen atom is shared between two silicon atoms, and each silicon atom located between four oxygen atoms allowing the formation of complex three-dimensional networks. In this form the resultant glass (100% fused silica) is amorphous and structurally very strong.
Network modifiers such as metal ions may be introduced, as oxides, into a silica-based network. These metal ions typically occupy open spaces bounded by the silicon-oxygen three-dimensional network, as it does so the metal ion tends to remove/displace at least one of the silicon-oxygen bonds of the network. Furthermore the bond between metallic ion and the network oxygen atom is non-directional resulting in a weaker and less viscous structure.

The metal ions can be introduced into a glass batch material as salts, for example: sodium carbonate, calcium carbonate, calcium phosphate, magnesium carbonate, zinc carbonate, nickel oxide, potassium carbonate, alumina, and the like. These components may be sourced from naturally occurring compounds, for example; magnesium and calcium introduced as dolomite, potassium and aluminium as feldspar, and fluorine introduced along with sodium and aluminium as cryolite, and sodium as trona and nephelene syenite.

It should be made clear that according to the present invention, the aforesaid metal compounds, sourced from naturally occurring materials, ores and/ or concentrates, are fluxed and assimilated as ions into, what are basically, a range of temporary at least partially vitrified structures.

The composition of the ore will typically be dependant upon the target metal and/or the feed stock target metal-containing mixture and the composition of the flux material will be similarly dependent.

Particularly preferred fluxes are sodium carbonate and/or caustic soda.

The composition of the flux material may be or include, but not be limited to, naturally occurring compounds whose compositions range as follows as an example for nickel laterites:

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>0.4-3.0%</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.04-1.6%</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.5-6.00%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.4-48.0%</td>
</tr>
<tr>
<td>Silica</td>
<td>8.0-60.0%</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.01-1.5%</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.2-3.0%</td>
</tr>
<tr>
<td>Iron</td>
<td>8.0-55.0%</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.05-10.0%</td>
</tr>
</tbody>
</table>
Zinc 0.05-0.1%
Copper 0.05-0.1%

A further preferred composition for nickel laterite may be:
Nickel 0.6-4.0%
Aluminium 0.5-18%
Magnesium 0.4-38%
Silica 1.3-55%
Calcium 0.01-50%
Chromium 0.2%-3.0%
Iron 8.0-85%
Manganese 0.12-1.5%

Typically, the metals will be present in the composition in an oxide or silicate form, for example aluminium present as aluminium oxide/silicate, magnesium present as magnesium oxide/silicate, calcium present as calcium oxide/silicate, chromium present as chromium oxide/silicate, iron present as ferric or ferrous oxide/silicate and manganese present as manganese oxide/silicate. This is particularly the case when the ore is a laterite.

Table 1.
Further novel temporary 'glass' flux compositions can incorporate naturally occurring ores and ore concentrates. By way of example, Table 1 illustrates the mechanical and chemical concentration steps from example specific ore bodies. Metal content in ores/concentrates can occur within any extensive range to the above.

A further embodiment of the invention is the treatment of sulphide ores where the grain size of individual particles is so fine that particle liberation cannot be successfully achieved with conventional grinding practices without generating excessive amounts of non-target material which forms slime which inhibit selective flotation separation processes. Target metal losses to tails become high in such circumstances.

The present invention allows for a coarser grind to produce a rougher concentrate which, in that state, has limited market potential, however making an ideal feed for present process. Metal losses to tails in this process are significantly reduced.

By way of example, a large silver-lead-zinc deposit with a very fine grain size has grade, recovery and losses as shown below:

<table>
<thead>
<tr>
<th></th>
<th>Ore Grade</th>
<th>Recovery</th>
<th>Losses to Tails</th>
<th>% Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>41g</td>
<td>29g</td>
<td>12g</td>
<td>30%</td>
</tr>
<tr>
<td>Lead</td>
<td>4.1%</td>
<td>2.66%</td>
<td>1.44%</td>
<td>35%</td>
</tr>
<tr>
<td>Zinc</td>
<td>9.2%</td>
<td>6.9%</td>
<td>2.3%</td>
<td>25%</td>
</tr>
</tbody>
</table>
While the invention process is able to assimilate the majority of the ore components, said invention process is equally able to assimilate the components of ore concentrates.

The process of the present invention can be used to treat ores known as refractory ores. An example of such an ore an/or concentrate occurs with gold and/or silver ores where the noble metals are locked within crystal lattice structures or sulphides such as pyrite and arsenepyrite. When these noble metals are contained in such a manner, their extraction by conventional cyanide processes is limited. The process of the present invention allows the liberation of both gold and silver into the melt matrix in their ionic form, so presenting such metals in a form which is readily recoverable using downstream processes such as cyanide separation.

The invention process is equally able to assimilate metals and compounds from mine tailings and other waste/effluent type sources. It should be understood that the invention process is most appropriate in the extraction of metals from mined ore, however it may be noted that in many existing metal processing steps where it is difficult to separate individual metals from alloys or mixtures, said invention process will provide an effective separation means.

In existing processes like smelting and similar metal extraction techniques, said invention process may provide an intermediate step or indeed alternative extraction method. This is particularly true when considering high melting point metals such as platinum, palladium, rhodium, niobium, tantalum, tungsten and the like.

Ores such as tantalite, niobium, columbite, tin and mixtures of these metals in an ore may be introduced into said invention process to form a molten ionic mixture with a base composition in a range as follows:

- Manganese oxide 5-12%
- Iron oxide 5-15%
- Niobium oxide 50-80%
- Tantalum oxide 65-90%
- Tin oxide 50-80%

Another molten ionic composition for use with the invention process includes the following or similar base components:

- Copper 1.0%-4.0%
Yet another mixed sulphide concentrate with the following base composition has been treated by the process of the present invention.

<table>
<thead>
<tr>
<th></th>
<th>Concentrate 1</th>
<th>Concentrate 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au g/t</td>
<td>60</td>
<td>6.5</td>
</tr>
<tr>
<td>Ag ppm</td>
<td>783</td>
<td>148</td>
</tr>
<tr>
<td>Cu%</td>
<td>10.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Zn%</td>
<td>2.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe%</td>
<td>13.5</td>
<td>20.7</td>
</tr>
<tr>
<td>As%</td>
<td>3.4</td>
<td>0.4</td>
</tr>
<tr>
<td>S%</td>
<td>24.1</td>
<td>25.1</td>
</tr>
<tr>
<td>SiO₂%</td>
<td>30.0</td>
<td>40.0</td>
</tr>
</tbody>
</table>

With sufficient applied temperature and the presence of fluxing agents most metals and indeed gases (including water vapour, chlorine, fluorine, hydrogen and the like) can be incorporated within a molten ionic matrix rather than expelled within the exhaust gases.

The molten ionic compositions of the present invention are designed to selectively place network formers and network modifiers found in naturally occurring ores into relatively unstable positions within the molten ionic matrix. This is preferably achieved by a combination of temperature control and chemical reaction.

Chemical reactions are initiated by the inclusion of phosphorous, chlorine, fluorine, sulphur, calcium, sodium, vanadium, lithium, potassium, boron, barium, zinc, and arsenic, either individually or in combination.

Although it is easier to use and calculate the effects of such components from their oxides, the major molten ionic materials used according to the present invention have natural bulk sources, for example:

- Phosphorous Apatite
- Boron & sodium & water Kemite
Boron & calcium & water Colemanite
Soda Ash Trona
Arsenic Arsenopyrite
with fluorides and chlorides providing both free and dissolved gases, and sulphates both sulphur and gas.

One important feature of the present invention is the treatment of sulphide ores including those ores where arsenic is present. The process of the present invention is an immersion process. New feed additions or ores are immediately immersed into an existing melt. This process considerably limits the emissions of sulphur and arsenic in furnace exhaust gases. Further, the invention utilises the ability of arsenic, like silica and borax for example to act as a glass former. Hence the arsenic contributes the formation of the glass in the melt. Such a glass is rendered hygroscopic by including an extra 5 to 8% of sodium carbonate.

A further preferred flux forming matrix used according to the invention has a composition as follows for nickel laterites:

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>0.4-3.0%</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.04-1.6%</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.5-6.0%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.4-48.0%</td>
</tr>
<tr>
<td>Silica</td>
<td>8.0-60.0%</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.01-0.5%</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.2-3.0%</td>
</tr>
<tr>
<td>Iron</td>
<td>8.0-55.0%</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.05-10.0%</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.05-0.10%</td>
</tr>
<tr>
<td>Copper</td>
<td>0.05-0.1%</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.0-30.0%</td>
</tr>
<tr>
<td>Boron</td>
<td>0.0-40.0%</td>
</tr>
<tr>
<td>Sodium</td>
<td>15.0-70.0%</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.05-12.0%</td>
</tr>
<tr>
<td>Water</td>
<td>0.02-10.0%</td>
</tr>
</tbody>
</table>

Yet another embodiment of said flux forming composition includes but is not limited to the following components:
Phosphorous: 10.0-30.0%
Boron: 10.0-40.0%
Sodium: 15.0-30.0%
Chlorine: 0.05-12.0%
Lithium: 0.5-15.0%
Water: 0.02-3.5%

To this basic formula range can be added between 10% and 60% of most naturally occurring metal ores.

The process of the present invention is also suitable for treatment of high grade silver ore in which the silver is contained within rich silica, the latter up to 95% silica.

The inclusion of other aforementioned ionic matrix forming materials will consequently enable selective extraction of target metals. For example the inclusion of arsenic and/or lithium compounds will assist ion mobility and general network sharing capacity.

The product ionic melt formed according to the method of the present invention may be soluble in a range of solvents including water, acids, and alkali solutions such as ammonia and ammonia carbonate. Other solvents may be used including but not limited to fused salts, and gases including but not limited to, steam, chlorine, sulphur dioxide, and carbon monoxide.

The melt product of the present invention will typically be hygroscopic due in large part to the composition of the flux material chosen. One of the by-products of the process of the present invention is silica gel which may be used or on-sold. The silica gel is typically formed when the carbon dioxide of the exhaust gases is passed through a solution containing sodium silicate.

According to preferred embodiments of the present invention, one or more "flux" material is included in order to achieve more or less complete melting of any "glass" which may form in the furnace and/or the target metal containing material at a lower temperature that would otherwise be needed in the absence of the flux material. For example, for common glasses such as soda-lime-silica, sodium and calcium are the fluxing agents for the silica component which itself would otherwise require a melting temperature of 1,700°C. The fluxing effect of calcium and sodium reduces that temperature by over 800°C.
Typically, the flux/target metal containing material ratio is between approximately 1:0.5 at the lower end and 1:3 at the upper end with an optimum ratio for nickel laterite in particular being approximately 1:1.

It is further preferred that when nickel laterites are to be treated, up to approximately 10% sulphur may be added to the melt as elemental sulphur or in a sulphide such as iron pyrite.

**FLUXES**

As mentioned briefly above, the purpose of the flux is preferably to reduce the melting point of the target material. The melting point of laterites can for example, be reduced from approximately 1800°C to under 950°C.

The flux can also act as high temperature solvents. Again, with laterites in a melt, they dissolve silica and silicates containing the nickel and cobalt, also the oxides and silicates of Fe, Al, Mg, Mn, and Ca.

Other examples of particular fluxes which may be used include soda ash, soft cake, potassium hydrate, ammonium nitrate, Borax or similar compounds. Typically, flux compounds are provided as low melting point temperature molten solid-phase compounds.

Using Na$_2$O based fluxes as Na$_2$CO$_3$ or NaOH, the presence of silica or silicates preferably provides the glass former.

It is preferred that the glass product created is soluble in water. This is typically provided by the glass former materials, Na$_2$O and SiO$_2$ combination forming Na$_2$SiO$_3$ (water glass), which is the aggressive destroyer of laterites and itself is soluble in water.

The preferred fluxes for treatment of nickel laterite are NaOH and Na$_2$CO$_3$. This choice is based on:

- NaOH can be manufactured on site
- NaOH changes to Na$_2$CO$_3$ in the presence of CO$_2$
- Both supply the Na$_2$O required to produce the water soluble water glass, fundamental to the disintegration of almost all rocks, including laterites.

NaOH has:

- The ability to be made onsite by electrolysis of common salt, NaCl, as found as rich, hypersaline brine ground water beneath the WA laterites, which may also provide a source of NaCl.
• Ability to be regenerated on site, with the presence of CO₂ converting the NaOH to Na₂CO₃ according to the equation:

\[ 2NaOH + CO₂ → Na₂CO₃ + H₂O \]

The chemical reaction for the conversion of a laterite to a diffused salt commences with, for example:

\[ Na₂CO₃ → Na₂O + CO₂, \]  
\[ 2NaOH → Na₂O + H₂O \]

The Na₂CO₃ and NaOH fluxes generate Na₂SiO₃ (water glass), according to the equations:

\[ Na₂CO₃ + SiO₂ → Na₂SiO₃ + CO₂, \]  
\[ 2NaOH + SiO₂ → Na₂SiO₃ + H₂O \]

Though Na₂CO₃ (or NaOH) alone do not dissolve Fe₂O₃ or MgO, however in combination with SiO₂ (to form Na₂SiO₃) these iron and magnesium compounds are readily dissolved in the melt.

The two main iron oxides (FeO and Fe₂O₃) are soluble in Na₂SiO₃. Most FeO will be oxidized in the furnace to Fe₂O₃.

The reaction of the breaking of the strong silica and silicate bonds, Si - O - Si is:

\[ Si - O - Si + Na₂O → 2Si - O^+ + 2Na^+. \]

It should be noted that the Si - O - Si reaction shows the breaking of only one Si- Si bond when every Si has a total of four bonds. However, in the present invention, because of the excess of soda, more bonds will typically be broken.

The Na₂SiO₃, itself soluble in water, attacks and renders soluble everything, including all the key components of laterites. These include both the oxides and silicates of Fe, Al, Mg, Mn and Ca. Aluminium silicate is of course the major component of clay minerals, which in turn contains nickel in some of the laterite deposits. Many laterite deposits contain both nickel and cobalt predominantly in clays (aluminum silicates) as well as in the iron oxides of limonite and goethite. One of the major and higher grade sources of nickel is saprolite and serpentine/garnetite ores. These ores are not processed by the HPAL system because they are rich in magnesium and magnesium consumes excess amounts of the sulphuric acid added to the autoclave. These ores can be processed by the method of the present invention.
Na$_2$CO$_3$ and NaOH in combination with SiO2 not only create fast dissolution of the rock material in any raw ore used but also increases solubility of the fused salt in water. The Na20 is typically highly mobile in the melt.

The melt if homogeneous, is a sound indication both the Ni and Co have been released and are in their ionic form.

If the nickel is not contained within the silica, say within an oxide, then an acidic oxide such as SiO$_2$, (OrB$_2$O$_3$, or P$_2$Os) may be required. However, the water glass melt will typically dissolve the nickel and cobalt contained in non-silicate forms and converts these elements in the melt to ions, which make them far more accessible for downstream processing.

It is important to obtain the correct balance of target-metal containing mixture and flux to ensure the combination provides a homogeneous and low viscosity melt and produces a pour which is hygroscopic.

Fluxes are one of the most important elements to the method of the present invention, including considerations such as:

- The optimum flux for the target metal containing material.
- The optimum target metal containing material/flux ratio
- The flux recovery/regeneration/recycle processes.

When using Na$_2$CO$_3$ or NaOH as the flux, a large part of the vitrified structure or melt does not dissolve in water, just disintegrates as SiO$_2$, Fe$_2$O$_3$, MnO, CaO and Al$_2$O$_3$, and/or hydroxides or carbonates of these elements, the latter to form a formless sludge. In a very basic environment, very small amounts of the SiO$_2$ and Al$_2$O$_3$ may dissolve.

The high temperature solvents for the ore should also be soluble in water, as are Na$_2$CO$_3$, NaOH and Na$_2$SiO$_3$.

The introduction of carbon monoxide, or sulphur into the furnace would reduce the nickel and cobalt to metals. However, CO is dangerous and should not be considered.

Cr$_2$O$_3$ does not dissolve easily in Na$_2$SiO$_3$. This can be improved by increasing the Na$_2$CO$_3$, or SiO$_2$.

The substitution of NaOH for Na$_2$CO$_3$ can be viewed when examining the molar weights. For example: Na$_2$CO$_3$ has a molar wt of 106g/mol and NaOH of 40g/mol. Therefore the molar equivalent of NaOH to Na$_2$CO$_3$ = 40 X 2 = 80 to
106g/mol. This means less NaOH is required than Na$_2$CO$_3$ in the ratio of 80 to 106 or 1 to 1.33.

NaCl has little value in dissolving silica. Also, it will not dissolve Fe$_2$O$_3$.

Borax as a flux material dissolves most components and reduces viscosity and increases the solubility of the glass. It also promotes a homogeneous pour. Even though borax appears to be cost prohibitive when compared with Na$_2$CO$_3$ or NaOH, it is possible to partially recover borax by evaporation.

For the higher magnesium ores such as serpentine/garnerite (MgO 25 - 38%), a little more silica and Na$_2$CO$_3$ or NaOH will be required to dissolve the magnesium.

The use of natural trona compared to the artificial Na$_2$CO$_3$ should have little influence in changing the glass chemistry and therefore on the process of the present invention. Trona, if readily available must be considered.

Dolomite does not make a good glass and importantly, it cannot dissolve silicates.

**Preferred Flux Regime for Nickel Laterite**

A laterite, LH2, sourced from Western Australia is treated as follows:

<table>
<thead>
<tr>
<th>LH2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Laterite</td>
<td>130g</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>130g or 1 to 1</td>
</tr>
</tbody>
</table>

The Na$_2$CO$_3$ is added initially as 100g to form the initial melt pool. To this melt, 3 separate lots of LH2 are added, together with 10g Na$_2$CO$_3$ with each LH2 addition.

A 50%mol/50%mol ratio of CaCl$_2$/NaCl may be more effective for a nickel laterite target metal containing material and may be effective at reducing the furnace operating temperature to 650°C-850°C. Other components that may be used in this flux include CaCl$_2$ or Na$_2$CO$_3$ to replace the CaCl$_2$.

**FURNACE**

The furnace of the present invention needs only to melt, dissolve then discharge. Therefore the comparative energy costs and resident times are much lower for the furnace of the invention. This equates to furnace production being much higher and unit costs much lower for the present invention when compared to an equivalent sized glass furnace.
Furnace operating temperatures are expected to range from 980-1000°C. This temperature will be dependent on the combinations of ore types, flux addition and particle size of the feed.

The furnace will preferably have similar refractory liners, waste-heat regeneration, exhaust, feed and heat supply systems and automated controls as for a production glass furnace. A heat regeneration/capture system may be provided.

The furnace will typically include one or more electrodes. The electrodes may be AC to boost the melt and stirring process or DC which may assist in metal recovery and/or the destruction of mineralogical bonds in the melt. The electrodes may be static or movable to provide either static or moving heat zones in the melt.

The electrodes may require additional protection from the aggressive environment in which they are used, said protection typically in the form of a layer of porous but toughened ceramic material.

At least some of the electrodes may be provided with AC power in order to supply bursts of heat to the melt if required.

The presence of CO2 in the exhaust gases of the furnace or the heating process for the furnace may be important as this gas can then be used as a part of the flux regeneration process.

QUenching

In a preferred embodiment, once metal fluxing and ion assimilation has taken place, said specific metal ions may be extracted from the glass body by quenching the molten 'glass' in neutral pH aqueous solutions or in aqueous solutions containing acids or alkalis. The resultant liquor is preferably an electrolyte; consequently direct electrowinning techniques may be applied during quenching or soon thereafter.

One particularly preferred quench fluid is brine or salt water.

As an alternative to quenching the melt, the melt exiting the furnace may be "sheet formed" to produce a thin layer of the melt. This can be accomplished in a number of ways including pouring the melt onto a tray and allowing/forcing the melt layer to cool rapidly with air cooling and/or water sprays. Typically, any water sprays will be directed so as not to wet the pour. The water sprays will therefore preferably be from beneath the melt or indirect.
Such unquenched material to be passed through a crusher, such as a rolls crusher. A solvent such as water is added and the mix vigorously agitated for up to fifteen minutes to convert the crushed particles to a formless sludge.

Post quench treatment may comprise sequential pH adjustment with or without inclusive electrowinning mechanisms.

A preferred quenching option utilises a fused salt bath containing molten sodium chloride and/or potassium or sodium nitrate; said bath may or may not incorporate electrolysing electrodes.

Another preferred quench procedure incorporates a molten metal bath containing appropriate metals either independently or in combination with other metals or salts; said bath may or may not incorporate stirring means, preferably in the form of moveable paddles.

Once the molten material enters the quench bath, immediate chemical changes occur. A large part of the glass will not dissolve in water but just precipitate as SiO₂, Fe₂O₃, MnO, CaO, MgO and Al₂O₃ or as carbonates or hydroxides of these metals. It is important that all the glass should be hygroscopic and disintegrate. Because of the strong basic condition of the melt, many of the components of the melt are precipitated to their oxides, hydroxides or carbonates. The changes include nickel and cobalt. This is because nickel and cobalt ions can not exist in water and immediately precipitates to Ni(OH)₂ and Co(OH)₂ respectively. Basic oxides, carbonates or even silicates might form. The key is that nickel and cobalt compounds are finely dispersed in the sludge. A likely equation is as follows:

\[ \text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 \]

Therefore, the majority of the nickel and cobalt will be found in the sludge and not the liquid. Similarly, the Fe, Mn, Ca, Mg and Al all precipitate to oxides or hydroxides. This means the quenched material will divide into a sludge and solution. The soluble compounds include unused flux and Na₂SiO₃ will be in the solution. The sludge should be of a formless nature.

Importantly, the nickel and cobalt in the sludge would be in a fine and more reactive form than when in the laterite and therefore far more accessible to downstream processing, including by solvents. An example of a reaction is:

\[ \text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 \]

The Ni²⁺ is released by the Na₂SiO₃, and the OH⁻ is derived from the
basic Na$_2$SiO$_3$ solution.

The volume of the quench solution should be in the order of 1 to 1 to the product mixture exiting the furnace and may require replacement or replenishment.

On some occasions, the quench water may be laced with salt. There are no obvious signs of this salt having any influence on the solubility of the pour. However, the salt will typically influence the recovery/regeneration of the Na$_2$CO$_3$.

A water quench dissolves only the soluble compounds. The Na compounds dissolved may later be recovered by evaporation. If NaCl is also present, this should be separated first, possibly by fractionation crystallization or by chemical separation.

With the laterites, after an apparent successful run, the quenched product is coloured a dark olive green. However, with exposure to the atmosphere, or water, the colour, and appearance, quickly changes to become a dark sticky toffee. This is a feature of the hygroscopic nature of the flux-laden poured material. This hygroscopic form is a preferred requirement.

A preferred pour, which should flow like medium to runny honey, will typically at best, make a slight sizzle when hitting the water. Again, the latter is a desirable feature as it indicates the stream of the poured material into the quench is thin, and quenching therefore is likely to be immediate and fully effective.

The solids of the quenched product, when mixed with water, may be allowed to sit for only a relatively short period before pressure or vacuum filtration. To reduce contact with CO2, the washing and filtration processes will preferably be conducted in enclosed vessels. The solids before washing and filtration are preferably crushed to reduce particle size to <3mm. When wash water is added, agitation preferably takes place to form both a sludge and solution. Ideally, the process will be continuous so that filtering takes place in a matter of hours from the time of the pour as this will typically decrease the amount of silica gel present in the mixed and quenched product.

 Preferably, the furnace temperature and residence time and pour conditions are such that the powder product is produced.

 Forced drying of the sludge may make the nickel and cobalt compounds less reactive and therefore should be avoided.
When attempting to wash the poured product, difficulties may be encountered due to the formation of insoluble silica gel (SiO$_2$). This gel binds all of the contents together so that physical separation by filtration is not possible. When washing the poured product, the wash solution will typically be maintained at a pH of approximately 12 or above, preferably through the addition of NaOH or similar basic solution. To overcome an ageing process where colloidal silica will form, even at this elevated pH, the wash solution will ideally be filtered within approximately 45 minutes of the commencement of washing. Filtration may be assisted either through pressure of vacuum. The NaOH will typically be recovered at a later stage in the flux regeneration process.

The formation of the silica gel is from the dissolution of the Na$_2$SiO$_3$ in water as:

$$\text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \rightarrow 2\text{Na}^+ + \text{SiO}_3^{2-}.$$ 

The silica gel becomes part of the sludge. This continues to react further to SiO$_2^{-}$ but still is in a very finely dispersed reactive form.

The presence of silica gel and sodium silicate are both strongly indicative of the break-down of the silica/silicate compounds within the laterite, and through this, the release of the nickel and cobalt.

As silica gel is very reactive, it may bind some nickel very loosely, if at all.

Quenching in a reaction vessel, with NH$_4$OH as the quench bath may be preferred. This should lead to immediate nickel and cobalt extraction, assisted by the elevated temperatures within the vessel. The reaction vessel should assist in the recovery of the ammonia for reuse.

Chemically, the silica gel should not influence the extraction of the nickel from the sludge, whilst physically, it typically does.

Warm brine is very aggressive against ordinary steel and aluminum. If metals are considered as transfer pipes or vessels, some types of stainless steel, would be required to replace the above metals. Plastics would be another alternative.

The NaCl of the brine will typically reduce the stability of silica gel.

The presence of silica gel should not influence the extraction of the nickel from the sludge. If NaOH is used as the quench this should keep the silica gel in solution.
Nickel and cobalt may appear in trace amounts in the quench bath. This possibility needs to be monitored to ensure any limits are not exceeded. However, this is a positive sign as it demonstrates these elements are in the sludge in a reactive form, with even water dissolving them slightly.

If nickel and cobalt are in the flux, this does not constitute a potential loss as the dried flux is returned as furnace feed.

The nickel and cobalt may form another compound in the quench, combining with say Fe, Al, Mg, or SiO₂.

It has been noted that when NH₄OH has been added to a sludge containing silica gel, the separation of liquids from solids was not a problem. However, when replacing the NH₄OH with H₂SO₄, the total beaker contents became a jelly.

The dried, washed sludge will have a higher nickel content than the dried, unwashed pour. This is simply because the Na₂SiO₃ and Na₂CO₃, both soluble, would have been removed from the sludge.

As the separation of the silica gel from the sludge may prove difficult, a physical means of separation such as a centrifuge or a porous membrane, or a chemical process, such as a flocculent may be used.

The target metal to flux ratio largely depends on the ability for the pour to disintegrate afterwards in the water quench to form sludge.

The separation of the sludge from the silica gel may be desirable to capture the target metals and also for the recovery of the silica gel as a by-product.

Small quantities of SiO₂ and Al₂O₃ as found in the sludge may also dissolve if the solution is sufficiently basic.

If cost effective acetic acid (CH₃COOH) is available as a quench, further options would be provided.

Where a laterite is deficient in SiO₂, Na₂SiO₃ from the quench may be added to the front of the furnace.

Time between pour and the downstream processing of the quenched pour may be a significant factor. This is because time may allow changes in the chemical composition of the quenched product which in turn may be deleterious to downstream processing.

The change of colour of the quenched solution from say a canary
yellow to dark brown indicates dissolution of the iron, and if this is the case also the
dissolution of nickel and cobalt is likely.

In order to produce finer particles rather than lumps within the cooled
pour, it is important to have low viscosity and a thin laminar flow of the pour.

Acetic acid dissolves most metal oxides, including those of nickel and
cobalt in laterites. SiO₂ is the exception. Acetic acid reacts with Na₂CO₃ driving out
CO₂. When reacting with Na₂SiO₃, acetic acid produces silica gel. Using acetic acid
may not be desirable in preference to a solvent that releases the target metal only,
such as provided by NH₄OH

Acetic acid should dissolve even more of the quenched laterite than
H₂SO₄

Ultrasound may greatly facilitate the disintegration process of glass in
water. Energy costs could be a deterrent.

Phase separation, should it occur after the pour enters the quench
would not be a problem providing all the pour disintegrates into sludge.

The presence of some nickel and cobalt in the quenched water could
indicate one of two things as, a) there are fine nickel and cobalt particles that have not
been filtered out, or b) nickel and cobalt are so reactive that even water can dissolve a
little of them.

When quenching the melt it is best to have low viscosity and higher
temperature of the pour immediately before quenching or air cooling.

The Na₂O in the melt and the NaOH in the quench solution both have
the same effect. They tend to convert SiO₂ to water soluble Na₂SiO₃ according to the
equations:

\[
\text{SiO}_2 + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 \\
\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}
\]

The difficulty may be that the above reactions are reversible. It is
possible the SiO₂ has a stronger affinity towards another compound such as Ni(OH)₂.
If the SiO₂ prefers to bond Ni instead of Na, we need to add sufficient Na is added to
set the SiO₂ free.

The addition of Na₂CO₃ or NaOH to the quench bath could assist in
releasing the Ni and Co from the sludge. The addition of extra Na₂CO₃ to the melt
may also assist.
NaOH if used in the quench bath should keep the silica gel in solution. Unfortunately, the one experiment conducted using the NaOH as the quench solution resulted in quite violent explosions as the pour hit the quench.

The sludge should not contain much Na. If it does it means either the washing and/or filtering are incomplete or the soluble glass is far from soluble.

The colour of the sludge is no definite indication that something is released. There should be very little release in water except soda and water glass. Cobalt hydroxide is orange to pink but when in combination with silica it is blue. If nickel is the dominant element in a nickel/cobalt mix, the blue colour will predominate. Nickel hydroxide is green and this colour is maintained in combination with silica. However, with NH₄OH, nickel becomes ultra marine blue.

From the quench bath, it is also possible to recover:

- Na₂CO₃ (surplus) Solution
- Na₂SiO₃ Solution
- NaOH (if this is the flux) Solution
- SiO₂ (silica gel) Solid

Quenching in atmospheric conditions is a preferred option. However, quenching at elevated or decreased pressures may be used. Oxidizing or reducing agents may also be used.

One preferred aspect of the invention method and device incorporates a moving-heat-zone means in both the primary vitrification furnace and high temperature quench bath. Said moving-heat-zone utilises conductive ceramic, e.g., silicon carbide, or graphite electrodes. A preferred moving-heat-zone electrode may utilise AC or DC currents. Where it is appropriate to use AC currents as a heating source, electrode materials may consist of carbon, molybdenum, conductive ceramic, tungsten, platinum, niobium, tantalum and the like can be used or alloyed as a combination or with other suitable materials.

A direct current will normally be used to electrowin the melt but either an alternative or direct current may be used to break or disrupt bonds in the melt.

However, a moving-heat-zone electrode assembly manufactured from a silicon carbide material is a preferred invention device. Said assembly may comprise solid structures or a mesh whereby as the assembly is traversed and/or rotated through the molten media, the majority of particles will pass through. Larger particles will of
course be held in contact with the electrode mesh structure enabling high-localized heating to encourage assimilation of said large particles into the molten bulk media.

The heat zone(s) may alternatively be provided as static heat zones.

**METAL RECOVERY**

The preferred rapid quench of a homogeneous and low viscosity melt into a quench bath preserves the ionic conditions of the target metal formed in the furnace. Rapid air cooling is also an effective means of producing an amorphous pour.

In a water quench bath the nickel and cobalt ions are immediately precipitated as hydroxides or carbonates.

As well as the nickel and cobalt precipitating out, so too do other elements and compounds in the laterite, namely the oxides of: Al, Mg, Fe, Mn, Ca, and SiO₂, all combining to form a formless sludge.

In this sludge the nickel and cobalt are in a finely divided form and are more readily accessible for downstream processing.

The form of the target metal in the sludge can be any one or more of: hydroxide, oxide, carbonate, silicate, or perhaps occurring as a chemical compound with another element, such as Fe. The form of the target metal is an important step in the process of deciding the path of recovery.

Once this form has been determined, the downstream steps in isolating and recovering the target metal can then be taken.

There are a number of options available. These include the use of ammonia or ammonia carbonates, H₂SO₄ or other specialized solvents. Ammonia, as NH₄OH, has advantages as it can be recycled.

The possibility of using ion exchanges to capture the nickel and cobalt once in ionic form needs to be considered with Na⁺ as a possible exchange ion. The clinoptilolite from natural zeolite may be used.

There may be electrowinning of the melt in the furnace as well as possibly in the quench bath. Electrowinning the melt will preferably take place by providing electrodes in the main production furnace which may be truncated towards the discharge end of the furnace to supply extra electrode space, or by discharging the formed melt into at least one secondary furnace specifically equipped and designed with electrodes for electrowinning the product melt. Any secondary furnaces may be provided in parallel to provide the flexibility of having an operating secondary
furnace and an inoperative secondary furnace to allow for the replacement of the electrodes whilst maintaining output.

The preferred method for electrowinning in the melt is to switch the electrodes provided in the furnace to provide additional heat in the melt, to DC current. As well as target metal recovery, this will typically break any of the remaining strong mineralogical bonds of the ore. This will materially assist with the capture of unrecovered target metals in conventional downstream processes.

In an alternative embodiment, of the target metal may be recovered using a forced precipitation mechanism. For example, addition of iron/steel to the melt will typically cause or force precipitation of the nickel and cobalt contained in a nickel laterite melt, into a relatively pure although molten metal form. Using iron/steel will typically precipitate the nickel and cobalt from a nickel laterite melt in preference to any other metals contained in the melt.

Normally, the molten metal nickel and cobalt precipitating out will settle to the base of the melt pool on the basis of density where these target metals may be drawn off separately from other waste or less desired metal components of the melt.

Without wishing to be limited by theory, iron, nickel and cobalt have similar atomic weights. Therefore, the quantity of iron/steel added to the melt in order to force precipitation of the nickel and cobalt will normally be at a rate substantially equivalent to the combined percentage content of nickel and cobalt in the ore. The approximation of the percentage content of nickel and cobalt in the ore can be obtained by sample in the feedstock. In principle, the same addition protocol can be used for other target metals based on the addition of a precipitate forming material of a substantially similar molecular weight.

For example, if the nickel and cobalt content in the ore are approximately 1.6 and 0.07 weight percent respectively, then the amount of iron/steel to be added is approximately equivalent to 1.67 weight percent. A redundancy margin in order to ensure as much as possible that the precipitate forming material contact the target metal may be built in of approximately 5% of the precipitate forming material, above the approximate weight percent of the target metals.

It is further preferred that the precipitate forming material is added in particulate form in order to increase the surface area per unit volume of the precipitate
forming material. Increased mobility of the precipitate forming material through the melt may be achieved through agitation and/or stirring of the melt after the addition of precipitate forming material thereto.

**FLUX REGENERATION**

With the very high levels of flux which will likely be required for the successful melting of target metal containing ores, it is important to the present invention, that the fluxes can be generated and/or regenerated on site.

As an example, there are two preferred flux options for nickel laterite and sulphide ores. These are Na$_2$CO$_3$ and NaOH, both suppliers of the required Na$_2$O to the melt and through its combining with the essential silica, forms the soluble Na$_2$SiO$_3$.

**Sodium Carbonate** (Na$_2$CO$_3$)

There are two well known artificial manufacturing processes, named after the inventors. These are the Solvay and Hue processes. Both processes use salt to produce Na$_2$CO$_3$.

The basic process is:

\[ \text{NaCl} + \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl} \]

The NaHCO$_3$ precipitated from this reaction is dried to produce:

\[ 2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2. \]

The NH$_4$Cl is sold as a fertilizer.

Note: Additional to NaCl necessary for the manufacture of both Na$_2$CO$_3$ and NaOH, Na$_2$CO$_3$ also requires CO$_2$ and NH$_3$. The burning of limestone is necessary to produce CO$_2$. The manufacture of NH$_3$ requires a complex plant to separately supply each of the nitrogen and hydrogen. An extensive industrial chemical process facility is therefore necessary to produce Na$_2$CO$_3$. An advantage is that the NH3 is recovered.

**On-Site regeneration**

The key ingredients for the on-site manufacture of Na$_2$CO$_3$ are CO$_2$ and sodium, the latter produced from Na$_2$SiO$_3$, a by-product of the process of the present invention when used to treat nickel laterite and/or sulphide ores/concentrates.

One source of the CO$_2$ is from the exhaust gases from the production furnace. Where necessary, additional CO$_2$ may be required from other on-site industrial exhaust systems.
The energy sources of the production furnace can be varied. These will typically include fuel oil, powdered coal, natural gas and a diesel/sump oil mix. With methane as an example:

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]

The \( \text{CO}_2 \) used in regeneration does not have to be pure. Traces of \( \text{O}_2, \text{N}_2, \text{NO} \) and \( \text{SO}_2 \) do not have to be removed. This simply means the exhaust gas can be captured and applied. There will also be large quantities of nitrogen, resulting from the use of air in combustion.

Bubbling \( \text{CO}_2 \) through the quench solution and sludge therefore preferably accomplishes two things, a) precipitates the silica gel and b) regenerates the \( \text{Na}_2\text{SiO}_3 \) to \( \text{Na}_2\text{CO}_3 \).

**Basic Steps**

1. Collect the exhaust gases, and specifically the \( \text{CO}_2 \) component
2. The sludge wash-water will contain \( \text{Na}_2\text{SiO}_3 \), plus any remaining \( \text{Na}_2\text{CO}_3 \), both soluble in water.
3. Pass the \( \text{CO}_2 \) through this solution, to produce \( \text{Na}_2\text{CO}_3 \) according to the equation:

\[ \text{Na}_2\text{SiO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{SiO}_2 \]

The insoluble \( \text{SiO}_2 \) precipitates as silica gel. This should be collected and stored.

4. Evaporate off the water to recover the \( \text{Na}_2\text{CO}_3 \).

5. In the presence of any \( \text{CO}_2 \), including atmospheric furnace combustion, the \( \text{NaOH} \) is converted to \( \text{Na}_2\text{CO}_3 \) as:

\[ 2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \]

Accordingly in practical terms the \( \text{NaOH} \) cannot be recycled. This factor has no impact on the nature of the flux as it is the \( \text{Na}_2\text{O} \) that is required.

**Sodium Hydroxide \( (\text{NaOH}) \)**

Manufactured by the electrolysis of brine (\( \text{NaCl} \)). This is known as the "chloralkali" process.

The electrolysis formula are:

\[ \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \text{ (dissolution in water)} \]
\[ \text{Na}^+ + \text{e}^- \text{ (reaction on the cathode)} \]
\[ 2\text{Cl} + 2\text{e} \rightarrow \text{Cl} \text{ (reaction on the anode)} \]
\[ 2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2 \]
In the presence of any CO₂, including atmospheric CO₂, the NaOH is converted to Na₂CO₃ as:

$$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$

Accordingly NaOH cannot be recycled as noted above.

To recover the Na₂CO₃/NaOH, first precipitate the silica gel. (This precipitation is a common industrial procedure). After precipitation of the silica gel, the solution and gel are separated by such processes as a centrifuge or decantation. The Na₂CO₃ remains in solution, the later recovered by evaporation.

Production of NaOH on site normally uses brine or saltwater. One by-product of this process is chlorine gas which may find an integrated use in the process of the present invention through conversion to HCl to leach Ni and Co from the quench sludge, when treating laterites.

A most preferred process of the present invention normally comprises the following steps:

1. Formulation and preparation of an appropriate temporary' glass' composition.
2. Introduce composition into a glass melting type furnace.
3. Apply fluxing and fusing temperature (950°C-1150°C) using gas, fuel oil, electricity, or other available energy source via appropriate burners and/or electrodes.
4. Once the bulk 'glass' is molten, apply current to said moving-heat-zone assembly and traverse it through the molten section of the furnace contents so that extra localised heat is applied (approx. 1250°C). This could be performed at least twice to achieve optimum feed material assimilation.
5. Once assimilation is complete the furnace exit gate is opened to allow a controlled flow of said molten temporary' glass' into the quenching tank, or rapid air cool.
6. In some instances said quench tank may contain a concentrated brine solution and/or sodium hydroxide, or a mild acid solution for example HCl. It may be necessary depending on metal extraction selectivity to use a fused salt such as potassium nitrate as a quenching medium. On other occasions it may be useful to quench with a molten metal for example tin or lead.
7. Generally the result of said quenching cause the precipitation of the majority of melt components out of the melt. The quench solution may additionally be
an electrolyte in which electrowinning techniques can immediately or subsequently be applied. Electrolyte thus generated can be conveniently pumped to extra electrowinning tanks, or for storage and additional physical and chemical treatments.

8. Further chemical and heat treatments can be applied to the electrolyte to assist the sequential removal of mineral or metallic constituents.

9. Many of the residual constituents of the original "glass" composition can either be directly recycled into the process and/or utilized as non-toxic aggregate materials for agricultural and building applications including pozzolanic substances including silica.

The process of the present invention is designed to allow balanced output-input-replenish schedules; fusing chamber and quench tank capacities are therefore increased accordingly.

It is preferred that the apparatus and method of the present invention are used to treat platinum group elements (PGE), refractory gold, base metal concentrates and high silicon silver amongst other metals and ores. The invention provides the capability of treating the full and extensive range of nickel laterite ore types, PGE's and refractory gold, a situation not possible with any one existing treatment and recovery process.

The present process also gives the ability to separate many rare earth metals both from each other and from the accompanying ore matrix. Rare earths that may be separated using the present invention include lanthanum, cerium, praseodymium. Neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, yttrium, and scandium. The process may also be used on environmentally dangerous metals such as cadmium and mercury. Further, the separation of magnesium from the mineral magnesite has been proven.

Typically, the process for the separation of rare earth metals will include mixing of the rare earth-containing ore with a flux such as borax, sodium carbonate or caustic soda with approximately 35% silica to form a "glass" at a furnace temperature of between approximately 1050°C to 1350°C.

There are three separate likely metal recovery methods with the present invention. These include:
from the cathode;
2 from the solution, and
3 from the sludge (there are current methods of heap-leaching nickel laterite ores. Because of the tight mineralogical bonds these heap-leaching methods so far, are proving to be inefficient and bordering on being uneconomical, even at high metal prices. However, with the furnace treatment of the present invention alone, and specifically if electrowinning in the melt is included, the target metals become far simpler to capture and recover.

Addition of iron to the melt preferably precipitates nickel and cobalt.

Where used in this specification, the term "glass" is not used to convey a crystalline structure but rather an ionic melt structure which when cooled is hygroscopic and typically amorphous. It may be partially vitrified when cooled but typically when an appropriate flux material is used, will typically retain a non-solid and non-crystalline structure.

**Brief Description of the Drawings.**

Various embodiments of the invention will be described with reference to the following drawings, in which:

Figure 1 is a sectional side view of a process apparatus according to a preferred embodiment of the present invention.

Figure 2 is a sectional plan view of the process apparatus illustrated in Figure 1.

Figure 3 is a sectional side view of a process apparatus according to a second preferred embodiment of the present invention.

Figure 4 is a sectional plan view of the process apparatus illustrated in Figure 3.

Figure 5 is a sectional side view of a process apparatus according to a third preferred embodiment of the present invention.

Figure 6 is a sectional plan view of the process apparatus illustrated in Figure 5.

Figure 7 is the front page of a result sheet from a trial of a preferred embodiment of the method of the present invention.

Figure 8 is the reverse of the result sheet illustrating Figure 7.
Figure 9 is the front page of a result sheet from a trial of a preferred embodiment of the method of the present invention.

Figure 10 is the reverse of the result sheet illustrating Figure 9.

Figure 11 is the front page of a result sheet from a trial of a preferred embodiment of the method of the present invention.

Figure 12 is the reverse of the result sheet illustrating Figure 11.

Figure 13 is the front page of a result sheet from a trial of a preferred embodiment of the method of the present invention.

Figure 14 is the reverse of the result sheet illustrating Figure 13.

Figure 15 is the front page of a result sheet from a trial of a preferred embodiment of the method of the present invention.

Figure 16 is the reverse of the result sheet illustrating Figure 15.

**Detailed Description of the Preferred Embodiment.**

According to a particularly preferred embodiment, a method and device for the removal of metals from their naturally occurring ores and mineral concentrates using vitrification processes are provided.

The only ores considered in this discussion of the operation of a preferred embodiment, are nickel/cobalt laterites even though the process can similarly be used to treat sulphide ores/concentrates including refractory gold and refractory gold with arsenopyrite present.

Testing has been performed to date with three laterites, two from India and one from Western Australia. Initial focus has been on laterites from Western Australia.

Two separate samples, LH and LH2 respectively have been used. A typical component analysis of LH2 is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.73</td>
</tr>
<tr>
<td>CoO</td>
<td>0.074</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.10</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.93</td>
</tr>
<tr>
<td>CaO</td>
<td>0.04</td>
</tr>
<tr>
<td>MgO</td>
<td>3.15</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>14.31</td>
</tr>
<tr>
<td>SiO2</td>
<td>50.69</td>
</tr>
<tr>
<td>LOI %</td>
<td>19.2</td>
</tr>
</tbody>
</table>

The composition of the glass forming substrate used in the illustrative embodiment for the nickel laterite processed is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>0.4-3.0%</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.04-1.6%</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.5-6.00%</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.4-48.0%</td>
</tr>
</tbody>
</table>
The process to which the nickel laterite is subjected is as follows:

1. Preparation of the appropriate temporary glass' composition as above.
2. Introduce the composition into a glass melting type furnace.
3. Apply fluxing and fusing temperature (950°C-1 150°C) using gas, fuel oil, electricity, or other available energy source via appropriate burners and/or electrodes.
4. Once the bulk material is molten, apply current to said moving-heat-zone assembly and traverse it through the molten section of the furnace contents so that extra localised heat is applied (approx. 1,250°C). This could be performed at least twice to achieve optimum feed material assimilation.
5. Once assimilation is complete the furnace exit gate is opened to allow a controlled flow of said molten temporary glass' into the quenching tank or rapid air cooling.
6. In this illustrative embodiment, the quench tank contains a brine solution.
7. The result of said quenching cause the precipitation of the majority of melt components out of the melt.

Three alternative forms of a production apparatus used in the above process, are illustrated in Figures 1 to 6.

Figure 1 shows both a cross section and plan view of a first preferred embodiment of a 'glass' fusing chamber or furnace A and quenching tank B. In Figures 1 to 6, the following components of the system are present:

- molten 'glass'.
- electrode assembly creating a moving-heat-zone or high temperature zone
- raw material entry point
- inner glass exit plug
outer glass exit plug
electrowinning assembly
electrowinning assembly
quenching fluid/electrolyte (g,h,i, options only)
metal tank material (with corrosive materials this is an option only)
high temperature zone
quenching fluid/electrolyte outlet valve

Figures 1 and 2 show a cross section view of the furnace or melting chamber and quenching tank with ionic melt exit plugs 14 and 15 in their open positions allowing the ionic melt 10 to enter quenching tank B. Moving-heat-zone electrode assembly 11 is shown in its exit position after at least two traverses of the fusing chamber A.

The embodiment of the invention illustrated in Figures 1 and 2 also has a pair of burners 25 for heat addition to the furnace A and an exhaust 26 for heat capture.

Also illustrated in embodiment of Figures 1 and 2 is a subsurface gas inlet system 23 which although illustrated closer to the discharge end of the furnace A, will normally be located towards the inlet end. The subsurface gas inlet system 23 is provided to promote mixing in the furnace A. It may use air and/or steam and will allow for pulsed or intermittent injections as well as steady flow injection.

The quenching tank B has a liquid outlet 21 and a sludge removal outlet 22. The sludge removal outlet 22 is located in a lower portion of the tank B below a grading grill 24 which will typically act to break down any larger sludge lumps that may form upon entry of the molten mixture 10 into the quenching tank B.

Figures 3 and 4 illustrate an alternative embodiment of the production furnace and quenching tank. In these Figures, the preferred moving electrode assembly 11 to create a higher temperature area within the melt is illustrated as is the moving heat zone 20 which is created. In most other respects, the embodiment illustrated in Figures 3 and 4 is similar to that illustrated in Figures 1 and 2.

Figure 5 and 6 show views of an ionic melt chamber and quenching tank, illustrating exhaust heat recuperation/regeneration chamber 27 and burner assembly 25. It should be noted that multiple burner/exhaust assemblies can be employed for larger capacity chambers and/or to increase heat transfer efficiencies.
All proof of concept experiments to date (over 300 separate runs) have been conducted in a small crucible furnace. This furnace is fire-brick lined, insulated, all encased in a steel liner. This furnace is designed to take a ceramic crucible that can comfortably take a 300g charge. The furnace has a central, hinged lid, with a central port. This port serves three main purposes. The first is to observe the charge, the second provides access to a stirring rod while the third is to provide the one and only exhaust.

The furnace is fired by propane gas, using conventional household cylinders. The gas enters through a lower, tangential port. The gas is assisted by a small electrically powered centrifugal blower which allows temperature to reach up to $1150^\circ$C. This blower is normally activated after the furnace temperature reaches $300^\circ$C. A removable thermocouple is located opposite to the gas port. This thermocouple in turn is wired to a wall-mounted temperature display panel.

It is in this test furnace that the results illustrated in Figures 7 to 16 have been obtained to prove the invention.

The first step is to add the flux only then melt so generating an initial molten flux pool.

Coarser particles (2-8m) have proved more reactive, as observed by increased effervescence (efc), when compared to the additions of finer particles. Thus ore feed of a production furnace will typically not have to be ground. The avoidance of grinding becomes a major cost benefit of the present invention. Crushing to 10 mm should be adequate. The highly aggressive nature of the flux suggests the feed size could even be greater than 10mm.

The procedure is to add the laterite and additional flux in a number of smaller amounts, stirring after each addition.

Fresh additions tend to fuse into 'lumps'. When breaking these sintered lumps, some of the fines of the core become airborne. In a production furnace, this may constitute losses. However, on a mass scale, with a thin feed stream and air jet agitation, this loss will not occur.

The crucible stirring rod, after each stirring, quickly gains a thick wad of crucible contents on the tip. This wad, immediately after each stirring, is broken off and returned to the crucible and allowed to re-melt.

Frequently, immediately prior to the pour, there is effervescence and/or
bubbling within the crucible contents. This suggests the crucible contents have not yet reached their final temperature and digestion is not complete. Providing the laterite particles have been digested, the pour is homogeneous and fluid, and the final temperature has been reached, the pour should proceed. This suggests that increased residence time has little benefit.

The aim is to have the shortest furnace residence time as possible, then expel. This allows for increasing furnace production rates and efficiencies.

The commercial/production aspects of the balance between increased furnace temperatures and residence time will need to be carefully assessed on a case by case basis. Current findings are showing the time span between the first ore addition and pour to be under 40 minutes. The time span between the last ore addition and pour is 5-10 minutes.

The pour should be homogeneous. This illustrates the ore to flux ratios are in balance. In earlier times, the pour of the ore contents was preceded by an initial run of fluxes, which cooled to a canary-yellow mass. This non-homogeneous pour indicated either a surplus of flux in the mix, or the wrong fluxes that were not contributing to the break-down of the ore particles, e.g., excessive amounts of sodium chloride. Analysis of this flux showed the presence of only trace quantities of nickel.

Just prior to the pour, it is desirable to ensure the temperature is elevated to plus 1000°C. This will assist in reducing the viscosity of the pour approximating a medium to runny honey-like consistency.

**Production Furnace**

Calculations have been made of the size of a possible production furnace according to the present invention. Based on a production rate of 3 dry tonnes of laterite per minute, or 4,300 dry tonnes per day and a total residency time of 35 minutes, the furnace size calculates at an internal area of 7 x 20 meters.

Furnace design and construction engineers have provided a pre-feasibility estimate for an equipped, installed and commissioned 7 x 18 meter internal dimensions production furnace with an estimate of natural gas consumption for the furnace at 40,000 cubic meters per day.

Therefore, for a furnace size expanded from 7x18 to 7x 20 meters 50,000 cubic meters per day should be allowed.

The increased throughput of the furnace of the present invention
compared to a conventional glass furnace suggests increased wear. Therefore, provision needs to be made both in initial construction and major maintenance programmes to accommodate this aspect. The operating life of a production furnace before re-lining is required, is expected to be in excess of four years.

The feed into the furnace will be along the lines of a conventional large scale glass furnace. The ore plus any fluxes will be pre-mixed.

In a production furnace, the feed will be pre-heated with waste heat. The ore feed moisture content of Western Australia laterites can range from 25 - 30%. Some of this moisture will be lost in the pre-heating. However, the addition of moist ore directly into the furnace is not expected to create problems. In fact, the generation of steam may also assist with the stirring.

A practical method to assist mixing of the contents of the furnace is to have floor-mounted air jets. These jets would typically be fed with a constant low pressure, with periodic pulses of higher pressure. In practice these subsurface jets will be located towards the feed end, rather than the discharge end.

The use of sub-surface low pressure air, possibly with steam included, will assist in mixing the furnace contents. Pulsing of the introduced air/steam would assist even further.

The production furnace design contains electrodes protruding into the melt. Glass conducts electricity in the molten state, but not as a solid. These electrodes may be either AC to boost the melt and stirring process, or DC. DC electrodes have recently been trialed in the crucible experiments. Duration in the melt has been as little as 8 minutes. The most recent trial of LH2 material was 10 minutes at 2 volts and 3 amps. These electrodes were both carbon, but the cathode should be of another element, such as molybdenum. The purpose of the DC electrodes is primarily to assist in the breaking of any of the silica bonds of the compounds within the melt.

It is also preferred that the electrodes be oriented horizontally rather than vertically.

Electrowinning (EW) in the melt may be used as a means of the direct winning of both the nickel and cobalt onto the cathode provided that the electrowinning of iron can be minimised.

In order to protect the electrodes in a high production furnace, the
Electrodes may be encased within a loose sleeve of a high quality, porous ceramic.

Electrodes used so far have been carbon. As carbon electrodes burn in the air component of the furnace atmosphere other electrodes such as molybdenum will be required in production furnaces.

The use of a rotary furnace has been considered. The only possible use of a rotary furnace would be to pre-heat the feed to the main furnace. However, it would appear that through conventional pre-heat processes, a rotary furnace would not be required.

It may be required that furnace gases be cleaned of solids by electrostatic precipitators. Also HCl, SO₂ and NO gases may need to be recovered for environmental reasons.

In the present specification and claims (if any), the word "comprising" and its derivatives including "comprises" and "comprise" include each of the stated integers but does not exclude the inclusion of one or more further integers.

Reference throughout this specification to "one embodiment" or "an embodiment" means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, the appearance of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more combinations.

In compliance with the statute, the invention has been described in language more or less specific to structural or methodical features. It is to be understood that the invention is not limited to specific features shown or described since the means herein described comprises preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims (if any) appropriately interpreted by those skilled in the art.
Claims
1. A method of extraction of a metal from an ore or ore concentrate, including the steps of melting a target metal-containing mixture in a heated process vessel at a minimum temperature to form a homogeneous melt in the presence of an appropriate flux material to lower the melting temperature of the target metal-containing mixture, to produce a molten ionic matrix which is largely amorphous and hygroscopic and cooling the matrix.
2. A method of extraction of a target metal from a target metal-containing mixture, including the steps of melting a target metal-containing mixture in a heated process vessel at a minimum temperature to form a homogeneous melt containing at least the target metal and silica in the presence of an appropriate flux material to lower the melting temperature of the target metal-containing mixture, to produce a molten ionic matrix and cooling the matrix.
3. A method as claimed in either claim 1 or claim 2 wherein silica is present in the molten ionic matrix in the order of approximately 30% of the total by mass.
4. A method as claimed in claim 3 wherein silica is added to the molten ionic matrix if not present due to the composition of the target metal-containing mixture or appropriate flux material.
5. A method according to any one of the preceding claims wherein the molten ionic matrix is an amorphous soluble admixture.
6. A method according to any one of the preceding claims wherein the flux is added to a process vessel and then heated to form a molten flux pool with the target metal-containing mixture gradually added to the molten flux pool.
7. A method according to any one of the preceding claims wherein a flux/target metal containing material ratio is between approximately 1:0.5 at the lower end and 1:3 at the upper end.
8. A method as claimed in claim 7 wherein an optimum flux/target metal containing material ratio is approximately 1:1.
9. A method as claimed in any one of the preceding claims further including the step of electrowinning the molten ionic matrix.
10. A method according to any one of the preceding claims including the further step of quenching the molten ionic matrix in a fluid quench.

11. A method as claimed in claim 11 wherein the fluid is a gas.

12. A method as claimed in claim 11 or claim 12 further including the step of electrowinning the fluid quench.

13. A method according to any one of the preceding claims including a further step of recovering the target metal using a forced precipitation mechanism.

14. A method according to claim 11 further including the regeneration of the flux material using CO₂ produced from a combustion process to heat the heated process vessel.

15. An apparatus for the extraction of a target metal from a target metal-containing mixture, the apparatus including a heated process vessel to melt a target metal-containing mixture at a minimum temperature to form a homogeneous molten ionic matrix containing at least the target metal in the presence of an appropriate flux material to lower the melting temperature of the target metal-containing mixture and an associated cooling assembly adapted to cool the homogeneous molten ionic matrix.

16. An apparatus as claimed in claim 16 wherein the heated process vessel is further provided with one or more electrodes.

17. An apparatus as claimed in claim 17 wherein the one or more electrodes are provided with AC current to boost heat in the molten ionic matrix.

18. An apparatus as claimed in claim 17 wherein the one or more electrodes are provided with DC current.

19. An apparatus as claimed in any one of claims 17 to 19 wherein the one or more electrodes are movable within the heated process vessel.
WITH ELECTRODES (DS) INTO MELT

CRUCIBLE FURNACE
TEST PROCESSES

SOURCE MATERIAL
HEIDE (2.)

WEIGHTS
Fluxes
\( \text{Ni}_2\text{CO}_3 \) 11.0 gm

Test material
LH2
Sub total 1.6

Total weight of Charge 285 gm

Preheat Time In Time Out Total
11:45 AM PM 12:58 AM PM 12:58
75 Minutes

CRUCIBLE CONTENTS OBSERVATION

TIME
11:43
12:11
12:18
12:26
12:33
12:36
12:40
12:58

OBSERVATION
End of Cycle furnace
109 No. C
5% Squeezed 230 mg.
3% Squeezed 120 mg.
4% Squeezed 250 mg.
100% Squeezed 800 mg.
100 No. C
5% Squeezed 230 mg.
4% Squeezed 250 mg.

Viscosity at Pour
Fluid: Semi fluid: Viscous (Sticky honey): Very viscous (Sticky pudding)

Temp: as crucible added
1073 C
Max Temp 1116 C.

Comments
No explosion. A number of lumps and finer grained, initially dark olive green in colour.

Signature

Figure 7
\begin{align*}
\text{Li}^+ & : 20 \quad 15 \quad 15^\circ \quad 20 \quad 20 \quad 20 \quad 15^\circ \\
(\alpha_h) & \quad (\alpha_h) \quad (\alpha_h) \\
\text{Na}_2\text{CO}_3 & : 10 \quad 10 \quad 10 \quad 10 \quad 10 \quad 10 \\
\end{align*}

EW. Initially 15 V for 1 min.
Turned up to 30 V. Amper quickly picked up around 8-12.
Volts up to 30. Amps came to 12.
Turned back to 10 x 9.3 A.
Total time in melt 7 minutes.

Bowl 223 36
E 41

Figure 8
**MELT IN THE CRUCIBLE FURNACE**

**SAMPLE NO.** L112-103/20

**SOURCE MATERIAL:** NICKEL LATERITE

**TEST PROCESSES**

<table>
<thead>
<tr>
<th>Fluxes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃</td>
</tr>
<tr>
<td>Sub total</td>
</tr>
<tr>
<td>Na₂CO₃ added</td>
</tr>
</tbody>
</table>

**FURNACE**

- Crucible in furnace: 9:28 AM
- Crucible out of furnace: 11:31 AM
- Total time in furnace: 123 minutes
- Energy source: Propane and oxygen unless stated

**PRE-HEAT**

<table>
<thead>
<tr>
<th>Time In</th>
<th>Time Out</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:28 AM</td>
<td>11:31 AM</td>
<td>230</td>
</tr>
</tbody>
</table>

**FURNACE OBSERVATIONS**

- Temp. as crucible added: 23 °C
- Temp. as crucible removed: 1025 °C
- Air Temp: 1044 °C

**CRUCIBLE CONTENTS OBSERVATION**

<table>
<thead>
<tr>
<th>TIME</th>
<th>OBSERVATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:28</td>
<td>2nd charge</td>
</tr>
<tr>
<td>10:30</td>
<td>NR 1/34 fully molten</td>
</tr>
<tr>
<td>10:40</td>
<td>479.14 2nd</td>
</tr>
<tr>
<td>10:54</td>
<td>Stirred, v. dark &amp; sticky</td>
</tr>
<tr>
<td>10:55</td>
<td>NR 310.1 molten</td>
</tr>
<tr>
<td>11:05</td>
<td>130 mtl</td>
</tr>
<tr>
<td>11:16</td>
<td>Stirred, sticky, tacky, spreadable</td>
</tr>
</tbody>
</table>

**Viscosity at Pour**
- Fluid: Semi-fluid
- Viscous: Sticky honey
- Very viscous (Sticky pudding)

**Comments**
- Quenched, sticky, very dark gray to black in colour. Mainly fractured, fragments.

**Signature**

10:30: Fully molten, EFT
10:25: After 339 L112
11:01: Stirred with difficulty, many lumps
11:13: 998 Electro core into melt
11:31: Powder
LiH₂ 374 33 \( \text{Total} \) \( \frac{100}{100} \)
Na₂CO₃ 10 10 10 30

Gross wt. Bowl 233.42 84.14
Net 149.34

1. Electrodes into melt 11.13 Both carbon out of melt 11.27 Duration 14 min.

2. Temp when in melt 998° out of melt 1012°

3. Electrode switching one minute once only

4. Electrode appearance

5. Volts Amps
   1 1.6 2.0 on 1.8

Figure 10
N.B. NH₄OH Reaction
(about 1/2 L/100)

Note: Allowed to drip
to 1400 but had to
increase to get a melt.

CRUCIBLE FURNACE

SOURCE MATERIAL
HERON (Z)

TEST PROCESSES

CONTACT NAME
NICKEL LATEX

WEIGHTS

Fluxes

Test material
LH 2

Sample No. LH 2, 98/211

Date: 06-28-98

WEIGHTS

Sub total
160

Added Beth 500 g
N₂O₅ as slurry

Preheat Time In Time Out Total

FURNACE
Cruible into furnace
Cruible out of furnace
Total time in furnace
Energy source (Propane and Oxygen unless stated)

FURNACE OBSERVATIONS

Temp. as crucible added
Temp as crucible removed

CRUCIBLE CONTENTS OBSERVATION

TIME

OBSERVATION

11:47 AM/PM
11:25 AM/PM
11:59 AM/PM
11:51 AM/PM
11:33 AM/PM

- Colder than expected
- Add 200 m1 LH 2
- Drain 100 mL of N₂O₅
- Some gas
- 
- 
- 
- 
- 

Viscosity at pour: Fluid, Semi fluid, Sticky (shiny, sticky honey) Very viscous (sticky)

Flower a flower design next. 210. Still had to be
scooped. Some sizzling in the NH₄OH furnace.


Comments

Some smooth, shiny, sticky nodules.
No added material of note:
Break up nodules with a hammer, semi smooth.

Signature: [Signature]

Figure 11
Figure 12
Note: BNTES = Bunsen needed to be stirred.

CRUCIBLE FURNACE

TEST PROCESSES
Sample No. PS2/213
Date 08-02-08
Sitampundi (Platinum Group Elements)

SOURCE MATERIAL
Contact Name

WEIGHTS
Fluxes

\[ \text{Na}_2\text{CO}_3 \quad \text{gm} \quad 1.3 \]

Test material
Sub total 190.4
Plus fluxes 1.9
Total weight of Charge
29.5

Preheat, Time in
11.03 AM/PM First Ps
58 Minutes

FURNACE
Crucible into furnace
Crucible out of furnace
Total time in furnace
Energy source (Propane and Oxygen unless stated)

FURNACE OBSERVATIONS
Temp. as crucible added
320°C
Temp. as crucible removed
1272°C
Furnace Temp 1127°C

CRUCIBLE CONTENTS OBSERVATION

TIME
11.29
11.32
11.34
11.39
11.41
11.43
11.46
11.47
11.50
11.52
12.01

OBSERVATION
320°C first cooled frame
180°C fully melted
170°C drained Ps
160°C drained BNTES
140°C drained O3
130°C BNTES
120°C O3

Flowed a little. Pot may Ps1 but not to be scraped
Either one of 11.34/11.41 higher than 23°C temp.
Comments
May have resisted to heat soak time
A greater number of smaller nodules. Dark browning in color
Note: Frozen broken material appeared to be an expl

Signature

Figure 13
**Notes:**
1. Replace 20g Na₂CO₃ with 20g Na₂Cl to Na₂P₂O₅
2. Added NaCl to the ground

**CRUCIBLE FURNACE TEST PROCESSES**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>LH2-09/02/05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>30-11-07</td>
</tr>
<tr>
<td>Crucible</td>
<td>42</td>
</tr>
</tbody>
</table>

**SOURCE MATERIAL**

- **Na₂CO₃**
- **NaCl**

<table>
<thead>
<tr>
<th>Weight</th>
<th>g</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

Test material: LH2
Sub total: 110g

**Preheat Time In**

- **9.58 AM/PM First LH2**
- **10.29 AM/PM Poured**
- **71 Minutes Duration**

**FURNACE OBSERVATIONS**

- Temp. as crucible added: 20°C Max Temp. 1114°C
- Temp as crucible removed: 1092°C

**CRUCIBLE CONTENTS OBSERVATION**

<table>
<thead>
<tr>
<th>Time</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-59</td>
<td>20 Fire flint, 20g Shred Graphite, 20g Shred Vitun</td>
</tr>
<tr>
<td>10-62</td>
<td>20g Shred Graphite, 20g Shred Vitun, 20g Shred Graphite, 20g Shred Vitun</td>
</tr>
<tr>
<td>10-62</td>
<td>10g Shred Graphite, 10g Shred Vitun</td>
</tr>
<tr>
<td>10-60</td>
<td>10g Shred Graphite, 10g Shred Vitun</td>
</tr>
</tbody>
</table>

**Comments:**

Dark olive green, quickly become dark olive after

Note: Plenty of small, dark spots but one larger one;

Will need to start the quenching drum.

**Signature:**

- June 6, Shred Shred
- June 6, Shred Shred
- June 6, Shred Shred

**Figure 15**
Figure 16
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C22B 3/04 (2006.01)  C22B 9/10(2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPIDOC and WPI IPC Marks (MELT??? OR MOLTEN) AND (SODIUM) AND (+SILICA+ OR +SI02+) AND (AMORPHOUS) AND (HYGROSCOP+)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 4790872 A (BOWMAN) 13 December 1988 Column 1 lines 52-54; Column 5 line 27; Example in column 6</td>
<td>2-6, 9-19</td>
</tr>
<tr>
<td>X</td>
<td>US 3264096 A (AGARWAL ET AL) 2 August 1966 Column 1 line 70 to column 2 line 62; column 3 line 31</td>
<td>1, 5, 7-8, 10-11, 15</td>
</tr>
<tr>
<td>X</td>
<td>GB 1418060 A (SWARSAB MINING EXPLORATION &amp; DEVELOPMENT COMPANY, (PROPRIETARY) LIMITED) 17 December 1975 Page 3 lines 34-54</td>
<td>1, 5, 10-11, 15</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents:

'A' document defining the general state of the art which is not considered to be of particular relevance

'E' earlier application or patent but published on or after the international filing date

'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

'O' document referring to an oral disclosure, use, exhibition or other means

'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

'&' document member of the same patent family

Date of the actual completion of the international search 23 October 2009

Date of mailing of the international search report 30 OCT 2009

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