REFINING OF PLATINUM GROUP METALS CONCENTRATES

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ABSTRACT
This invention relates to a process in which a Platinum Group Metal (PGM)-rich residue from a BMR (Base Metals Refinery) process is subjected to a high temperature roast to remove contaminants, typically volatile elements (for example Se, Te, As, S, Bi, Os) and obtain a roast product. The roast product is smelted with a flux to form a slag phase and an alloy phase, and to vaporize sulphates and heavy metals like Pb, Te, and remove stable oxide compounds such as SiO2 and oxides of Fe, Ni, Co, Cu, Cr, Te, Bi to the slag phase. The alloy and the slag phase are separated, and the alloy phase is then melted and atomized with a gas or liquid atomization process to form fine alloy particles that can be dissolved in water and treated in a hydrometallurgical PMR (Precious Metals Refinery) process.
Fig. 1

- Off-gas handling from roasting operation (22)
- Off-gas handling from smelting operation (38)
- Reductive roast (16A)
- Oxidative roast (16B)
- Reductive melt (26A)
- Pressure lowering (26B)
- Oxidation agent addition (26C)
- Casting in mould (42)
- Manual separation (44)
- Melt for atomization (50)
- Atomization (52)
- Dissolve (54)
- Return slag to smelter (46)
REFINING OF PLATINUM GROUP METALS CONCENTRATES

BACKGROUND TO THE INVENTION

[0001] This invention relates to the production of Platinum Group Metals (PGMs) (which includes Pt, Pd, Rh, Ru, Ir) and gold (Au), which normally consists of a flotation step during which most of the PGMs and sulphide minerals are concentrated in slurry. Floatation is quite selective and typical PGM recoveries >80% can be achieved with mass pull (mass % of feed reporting as concentrate) figures of 1.8% to 4%. Unfortunately, some elements are often associated with the sulphide or PGM mineralogy (elements like As, Se, Te, Bi, Cd, Hg, Pb) and some of these elements also carry over with the floatation concentrate to become smelter feed material.

[0002] In the typical smelting step of PGM production, concentrates are first melted in an AC or DC furnace where the sulphide minerals separate from the oxide minerals to form a distinct furnace matte and slag layer respectively. These layers are tapped separately on different elevations in the furnace. PGMs tend to follow the matte phase and recoveries in the smelting step achieves >95%. However, minor contaminant elements (As, Se, Te, Bi, Cd, Hg, Pb) also follow the matte phase with varying recoveries. A converting step follows the smelting step in which FeS is removed from the furnace matte. During converting, air (with or without O₂ enrichment) is injected into the converter to oxidize FeS to FeO and SO₂. Some oxidation and minor desulphurisation of the molten base metal sulphides may also occur during converting. The final product from the smelting operation is mostly referred to as converter matte. Converter matte not only contains contaminant materials (As, Se, Te, Bi, Pb), but also contains minerals that are artefacts of the converting operation and are present due to slag carryover or entrainment. This normally includes SiO₂ and spinel-type oxides like magnetite and Trevorite (or other similar Ni/Cu/Fe oxides). Trace amounts of Cr₂O₃, CaO, MgO (also with the origin of slag carry over) are also present in converter matte.

[0003] Converter matte can either be granulated or atomized and sent to a Base metal removal/refining step where sulphide minerals (being mostly Ni, Cu and Fe sulphides) are leached to produce a >40% PGM containing residue (dry basis).

[0004] In another practice, converter matte can be slow cooled to separate the PGM’s in an alloy phase from the Base Metal Sulphides. Following slow cooling, the alloy-sulphide mass is crushed and the alloy is recovered into a crude magnetic fraction, whereas the base metal sulphides are recovered to the non-magnetic concentrate. Complete physical separation between these two phases is seldom feasible so that the alloy phase is normally treated with acids and alkalis under oxidising environments to remove the intergrowths of base metal contaminants. Subsequently, the PGM alloy concentrate is sent directly to the PMR.

[0005] Although the BMR process is primarily aimed at removing sulphide minerals, the refineries often contain circuits that are aimed at removing some of contaminants from the BMR residue material before it is sent to the Precious Metal Refinery (PMR). This includes circuits to remove Se, Te, Pb, SiO₂, and oxidic Fe/Ni complexes. The circuits are normally used at the BMR which tends to be a sulphate base process. Contaminants that are easier to be removed in or from a sulphate solution matrix are therefore better treated in a BMR. Conversely, contaminants that are easily removed using a chloride, nitrate or cyanide solution matrix are better removed at a PMR.

[0006] The final steps in producing PGMs (including Pt, Pd, Rh, Ru, Ir, Os) as well as Au and Ag are done in the Precious Metal Refinery. This Precious Metal concentrate derived from the BMR is typically leached in a chlorinate and hydrochloric acid environment to solubilise the PGMs. The PGM-containing solution is then separated into its constituent metals through a number of processes that may include any of a range of repeated precipitation and dissolution processes, solvent extraction, ion exchange or molecular recognition technology.

[0007] Typical feed grade to the PMR for the Platinum industry is around 40% to 75%, but typically 65% (sum total of Pt, Pd, Rh, Ru, Ir, and Au). The remaining content is a complex mixture of compounds of As, Pb, Se, Te, Bi, SiO₂, Fe/Ni oxides, metallic/sulphide Fe, unleached BMS (Base metal Sulphides), stable sulphates/hydroxysulphates formed during the BMR process, CaO, MgO, Cr₂O₃, and crystal water. This list of contaminants reports into different streams of the PMR process, and tend to produce residues in the PMR process. These residues need to be retreated with associated processing cost, inventory time, etc. The contaminants might also negatively impact on overall recoveries of Precious Metals and pipeline time for delivery of the metals to the market.

[0008] Currently all contaminants contained in PMR main feed material stream are handled through Hydrometallurgical processing steps (with circuits either introduced in the BMR or PMR process). Most refineries have pyrometallurgical process steps on recycle/residue/toll materials, but there is no existing Pyrometallurgical process slotted to treat the main feed material stream after the bulk of the Cu, Ni and S are removed and before the material is brought into dissolution for a PMR process.

SUMMARY OF THE INVENTION

[0009] According to the present invention, there is provided a process in which a Platinum Group Metal (PGM)-rich residue (typically greater than 40% by mass of Precious Metals in the residue are PGMs) and typically containing less than 10% by weight Base Metals is subjected to a high temperature roast to remove contaminants, typically volatile elements (for example Se, Te, As, S, Bi, Os) and obtain a roast product.

[0010] Preferably, the roast product described above is smelted with a flux to form a slag phase and an alloy phase, and to vaporize sulphates and heavy metals like Pb, Te, and remove stable oxide compounds such as SiO₂ and oxides of Fe, Ni, Co, Cu, Cr, Te, Bi to the slag phase and, whereafter the alloy and the slag phase are separated.

[0011] The alloy phase described above may subsequently be melted and atomized with a gas or liquid atomization process to form fine alloy particles that can be dissolved in water and treated in a hydrometallurgical PMR (Precious Metals Refinery) process.

[0012] The principle of the invention allows for the removal of a wide range of contaminants by a pyrometallurgical process, by making use of the noble nature of the PGM materials at high temperatures (resistance to oxidation and low vapour pressures). The abundance of PGM’s allows the formation of a PGM alloy phase (without the addition of a collector) that can be atomized. The proposed process can produce 90% 6
Roasting temperatures need to be high enough to vaporize the necessary compounds (like TeO₂, SeO₂, TeO₂, As₂O₃, and Os₂O₆) and to decompose stable compounds (like sulphates) and may require temperatures above 500°C and below 1000°C, preferably from 600°C to below 900°C, most preferably 700°C to 850°C. At the lower temperatures, the PGM’s (specifically Pd, Ru, Rh, Ir) tend to oxidize and the vapour pressures of the PGM oxides are orders of magnitude greater than the pure metals. To avoid PMG oxide vaporization (especially of Ru), roasting temperatures should be kept below 900°C. The roasting step comprises an oxidative roast, with the addition of an oxidation agent, such as air. Typically, from 100 to 150 g, preferably 130 to 150 g of air is added per 100 g residue.

Although all the volatile components are oxides and therefore require an oxidative roast in air, the oxidation state and mineralogical association of the elements determine the roasting conditions. A reductive roast might also be necessary to form the correct oxidation state of certain elements, prior to or following on the oxidative roast. The reductive roast may be conducted at a temperature of from 550°C to 650°C, typically about 600°C, with a reducing agent such as coal or petroleum coke.

The smelting step should be done slightly higher than the liquidus temperature (lowest temperature where all solids disappear and become completely molten) of the alloy phase to decompose stable compounds (like sulphates), remove Pb (and other heavy metals) to the gas phase and allow stable oxides (such SiO₂, Cr₂O₃, and spinels) to dissolve in the slag phase, typically the smelting step is carried out at a temperature of 1300°C to 1600°C, preferably 1400°C to 1500°C.

Preferably, the smelting is carried out under reducing conditions, typically by adding as reductant such as carbon, for example by adding 5 g to 15 g per 100 g feed material of a carboylute such as flour.

A synthetic slag should also be added to the melt, making use of the low melting point and viscosity of a Ca or Mg oxide, silicate, aluminate, alkali oxide, preferably a CaO–SiO₂—Al₂O₃—Na₂O—K₂O flux system, for example the flux may contain 10-40% by weight SiO₂, 5-15% by weight Al₂O₃, 30-70% by weight CaO and 15-25% by weight Na₂O. Slag additions can vary from 20 g to 100 g slag per 100 g of roast product feed, but typical additions of 50 g slag per 100 g roast product feed will allow slag capacity to dissolve stable spinel type compounds in the roast feed material.

The smelting step may be carried out without adding a collector.

If induction is used to achieve smelting, a graphite receptor vessel lined with ceramic should preferably be used as crucible.

Preferably, the smelting is carried out in three steps:

1) a reductive melting step;

2) lowering of pressure, preferably lowering the absolute pressure to below 0.5 atm, typically about 0.1 atm, for a period of 10 to 30 minutes to remove Pb, Te and/or other heavy metals; and/or

3) addition of an oxidation agent such as K₂NO₃, NaNO₃, O₂, air NaNO₂, or MnO₂, preferably NiO₂, to ensure good partitioning of contaminants such as Fe and Ni to the slag phase.

Atomization of the alloy can be done by either gas or liquid cooling. High pressure water jets are a well-established method of atomization and can achieve very fine particulate (D50 around 10 to 20 micron if required). Atomization done with liquid (like water) forms rapidly cooled meta-stable phased and uneven (often hollow) particles with a high surface area that allows rapid dissolution. It is also possible to use high pressure inert gas (like N₂ or Ar) jets, or centrifugal gas cooling to atomize the alloy to a D50 around 40 micron. Particles are more spherical and cooling is less rapid than in water.

Materials handling, dissolution behavior and metal accounting will drive the decision on the type of atomization used.

The process of the invention may be inserted:

1) after a Slow Cooling process,

2) in a Base Metals Recovery (BMR) process, or

3) in-between a BMR process and a PMR process.

By “Slow Cooling” process is meant a process where a matte is slow cooled to separate the PGM’s in an alloy phase from the Base Metal Sulphides.

By “BMR process” is meant any process that removes the bulk (>95%) of the base metals and sulphur from a feed (e.g., a sulphate based hydrometallurgical process).

An example of a position for the process of the invention would be to melt concentrate from a BMR process directly after the pressure leach that is aimed at removing Cu. This will eliminate sections of an existing BMR aimed at removing the last remaining BMS, SiO₂, Fe/Ni oxides, metallic/sulphidic Fe, Pb and amphoteric elements.

By “PMR Process” is meant hydrometallurgical processing steps where PGMs are separated and recovered from PGM concentrate.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a flow sheet for a process of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention relates to a Pyrometallurgical process that has the capacity to remove a large array of contaminants from material feed to a PMR (Precious Metals Recovery) process in a single processing step, while being very selective to remove contaminants (but not PGM’s, apart from Os). As a number of contaminants can be removed in a single step, current BMR (Base Metals Recovery) and PMR process flows can potentially be simplified with associated cost saving.

A process is described in which contaminants (including but not limited to As, Pb, Se, Te, Bi, SiO₂, Fe/Ni oxides, metallic/sulphidic Fe, unleached Base metal Sulphides, stable sulphates/hydroxi-sulphates, CaO, MgO, Cr₂O₃) is wholly or partly removed by a Pyrometallurgical process from PMR feed material. The Pyrometallurgical process consists of a Roasting process followed by a Smelting step. The roasting step removes volatile elements to the gas phase (for example Se, Te, Os, S, Bi, As). The smelting step decomposes stable compounds (like sulphates), removes Pb (and other heavy metals) to the gas phase and allows stable oxides (like SiO₂, Cr₂O₃, and spinels) to dissolve in the slag phase. The smelting step forms an alloy and slag phase that
can be casted and physically separated. The alloy phase can be re-melted and atomized in order to facilitate alloy dissolution in the PMR process.

[0037] Table 1 below contains a typical feed of material that can be treated by the proposed process of the invention. Mineralogical speciation and mineral association is critical to understand process optimization.

<table>
<thead>
<tr>
<th>Specie</th>
<th>% content</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>3.65</td>
</tr>
<tr>
<td>CuS</td>
<td>6.10</td>
</tr>
<tr>
<td>Co3O4</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe3O4</td>
<td>6.71</td>
</tr>
<tr>
<td>Se</td>
<td>3.43</td>
</tr>
<tr>
<td>Te</td>
<td>0.54</td>
</tr>
<tr>
<td>As</td>
<td>1.98</td>
</tr>
<tr>
<td>PbSO4</td>
<td>6.13</td>
</tr>
<tr>
<td>SiO2</td>
<td>4.05</td>
</tr>
<tr>
<td>S</td>
<td>5.88</td>
</tr>
<tr>
<td>Pt</td>
<td>24.33</td>
</tr>
<tr>
<td>Pd</td>
<td>11.72</td>
</tr>
<tr>
<td>Au</td>
<td>0.60</td>
</tr>
<tr>
<td>Rh</td>
<td>4.04</td>
</tr>
<tr>
<td>Ru</td>
<td>6.20</td>
</tr>
<tr>
<td>Ir</td>
<td>1.51</td>
</tr>
<tr>
<td>Ag</td>
<td>0.72</td>
</tr>
<tr>
<td>Os</td>
<td>4.57</td>
</tr>
<tr>
<td>H2SO4</td>
<td>0.55</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.46</td>
</tr>
<tr>
<td>CaO</td>
<td>0.14</td>
</tr>
<tr>
<td>CuO</td>
<td>0.39</td>
</tr>
<tr>
<td>MgO</td>
<td>0.54</td>
</tr>
<tr>
<td>Total</td>
<td>94.24</td>
</tr>
<tr>
<td>6E</td>
<td>48.61</td>
</tr>
</tbody>
</table>

[0038] The heart of the roasting step lies at the formation of volatile oxides (being primarily SeO2, TeO2, As2O3, Os2O6 and SO2). Air is a sufficiently strong oxidizxation agent to achieve this purpose. Apart from air being available with no associated cost, it also contains 79% N2 that plays an important part to allow enough gas volume to remove volatile species (especially TeO2).

[0039] For the feed material under investigation, around 140 g of air per 100 g of feed material was necessary to achieve sufficient removal. There would be little consequence to having more gas flow (volumes), apart from the longer roasting time and roasting cost increase.

[0040] A temperature of around 800° C, works for the oxidative roasting step. Higher temperatures will serve to decompose stable sulphates, but some Ru losses (as RuO2 and RuO3) will be experienced above 900°C. Ru, Rh, Ir and Pd all form oxides at roasting temperatures and the vapour pressure of these oxides are orders of magnitude greater than the pure metal (apart from Pd).

[0041] The roasting temperature should be optimized for the feed material properties. As an example, another leach residue from the SeTe precipitation circuit in the BMR started melting around 750° C. and roasting temperatures were limited to 700° C. Despite the poor removal of Te in the roasting circuit, the Te could be sufficiently removed in the pressure lowering smelt.

[0042] Roasting can be done in a fluid bed (circulating bed fluid reactor or bubbling bed reactor), rotary drum roaster, multiple hearth furnace or static bed (multiple trays manually loaded in a muffle furnace). The preference would be the high efficiency fluid bed reactors, but particle size, required throughput rates and the need for batch processing would play a crucial role in the choice of technology. In the case of the studied material, some micro agglomeration was done to control particulate suspension. Binders used for micro agglomeration will decompose/dissolve to the slag phase during the smelting step. Heat for the roasting can be supplied by electricity/gas or combustion.

[0043] For the material studied, As removal with air roasting was not as efficient as predicted by modelling. This was probably true due to the incorrect assumed speciation in the feed material, with the presence of arsenates (As(3+)) which are not volatile, and pyrrhotite which is quite refractory to oxidation. In order to remove As, reduction to trivalent As is necessary. A pre-reductive roast can be done with coal or petroleum coke at around 600°C. If a dual step reductive/oxidative roast is necessary, a batch reaction is better where a simple switch-over of gas can be done in a single vessel.

[0044] With reference to FIG. 1, BMR feed material 10, reductant 12 and an inert gas 14 are fed into a reductive roasting step 16A in a roaster 16. Thereafter, air 18 is supplied to provide an oxidative roasting step 16B following the oxidative roasting step to the same roaster 16.

[0045] Typical recovery values to the gas phase of a roast at 800° C, can be seen in Table 2 below. Almost all Se, As, Os, Te and most S can be volatilized.

<table>
<thead>
<tr>
<th>Element</th>
<th>Removal to gas phase (Mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.0%</td>
</tr>
<tr>
<td>Au</td>
<td>0.0%</td>
</tr>
<tr>
<td>Pt</td>
<td>0.0%</td>
</tr>
<tr>
<td>Ir</td>
<td>0.0%</td>
</tr>
<tr>
<td>Os</td>
<td>100.0%</td>
</tr>
<tr>
<td>Te</td>
<td>95.0%</td>
</tr>
<tr>
<td>Ag</td>
<td>0.0%</td>
</tr>
<tr>
<td>Pd</td>
<td>0.0%</td>
</tr>
<tr>
<td>Ru</td>
<td>0.0%</td>
</tr>
<tr>
<td>Se</td>
<td>100.0%</td>
</tr>
<tr>
<td>As</td>
<td>90.0%</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0%</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0%</td>
</tr>
<tr>
<td>Co</td>
<td>0.0%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0%</td>
</tr>
<tr>
<td>S</td>
<td>90.0%</td>
</tr>
</tbody>
</table>

[0046] Off gas 20 formed during roasting should be captured and presented to a gas cleaning/metal recovery step 22 as the gas will contain harmful species (such as oxides of Se, As, Os and SO2). This will be discussed in more detail below.

Melting Step

[0047] A smelting step follows roasting, and oxidised material 24 from the roaster 16 is supplied to a smelter 26, together with reductant 28, inert gas 30 and fluxes 32. Smelting allows the formation of an alloy phase and a slag phase. The slag phase will absorb SiO2, oxides of Fe, Ni, Co, Cu, Cr,
Te, Bi, etc. while sulphates/oxysulphates will decompose and allow the resulting oxides to be absorbed in the slag phase. PGM’s are concentrated in the alloy phase, and by atomizing the alloy phase. PGM’s are reactive enough to enter a PMR refining circuit through the existing dissolve circuit.

[0048] In this embodiment of the invention, the smelter 26 is an induction furnace, although AC and DC technology can also be used. Induction melting can facilitate batch operation by heating and cooling in a crucible arrangement, while allowing a pressure modification step easier than either AC or DC furnaces. Preliminary results of induction melting show that heat needs to be transferred to the material via a receptor crucible, as direct coupling cannot be achieved to the roasted material. Graphite is suggested as the receptor crucible as it can facilitate temperatures up to 1800°C, without any problems and can be heated and cooled very fast. The study showed that graphite does interact with the melt and a ceramic crucible (preferably high Magnesia content) should be used to line the graphite and be in contact with the melt.

[0049] Smelting should be performed just above the liquidus temperate (lowest temperature where all solids become completely molten) of the alloy. The liquidus temperature of the alloy phase is driven by the relative concentration of the different PGM metals and the alloying effect of the base metals (like Cu and Ni) and Fe. The higher the PGM content (especially of the higher melting metals like Ru), the higher the liquidus temperature. For the BMR leach residues studied. Ru is the last metal to dissolve in the alloy and the liquidus temperature is between 1430 and 1450°C. A temperature of 1450°C to 1500°C, was found to be suitable in the test work. Temperatures above 1500°C leads to some losses (0.3% at 1500°C) of Pd, as Pd has the highest vapour pressure of the PGM metal group.

[0050] The smelting operation can be best described as 3 distinct steps, being 1) slightly reductive melting step 26A, 2) Pb, Te and other heavy metal removal by lowering of pressure 26B, and 3) oxidation agent addition 26C to ensure good partitioning of contaminants (including some Fe and Ni) to the slag phase. As smelting is done as a batch process, the 3 steps can be adjusted consecutively from charging to casting. Casting follows after the last oxidation step.

[0051] As the vapour pressure of PGM oxides (Ru, Ir and to a lesser degree Rh) are great enough to lead to losses during heating a mild reducing agent 28 should be added together with synthetic slag 32 (i.e. the slag is not a naturally slag, but a slag made from the constituents thereof) and mixed with the roasted feed material before melting. The reductant can be a carbohydrate (like wheat flour) and should be in the order of around 5 g to 10 g flour per 100 g roasted feed material. Too reducing conditions will force most of the Fe and Ni to the alloy phase. Once in the alloy phase, these elements are difficult to selectively oxidize to a great extent. Inert gas 30 is supplied to the smelter 26, and an inert gas atmosphere should be maintained above the melt throughout the entire smelting operation.

[0052] After all the material is molten, the pressure of the atmosphere above the melt can be lowered. This can be facilitated by closing a pressure chamber and drawing a vacuum with a vacuum pump in the chamber. Pb often creates particular problems in the PMR (especially during Rh refinement). Due to the required Pb specification, a Pb removal step to the gas phase needs to be included in the melting operation. Around 95% Pb removal (together with Te and some other heavy metals) can be achieved very effectively by lowering the absolute pressure to around 0.1 atmosphere. Pb is vaporized as both PbO and Pb. After a period of 10 to 30 minutes at the lower pressure, the vacuum can be broken. Around 50% of the Ag is lost to the gas phase is experienced with the lowering of pressure.

[0053] After the vacuum chamber is opened and normal pressure is restored to the melt, an oxidation agent 34 can be added to the slag in order to ensure optimum partitioning of contaminants to the slag phase. Limited oxidation of Fe, Ni and to a lesser extent Cu can also be achieved by the oxidation agent addition. An addition of around 2.5 g oxidation agent per 100 gsm roasted product feed can lift the final alloy PGM grade from 87% to 92%. NaNO3 and MnO2 can both be considered as oxidation agents, but NaNO3 is preferred.

[0054] It is important to note that the specification on certain elements at a plant will drive the melting step complexity. Both the pressure lowering steps and the oxidation steps can be eliminated if the tolerance on Pb, Ni, etc. in the alloy can be lowered. The slightly reductive melt will yield an alloy with a 6 PGE grade of around 83%.

[0055] Table 3 below shows the typical recovery to the alloy phase across the melting step of Roasted product at 1450°C with a flour addition of 7 g per 100 g of roasted product. A person skilled in the art will be able to recalculate the mass addition required if alternative carbohydrates are used.

<table>
<thead>
<tr>
<th>Element</th>
<th>Recovery to alloy phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>29.35%</td>
</tr>
<tr>
<td>Te</td>
<td>1.46%</td>
</tr>
<tr>
<td>As</td>
<td>2.45%</td>
</tr>
<tr>
<td>Pb</td>
<td>0.22%</td>
</tr>
<tr>
<td>Au</td>
<td>99.58%</td>
</tr>
<tr>
<td>Pt</td>
<td>100.00%</td>
</tr>
<tr>
<td>Ir</td>
<td>99.99%</td>
</tr>
<tr>
<td>Ag</td>
<td>36.42%</td>
</tr>
<tr>
<td>Pd</td>
<td>99.75%</td>
</tr>
<tr>
<td>Rh</td>
<td>100.00%</td>
</tr>
<tr>
<td>Ru</td>
<td>99.42%</td>
</tr>
<tr>
<td>Cu</td>
<td>64.16%</td>
</tr>
<tr>
<td>Ni</td>
<td>26.39%</td>
</tr>
<tr>
<td>Co</td>
<td>7.93%</td>
</tr>
<tr>
<td>Fe</td>
<td>3.70%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.06%</td>
</tr>
<tr>
<td>Ca</td>
<td>0.00%</td>
</tr>
<tr>
<td>S</td>
<td>0.00%</td>
</tr>
<tr>
<td>Si</td>
<td>0.00%</td>
</tr>
<tr>
<td>Al</td>
<td>0.00%</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

[0056] A synthetic slag needs to be added to the melt in order to absorb the unwanted oxides from the melt. The CaO—SiO2—Al2O3—Na2O system is suggested as flux as has a low melting temperature (liquidus temperature around 1150°C. For the suggested slag composition), low viscosity (around 0.4 log(poises) at 1450°C), a good capacity to absorb all oxides and a very low capacity to absorb...
Magnesia based linings. The aimed slag composition (from an addition perspective) is shown in Table 4 below:

**TABLE 4** Proposed Fluxing agent composition ratio

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>30</td>
</tr>
<tr>
<td>Al2O3</td>
<td>10</td>
</tr>
<tr>
<td>CaO</td>
<td>40</td>
</tr>
<tr>
<td>Na2O</td>
<td>20</td>
</tr>
</tbody>
</table>

The fluxing addition rate is suggested around 50 g total flux per 100 g roasted product feed material. This addition rate is important to allow enough absorptive capacity to absorb spinels that would otherwise be present as a solid. Spinels are present due to the converting operation (for instance magnetite and trevorite), but some can also form during the roasting due to the presence of Mg, Fe, Ni, Al and Cr.

The slag at the end of the smelting operation has a very low viscosity (calculated as 0.13 log (poise)), due to the additional fluxing capacity of oxides absorbed from the melt (for example FeO, Fe₂O₃, NiO, MgO).

Off-Gas Handling from Roasting Circuit

The smelting circuit will yield a hot, concentrated gas stream that will contain the bulk of the gas species that are hazardous to the environment and people. As some suspension of particulate to the gas phase is almost inevitable from the smelting operation, a particulate separation step needs to be included in this gas circuit. Ideally this particulate removal step should be performed while the gas is still hot (above dew-point/de-sublimation point) of the gas species. A ceramic candle filter is an example of hot particulate removal equipment that can be used. Particles removed from the gas may be returned to the roaster.

In order remove most of the harmful gaseous species from the off-gas, it would be possible to scrub in a wet circuit (alkali based preferably). It is also possible to recover some of the valuable gas species (Se, Te, Os) by selective condensation/de-sublimation. This might require reduction and a cool surface area to condense on.

If a reductive roasting step is required, the presence of combustible gas species needs to be designed for. Off-gas handling will be driven by legislation, existing infrastructure and the potential market/value of metals.

It is also possible to treat both the roasting and smelting off-gas in existing plant scrubbing circuit (post particulate recovery).

Off-Gas Handling from Melting Circuit

Off-gas from the smelting operation will have to be extracted from above the furnace and treated, and is treated in an off-gas handling operation. The off-gas handling might or might not require particulate removal and scrubbing. The off-gas stream could be combined with that of the roasting operation or could be combined with existing plant circuits.

Roast Melt and Oxidative Melt—Casting in Mould

Molten alloy and slag from the smelter is cast into a mould. Induction furnaces (and smaller AC and DC furnaces) can normally be tilted with hydraulics in order to pour the melt into moulds. Bottom tapping would also be possible for a batch operation.

Casting can be done into either a stationary type of mould, or in a gravity-driven flow-over bucket type of mould arrangement. Upon solidification, the content of the mould’s can be removed. The major loss mechanism of PGM’s to the slag is not dissolution in the slag phase, but suspension (entrainment) and freezing of alloy particles in the slag phase during the casting process. A very important aspect of casting is to allow the slag to be sufficiently fluid to facilitate quantitative alloy settling from the slag to the molten alloy pool. A distinct flat surface between slag and alloy is necessary for easy and clear separation and is readily achieved.

In the case where stationary AC or DC furnace technology is used for melting, tapholes can be maintained in the refractory lining that can be opened and plugged as required (but tilting can also be done on small AC and DC furnaces). Slag and alloy can be tapped from different elevations effectively removing the suspension of alloy during the casting operation. The advantage of this is that the slag will be more devoid of Precious Metals and this will limit material locked up in process.

Manual Separation of Slag and Alloy

Alloy and slag are separated in a simple manual separation process. The slag can simply be knocked off the alloy phase mechanically. If casting was done with good control, the surface between slag and alloy should be quite smooth and separation is easily affected. Alloy ingots and slag pieces can then be manually sorted and batched for further processing. The alloy ingots should be clean with very little slag carry over with the alloy phase, as this slag will enter the PMR process with the alloy after atomization.

Slag Return to Smelter

Slag is separated from the alloy will contain some PGMs, mostly due to entrainment of alloy in the form of small suspended particles. PGMs in the slag phase can be recovered by re-processing the slag in the smelter plant furnace (referencing to existing smelting operations, for instance the concentrate smelting done prior the converting step and the BMR). The Base Metal Sulphide material draining through the slag will act as collector and reclaimed PGM’s will pass through the converting process once again. Typical smelting operations have recoveries >98%, so a second pass of slag should have the opportunity to reclaim any losses quite efficiently.

Atomization Melt

It is necessary to dissolve the separated alloy into the Precious Metal Refinery. In order to achieve this efficiently with an alloy, the surface area needs to be large enough, and the surface needs to be reactive enough. Atomization of the alloy to a fine powder achieves this goal.

In order to atomize a liquid stream of alloy, the alloy must once again be melted. Induction furnace technology is by far the most suitable for this cause, as coupling and transfer of energy can be done directly to the alloy. This makes the melting process very fast and efficient. It is proposed to melt the alloy in an Alumina crucible, but graphite can also be used. Temperature of the melt should not be higher than 50°C above the temperature where all the alloy is liquid (liquidus temperature). The required atomization melt tem-
perature is in the order of 1500°C to 1550°C. An inert gas atmosphere should be maintained above the crucible to avoid oxidation of the alloy and crucible.

[0072] In order to present a controlled liquid stream of alloy (controlled in both the mass flow and the direction of flow) to the high pressure gas or water sprays, a graphite funnel can be used. This graphite funnel can once again be heated by an induction coil to prevent any material from freezing inside the funnel. An inert gas atmosphere should be maintained across the graphite to prevent oxidation of the alloy and crucible. The funnel receives and queues liquid metal into the high pressure gas/water jets. Temperature of the funnel can be controlled at 1500°C.

[0073] An extraction hood should be located above the induction furnace in order to remove fumes. The gas from this melt could be combined with other gas streams, like gas from the roasting and/or primary smelting steps for scrubbing. There should not be any need for particulate removal from this gas stream.

[0074] Atomization

[0075] Atomization 52 of the alloy can be done by either gas or liquid cooling. If liquid is used, water is preferred, while an inert gas, like N₂ or Ar is preferred as gas cooling media. High pressure water jets are a well-established method of atomization and can achieve very fine particulate (D₅₀ around 10 to 20 micron if required). Atomization done with liquid (like water) forms rapidly cooled meta-stable phases and uneven (often hollow) particles with a high surface area that allows rapid dissolution. For the materials evaluated, at least 2 phases formed during cooling, a high melting phase that contains most of the high melting PGM’s (Rh, Ir, Ru and Pt) and a secondary phase that contains some Pd and most of the remaining Fe, Ni and Cu.

[0076] It is also possible to use high pressure gas jets, or centrifugal gas cooling to atomize the alloy to a D₅₀ around 40 micron. Particles are more spherical and cooling is less rapid than in water. Materials handling, dissolution behaviour and metal accounting will drive the decision on the type of atomization used.

[0077] If water is used, it is proposed to use water jets at a pressure between 60 bar and 160 bar. The water to alloy (weight to weight) ratio during atomization can be between 5 and 10. Managing the water to alloy ratio will allow the alloy slurry to be pumped directly to dissolution vessels. If this cannot be done, a filtering step will be required to remove water from the slurry.

Dissolution into PMR Circuit

[0078] Atomized alloy can be directly submitted to a dissolution process 54, although the dissolution rate might force better temperature control on the vessels. The reactivity of the alloy was found to be slightly higher than normal PMR feed material, and the solution heated faster with the alloy after the chlorine was opened. However, temperature control and redox potential control could be achieved on similar levels to normal PMR feed material on lab scale.

Process Variations not Limiting the Invention

[0079] This invention is not limited or constrained by any of the following:

[0080] The way in which converter matte is prepared from furnace matte, or any technology or processing method prior to producing converter matte.

[0081] The way in which PGM’s are concentrated from converter matte (the way the base metals are removed either physically or chemically)

[0082] The process steps in the BMR (if PGM’s pass through the BMR) — as an example the technology choice between atmospheric and pressure leach for Ni-Cu removal.

[0083] The process steps in the PMR — as an example the technology choice between repeated precipitation and dissolution processes, solvent extraction, ion exchange or molecular recognition technology.

[0084] Type of furnace — AC, DC or induction for primary melting. Induction should be best for atomization (rate of heating, efficiency through direct coupling)

[0085] Smelting process — inclusion or exclusion of pressure control, inclusion or exclusion of oxidation agent addition to slag

[0086] Type of crucible/refractory

[0087] Type of atomization — gas or liquid as cooling medium

[0088] Type of casting mould — gravity overflow arrangement type, single large mould, etc.

[0089] Method of slag cleaning — could put back in existing smelting operation or could introduce separate slag cleaning melt and discard slag

[0090] Type of roaster — static bed, rotary type, multiple hearth, fluidized bed roasting

[0091] Type of roasting requirement — necessity of reductive roast before or after the oxidative roast

[0092] Type of gas cleaning and solids recovery used

[0093] Type of method (if used) for the recovery of valuable metals from the off-gas stream, like Se, Te and Os

[0094] A major advantage of the process of the present invention is that it can fit into any existing precious metal refinery where the feed material contains contaminants, including but not limited to As, Pb, Se, Te, Bi, Cd, Hg, SiO₂, Fe/Ni oxides, metallic/sulphidic Fe, unleached BMS (Base metal Sulphides), CaO, MgO, Cr₂O₃.

[0095] The following list of advantages is foreseen by the process of the present invention:

[0096] The amount of residues generated in the PMR process can be lowered. Costs on tolling/re-processing of residue materials will be saved.

[0097] The amount of effluent from the PMR process should reduce with associated reduction in PGM losses in the effluent.

[0098] Increased first pass recoveries in the PMR circuit due to less tie-up of PGM’s in residue and effluent streams may be achieved.

[0099] The PMR processing time could decrease (from a more reactive and faster primary leach to contaminant removal steps). This lowers inventory in the process and increases the capacity of the PMR.

[0100] Operational challenges in the PMR related to contaminant presence (especially the periodic high SiO₂ and Pb feed to the PMR) may be resolved. The smelting step will stabilise PMR feed grade by removing contaminants that do not have controlling steps in the rest of the process.

[0101] The BMR and or PMR process can be simplified by bypassing hydrometallurgical contaminant removal steps. This will also eliminate the creation of the effluent streams of this bypassed step (with lower associated
PGM losses). Labour and cost savings can be achieved by contaminant removal processes that are bypassed.

This patent application claims priority from ZA 2011/00894, the content of which is incorporated herein by reference.

1. A process in which a Platinum Group Metal (PGM)-rich residue, wherein greater than 40% by mass of Precious Metals in the residue are Platinum Group Metals (PGMs), containing less than 10% by weight base metals, is subjected to a high temperature roast which includes an oxidative roast wherein the roasting temperature is above 500°C and below 1000°C to remove contaminants including Se, Te, As, S, Bi, Os and obtain a roast product; and the roast product is smelted with a flux at a temperature of 1300°C to 1600°C to form a slag phase and an alloy phase, which are separated.

2. The process as claimed in claim 1, wherein the roasting temperature is from 600°C to below 900°C.

3. The process as claimed in claim 2, wherein the roasting temperature is from 700°C to 850°C.

4. The process as claimed in claim 1, wherein an oxidation agent is added to the oxidation roast.

5. The process as claimed in claim 4, wherein the oxidation agent is air.

6. The process as claimed in claim 5, wherein from 100 to 150 g of air is added per 100 g residue.

7. The process as claimed in claim 6, wherein from 130 to 150 g of air is added per 100 g residue.

8. The process as claimed in claim 1, wherein the roasting step includes a reductive roast prior to or after the oxidative roast.

9. The process as claimed in claim 8, wherein the reductive roast is carried out at a temperature of from 550°C to 650°C.

10. The process as claimed in claim 9, wherein the reductive roast is carried out at a temperature of about 600°C.

11. The process as claimed in claim 8, wherein a reducing agent is added to the reductive roast.

12. The process as claimed in claim 11, wherein the reducing agent is coal or petroleum coke.

13. The process as claimed in claim 1, wherein the roast product is smelted at a temperature of 1400°C to 1500°C.

14. The process as claimed in claim 13, wherein the smelting is carried out under reducing conditions.

15. The process as claimed in claim 14, wherein a reductant is added to the smelting step.

16. The process as claimed in claim 15, wherein the reductant is a carbohydrate.

17. The process as claimed in claim 16, wherein the reductant is flour.

18. The process as claimed in claim 17, wherein 5 g to 15 g of flour is added per 100 g feed material.

19. The process as claimed in claim 1, wherein the slag is a synthetic slag.

20. The process as claimed in claim 1, wherein the flux is a Ca or Mg oxide, silicate, aluminate, alkali oxide flux.

21. The process as claimed in claim 20, wherein the flux is a CaO—SiO₂—Al₂O₃—Na₂O flux.

22. The process as claimed in claim 21, wherein the flux contains 10-40% by weight SiO₂, 5-15% by weight Al₂O₃, 30-50% by weight CaO and 15-25% by weight Na₂O.

23. The process as claimed in claim 1, wherein the slag additions are from 20 g to 100 g slag per 100 g of roast product feed.

24. The process as claimed in claim 23, wherein the slag additions are about 50 g slag per 100 g of roast product feed.

25. The process as claimed in claim 1, wherein the smelting step is carried out without adding a collector.

26. The process as claimed in claim 1, wherein induction is used to achieve smelting in a graphite reactor vessel lined with ceramic.

27. The process claimed in claim 1, wherein the smelting is carried out in three steps:

1) a reductive melting step;
2) lowering of pressure, preferably lowering the absolute pressure for a period of 10 to 30 minutes to remove Pb, Te and/or other heavy metals; and/or
3) addition of an oxidation agent such as K₂NO₃, Na₂O₂, O₂ gas, air NaNO₃ or MnO₂, preferably NaNO₃ to ensure good partitioning of contaminants such as Fe and Ni to the slag phase.

28. The process claimed in claim 27, wherein the absolute pressure lowered below 0.5 atm.

29. The process claimed in claim 28, wherein the absolute pressure is lowered to about 0.1 atm.

30. A process in which the alloy product of a process as defined in claim 1 is melted and atomized with a gas or liquid atomization process to form fine alloy particles that can be dissolved in water and treated in a hydrometallurgical PMR (Precious Metals Refinery) process.

31. A process as defined in claim 1 carried out: after a Slow Cooling process, in a Blase Metals Recovery (BMR) process, or in-between a BMR process and a PMR process.