FIRE ASSAY FLUX COMPOSITION FOR THE ANALYSIS OF PGM AND GOLD CONTAINING MINERAL SAMPLES

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ABSTRACT

This invention relates to a novel fire assay flux composition including, inter alia, a dispersant in the form of a source of phosphate; a primary reductant in the form of iron powder comprising particles having a particle size of 60 mesh and finer, at least one basic flux and at least one acidic flux. The fire assay flux composition is useful for the fire assay analysis of Platinum Group Metals and gold in low and medium grade samples such as ores and floatation concentrate including furnace mattes and slags. The invention further extends to the use of such components in the preparation of a fire assay flux composition for fire assay analysis of PGM and gold in low and medium grade samples such as ores and floatation concentrate including furnace mattes and slags.
FIRE ASSAY FLUX COMPOSITION FOR THE ANALYSIS OF PGM AND GOLD CONTAINING MINERAL SAMPLES

[0001] This invention relates to a novel flux composition for use in a fire assay, and particularly for use in fire assay analysis of Platinum Group Metals and gold in low and medium-grade samples such as ores and flotation concentrate including furnace mattes and slags.

BACKGROUND TO THE INVENTION

[0002] Those who are engaged in the extractive metallurgical and pyrochemical industries will appreciate that fire assay is a method of analysing the quantity of precious metals in ores and metallurgical products. Fire assay analysis is commonly employed to collect Platinum Group Metals (hereafter "PGM") and gold for analysis purposes in low-grade samples, such as ores, where the PGM concentration is too low to measure directly.

[0003] PGM and gold fire assay typically involves fusing a finely ground ore sample with a suitable flux, which is generally a lead oxide (litharge) based flux, in the presence of a reductant and at high temperatures (±1200°C). A reaction occurs that liberates the PGM and separation of the precious metals from the gangue is facilitated. More particularly, the litharge in the flux is reduced to minute globules of lead that fall through the melting mass, collecting particles of precious metals, and coalescing as a lead alloy button at the bottom of a crucible. Barren material from the sample, such as chromite and silicate, are dissolved with other components in the flux to form a molten slag. On cooling the slag and lead solidify and the lead button containing the precious metals is mechanically separated. The lead button is then analysed for its PGM or gold content through any one of a variety of methods.

[0004] In traditional fire assays, lead is removed from the lead alloy button through oxidizing fusion (also known as cupellation) to isolate the precious metals from the lead alloy, after which the precious metals so isolated are analysed. However, automated fire assays, which are now being introduced, involve direct analytical measurements of the PGM in the lead alloy button through processes such as spark optical emission spectrometry. It is accordingly of utmost importance that the lead alloy button is free from any unwanted impurities that could interfere with the PGM measurements.

[0005] The selection and proportions of flux components are the most important factors in effecting successful fire assay analysis. From a practical point of view, a flux should be a relatively common, cheap material that does not readily attack a crucible or furnace lining. In addition, factors such as solubility of PGM in the slag and slag viscosity should be borne in mind. Determination of the optimum flux composition requires knowledge of the ore type, an understanding of basic pyrochemical principles, accurate interpretation of phase diagrams, and trial-and-error.

Flux Components

[0006] Traditionally, the main constituents of fluxes for fire assay are sodium carbonate (Na₂CO₃), sodium tetraborate (Na₂B₄O₇), silica (SiO₂) and litharge (PbO), together with some or other reductant. More particularly, traditional fluxes for PGM analysis comprise approximately 40% sodium carbonate, 15% sodium tetraborate, 10% silica and 22-28% litharge. The litharge is reduced by the reductant to form metallic lead, which serves as the PGM carrier, while the sodium carbonate, sodium tetraborate and silica are slag formers. The sodium carbonate, sodium tetraborate and silica form an oxide slag that dissolves silicates and chromites from the ore sample.

[0007] Although traditional fire assays use sodium carbonate, in automated fire assays sodium carbonate has proven to be problematic because of its slow kinetics, resulting in long fusion times. The decomposition of sodium carbonate produces carbon dioxide that is released upon reaction with the sample. During automated analysis, where the flux and/or sample mixture are charged into a hot crucible, the carbon dioxide gas causes spitting of the charge, which results in physical losses of the sample and slag. This is detrimental to the furnace, as the slag is corrosive. Also, the physical losses may impair the accuracy of the assay.

[0008] In an effort to overcome this difficulty, it has been proposed to use sodium hydroxide instead of sodium carbonate in automated fire assay analysis. However, laboratories experience problems with the use of sodium hydroxide, because it is extremely hygroscopic and tends to stick together forming a corrosive alkaline sludge, coating and damaging equipment. As such, the applicant has identified a need to develop a flux for automated fire assays that does not require the use of sodium hydroxide, but at the same time will address the shortcomings associated with the use of sodium carbonate.

[0009] One of the difficulties associated with fire assay analysis is that PbO is a toxic powder. As such, special extraction equipment is necessary in plant environments where PbO is used and operators are required to wear dust masks to prevent inhalation of the toxic dust. Moreover, PbO comprises of fine particles that have poor flow character and tends to choke pipes and equipment in the plant. It is therefore usually necessary to add a binder to the flux composition to granulate the flux for improved handling purposes.

Carbon Reductant

[0010] In fire assay analysis the reductant is typically carbon based and is commonly added in the form of finely powdered wood charcoal, maize meal or flour, and particularly constitutes between 1%-2% of the flux composition. Carbon is a strong reductant that reduces litharge to metallic lead, with the evolution of carbon monoxide and/or carbon dioxide.

[0011] One of the primary difficulties encountered with the use of carbon as primary reductant in automated fire assay analysis is the reporting of impurities in the lead alloy button when fusing sulphide containing silicate samples. More particularly, because carbon is such a strong reductant, it reduces base metals, copper, nickel and sulphur species, present in the sample/slag and introduces high quantities of these into the lead alloy button. These impurities overlap in wavelength with PGM and cause analytical interferences during spark analysis. In addition, high sulphur content in the lead alloy button makes the lead button inhomogeneous so that different analytical readings are obtained at different positions on the button.

Iron Nail Assay

[0012] In an attempt to overcome the disadvantages associated with carbon reductant, it is known in the assay of ores
containing sulphides to effect decomposition of the sulphides by the addition of iron nails, in what is commonly referred to as iron nail assay. In these reactions, the sulphur is reduced by the iron nails to form ferrous sulphide (FeS), which remains in the slag, provided the slag is basic enough.

[0013] A primary disadvantage of iron nail assay is that the process is generally not based on accurate mass-balanced chemical reactions, which results in a host of potential problems. Classical iron nail assay tends to use an excess of iron, commonly in the form of large six-inch iron nails, which are removed prior to casting. In some applications an excess of iron fillings or several small one-inch nails are also used. However, because these iron fillings or iron nails generally do not react completely, it leaves iron impurities in the slag, which cause spectrographic problems in spark analysis. This problem is exacerbated when high chromite content ore samples are fused and accordingly iron nail assay is generally not applied to the analysis of high chromite samples. Therefore, classical fluxes containing iron usually cannot robustly be applied for the analysis of both chromite and silicate sample types. Moreover, too much iron causes formation of refractory iron oxides such as hematite and magnetite in the slag. Excess iron is also problematic in cupellation.

[0014] Iron nail analysis has proved satisfactory with some sulphides, but it is, however, not suitable for samples of high sulphide concentration. With such samples, it often happens that there is not enough iron in the reaction, which causes unacceptable levels of sulphur nevertheless to collect in the lead alloy button. Iron nail assay works reasonably well in traditional, non-automated fire assay, where there is enough time for reactions to occur, but the automation of fire assay analysis, where fusion time is shortened, has precipitated the need to have increasingly controlled pyrochemical conditions.

Chromite Samples

[0015] It will be appreciated that particular challenges are encountered when it comes to analysing ore samples, which are high in chromite content, for their PGM content. Chromite is very refractory and does not fuse easily. Moreover, undissolved chromite retains lead in the slag and the physical loss will result in inaccurate analysis and low analytical bias.

OBJECT OF THE INVENTION

[0016] It is accordingly an object of the present invention to provide a novel flux composition for use in fire assay analysis of PGM and gold that will overcome or alleviate the disadvantages associated with known flux compositions, or at the very least will provide a useful alternative to existing flux compositions of this nature.

[0017] It is particularly an object of the invention to provide a universal flux composition for use in automated fire assay analysis of PGM and gold, and in both silicate and chromite sample types, that will alleviate the prior art problems associated with automated fire assay analysis, but at the same time will be suitable for use in traditional, non-automated fire assay analysis.

[0018] It is another object of the invention to provide a flux composition for automated fire assay analysis of PGM and gold in sulphide containing silicate samples that will overcome or at least alleviate the problems associated with reporting of sulphur species in a lead alloy button.

[0019] It is a further object of the invention to provide a flux composition suitable for automated fire assay analysis of PGM and gold that will reduce base metals in the lead alloy button and physical losses of lead associated with high chromite slags.

[0020] It is yet another object of the invention to provide a flux composition for fire assay analysis of PGM and gold with improved flow character and handling properties that will alleviate the prior art problems associated with choking.

SUMMARY OF THE INVENTION

[0021] The applicant anticipates that the flux composition according to the invention would be equally suitable for use in fire assay analysis of PGM and gold and accordingly any reference to PGM in the specification should be interpreted also to be a reference to gold.

[0022] The applicant refers to the size of a particle by means of a mesh size. The term mesh herein refers to the classification of a collection of particles according to a range of sizes of such particles, and is derived from the sizes of the opening in standard or test sieves used for classifying such particles. For present purposes the United States standard, namely the Tyler designation, was used and all test screens were metric and the nearest equivalent mesh size was taken.

[0023] Classification is to be understood as the process in which two or more sieves are used to separate specific cuts of particles that have sizes falling in a particular size range, from a body of particles having a larger size range.

[0024] It will be appreciated that the expression of particle size by reference to mesh size is more practical from a commercial/industrial perspective, wherein a person wanting to identify whether a body of particles has a particular particle size would employ the classification process as discussed herein.

[0025] According to a first aspect of the invention there is provided a fire assay flux composition for fire assay analysis of PGM and gold, the flux composition comprising a dispersant in the form of a source of phosphate.

[0026] The composition may include between 0.1% and 12% (m/m of total composition) phosphate, and preferably may include 1.0% (m/m of total composition) phosphate.

[0027] The source of phosphate may be monopotassium phosphate, although the applicant anticipates that the source of phosphate may be selected from the group consisting of potassium phosphates, sodium phosphates, lithium phosphates, their poly phosphates and their hydrates. The potassium phosphates may be in the form of di-potassium and tri-potassium phosphates and indeed any potassium polyphosphate such as potassium pyrophosphate.

[0028] The invention particularly provides a fire assay flux composition for automated fire assay analysis of PGM and gold in low-grade samples with high chromite content, wherein the flux composition comprises a source of phosphate.

[0029] The flux composition also may include iron powder with a particle size of 60 mesh or finer, and preferably with a particle size of 100 mesh, as a primary reductant. The flux composition may include between 0.5% (m/m of total composition) and 5% (m/m of total composition) iron powder, and preferably may include 2.2% (m/m of total composition) iron powder. The iron powder may be used in the presence of a basic fire assay slag.

[0030] In a preferred form of the invention, the iron powder is preferably of a high purity, typically being 99% pure and
having less than 10 ppb (ng.g\(^{-1}\)) of impurities such as platinum, palladium, gold, rhodium, ruthenium and iridium.

[0031] The flux composition may include a secondary reductant selected from the group comprising carbon, magnesium, calcium, silicon and aluminum. In a preferred form of the invention, the secondary reductant is carbon and more particularly powdered steam activated carbon having a particle size of 70 mesh or finer. The flux composition may include between 0.01% (m/m of total composition) and 1.0% (m/m of total composition) powdered steam activated carbon, and preferably may include 0.3% (m/m of total composition) powdered steam activated carbon.

[0032] The flux composition may also include at least one basic flux as well as at least one acidic flux. The at least one basic flux may be selected from the group consisting of sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, lime (calcium oxide), calcium carbonate, calcium hydroxide, bismuth oxide (Bi₂O₃) and lead oxide (PbO). The at least one acidic flux may be selected from the group consisting of boric acid, sodium tetraborate, sodium carbonate, potassium carbonate, and potassium phosphates, sodium and potassium sulfates, alumina, silica, calcium silicates and sodium metasilicate calcium/sodium silicate glasses.

[0033] In a preferred form of the invention, sodium carbonate and PbO may be included as the basic fluxes and all of boric acid, sodium tetraborate, silica and sodium metasilicate may also be included as the acidic fluxes.

[0034] More particularly, the flux composition may include boric acid as a partial substitute for traditionally used sodium tetraborate. More specifically, the composition may include between 0.1% (m/m of total composition) and 12% (m/m of total composition) boric acid, and preferably may include 0.9% boric acid. The flux composition may include between 5% (m/m of total composition) and 20% (m/m of total composition), and preferably may include only 13.4% (m/m of total composition) sodium tetraborate.

[0035] The flux composition may also include sodium metasilicate as a substitute for traditionally used silica and sodium carbonate. More particularly, the composition may include between 5% (m/m of total composition) and 40% (m/m of total composition) sodium metasilicate, and preferably may include 16.8% (m/m of total composition) sodium metasilicate.

[0036] The flux composition may be characterized therein that it includes an excess quantity of PbO of between 15% (m/m of total composition) and 80% (m/m of total composition) PbO, and preferably may include 27% (m/m of total composition) PbO.

[0037] The flux composition may also additionally include between 5% (m/m of total composition) and 40% (m/m of total composition) and preferably approximately 18.5% (m/m of total composition) sodium carbonate.

[0038] In a preferred form of the invention, the primary and secondary reductants, together with the at least one basic oxide flux and the at least one acid oxide flux may be granulated to form a plurality of granules. At least 80% of the granules so formed have a particle size of between 12 mesh and 32 mesh.

[0039] It is also preferable, but not necessary, to co-granulate the dispersant in the form of a source of phosphate with the primary and secondary reductants as well as at least one basic oxide flux and at least one acid oxide flux.

[0040] In one embodiment of the invention, the fire assay flux composition may be provided in the form of granules. In another embodiment of the invention, and wherein components are included which are not co-granulated, the fire assay flux composition may comprise a granular portion and the components, which components are blended together with the granules. It will be appreciated that in alternate embodiments of the invention, the flux composition may be in powder form.

[0041] In a modified form of the invention, the fire assay flux composition also may include one or more hydrates characterized therein that they have very low melting points, typically below 100°C, so as to dehydrate rapidly to form a barrier to gas movement in the charge, which hydrates may be selected from a group including, although not limited to, hydrated compounds of the various sodium, potassium and lithium silicates and/or borates; hydrated phosphate compounds, such as dibarium hydrogen orthophosphate trihydrate (K₂HPO₄·3H₂O); hydrated carbonates, such as sodium carbonate decahydrate (Na₂CO₃·10H₂O); and their derivatives.

[0042] The hydrates may have a particle size between 32 mesh and 150 mesh, and are preferably blended together with granules as herein before described.

[0043] In an embodiment of the invention, the fire assay flux composition may include sodium metaborate tetrahydrate and sodium perborate tetrahydrate, added in combination. The particle size of the sodium metaborate tetrahydrate and sodium perborate tetrahydrate is between 32 mesh and 60 mesh. More particularly, the composition may include between 0.5% and 20% (m/m of the total composition) sodium metaborate tetrahydrate, and preferably 4.0% (m/m of the total composition); as well as between 0.5% and 5.0% sodium perborate tetrahydrate; and preferably 1.0% (m/m of the total composition).

[0044] In another embodiment of the invention, the fire assay flux composition may include sodium tetraborate decahydrate and sodium metasilicate pentahydrate, added in combination. The particle size of the sodium tetraborate decahydrate is between 48 mesh and 150 mesh, while the particle size for the sodium metasilicate pentahydrate is between 32 mesh and 60 mesh. At least 80% of the particles fall within the above mesh ranges. More particularly, the composition may include between 0.5% and 20% (m/m of the total composition) sodium tetraborate decahydrate, and preferably 9.0% (m/m of the total composition); as well as between 0.5% and 20% sodium metasilicate pentahydrate; and preferably 4.0% (m/m of the total composition).

[0045] According to a second aspect of the invention there is provided a fire assay flux composition for use in fire assay analysis of PGM and gold containing samples, the flux composition comprising high purity iron powder with a particle size of 60 mesh or finer, and preferably with a particle size of 100 mesh, as a primary reductant. The flux composition may include between 0.5% and 5% (m/m of total composition) iron powder, and preferably may include 2.3% (m/m of total composition) iron powder. The iron powder may be used in the presence of a basic fire assay slag.

[0046] According to a third aspect of the invention there is provided a fire assay flux composition for use in fire assay analysis of PGM and gold containing samples, the flux composition comprising between 0.1% (m/m of total composition) and 12% (m/m of total composition) boric acid, and preferably 0.5% (m/m of total composition) boric acid as a partial substitute for sodium tetraborate. The flux composi-
tion accordingly may include only approximately 13.4% (m/m of total composition) sodium tetraborate.

[0047] The invention extends to the use of any one or more of a phosphate, and preferably monopotassium phosphate; high purity iron powder with a particle size of 60 mesh or finer, and preferably with a particle size of 100 mesh; powdered activated carbon with a particle size of 70 mesh or finer; boric acid; hydrates, as herein before described and/or sodium metasilicate in the preparation of a flux composition for fire assay analysis of PGM and gold containing samples, and particularly for automated fire assay analysis of PGM and gold in low grade samples.

[0048] The invention also extends to the use of high purity iron powder with a particle size of 60 mesh or finer, and preferably with a particle size of 100 mesh and as a primary reductant in a flux composition for fire assay analysis of PGM and gold of high chromite content samples.

[0049] The invention also includes the use of between 0.1% (m/m of total composition) and 12% (m/m of total composition) boric acid, and preferably 0.9% (m/m of total composition) boric acid, as a granulator in a flux composition for automated fire assay analysis of PGM and gold containing samples.

SPECIFIC EMBODIMENT OF THE INVENTION

[0050] Without limiting the scope thereof, three embodiments of the invention will now be described by way of the following examples.

Example 1

[0051] The applicant prepared a flux composition for fire assay analysis of PGM and gold according to the following formulation.

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical formula</th>
<th>% of total flux composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead oxide</td>
<td>PbO</td>
<td>32.0</td>
</tr>
<tr>
<td>High purity iron powder</td>
<td>Fe</td>
<td>2.6</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>C</td>
<td>0.4</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>24.0</td>
</tr>
<tr>
<td>Sodium tetraborate</td>
<td>Na₄B₆O₁₅</td>
<td>19.0</td>
</tr>
<tr>
<td>Sodium metasilicate (anhydrous)</td>
<td>Na₂SiO₃</td>
<td>20.0</td>
</tr>
<tr>
<td>Boric acid</td>
<td>H₃BO₃</td>
<td>1.0</td>
</tr>
<tr>
<td>Monopotassium phosphate</td>
<td>K₂HPO₄</td>
<td>1.0</td>
</tr>
</tbody>
</table>

[0052] The real test of a flux is the ability to get a known value on a reference sample. Often the preferred choice is SARM 7B, which is a Merensky Reef sample derived from the South African Bushveld Complex and which is a platinum bearing ore. The method to test the flux can affect the results and these parameters ideally need to be similar.

[0053] For the testing of this flux composition, the individual components were weighed out and blended together in a drum mixer. The powdered flux composition was then blended with approximately 6% by mass of water and mixed thoroughly to form small granules. The granules were screened through a 2 mm screen and dried overnight in steel pans at 140° C., after which the dry granules were blended together. Boric acid was included in the flux composition so as to facilitate the granulation.

[0054] A mass of 50 g sample material was weighed out and mixed with 250 g of the flux composition. The mixture was charged into a pre-heated fire clay crucible, which was closed with a ceramic lid and loaded into a bottom loading fusion furnace with a set temperature of 1200° C. The charge was allowed to fuse for 15 minutes after which the charge was cast and the liquids separated. A rapidly chilled lead disc was prepared in this fashion.

[0055] The lead disc was weighed and its surface milled before it was analysed for its chemical content using spark optical emission spectrometry. From the PGM content of the lead disc and its mass, the content of the original sample was determined. In addition to the PGM content, the unwanted base metal impurities in the lead sample were also determined. The results for the reference material are summarised in the table below.

<table>
<thead>
<tr>
<th>Component</th>
<th>Pt grade/ g ton⁻¹</th>
<th>Pd grade/ g ton⁻¹</th>
<th>Au grade/ g ton⁻¹</th>
<th>Rh grade/ g ton⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analyzed</td>
<td>3.71 ± 0.2</td>
<td>1.58 ± 0.08</td>
<td>0.33 ± 0.16</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>Certified</td>
<td>3.74 ± 0.045</td>
<td>1.53 ± 0.032</td>
<td>0.31 ± 0.015</td>
<td>0.24 ± 0.013</td>
</tr>
</tbody>
</table>

[0056] There is good agreement of the analysis using the new flux composition with the accepted values for this reference material.

[0057] For the evaluation of the base metal impurities the same Merensky feed sample was analysed after fusing with different fluxes.

<table>
<thead>
<tr>
<th>Lead impurities</th>
<th>Cu/ ppm</th>
<th>Ni/ ppm</th>
<th>S/ ppm</th>
<th>S % RSD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>New flux composition</td>
<td>428</td>
<td>420</td>
<td>260</td>
<td>0.7</td>
</tr>
<tr>
<td>Classical flux composition 1</td>
<td>393</td>
<td>437</td>
<td>508</td>
<td>12.8</td>
</tr>
<tr>
<td>Classical flux composition 2</td>
<td>610</td>
<td>891</td>
<td>956</td>
<td>30.7</td>
</tr>
</tbody>
</table>

* S % RSD = percentage relative standard deviation

[0058] Despite collecting the PGM in a smaller mass of lead with the new flux composition, the concentration of the base metal impurities from the sample in the lead was lower for the new flux composition for sulphur and nickel where the opposite would be expected. This is as a result of the greater selectivity of the iron reductant for the new flux composition. The classical flux composition contained only carbon as a reductant. The classical flux composition 2 was fused in a similar manner to the new flux composition while the classical flux composition 1 was fused with the traditional method using cold crucibles in a large front-loading fire assay furnace at 1200° C. for 60 minutes.

[0059] The lowered sulphur content of the sample improved the homogeneity of the spark analysis as was depicted by the percentage relative standard deviation (% RSD) agreement between the spark analyses from different parts of the sample. The greater homogeneity ensures greater accuracy of the analysis.

[0060] The fineness of the iron reductant was investigated with a controlled experiment to examine the effect of the iron impurity in the collector after a 15-minute fusion as explained above. A 100-mesh iron powder was found to be the most
efficient reductant for the application as there were no unreacted iron impurities in the lead collector. While the finer iron powder tended to be carried away with the off gas yielding a slightly smaller lead mass, it was nevertheless efficient and the analysis was accurate. The most usable forms of iron appear to be 60 mesh or finer.

<table>
<thead>
<tr>
<th>Iron powder</th>
<th>Top size/µm</th>
<th>Lead mass/g</th>
<th>Fe impurity/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 mesh</td>
<td>75</td>
<td>51.4</td>
<td>0</td>
</tr>
<tr>
<td>100 mesh</td>
<td>150</td>
<td>51.8</td>
<td>0</td>
</tr>
<tr>
<td>18 mesh (filings)</td>
<td>850</td>
<td>51.5</td>
<td>32</td>
</tr>
</tbody>
</table>

The iron impurity in the lead collector is essential when analysing the lead collector using spark analysis for the PGM as it is a major source of analytical interference which, because of the poor solubility and inhomogeneity of iron in the lead collector, is difficult to correct for. This is the reason why iron nails or iron filings are not used for this application.

The iron powder is the primary reductant because it is a good reductant for sulphides present in PGM ores: it selectively removes sulphur as iron sulphide (FeS₂), which dissolves in basic fire assay slags. This helps to remove the sulphur as an impurity in the lead collector phase, and also reduces copper and nickel impurities in the lead. Moreover, the selective removal of these impurities also reduces losses during cupellation because of less scoria formation (due to nickel removal), surface tension and absorption problems (associated with sulphur). However, an excess of iron powder will cause problems resulting from the formation of iron oxide such as haematite and magnetite in the slag and usually increased iron oxide scoria formation during cupellation. It is therefore essential that a controlled percentage is added to the formulation.

The iron powder is used in the presence of a basic flux that reacts with the acidic portions of the flux composition to form a sodium-oxide slag. Sodium carbonate is the traditional choice as a sodium oxide source, but problems can arise from the excessively rapid carbon dioxide evolution at high temperatures. Therefore, the addition is kept as low as possible, and some of the sodium carbonate is substituted with sodium metasilicate to help control gas evolution while retaining slag basicity. A measure of sodium carbonate and carbon dioxide evolution is required for efficient mixing, but needs to be controlled to avoid spitting and frothing of the charge during fusion.

The applicant has found that the use of monopotassium phosphate is particularly beneficial in the analysis of chromite samples, as it prevents adhesion of chromite grains in the slag that form agglomerates in the traditional methods. This prevents the losses of the lead collector to the slag, which is essential for accurate analysis. Monopotassium phosphate is the preferred choice due to its low melting point, but the applicant anticipates that di-potassium, tri-potassium phosphates, potassium poly-phosphates such as potassium pyrophosphate, their hydrates and their sodium and lithium phosphate variants could also work.

The applicant has elected to add sodium metasilicate as a partial substitute for traditionally used silica, because it is not as acidic as silica and requires the use of less sodium carbonate. Sodium metasilicate facilitates control of the fusion when charging into a preheated crucible for automation, and also accelerates the fusion process.

Boric acid, which is an acidic fire assay flux, has been used because of its low melting point and because it acts as a coagulant in the early part of the fusion, especially when charging into a hot crucible for automation. It also acts as a binding agent and is useful for granulation purposes.

It will be apparent from the above formulation, that the applicant has used an excess percentage of PbO as it has good thermal properties for heat conduction, promoting a faster fusion. Classical fluxes for PGM run with compositions having 22-28% PbO.

The powdered activated carbon of 70 mesh or finer was added as a secondary reductant to ensure a consistent button size. Powdered activated carbon is preferred to more classical reductants such as flour and maize meal, but it should be borne in mind that the carbon could be substituted by one or more of the elements selected from a group including magnesium, calcium, silicon and aluminum.

Example 2

After successfully testing the flux composition of the universal flux of Example 1, it was discovered that a few QC samples derived from the UG2 reef displayed anomalous behaviour. The results from some of these QC samples tended to give lower analytical results on palladium and rhodium. Examining this phenomenon carefully, it was discovered that the very fine nature of these carefully prepared QC materials meant that the sample material had been ground very fine, producing a substantial percentage of sample particles of less than 1 µm in diameter.

During fusion for the automated analysis application, while dosing the material into a hot crucible, there were some dust losses as air was expelled from the mixture while charging the crucible and during the early stages of the fusion. This ultra fine material was captured in the chimney of the furnace and was being removed from the charge. Unfortunately, even though the mass loss was relatively insignificant (in the order of only 100 mg), the ultra-fine material from the UG2 is characterized with higher concentrations of the PGM compared to the bulk of the sample. This resulted in losses of the PGM during the fusion and a low bias of the analytical result. This phenomenon was never observed in any of the silicate samples.

The effect was considerably reduced when a powdered form of the flux composition was used however this lead to problems with regard to the handling of the flux composition in the automated system due to the poor flow characteristics of the flux composition in powder form. The applicant identified that while changes were required to the flux composition to prevent these losses and retain the ultra fine portions of the sample, granules would still have to be used.

Accordingly, after some investigation it was decided to try various fine flux components to be blended with the granules, comprising the components set out in Example 1, so as to provide a flux composition which included a granular portion and the additional components blended therewith. The fluxes, potassium phosphate, boric acid, sodium metaborate tetrahydrate and potassium nitrate were used first to try to prevent the dust losses. These compounds have various melting points lower than normal standard fire assay fluxes such as sodium tetraborate and sodium carbonate.
It was discovered that the boric acid and potassium phosphate helped to reduce the effect of the dusting and results improved. However, the sodium metaborate tetrahydrate was extremely efficient in preventing the losses completely. Upon examining the melting point of the compound, it was surprisingly found that the crystals melt in their own water of crystallization, forming a porous mass (much like popcorn) that trapped the sample within the charge, thereby preventing dusting losses. This was in contrast to what was expected as the H₂O(g), given off by the compound as it rapidly dries, was expected to increase the dusting losses.

The applicant expects that a host of suitable compounds would perform this function, including hydrates of the various sodium, potassium and lithium silicates, as well as any number of the hydrated compounds of the sodium, potassium and lithium borates. Similarly, the hydrated phosphate compounds, such as di-potassium hydrogen orthophosphate tri-hydrate (K₂HPO₄·3H₂O), and the carbonates such as sodium carbonate deci-hydrate (Na₂CO₃·10H₂O), as well as their derivatives may all be suitable for this application. Needless to say there may be many other hydrated compounds that will be suitable for this function, but the key is that the compound should have a very low melting point due to its water of crystallization, which will dehydrate rapidly forming a barrier to gas movement in the charge. This prevents the dust loss during the charging and early stages of the fusion that may bias the result.

The two compounds that have been identified to be best suited to this application are the sodium metaborate tetrahydrate and sodium perborate added in combination. The sodium perborate tetrahydrate is very similar in behaviour to the sodium metaborate tetrahydrate, but it is a mild oxidant and adds additional selectivity in the base metal impurity removal from the lead during the fusion. Sodium metaborate (NaB₃O₃), once it is dehydrated, has very favourable thermodynamic properties, as its heat capacity is low. Therefore, it may promote conduction of heat into the charge. This is illustrated in the graph below:
To facilitate the change in the flux composition, the composition as set out in Example 1 was modified slightly to accommodate the addition of sodium metaborate tetrahydrate and sodium perborate tetrahydrate. Some of the sodium carbonate and sodium tetraborate were substituted with these compounds. However the final slag composition after the fusion was unchanged by this modification.

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical formula</th>
<th>% Comp.</th>
<th>% Comp. range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead oxide</td>
<td>PbO</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td>Iron powder</td>
<td>Fe</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>C</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>Sodium tetraborate</td>
<td>Na₂B₄O₇</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>Sodium metasilicate</td>
<td>Na₂SiO₃</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>Boric acid</td>
<td>H₃BO₃</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Monopotassium phosphate</td>
<td>K₂HPO₄</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Sodium metaborate tetrahydrate</td>
<td>Na₂B₄O₇·4H₂O</td>
<td>4.0</td>
<td>0.5-20.0</td>
</tr>
<tr>
<td>Sodium perborate</td>
<td>NaBO₂·4H₂O</td>
<td>1.0</td>
<td>0.5-5.0</td>
</tr>
</tbody>
</table>

The bulk of the flux components were weighed and blended together, wetted with water and thoroughly mixed to form granules. The wet granules were forced through a 2 mm wedge wire screen and the resulting granules were dried. Thereafter the powdered sodium metaborate and sodium perborate were blended with the granules. Addition of the powdered flux was a total of 10% of the flux mass, while additions of up to 20% of the total flux mass are feasible, although conceivably this could be as high as 64% with only the lead and reductant components along with the boric acid being granulated.

A mass of 250 g of the flux composition as described above was weighed out and blended with 40 g of sample material. This mixture was added to a pre-heated pot and fused for 15 minutes at a set temperature of 1200° C. The molten material was cast into an iron mould and cooled. The lead was mechanically separated from the slag and the remaining slag was leached off the lead using dilute hydrochloric acid. The lead was washed with water and dried.

A disc was formed by pressing the lead in a die with a hydraulic press. The disc was subsequently milled and analyzed, using spark optical emission spectrometry. The grade of the ore was calculated from the lead mass, concentration of PGM in the lead and the sample mass. The results from the UG2 reference materials SARM 65 and 72 were compared to the consensus values and showed excellent agreement. In addition, the Merensky sample SARM 7B was also analyzed and showed superb agreement, satisfying the requirements as a universal flux composition for the analysis of both UG2 (chromite) and Merensky (silicate) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt grade/ g.ton⁻¹</th>
<th>Pd grade/ g.ton⁻¹</th>
<th>Rh grade/ g.ton⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>SARM 65</td>
<td>2.76</td>
<td>1.28</td>
<td>0.53</td>
</tr>
<tr>
<td>SARM 7B</td>
<td>3.82</td>
<td>1.53</td>
<td>0.24</td>
</tr>
<tr>
<td>SARM 72</td>
<td>3.88</td>
<td>4.13</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Addition of sodium metaborate as a solution to the compounds. However the final slag composition after the fusion was unchanged by this modification. In addition, the Merensky sample SARM 7B was also analyzed and showed superb agreement, satisfying the requirements as a universal flux composition for the analysis of both UG2 (chromite) and Merensky (silicate) samples.

Further example of a flux composition according to the invention is set out below.

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical Formula</th>
<th>% Composition (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead Oxide</td>
<td>PbO</td>
<td>33.70</td>
</tr>
<tr>
<td>Iron Powder</td>
<td>Fe</td>
<td>2.70</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>C</td>
<td>0.4</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
<td>22.0</td>
</tr>
<tr>
<td>Sodium tetraborate</td>
<td>Na₂B₄O₇</td>
<td>16.80</td>
</tr>
<tr>
<td>Sodium metasilicate</td>
<td>Na₂SiO₃</td>
<td>20.00</td>
</tr>
<tr>
<td>Boric acid</td>
<td>H₃BO₃</td>
<td>1.10</td>
</tr>
<tr>
<td>Monopotassium phosphate</td>
<td>K₂HPO₄</td>
<td>1.10</td>
</tr>
</tbody>
</table>

As in the case of example 2, the bulk of the components above were weighed and blended together, wetted with water and thoroughly mixed to form granules. More particularly it is preferable to sandwich the lead oxide, iron powder and activated carbon between the other components for efficient mixing of the more dense components.

The components were added to a mixer, which is to be sealed after addition in order to prevent loss of any of the components, in the following order: sodium carbonate, sodium tetraborate, lead oxide, activated carbon, iron powder, sodium silicate, potassium phosphate and boric acid.

The above components were then dry blended until a homogeneous powdered mixture was formed, after which about 8% to 11% water by mass was added to form the desired granules. Preferably the water is to be added as a fine mist.)

The granules were then screened through a screen having a mesh size of 2 mm and then subsequently dried until the moisture content thereof was reduced to less than 1% of water by mass. The drying was effected by convection heating the granules at a temperature of from 100° C. to 140° C., and
typically at 105°C for a period of 2 hours. It is important that the granules be checked so that at least 80% of the granules so formed have a particle size of between 32 mesh and 12 mesh.

The granules so formed are then blended with the following components to provide the fire assay flux composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Chemical Formula</th>
<th>% Composition (m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granules prepared as above</td>
<td>—</td>
<td>80.00</td>
</tr>
<tr>
<td>Sodium tetraborate decahydrate</td>
<td>Na₄B₄O₆·10H₂O</td>
<td>9.00</td>
</tr>
<tr>
<td>Sodium metasilicate pentahydrate</td>
<td>Na₂SiO₅·5H₂O</td>
<td>4.00</td>
</tr>
<tr>
<td>Silica</td>
<td>SiO₂</td>
<td>7.00</td>
</tr>
</tbody>
</table>

The sodium tetraborate decahydrate and sodium metasilicate pentahydrate were screened through a 0.5 mm screen to remove or break up lumps or agglomerates. It is important that at least 80% of the particles of the sodium tetraborate decahydrate have a particle size of between 48 mesh and 150 mesh. It is further important that at least 80% of the particles of the sodium metasilicate pentahydrate have a particle size of between 32 mesh and 60 mesh.

The sodium tetraborate decahydrate, sodium metasilicate pentahydrate and silica were added on top of the dry granules in a mixer and blended to ensure a uniform distribution so as to provide the fire assay flux composition having a granular portion and the additional components being blended therewith.

The flux material prepared above was used in an automated fire assay laboratory to test the comparability of the material with the flux dosing systems and general handling. The trials that were carried out also tested for the accuracy of the system as certified reference materials were analysed. The reference materials were SARM 72 (South African Reference Material), a UG2 ore sample from the Bushveld Complex, AMIS 5 and 10 (African Mineral Standard) also UG2 ore samples from the Bushveld Complex and finally AMIS 7 and AMIS 10 ore samples from the Merensky reef of the Bushveld Complex. These reference materials are representative of typical platinumiferous ores.

The robotic system comprised a sample fluxing machine, fusion furnace, a molten slag/collector separator with a water cooled mould. Samples were introduced into the system and the analysis was fully automated with sample manipulation being performed with an articulated robot. An automated spark optical emission spectrometer was used at the end of the system to analyse the lead disc from the fusion circuit in the automated laboratory.

A mass of 300 grams of flux composition was dosed with the fluxing machine. The system added 2 doses of sample (30-50 grams) and the sample/flux composition mixture were mixed for 60 seconds. The system discharged the flux composition/sample mixture into a preheated alumina crucible. The flux composition/sample mixture was fused in an automated bottom loading furnace for 16 minutes with a temperature of 1260°C. The molten mixture was then cast into an automated separator device which physically separated the molten glass slag and the metallic lead collector. The lead was received in a water cooled mould and rapidly quenched. The solid lead disc so formed was then transported with a belt to a spark optical emission spectrometer. The lead disc was weighed, milled and then analysed using spark optical emission spectrometry. The grade of the sample was calculated from the concentration measured in the lead specimen, the sample mass and the mass of the lead disc.

The results obtained are tabulated below:

<table>
<thead>
<tr>
<th>Analyzed values</th>
<th>Reference values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt grade/ g/ton⁻¹</td>
<td>Pt grade/ g/ton⁻¹</td>
</tr>
<tr>
<td>AMIS 0005</td>
<td>3.473</td>
</tr>
<tr>
<td>AMIS 0010</td>
<td>2.144</td>
</tr>
<tr>
<td>AMIS 0007</td>
<td>2.515</td>
</tr>
<tr>
<td>SARM 72</td>
<td>4.083</td>
</tr>
</tbody>
</table>

The results analysed for the reference materials showed good agreement with the reference values for these materials and were typically within the 95% confidence intervals specified for them. The handling and feeding of the flux composition in the robotic system was seamless without any significant problems. In this manner it was determined that the granulated universal flux composition was compatible with the automated system and produced accurate quantitative analysis of ore samples.

It will be appreciated that many other embodiments of the invention may be possible without departing from the spirit or scope of the invention as set out in the consistory clauses hereinbefore.

1-32. (canceled)
33. A PGM fire assay flux composition including:
   a. a reductant in the form of iron powder comprising iron particles having a particle size of 60 mesh or finer;
   b. at least one basic flux and at least one acidic flux; and
   c. a dispersant in the form of a source of phosphate.
34. The fire assay flux composition of claim 33, wherein the iron powder is a primary reductant.
35. The fire assay flux composition of claim 33, wherein the phosphate is present in the amount of between 0.1% and 12% (m/m of total composition).
36. The fire assay flux composition of claim 33, wherein the source of phosphate is selected from the group consisting of potassium phosphates, sodium phosphates, lithium phosphates, their poly phosphates and their hydrates.
37. The fire assay flux composition of claim 33, wherein the source of phosphate is monopotassium phosphate.
38. The fire assay flux composition of claim 34, wherein the iron powder has a purity of at least 99% and less than 10% purity.
ppb (ng·g⁻¹) of impurities such as platinum, palladium, gold, rhodium, ruthenium and iridium.

39. The fire assay flux composition of claim 34, wherein the iron powder is present in the amount of between 0.5% and 5% (m/m of the total composition).

40. The fire assay flux composition of claim 33, wherein at least one hydrate is included, the at least one hydrate having a melting point of below 100°C.

41. The fire assay flux composition of claim 40, wherein the at least one hydrate has a particle size of between 32 mesh and 150 mesh.

42. The fire assay flux composition of claim 40, wherein the at least one hydrate is selected from the group consisting of sodium, potassium and lithium silicates; sodium, potassium and lithium borates; hydrated phosphate compounds and their derivatives.

43. The fire assay flux composition of claim 40, wherein the at least one hydrate is selected from the group consisting of sodium metaborate tetrahydrate, sodium perborate tetrahydrate, sodium tetraborate decahydrate and sodium metasilicate pentahydrate.

44. The fire assay flux composition of claim 43, wherein a first hydrate in the form of sodium metaborate tetrahydrate and a second hydrate in the form of sodium perborate tetrahydrate is included in the amounts of between 0.5% and 20% (m/m of the total composition) and between 0.5% and 5.0% (m/m of the total composition) respectively and each having 80% of particles between 32 and 60 mesh respectively.

45. The fire assay flux composition of claim 43, wherein a first hydrate in the form of sodium tetraborate decahydrate and a second hydrate in the form of sodium metasilicate pentahydrate is included in the amounts of between 0.5% and 20% (m/m of the total composition) and between 0.5% and 20% (m/m of the total composition) respectively and each having 80% of particles between 48 and 150 mesh and 32 and 60 mesh respectively.

46. The fire assay flux composition of claim 43, wherein a secondary reductant selected from the group consisting of carbon, magnesium, calcium, silicon and aluminium is included.

47. The fire assay flux composition of claim 46, where the secondary reductant is powdered steam activated carbon.

48. The fire assay flux composition of claim 47, wherein the powdered steam activated carbon has a particle size of 70 mesh or finer.

49. The fire assay flux composition of claim 47, wherein between 0.01% and 1.0% (m/m of the total composition) of powdered steam activated carbon is included.

50. The fire assay flux composition of claim 33, wherein the at least one basic flux is selected from the group consisting of sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, lime (calcium oxide), calcium carbonate, calcium hydroxide, bismuth oxide (Bi₂O₃) and lead oxide (PbO).

51. The fire assay flux composition of claim 33, wherein the at least one acidic flux is selected from the group consisting of boric acid, sodium tetraborate, sodium metaborate, sodium and potassium phosphates, sodium and potassium sulphates, alumina, silica, calcium silicates and sodium metasilicate calcium and sodium silicate glasses.

52. The fire assay flux composition of claim 33, wherein the following additional components are included:
   a. between 0.1% (m/m of the total composition) and 12% (m/m of the total composition) of boric acid;
   b. between 5% (m/m of the total composition) and 40% (m/m of the total composition) of sodium tetraborate;
   c. between 5% (m/m of the total composition) and 40% (m/m of the total composition) of sodium metasilicate;
   d. between 15% (m/m of the total composition) and 80% (m/m of the total composition) of lead oxide; and
   e. between 5% (m/m of the total composition) and 40% (m/m of the total composition) of sodium carbonate.

53. The fire assay flux composition of claim 33, wherein the primary reductant is co-granulated with a secondary reductant, at least one basic flux and at least one acidic flux to form granules having a particle size of between 12 mesh and 32 mesh.

54. The fire assay flux composition of claim 53, wherein at least 80% of the granules have a particle size of between 12 mesh and 32 mesh.

55. The fire assay flux of claim 33, wherein the primary reductant and the dispersant are co-granulated with a secondary reductant, at least one basic flux and at least one acidic flux to form granules having a particle size of between 12 mesh and 32 mesh.

56. Use of a dispersant in the form of a source of phosphate in the preparation of a fire assay flux composition for fire assay analysis of PGM and gold containing samples, wherein the fire assay flux composition includes:
   a. a reductant in the form of iron powder comprising iron particles having a particle size of 60 mesh or finer; and
   b. at least one basic flux and at least one acidic flux.

57. Use of iron powder comprising particles having a particle size of 60 mesh or finer in the preparation of a fire assay flux composition for fire assay analysis of PGM and gold containing samples, wherein the fire assay flux composition includes:
   a. a dispersant, in the form of a source of phosphate; and
   b. at least one basic flux and at least one acidic flux.

58. The use of claim 57, wherein a controlled amount of iron powder is provided, the amount being between 0.5% and 5% (m/m) of the total fire assay flux composition.

59. Use of hydrates having a melting point of below 100°C. in the preparation of a fire assay flux composition for the automated fire assay analysis of ores and other samples for the determination of PGMs and gold containing samples, wherein the fire assay flux composition includes:
   a. a reductant in the form of iron powder comprising iron particles having a particle size of 60 mesh or finer;
   b. a dispersant, in the form of a source of phosphate;
   c. at least one basic flux and at least one acidic flux; and
   wherein the reductant, dispersant, the at least one basic flux and the at least one acidic flux are co-granulated into granules having a particle size of between 12 mesh and 32 mesh.

60. Use of boric acid in the preparation of a fire assay flux composition for automated fire assay analysis of PGM and gold containing samples, wherein the fire assay flux composition includes:
   a. a reductant in the form of iron powder comprising iron particles having a particle size of 60 mesh or finer;
   b. a dispersant, in the form of a source of phosphate;
   c. at least one basic flux and at least one acidic flux; and
   wherein the boric acid is used as a granulator so as to co-granulate the reductant, the dispersant, the at least one basic flux and the at least one acidic flux into granules having a particle size of between 12 mesh and 32 mesh.
61. Use of the following components in the preparation of a fire assay flux composition for automated fire assay analysis of PGM and gold containing samples:
   a. iron powder in the amount of between 0.5% and 5% (m/m of the total composition) comprising particles having a particle size of 60 mesh and finer, as a primary reductant;
   b. monopotassium phosphate in the amount of between 0.1% and 12% (m/m of the total composition) as a dispersant;
   c. powdered steam activated carbon in the amount of between 0.01% (m/m of the total composition) and 0.1% (m/m of the total composition) having a particle size of 70 mesh or finer, as a secondary reductant; and
d. boric acid in the amount of between 0.1% (m/m of the total composition) and 12% (m/m of the total composition) as a granulator.
62. The use of claim 61, wherein at least one hydrate having a melting point of below 100° C. is used.
   * * * * *