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REPUBLIC OF SOUTH AFRICA

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THE PATENTS ACT, 1952, AS AMENDED

APPLICATION FOR A PATENT.

(WITH AUTHORISATION OF AGENT)

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I/We do hereby declare that I am/we are in possession of an invention the title of which is

"A PROCESS FOR THE TREATMENT OF MIXTURES OF PLATINUM GROUP METALS AND GOLD"

I/We are the assignee(s)/legal representative(s) of the inventor(s). To the best of my/our knowledge and belief there is no lawful ground of objection to the grant of a patent to me/us on this application and I/we pray that a patent may be granted to me/us for the invention.

I/We enclose the provisional/complete specification.

I/We hereby appoint the partners and qualified staff of the firm of W. E. JOHN & KERNICK, jointly and severally, to act for me/us in all matters relating to this application and any letters patent granted thereon.

Dated this 12th day of January 1975

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Table of Classification

| Class | Sub-class |
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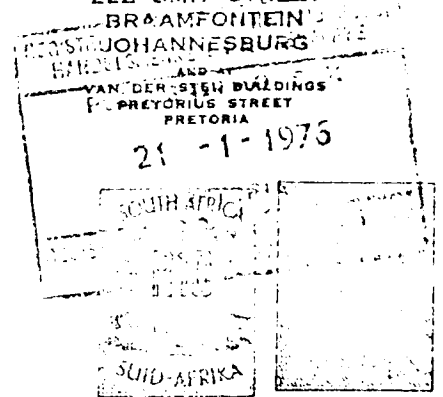


Signature of Applicant's and Capacity

PATENTS
Form No. 3

P 6873
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Application No. 75/0593



REPUBLIC OF SOUTH AFRICA

The Patents Act, 1952
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COMPLETE SPECIFICATION
=====

(a) Here insert title verbally agreeing with that in the application form. (a)

"PROCESS FOR THE TREATMENT OF PLATINUM GROUP METALS AND GOLD"

(b) Here insert (in full) name, address, and calling of applicant(s) as in application form. (b)

NATIONAL INSTITUTE FOR METALLURGY of
1 Yale Road, Milner Park, Johannesburg,
Transvaal Province, Republic of South Africa,

do hereby declare this invention, the manner in which and the method by which it is to be performed, to be particularly described and ascertained in and by the following statement :--

This invention relates to a process for the treatment of mixtures of platinum group metals, gold and silver, and is more particularly concerned with the treatment of so-called platinum group metal concentrates such as matte leach residues and the like, and also various intermediate solid products such as leach insolubles etc. which may arise during the processing of such materials.

All commercial refining methods for the platinum group metals are basically hydrometallurgical in nature. Thus the first and key operation in these processes is the dissolution of the valuable components from the source material.

However the platinum group metals are extremely difficult to dissolve, and extended leaching periods with highly active media such as aqua regia are commonly used. Even under very vigorous leach conditions complete dissolution of the values is not generally achieved, and in particular the secondary platinum metals (rhodium, ruthenium, iridium and osmium) are attacked to only a small extent. In addition the degree to which the metals dissolve is often highly variable

from batch to batch and is generally dependent on the nature of the process steps to which the source material has been subjected prior to the platinum metal leaching step.

5 Because of these effects it is common practice to use a multi-stage process involving both pyrometallurgical and hydrometallurgical steps to effect dissolution of the platinum metals. One commonly used series of operations is as follows:-

- 10 (1) performing an initial aqua regia leach on a concentrate of platinum group metals, gold and silver;
- (2) smelting the residue with litharge and a reductant to form a lead-platinum group metal alloy;
- 15 (3) parting of the lead bullion so formed with nitric acid
- (4) leaching the residue from step (3) with aqua regia which dissolves most of the platinum and palladium but little of the secondary platinum group metals;
- (5) fusing the residue which is rich in secondary
- 20 (6) leaching of the fusion mixture with water and neutralising with hydrochloric acid to produce a chloride solution of the secondary platinum group metals.

Various recycle streams are also involved in the practical performance of this currently used procedure.

Thus a large number of operations is involved and a major proportion of the platinum metals is locked up in recycle streams. Many of the recycle streams are initially in the form of solutions; in order for the values contained in these streams to be recovered they must first be treated to render the precious metals insoluble. Commonly, reduction to metal using zinc as the reductant is employed, and this operation is time consuming, expensive and not entirely effective.

Furthermore it is commonly found with many precious metal bearing source materials that a large proportion of the base metal content cannot be effectively separated out before the platinum group metal leach by, for example, a milder leach such as sulphuric acid leaching. These base metals therefore contaminate the leach liquors containing the precious metals and render both refining operations and recycle considerably more difficult.

It is the object of this invention to overcome the above difficulties in platinum refining by providing:-

- (1) a process whereby a large proportion of the base metal content of the feed material can be effectively leached from the precious metal content before the leaching of the precious metals themselves, and/or
- (2) a process whereby a large proportion of the precious metal content of the feed material can be dissolved in a single leach using chlorine as the oxidant and hydrochloric acid as the dissolving medium, and/or
- (3) a process whereby liquid recycle streams containing precious metals can be easily processed to recover the precious metal content without an intermediate zinc reduction step, by achieving reduction during base metal removal.

In this specification for the sake of clarity the term "precious metals" will be applied to mixtures of some or all of the platinum group metals and which may in addition contain gold and/or silver. The term "base metals" as used herein includes all metals other than the "precious metals".

In accordance with this invention there is provided a process for the treatment of a precious metal concentrate comprising the formation of an alloy of aluminium and precious metals and recovering at least the majority of the precious metals in solution by a suitable leaching procedure.

Further features of the invention provide for the alloy to be subjected initially to a leaching step adapted to remove base metals and for the precious metals to be recovered subsequently by a second leach step carried out under strong oxidizing conditions and for the base metal leach to be performed in two stages, the first of which is carried out by weak acid under reducing conditions and the second of which is carried out under conditions suitable for the dissolution of copper.

The aluminium precious metal alloy preferably has an aluminium to precious metal ratio of between about 10:1 and 1:1.

The formation of the aluminium alloy can be accomplished in a number of ways but it is most efficiently performed according to one of three techniques which are applicable to concentrates of various grades and compositions as follows:-

- (1) Concentrates having a high precious metal content (above about 50%) and which is essentially

metallic in character (e.g. lead bullion residue after parting) may be treated as follows:-

5 (a) The material may be simply melted together with an equal weight of aluminium at a temperature in excess of 1000°C under a protective atmosphere to reduce oxidation of the aluminium.

10 (b) The material may be mixed with a small proportion (5% - 25%) by weight of a suitable base metal oxide or sulphide, preferably ferric oxide or ferrous sulphide and sufficient aluminium powder, preferably a weight equal to the concentrate. This mixture is then ignited by a suitable technique where-
15 upon the base metal oxide and the aluminium react, and the aluminothermic reaction so initiated provides sufficient heat to accomplish the alloying.

20 (2) Concentrates having a medium precious metal content (between about 30% and 50%) with a high base metal content but where silica is present in low concentrations (less than 5%) or is preferably
25 absent. This may be treated in similar fashion to the above except that often sufficient base metal oxides or sulphides are already present in

the material to render the addition of further ferric oxide or ferrous sulphide unnecessary. Addition of some flux such as calcium oxide (CaO) may be helpful in rendering the aluminium oxide formed in the reaction soluble in the base metal leach. Certain matte leach residues and initial leach residues fall into this class of concentrate.

5

(3) Material of medium or low precious metal content (precious metal content of less than 30%) with high base metal content and high silica content.

10

The preferred technique here is to form an intermediate alloy of precious metals and iron which is then alloyed further with aluminium to form typically an alloy containing about 30% Fe, 30% Al, 30% precious metals and 10% other base metals such as Ni, Pb, Cu etc. This operation is typically but not necessarily carried out in an arc furnace as follows:-

15

(a) The concentrate is mixed with carbon and lime, pelletised, and roasted at about 800°C to reduce any precious metal oxides to metal.

20

(b) The roasted material is smelted together with scrap iron in an arc furnace to produce an alloy of roughly 50% precious metal content and a calcium-iron-silica slag which is low in precious metals.

25

(c) The slag is poured off and aluminium scrap is added to the iron alloy in sufficient quantity to form an alloy of roughly 30% Al content.

5 This technique applies especially to concentrates of high silica content and low precious metal content such as certain matte leach residues but of course could be applied in other cases as well.

In all the above cases the alloy so formed is preferably treated as follows:-

- 10 (1) The aluminium and iron content of the alloy are leached together under highly reducing conditions, using weak acid to do the leaching. Any recycle streams that are acidic and contain precious metal values can be used in this step. Very effective
- 15 cementation of the precious metal values has been experienced and the exhausted leach liquor will contain very low precious metal values.
- (2) The residue from the first leach is then subjected to a more intensive leach at a potential sufficient to
- 20 dissolve copper. Many known methods are available for doing this and in particular the controlled potential leach system of Falconbridge (Journal of Metals, May 197 p 6-9 "The recovery of nickel copper and a precious metal concentrate from high grade precious metal mattes"
- 25 L.R. Hougan, H. Zacharissen) using chlorine gas as the oxidant would be applicable here.

(3) The residue from the second leach is then leached in hydrochloric acid of commercial strength (about 10 Molar) using chlorine gas as the oxidant. Leaching has been found to be rapid and complete and the leach residue, if present, consists of insolubles such as silica and alumina with low precious metal content, typically less than 5000 ppm total precious metals.

5

Various experiments conducted thus far will now be described in order to demonstrate the operation of the invention.

10

Example I

The concentrate treated here was a moderately rich platinum group metal concentrate obtained from a copper-nickel matte leach plant and which analysed roughly 30% precious metals (platinum group metals + Au + Ag) and approximately 30% base metal, the remainder being oxygen, sulphur and silica. A sample of this material was firstly leached in 12M hydrochloric acid using chlorine as the oxidant and the following percentage dissolutions were obtained:-

20

| Pt | Pd | Rh | Ru | Ir |
|-------|-------|-------|-------|-------|
| 80.8% | 70.7% | 32.7% | 14.6% | 64.8% |

These results were improved considerably by performing a reduction roast prior to leaching on another sample of the

material, but complete dissolution could still not be obtained, the percentage dissolutions being as follows:-

| Pt | Pd | Rh | Ru | Ir |
|-------|-------|-------|-------|-------|
| 98.4% | 98.3% | 81.9% | 52.4% | 96.9% |

5 A third sample of the material was then aluminothermically reduced with an equal weight of aluminium powder, by mixing the two ingredients and igniting the mixture by heating to about 1000^oC. The reacted material was firstly leached with 12M hydrochloric acid in order to remove
10 aluminium and base metals, and thereafter with 12M hydrochloric acid with Cl₂ as the oxidizing agent in order to dissolve the platinum group metals. The results obtained upon leaching the reacted mass were as follows:-

| Pt | Pd | Rh | Ru | Ir |
|-------|-------|-------|-------|-------|
| 99.6% | 99.4% | 87.8% | 96.9% | 96.9% |

15 Thus the residue left after leaching was significantly poorer in platinum group metal content and in practice could be recycled to the matte smelting furnace.

Example II

20 The concentrate used in this example was similar to that described above but had a lower precious metal content (+ 20%), and was very much more refractory in nature. Results obtained on the raw material on leaching with 12M

hydrochloric acid with Cl_2 were as follows:-

| Pt | Pd | Rh | Ru | Ir |
|-------|-------|-------|-------|-------|
| 63.9% | 53.7% | 30.9% | 16.4% | 45.2% |

5 In this case, treating the material by means of a reducing roast prior to leaching did not produce as marked an improvement as in Example I, the results being the following percentage dissolutions:-

| Pt | Pd | Rh | Ru | Ir |
|-------|-------|-------|------|-------|
| 89.2% | 94.2% | 38.1% | 3.4% | 16.5% |

10 However, after aluminothermic reduction had been carried out in a manner identical to that described in Example I, very good subsequent dissolutions were obtained:-

| Pt | Pd | Rh | Ru | Ir |
|-------|-------|-------|-------|-------|
| 99.3% | 99.4% | 97.6% | 95.6% | 87.3% |

15 This example also illustrates that base metals can be removed almost completely before HCl/Cl_2 leaching by leaching in sulphuric acid, under oxidizing conditions. The following percentage dissolutions were found to be typical:-

| Cu | Ni | Fe | Cr | Al |
|-------|-------|-------|-------|-----|
| 91.2% | 85.5% | 87.7% | 25.5% | 95% |

20 The amount of platinum group metals dissolved together with the base metals was negligibly small.

Example III

The concentrate treated here was a secondary platinum group concentrate obtained from the parting and aqua regia treatment of lead bullion obtained as above described, and this contained about 60% platinum group metals, 20% lead and 20% other base metals.

Both direct leaching with HCl/Cl₂ and leaching in the same way following hydrogen reduction of this material proved to be almost completely ineffective, as shown below:-

| | Ru | Rh | Ir |
|----------------------------------|------|-------|------|
| no pre-treatment | 0% | 18.5% | 2.2% |
| hydrogen reduction pre-treatment | 5.7% | 14.6% | 6.7% |

A sample of this concentrate was then treated by mixing it with an equal weight of aluminium powder, and 20% by weight FeS. This mixture was ignited by heating at 1000°C and the reacted mass leached firstly in 200 g/l sulphuric acid to remove the base metals and aluminium and subsequently in 12M HCl/Cl₂. The percentage dissolutions obtained after leaching for two hours were as follows:-

| Ru | Rh | Ir |
|-------|-------|-------|
| 89.6% | 92.9% | 95.8% |

This experiment was repeated on a larger scale and it was found that almost all of the base metals added and

originally present were leached in the sulphuric acid leach. Subsequent HCl/Cl₂ leaching for two hours gave similar dissolutions, viz:-

| | Ru | Rh | Ir |
|---|-------|-------|-------|
| 5 | 90.8% | 93.1% | 90.3% |

A third test on this concentrate was conducted wherein 5 kg of concentrate were treated in a similar fashion to the above. The alloy was subjected to an initial leach in 10M HCl with the addition of 500 g Fe₂O₃ until the precious metals just started to dissolve. Filtration was effected immediately and showed on analysis 45 ppm precious metals, 7 g/l Fe, 3 g/l Pb and 120 ppm Cu. Leaching in 10M HCl/Cl₂ was then effected and was continued for eight hours as opposed to the two hour leach times above. The extension of the leach time increased the percentage dissolved substantially to that given below:-

| | Ru | Rh | Ir |
|--|-------|-------|-------|
| | 99.1% | 99.5% | 99.3% |

This leach liquor contained 54 g/l precious metals, 150 ppm Cu and 1,6 g/l of other base metals thus illustrating that the majority of base metals had been removed.

The above leach procedure was carried out in a two step manner as opposed to the preferred three step procedure set out above. The results of the three step procedure are, at this time, not available but the following are the

reasons for preferring a separate copper leach. In the leaching of iron, aluminium and similar base metals strongly reducing conditions are present when the alloy is leached with HCl or H₂SO₄ solution. Thus in that leach step there is virtually no possibility of dissolving precious metals. In the second step in which copper would be leached more oxidizing conditions exist thereby increasing the chance of precious metals being dissolved. Also, a substantially smaller vessel is required to effect the subsequent copper leach thereby resulting in smaller volumes of leach liquor to be treated for dissolved precious metals. The conditions in each stage of a two stage initial leach can be optimised and a plant can more readily be efficiently designed.

15 Example IV

This example illustrates an alternative method of performing the invention. A concentrate similar to that used in Example III was mixed with an equal weight of aluminium powder, and the mixture melted in a muffle furnace at 1000°C for two hours. The molten mass was allowed to cool and then leached with 200 g/l H₂SO₄ to remove the aluminium and base metals and the residue was dissolved in 12M HCl/Cl₂. The percentage dissolutions obtained in this case were

as follows:-

| Ru | Rh | Ir |
|-------|-------|-------|
| 95.6% | 91.5% | 96.3% |

Example V

5 A concentrate containing about 20% precious metals, 16% silica and 14% iron oxides was heated at 800°C with carbon for one hour. The amount of carbon added is dependent on the iron and platinum group metals that are present as oxides. The period of roasting is dependent
10 on the kinetics of the reduction process and this will vary with temperature, composition, particle size and the mineralogy of the material.

The reduced material was split into two batches, each of which was treated as follows.

15 The reduced material together with lime (CaO) in an amount of about 1 part was melted at 1600°C; iron scrap was added and the melt cooled. The metal was separated from the slag, and alloyed with aluminium in the ratio of 0,4:1 Al:precious metal alloy at 1600°C by first melting
20 the metal and adding solid aluminium to the metal. After cooling the aluminium alloy was leached in concentrated (10M) HCl acid and the residue leached in concentrated (10M) HCl and Cl₂. After this leach there was no residue remaining. The recovery of the various platinum group
25 metals in the final leach liquors is given in the following table:-

T A B L E

| | Pt | Pd | Rh | Ru | Os | Ir | Au |
|--|----------------------------------|----------------|----------------|----------------|--------------|--------------|--------------|
| Precious metals in head sample mass % | 1,11 (") | 6,40 (") | 2,99 (") | 6,51 (") | 1,43 (") | 0,44 (") | 670 (") |
| Precious metals in in slag (ppm) | ←————— 2434 —————→ (920) | | | | | | |
| Precious metals in HCl leach liquor (ppm) | ←————— 1,4 —————→ (4,3) | | | | | | |
| Precious metals in HCl/Cl ₂ leach liquor (ppm) | 700 (743) | 5063 (5583) | 2019 (2019) | 4438 (4775) | 850 (835) | 315 (330) | 160 (175) |
| Precious metals recovered in slag % | ←————— 3% —————→ (1,4%) | | | | | | |
| Precious metals recovered in alloy % by difference | ←————— 97% —————→ (98,6%) | | | | | | |
| Precious metals recovered in alloy (calculated from HCl/Cl ₂ leach solution values) | ←————— 109,3% —————→ (108,1%) | | | | | | |

The discrepancies in the recovery of precious metals which are quite obvious were due to assay errors. The figures given in parentheses are for the second half of the initial reduced material.

5 Example VI

Finally the operation of the use of a precious metal containing simulated recycle stream was tested in order to observe the cementation effects with the aluminium alloy.

10 40 litres of an imitation recycle stream of approximately 2M HCl and containing

| Ru | Rh | Pd | Pt | Ir |
|----------|----------|---------|-------|----------|
| 6000 ppm | 5031 ppm | 735 ppm | 3 ppm | 1250 ppm |

were contacted with 1 Kg of crushed aluminium-precious metal alloy. The alloy had a particle size of 100% minus 15 $\frac{1}{2}$ inch mesh and the contacting was effected at 60°C for six hours.

The solution was filtered off and found to contain:-

| Ru | Rh | Pd | Pt | Ir |
|---------|------|---------|------|-------|
| 1,5 ppm | N.D. | 0,4 ppm | N.D. | 6 ppm |

(N.D. means not detectable)

Thus cementation apparently occurred with a high degree of efficiency.

The above tests which have been carried out demonstrate that a process according to the invention will operate effectively in use. It will be noted that where hydrochloric acid has been used the strength was
5 either 10M or 12M. As will be apparent to those skilled in the art any strength acid may be used with the more dilute acids simply taking longer to produce the desired effect. Also, any strength sulphuric acid could be used up to a maximum strength of about 500 g/l.

10 The invention therefore provides a process having the following characteristics:-

- (1) It allows the base metal content to be removed prior to the platinum group metal leach by leaching with dilute sulphuric acid or hydrochloric acid, and
- 15 (2) It increases the leachability of the platinum group metals in an oxidizing hydrochloric acid leach to a very great extent, so that in effect total dissolution can be achieved.

20 The process may be applied to any platinum group metal rich material arising at any stage of the conventional refining process, and in particular can be readily applied to the following materials:-

- (1) feed material to the refinery, thus eliminating

the need for subsequent treatment of the residue. In practice, because platinum group metals are so valuable, this residue, if present at all, although low in platinum group metals content, would be recycled to a point earlier in the process such as the matte smelter,

5

(2) the residue from the primary leach, and

(3) the residue from the parting and aqua regia leaching of the lead bullion in which use of the method is a replacement for the potentially hazardous sodium peroxide fusion.

10

Having now particularly described and ascertained our said invention and in what manner the same is to be performed we declare that what we claim is:-

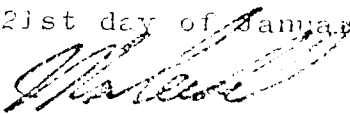
1. A process for the treatment of a precious metal concentrate comprising the formation of an alloy of aluminium and precious metals and recovering at least the majority of the precious metals in solution by a suitable leaching procedure.
5
2. A process as claimed in claim 1 in which the alloy is initially leached with acid to remove base metals, the leach being carried out under conditions which inhibit the dissolution of the precious metals, and the residue from the initial leach is leached under strong oxidizing conditions in order to dissolve the precious metals.
10
3. A process as claimed in claim 1 in which the alloy is initially leached with acid under strong reducing conditions to remove the majority of base metals, the first residue from this initial leach is then leached with acid under conditions suitable for the
15

dissolution of copper to provide a second residue,
and the latter residue is then leached under strong
oxidizing conditions to dissolve precious
metals.

- 5 4. A process as claimed in either of claims 2 or 3
 in which the initial leach for the removal of the
 majority of base metals is effected using
 hydrochloric or sulphuric acid.
5. A process as claimed in claim 4 in which the acid is
10 a recycle stream containing small amounts of
 precious metals which are cemented out during the
 leaching procedure.
6. A process as claimed in any of the preceding claims
 in which dissolution of the precious metals is
15 effected using hydrochloric acid and chlorine gas
 as an oxidant.
7. A process as claimed in any of the preceding claims
 in which the formation of the alloy is effected by
 mixing the concentrate with a suitable amount of
20 subdivided aluminium and the mixture is heated
 sufficiently to cause a molten alloy to form.

8. A process as claimed in claim 7 in which the mixture has sufficient base metal oxides and/or sulphides to enable a highly exothermic aluminothermic reaction to take place.
- 5 9. A process as claimed in any of claims 1 to 6 in which the aluminium alloy is formed by initially forming an iron-precious metal alloy, removing silica in the slag formed and adding the required aluminium to such iron alloy.
- 10 10. A process as claimed in any of the preceding claims in which the aluminium alloy has an aluminium to precious metal weight ratio of from 10:1 to 1:1.
- 15 11. A process substantially as herein described or exemplified.
12. Precious metals wherever produced using a process as claimed in any of the preceding claims.

Dated this 21st day of January, 1976.


JOHN AND KERNICK

Patent Agents for the Applicants