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FULL NAME(S) OF APPLICANT(S)

71 W.C. HERAEUS GMBH

FULL NAME(S) OF INVENTOR(S)

72 ALT, Hans-Joachim; PATZELT, Peter; VON EIFF, Hermann; ZELL, Bernd; MEYER, Horst; GREHL, Matthias

TITLE OF INVENTION

54 PROCESS AND DEVICES FOR REMOVING RUTHENIUM AS RuO₄ FROM RUTHENATE-CONTAINING SOLUTIONS BY DISTILLATION

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57 Abstract (not more than 150 words) and figure of the drawings to which the abstract refers, are attached.

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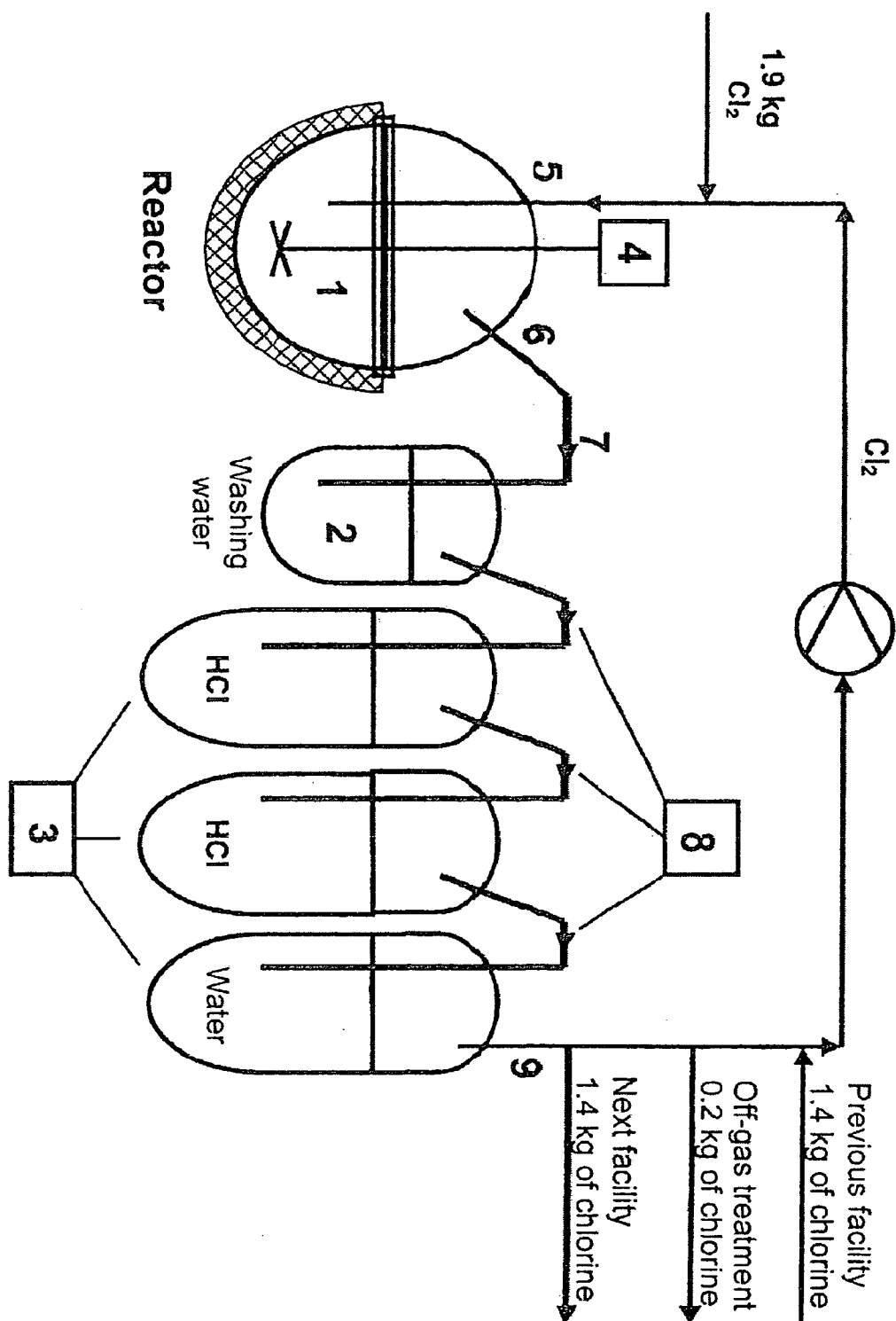


Abstract

5 A process for removing ruthenium by distilling RuO_4 from ruthenate-containing solutions, the process including at least the steps of:-

- I. treatment of the ruthenate-containing solution with an oxidising agent;
- II. distilling off of the RuO_4 formed; and
- III. absorbing the RuO_4 from step II in hydrochloric acid;

wherein the oxidising agent is recycled into step I following step III.



Hahn & Hahn Inc.
APPLICANTS ATTORNEY



**Processes and devices for removing ruthenium as
RuO₄ from ruthenate-containing solutions by distillation**

5. **Field of the Invention**

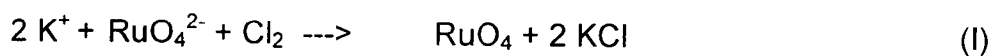
This invention relates to processes and devices for removing ruthenium as RuO₄ from ruthenate-containing solutions by distillation.

10 **Background to the Invention**

Parting products containing ruthenium (and, if applicable, osmium) are treated initially with an alkaline oxidising melt, for example, to recover the noble metals. Following leaching, solutions are obtained therefrom which contain K₂RuO₄ (and, if applicable, K₂OsO₄). The elements Ru and Os are advantageously partitioned oxidatively as tetrox-
15 ides. Suitable oxidising agents for this purpose are e.g. oxygen/ozone, H₂O₂/sulphuric acid, peroxodisulphate, bromine or chlorine. The tetroxides are separated off by distillation.

From JP61006130A, it is known to saturate ruthenate-containing aqueous solutions from alkaline melt leaching with chlorine gas, to decompose the hypochlorite formed by
20 acidification, to distil off RuO₄ and to take it up in HCl. A yield of 99% is indicated as being obtained on a laboratory scale.

To liberate RuO₄, chlorine is consumed:



25 During absorption in HCl, twice the quantity of chlorine is liberated:



30 When an oxidising agent such as chlorine or a chlorine/air mixture is passed through the ruthenate-containing solution on an industrial scale and acts as entrainer for RuO₄, a large quantity of oxidising agent is consumed in the process.

A need exists for providing a process for removing ruthenium as RuO₄ from ruthenate-containing solutions by distillation, in which process the oxidising agent is used as effi-

ciently as possible with a high yield. A further need exists for the provision of a process suitable for automation.

Summary of the Invention

According to the invention, there is provided a process for removing ruthenium by
5 distilling RuO_4 from ruthenate-containing solutions, the process including at least the steps of:-

I. treatment of the ruthenate-containing solution with an oxidising agent;

II. distilling off of the RuO_4 formed; and

III. absorbing the RuO_4 from step II in hydrochloric acid;

10 wherein the oxidising agent is recycled into step I following step III.

The oxidising agent, e.g. a chlorine/air mixture, is recycled within the distillation facility.

Advantageously, the reactor is heatable and coolable such that the temperature development can be controlled in an automated manner.

It is advantageous to connect several distillation facilities in series as modules. Appropriately, the process is controlled in such a way that as soon as excess oxidising agent,
15 e.g. chlorine, is developed in a facility, its gas mixture is pumped into the next facility. In this way, if chlorine is used as oxidising agent, chlorine produced in the process, too, is utilised for the oxidation of ruthenate. With this method of operation, approximately 1.9 kg of chlorine per kg of Ru, for example, are introduced from outside. As a result of the
20 recycling operation, approximately 0.2 kg of chlorine per kg of Ru pass into the off-gas purification facility.

If the pH of the alkaline ruthenate-containing solution is reduced with acid before introducing the chlorine, the violence of the reaction is easier to control.

It has proved to be advantageous to keep the concentration of hydrochloric acid in
25 which RuO_4 is taken up at a high level, appropriately above 5 mole/l, by introducing HCl gas to prevent RuO_4 from accumulating.

Appropriately, the process is integrated into a procedure for recovering ruthenium from partitioning products. In this case, the absorbed H_2RuCl_6 and the mother liquors which have arisen are worked up in a manner known to the expert.

According to a further aspect of the invention, there is provided a device for carrying out the process described above, which device exhibits at least one module including at least the following components:

- A a reactor with stirrer, gas inlet and gas outlet;
- B at least one scrubber connected in series downstream with the gas outlet via a line;
- C one or several gas absorbers connected in series downstream with the at least one scrubber via lines; and
- E at least one line from the optionally last absorber
 - for recycling into the gas inlet of the reactor
 - or into a further module
 - or into a facility for off-gas treatment.

Detailed Description of the Invention

The process according to the invention is elucidated by way of the following non-limiting example. Parts and percentages relate to the weight, as they do in the rest of the description, unless indicated otherwise.

Example

A ruthenium-containing melt cake from alkaline oxidising melt is leached with non-potable water with stirring. The potassium/sodium ruthenate solution obtained is introduced into a glass flask and subsequently pumped into a receiving vessel.

A 500 l reactor with a gas inlet, stirrer, gas outlet and a 50 l washing flask connected to it, which flask is connected to four absorber receiving vessels connected in series and filled with concentrated HCl (first receiving vessel), diluted HCl (2nd and 3rd receiving vessel) and water (4th receiving vessel) is supplied with 50 – 80 l of the potassium/sodium ruthenate solution and filled with service water to a level of 300 l. Depending on the predetermined concentration of potassium/sodium ruthenate solution, 5-10 l

of concentrated technical grade HNO_3 are added to the solution and the temperature is raised to 50°C .

$2.5 \text{ m}^3/\text{h}$ of chlorine are introduced into the solution via an inlet pipe. On termination of the temperature hike, heating is carried out.

- 5 All the liquid ruthenium tetroxide that has collected at the bottom of the distillation flask is distilled off and collected in the receiving vessels.

Before the end of the RuO_4 distillation, HCl gas is introduced into the first receiving vessel. RuO_4 reacts to form H_2RuCl_6 according to equation (II) in this process. The introduction is started once a temperature $80 - 85^\circ\text{C}$ has been reached in the distillation flask.

The reaction is terminated when the washing water in the washing flask becomes almost colourless, a temperature of at least 98°C has been reached in the reactor and no further RuO_4 is visible at the bottom of the washing flask.

The stream of chlorine is interrupted.

- 15 The stream of HCl into the receiving vessels is maintained for a further 1-2 h.

The residue in the reactor is treated with 3-4 l of 45-50% technical grade NaOH .

The $\text{H}_2\text{RuCl}_6/\text{RuCl}_3$ solution obtained is removed from the absorber receiving vessels.

Fig. 1 shows a module of an exemplary device for executing the process.

In the case of the module, a washing flask 2 is connected in series downstream to a reactor 1 with a stirrer 4, gas inlet 5 and gas outlet 6, in which washing flask the gas/vapour mixture distilled off is freed from possible salt mists originating from the reaction mixture. A line leads from the outlet of the gas scrubber to one or several absorbers 3 optionally connected in series. As regards the module of Fig. 1, several of it may be connected in series and jointly form a device for executing the process according to the invention. Optionally, the gas is recycled into the reactor through the outlet of the last absorber of a module or passed into a further module or into a facility for off-gas

treatment. It goes without saying that the off-gas treatment is carried out only after the last module of the device.

5 It is illustrated in the exemplary embodiment of the module of Fig. 1 that 1.9kg of chlorine are supplied from outside and 1.4 kg of chlorine arrive from a facility connected in front. Correspondingly, 1.4 kg of chlorine leaves this module in order to participate in the reaction in a facility connected in series downstream.

It has proved appropriate for the gasket of the stirrer 4, e.g. a sliding ring gasket, to be flushed with chlorine gas in order to avoid corrosion by RuO_4 penetrating into the gasket space.

10 It is to be appreciated, that the invention is not limited to the particular embodiment or device configuration as hereinbefore described and illustrated.

15 he claims which follow are to be considered an integral part of the present disclosure. Reference numbers (directed at the drawing) shown in the claims serve to facilitate the correlation of the integers of the claims with illustrated features of the preferred embodiment, but are not intended to restrict in any way the language of the claims to what is shown in the drawings, unless the contrary is clearly apparent from the context

Claims



1. A process for removing ruthenium by distilling RuO_4 from ruthenate-containing solutions, the process including at least the steps of:-
 - I. treatment of the ruthenate-containing solution with an oxidising agent;
 - II. distilling off of the RuO_4 formed; and
 - III. absorbing the RuO_4 from step II in hydrochloric acid;wherein the oxidising agent is recycled into step I following step III.
2. A process as claimed in claim 1, wherein the oxidising agent is recycled after at least one cycle into at least one further process connected in series downstream with further steps I to III.
3. A process as claimed in claim 1 or claim 2, wherein the oxidising agent is selected from the group including: oxygen/ozone, H_2O_2 /sulphuric acid, peroxodisulphate, bromine, and chlorine.
4. A process as claimed in any one of the preceding claims, wherein a mineral acid is added before step I.
5. A process as claimed in any one of the preceding claims, wherein the oxidising agent is bromine.
6. A process as claimed in any one of claims 1 to 4, wherein the oxidising agent is chlorine.
7. A process as claimed in any one of claims 2, 5 and 6, wherein the gas mixture is passed after step III into the process connected in series downstream when bromine or chlorine begins to develop after step III.
8. A process as claimed in claim 7, wherein the chlorine gas is freed from HCl gas by washing with water before recycling.

9. A process as claimed in any one of claims 5 to 8, wherein hydrochloric acid and/or nitric acid is added before step I.

10. A device for carrying out processes according to any one of the preceding claims exhibiting at least one module including at least the following components:

5 **A** a reactor (1) with stirrer (4), gas inlet (5) and gas outlet (6);

B at least one scrubber (2) connected in series downstream with the gas outlet (6) via a line (7);

C one or several gas absorbers (3) connected in series downstream with the at least one scrubber (2) via lines (8); and

10 **E** at least one line (9) from the optionally last absorber

- for recycling into the gas inlet of the reactor (1);
- or into a further module;
- or into a facility for off-gas treatment.

15 11. A device as claimed in claim 10, wherein a separate gas inlet is present on the stirrer (4) for producing a chlorine gas atmosphere in the space around the gasket of the stirrer.

20 12. A device as claimed in claim 10, wherein a separate gas inlet is present on the stirrer (4) for producing a bromine gas atmosphere in the space around the gasket of the stirrer.

25 13. A process according to the invention for removing ruthenium by distilling RuO_4 from ruthenate-containing solutions, substantially as hereinbefore described or exemplified.

30 14. A process for removing ruthenium by distilling RuO_4 from ruthenate-containing solutions including any new and inventive integer or combination of integers, substantially as herein described.

15. A device according to the invention, substantially as hereinbefore described or exemplified.

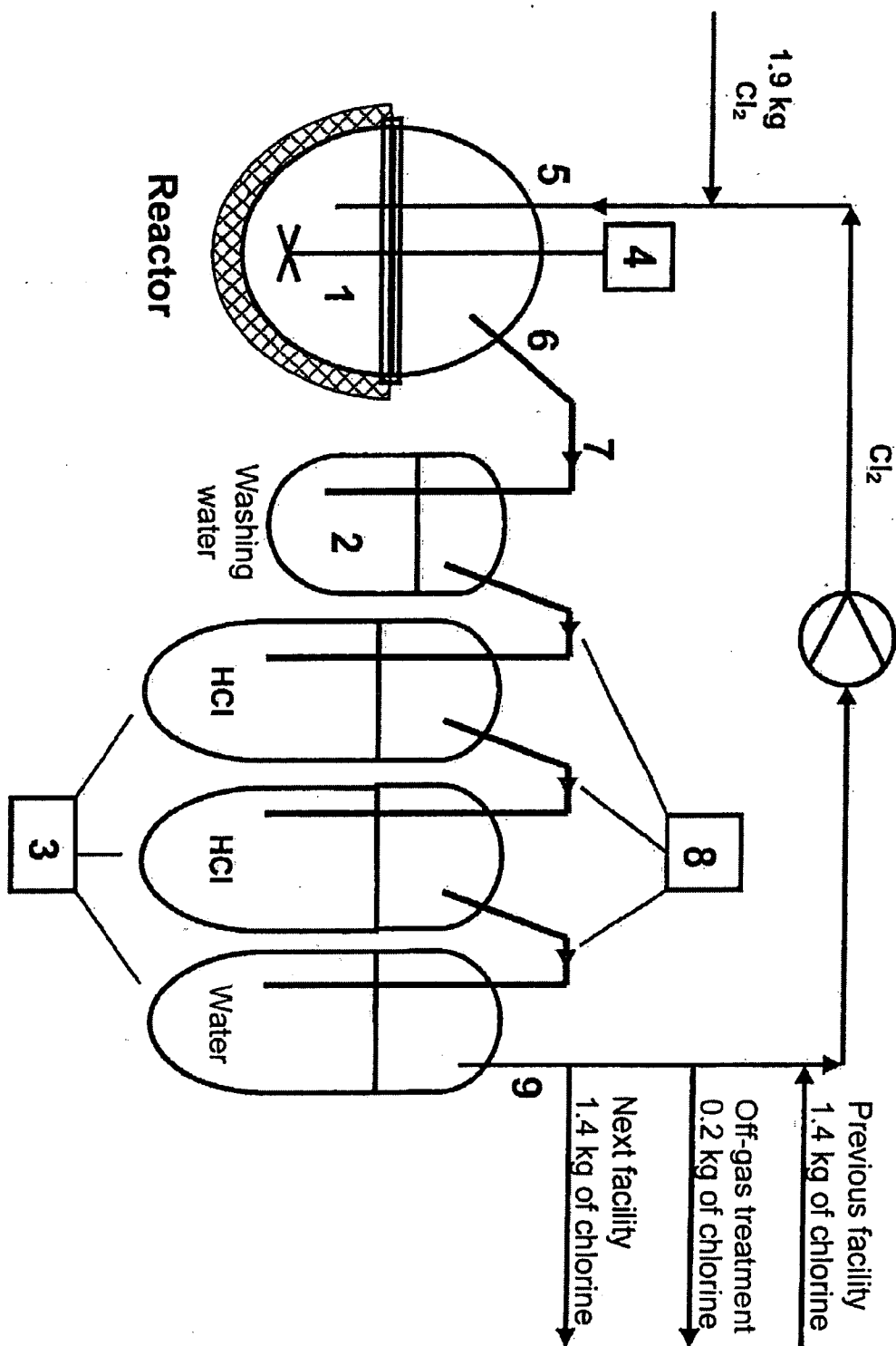
5 16. A device as specifically described with reference to or as illustrated in any one of the accompanying drawings.

17. A device, including any new and inventive integer or combination of integers, substantially as herein described.

10 **DATED AT PRETORIA THIS 28TH DAY OF JANUARY 2009.**

A handwritten signature in cursive script, appearing to read 'L. Bemdtt', is written over a horizontal line.

**HAHN & HAHN INC.
APPLICANT'S AGENTS**



Berndt
 HAHN & HAHN INC.
 APPLICANTS ATTORNEY