

US 20050139474A1

(19) **United States**(12) **Patent Application Publication**
Lewin et al.(10) **Pub. No.: US 2005/0139474 A1**(43) **Pub. Date: Jun. 30, 2005**(54) **ELECTROCHEMICAL CELL FOR METAL PRODUCTION****Publication Classification**(76) Inventors: **Robert Glynn Lewin**, Cumbria (GB);
Robert Charles Thied, Cumbria (GB)(51) **Int. Cl.⁷** **C25C 1/22**(52) **U.S. Cl.** **205/43; 204/280**

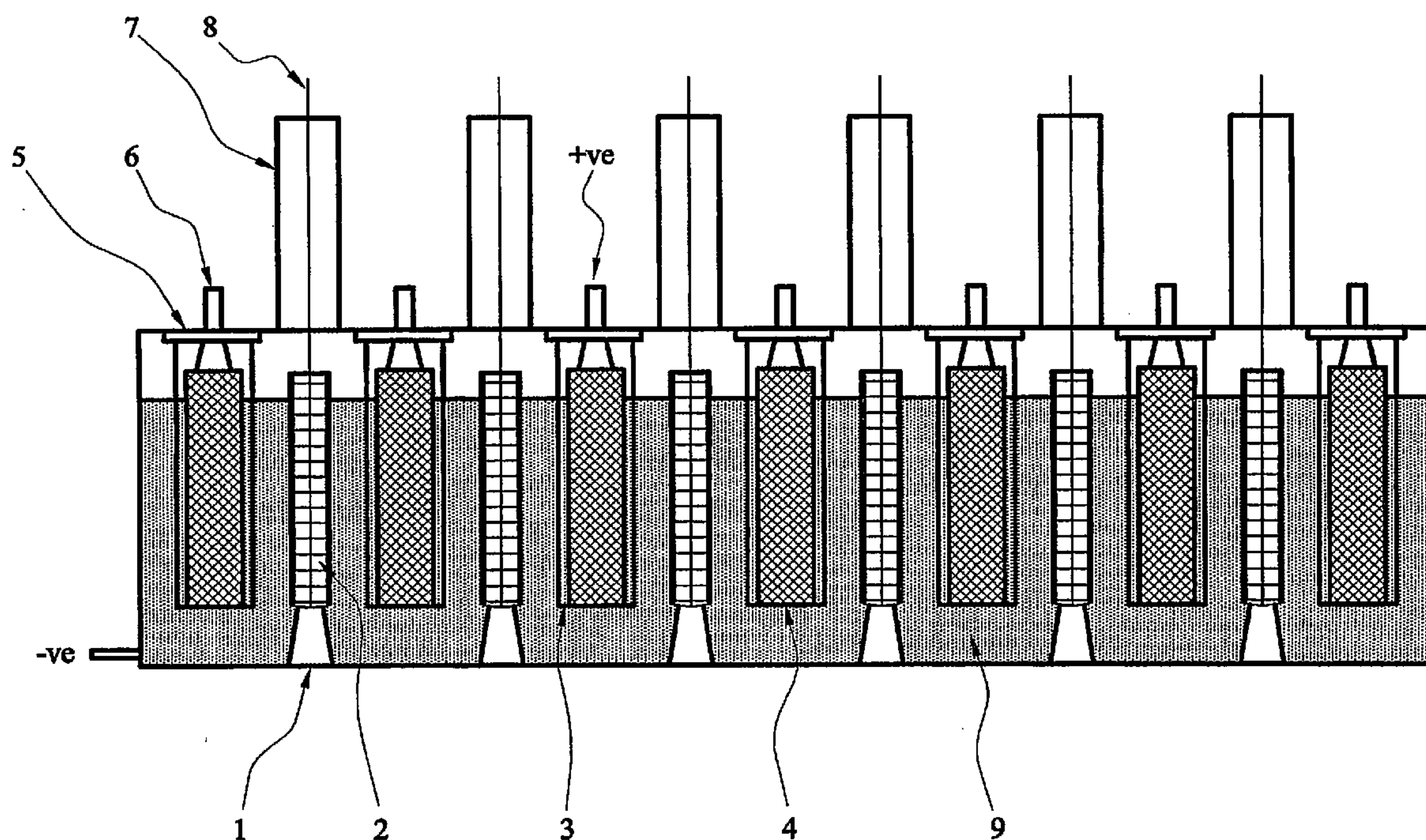
Correspondence Address:

MYERS BIGEL SIBLEY & SAJOVEC**PO BOX 37428****RALEIGH, NC 27627 (US)**(21) Appl. No.: **10/505,262**(22) PCT Filed: **Feb. 24, 2003**(86) PCT No.: **PCT/GB03/00792**(30) **Foreign Application Priority Data**

Feb. 28, 2002 (GB) 0204671.2

(57) **ABSTRACT**

A process for reducing to metallic form metal oxides includes cathodically electrolysing the oxide in the presence of a molten salt electrolyte whilst controlling the potential of the cathode so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt, and an apparatus for performing the said process. The apparatus is free from bolted or screwed fittings and includes an electrochemical cell that includes a body or housing, a cathode container, and a cathode connector, wherein the body or housing is maintained as the cathode.



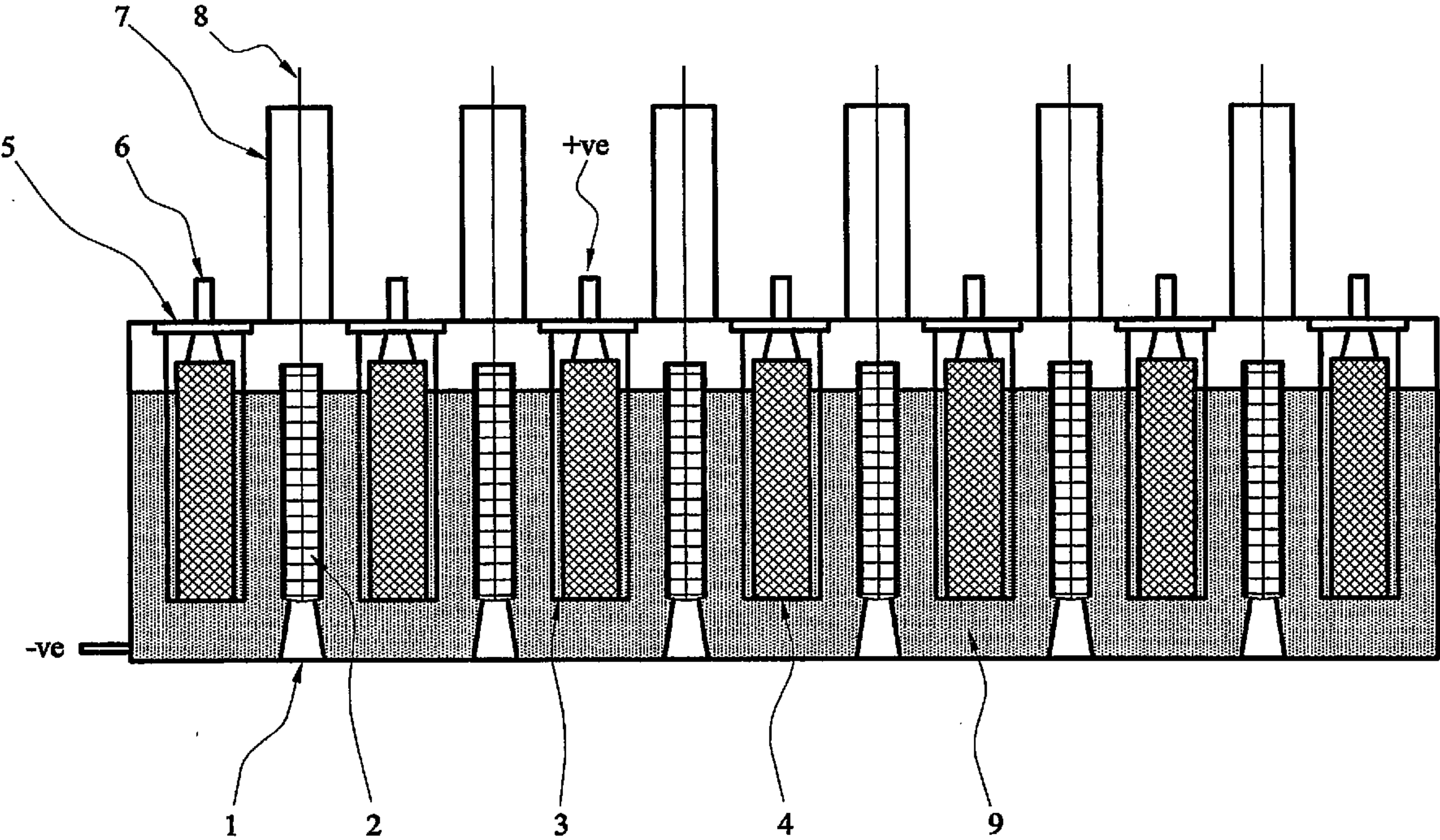


FIG. 1

ELECTROCHEMICAL CELL FOR METAL PRODUCTION

FIELD OF THE INVENTION

[0001] This invention relates to methods for the production of metals from oxides present in spent nuclear fuels and is particularly applicable to the production of actinides, specifically uranium. Methods of the present invention can be used in the treatment of irradiated fuels for producing actinides in metallic form suitable for use as feeds in subsequent electrorefining processes.

BACKGROUND OF THE INVENTION

[0002] In the established art, two processes have been developed for the treatment of irradiated nuclear fuel making use of molten salts. As used herein, the term "molten salts" is intended to cover salts such as lithium chloride which melts at an elevated temperature and also ionic liquids which typically are liquid at room temperature or which melt at a temperature up to about: 100 ° C.

[0003] The Dimitrovgrad SSC-RIAR process makes use of chemical oxidants (chlorine and oxygen gases) to react with powdered uranium dioxide fuel to form higher oxidation state compounds such as UO_2Cl_2 which are soluble in the molten salt. In an electrochemical cell the uranium compounds are reduced to UO_2 at the cathode, forming a dendritic deposit. This process has both technical and environmental limitations.

[0004] The second process, developed by the Argonne National Laboratory (ANL) is fundamentally an electrorefining technology which uses direct current to anodically oxidise uranium to form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and electrodeposited as dendritic uranium metal.

[0005] The ANL process requires a metal feed. If oxide fuels are to be treated, it is necessary to reduce the uranium oxide (usually UO_2 pellets) to the metal. This reduction process is carried out chemically, using lithium metal in a LiCl or LiCl/KCl molten salt or a Li/Cd alloy, at 500 to 600° C. Alternatively, a salt transport process can be used involving a Cu—Mg—Ca alloy and molten CaCl_2 salt. However, in both reduction methods the by-products, Li_2O and CaO respectively, need to be recovered from the molten salt phase by an electrolysis step. Effectively this means a two stage process.

[0006] A disadvantage of the lithium reduction process for producing a metallic feed from an oxide is the production of Li_2O by-product. This requires recycle to make the process economic, and this is done by an electrolytic recovery of lithium metal. Hence this is a two stage process, comprising a reduction step followed by a lithium recovery stage.

[0007] The prior art discloses many processes and apparatuses for the reduction of metal oxides to metals by cathodic electrolysis of the oxide in a molten salt. Thus, for example U.S. Pat. No. 5,378,325 discloses a low temper salt bath for the electrolysis of metal oxides to the corresponding metal, the bath comprising fluoride and chloride salts and including a low surface area carbonaceous anode. Alternatively, WO-A-00/40872 teaches a cell for the electrowinning of aluminium from alumina dissolved in a fluoride-containing molten electrolyte, the cell being provided with non-carbon metal-based anodes arranged to facilitate the circulation of electrolyte. As with these disclosures, however, much of the known prior art is merely concerned with metal

oxides in general, and makes no mention of the metal oxides to be found in spent nuclear fuel.

[0008] In co-pending PCT patent application WO-A-01141152 there is disclosed a single step process for reducing to metallic form a metal oxide present in spent nuclear fuel, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte, the potential of the cathode being controlled so as to favour oxygen ionisation over deposition of the metal from the cations present in the molten salt.

[0009] The process thereby involves the use of a single electrochemical process to reduce the metal oxide fuel to a metallic form, with oxygen, CO or CO_2 produced as the only by-products. The potential of the cathode is maintained and controlled so that only oxygen ionisation occurs and not the deposition of metal (eg Ca) from the cations (eg Ca ions) in the fused salt. Typically, the oxide comprises an actinide oxide, such as uranium oxide or irradiated uranium oxide.

[0010] U.S. Pat. No. 6,540,902 describes a similar single step process for reducing to metallic form a metal oxide present in spent nuclear fuel, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte, the potential of the cathode being controlled so as to prevent production of reductant metal from ions in the electrolyte, whilst the potential of the anode is controlled so as to prevent anode dissolution and gas evolution other than oxygen

[0011] The present inventors have, however, now effected an improvement to the processes described in WO-A-01141152 and U.S. Pat. No. 6,540,902, thereby allowing a more practical efficient and financially viable process to be adopted in the production of metals from oxides. The new process is particularly beneficial in that it facilitates the removal of bolted and screwed fittings from the apparatus used for the production of the metal.

STATEMENT OF INVENTION

[0012] Thus, according to a first aspect of the present invention there is provided an apparatus for performing a process for reducing to metallic form metal oxides, the said metal oxides comprising metal oxides present in spent nuclear fuel, wherein the apparatus comprises an electrochemical cell which comprises a body or housing, a cathode container, and a cathode connector, said body or housing being maintained as the cathode, and said electrochemical cell being free from bolted or screwed fittings.

[0013] The body or housing of the cell which comprises the apparatus according to the first aspect of the invention is most conveniently maintained as the cathode by the provision of an electrical connection from a power supply, provided by means of a connector from the cathode terminal to the body or housing of the cell. Typically, said connector comprises a bolted connection, but this is positioned externally to the cell. No bolted or screwed connections are present within the cell, wherein a cathode connector is provided which is affixed to an internal surface of the cell, most preferably the base of the cell, generally by welding. Preferably said cathode connector comprises a cathode rail.

[0014] In operation, the body or housing of the cell is maintained as the cathode, and said cathode is brought into contact with the cathode container by means of the cathode connector. Thus, contact is made between the cathode container and the cathode connector in order to facilitate the

electrolytic process. Contact may be most conveniently achieved by means of a simple press connection between the two components.

[0015] The cathode container preferably comprises a basket, such as a mesh basket, or vessel, typically a metal oxide retaining vessel, and—most preferably—comprises an assembly of such baskets or vessels. In order to effect electrical connection between such an assembly of cathode containers and the cell body during operation of the cell, it is necessary to provide a multiplicity of connectors and to effect contact between individual cathode baskets or vessels and individual connectors, preferably by means of a multiplicity of press connections.

[0016] Preferably the oxide is in contact with the cathode coder and it is preferred that the cathode is in the form of a mesh basket or, most preferably, an assembly of mesh baskets, with the oxide being contained within the said baskets. In this case, contact between the assembly of cathode containers and the cathode connectors is most simply achieved when the cathode connectors are in the form of a multiplicity of cathode rails which are welded to the base of the cell, allowing press contact to be brought about by the weight of the oxide feedstock in the cathode basket. This represents the most preferred embodiment of the first aspect of the invention. The anode may be any suitable inert anode, such as carbon.

[0017] According to a second aspect of the present invention, there is provided a process for reducing to metallic form metal oxides, the said metal oxides comprising metal oxides present in spent nuclear fuel, the process comprising cathodically electrolysing the oxide in the presence of a molten salt electrolyte in an apparatus according to the first aspect of the invention, the potential of the cathode being controlled so as to favor oxygen ionisation over deposition of metal from the cations present in the molten salt.

[0018] The molten salt electrolyte, may be any suitable molten salt or mixture of such salts, for instance chloride salts, preferably CaCl_2 and/or BaCl_2 .

[0019] Preferably, the oxide treated by the process according to the second aspect of the invention comprises an actinide oxide, such as uranium oxide or irradiated uranium oxide, or mixed uranium/plutonium oxides. The uranium oxide is commonly uranium dioxide. Alternatively, the oxide may comprise the oxide of a metal such as zirconium or hafnium.

[0020] In the said process, the fuel may be first treated mechanically to remove its zircaloy cladding before it is added to the electrolytic cell. Alternatively, the zircaloy cladding may be treated with the fuel. The fuel may require to be sheared into sections of small length prior to treatment in order to expose the oxide fuel to the molten salt.

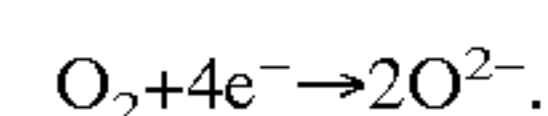
[0021] Said oxide may be in any physical form, and this is generally dependent on the particular chemical nature of the spent nuclear fuel and the processing to which the material has previously been subjected. For example, the fuel may comprise a powder, an amorphous mass, or a dense solid agglomerate. In any event, the material may be treated according to the method of the second aspect of the present invention by connection to an electrical circuit such that it serves as the cathode during electrolysis; as previously disclosed, connection to the circuit may be conveniently effected by the use of a cathode basket, into which the material is placed.

[0022] The process provides a single electrochemical process to reduce the metal oxide fuel to a metallic form, with oxygen produced as the only by-product. The potential of the cathode is maintained and controlled so that only oxygen ionisation occurs and not the deposition of metal (eg Ca) from the cations (eg Ca ions) in the fused salt.

[0023] The process according to the second aspect of the invention provides a more practical, efficient and financially viable means for the production of metal from oxides. The electrical continuity of the system which is provided is effective since all the components are held in the cathodic potential region and are, therefore, metallic in nature.

DETAILED DESCRIPTION OF THE INVENTION

[0024] In order to carry out an embodiment of the process according to the second aspect of the present invention, using a metal oxide which comprises spent nuclear fuel, an electrolytic cell is assembled which has a carbon anode, a mesh basket cathode and a cathode rail connector welded to the base of the cell. Irradiated oxide fuel is placed in the mesh basket. The electrolyte consists of a molten salt or a mixture of such salts comprising, for example, chloride salts such as CaCl_2 or BaCl_2 . A voltage is applied between the cathode and the anode. At the cathode the reaction involves the diffusion of oxygen atoms to the surface of the solid, followed by ionisation according to the reaction:



[0025] The oxide ions which are produced dissolve in the electrolyte and are transferred to the anode where they are re-oxidised to produce oxygen, CO or CO_2 gases. The potential at the cathode may be controlled, via a third reference electrode, to ensure that the reaction occurring at the cathode is oxygen ionisation and not deposition of eg Ca metal from the cations in the fused salt. Electrolysis at elevated temperatures results in an increased rate of oxygen diffusion, thereby also encouraging ionisation rather than metal deposition.

[0026] After electrolysis the irradiated fuel is left in the form of a metallic solid at the cathode. This metallic solid, which contains fission products, can be removed or used directly as the feed for an electrorefining process. The remaining components of the cell may be re-used immediately without the need for any cleaning.

[0027] In an alternative embodiment in accordance with the present invention the electrolytic ionisation of oxygen and the electrorefining processes are carried out in the same cell and the same salt system. In such cases a second cathode, or cathode assembly, may be required.

[0028] It is to be emphasised that the advantage of the apparatus and process of the present invention is that they facilitate the performance of an effectively single stage process which provides advantages over the prior art in terms of practicality, efficiency and cost. The process is advantageously used for the treatment of irradiated oxide nuclear fuel, possibly in the form of pellets and, most particularly, is applied to fuels such as uranium oxide, and mixed uranium and plutonium fuels.

[0029] In order to fully illustrate the above and other features of the apparatus according to the first aspect of the invention, without in any way limiting the scope of the invention, a preferred embodiment will now be described with reference to the drawing.

DESCRIPTION OF THE DRAWING

[0030] FIG. 1 shows an apparatus according to the first aspect of the invention which comprises a series of electrolytic cells, the bodies and housings of which are, in use, connected by means of cathode rails 1 to cathode baskets 2. The cells also comprise anodes 4, surrounded by anode protective sleeves 3, and connected to an electrical supply by means of electrical connections 6, these being protected by insulation shrouds 5.

[0031] In operation, the cathode baskets 2, which are equipped with basket handles 8, cooled by means of cooling chambers 7, are loaded with spent nuclear fuel pellets and lowered into the electrolyte 9 to a point at which contact is made with cathode rails 1 and, thereby, with the cell housing, which is maintained as the cathode, thereby allowing processing to commence.

1. An apparatus for performing a process for reducing to metallic form metal oxides, the metal oxides comprising metal oxides present in spent nuclear fuel, wherein the apparatus comprises:

an electrochemical cell which comprises:

- a body or housing;
- a cathode container; and
- a cathode connector;

wherein said body or housing is maintained as the cathode, and said electrochemical cell is free from bolted or screwed fittings.

2. An apparatus as claimed in claim 1 wherein said cathode connector is affixed to an internal surface of the cell.

3. An apparatus as claimed in claim 2 wherein said cathode connector is affixed to an internal surface of the cell by means of welding.

4. An apparatus as claimed in claim 1 wherein an electrical connection from the cathode container to the body or housing of the cell is provided by means of a cathode connector.

5. An apparatus as claimed in claim 4 wherein said electrical connection is provided by means of a press connection.

6. An apparatus as claimed in claim 1 wherein said cathode connector comprises a cathode rail.

7. An apparatus as claimed in claim 6 wherein said rail is welded to the base of the cell.

8. An apparatus as claimed in claim 1 wherein the cathode container comprises a mesh basket or metal oxide retaining vessel.

9. An apparatus as claimed in claim 1 wherein the cathode container comprises an assembly of cathode containers.

10. An apparatus as claimed in claim 9 wherein said assembly comprises an assembly of mesh baskets or metal oxide retaining vessels.

11. An apparatus as claimed in claim 1 wherein the electromechanical cell further comprises a carbon anode.

12. An apparatus as claimed in claim 1 wherein the body or housing of the cell is maintained as the cathode by the provision of an electrical connection from a power supply to the body or housing of the cell.

13. A process for reducing to metallic form metal oxides, said metal oxides comprising metal oxides present in spent nuclear fuel, the process comprising:

cathodically electrolysing the oxide in the presence of a molten salt electrolyte in an apparatus, the apparatus comprising:

an electrochemical cell which comprises:

- a body or housing;
- a cathode container; and
- a cathode connector;

wherein said body or housing is maintained as the cathode, and said electrochemical cell is free from bolted or screwed fittings;

controlling the potential of the cathode so as to favour oxygen ionisation over deposition of metal from the cations present in the molten salt.

14. A process as claimed in claim 13 wherein

maintaining the body or housing of the cell as the cathode while bringing the body or housing of the cell into contact with the cathode container by means of a press connection between said container and a cathode connector.

15. A process as claimed in claim 13 wherein the oxide comprises the oxide of zirconium or hafnium.

16. A process as claimed in claim 13 wherein the oxide comprises an actinide oxide.

17. A process as claimed in claim 16 wherein the actinide oxide comprises uranium oxide, irradiated uranium oxide and/or mixed uranium/plutonium oxide fuel pellets.

18. A process as claimed in claim 17 wherein the uranium oxide comprises uranium dioxide.

19. A process as claimed in claim 13 wherein the oxide is located in a mesh basket which forms the cathode.

20. A process as claimed in claim 13 wherein the molten salt electrolyte comprises at least one chloride salt.

21. A process as claimed in claim 20 wherein chloride salt is CaCl_2 or BaCl_2 .

22. A process as claimed in claim 13 wherein the spent nuclear fuel comprises cladding.

23. A process as claimed in claim 13, further comprising:

removing the cladding from the fuel prior to cathodically electrolysing the oxide and controlling the potential of the cathode.

24. A process as claimed in claim 13 further comprising:

using the metal oxides reduced to metallic form as the feed for an electrorefining process.

25. A process as claimed in claims 24 wherein the electrorefining process is carried out in a same electrolytic cell as cathodically electrolysing the oxide and controlling the potential of the cathode.

26. (canceled)

* * * * *