



US 20060169590A1

(19) **United States**

(12) **Patent Application Publication**  
**Hebditch et al.**

(10) **Pub. No.: US 2006/0169590 A1**

(43) **Pub. Date: Aug. 3, 2006**

(54) **PROCESS FOR SEPARATING METALS**

**Publication Classification**

(76) Inventors: **David John Hebditch**, Gloucestershire (GB); **Zara Banfield**, Cheshire (GB)

(51) **Int. Cl.**  
**C25C 1/22** (2006.01)  
**C25C 3/34** (2006.01)  
(52) **U.S. Cl.** ..... **205/46**

Correspondence Address:  
**MYERS BIGEL SIBLEY & SAJOVEC**  
**PO BOX 37428**  
**RALEIGH, NC 27627 (US)**

(57) **ABSTRACT**

An electrorefining apparatus is capable of operating in continuous mode, and includes a criticality control mechanism, preferably a geometric criticality control mechanism, for example, to control the dimensions of the apparatus. Electrochemical cells include a large surface area per unit volume, preferably in the form of thin, flat plates. Cells include a crusting liquid cathodes, a cast cathode, a fluidised cell or pulsed bed, a moving belt cathode, a consolidating cathode, or a liquid anode and a plate cathode. A continuous process for the isolation of metals, typically uranium, from spent nuclear fuels includes electrochemically treating the spent nuclear fuels in the apparatus.

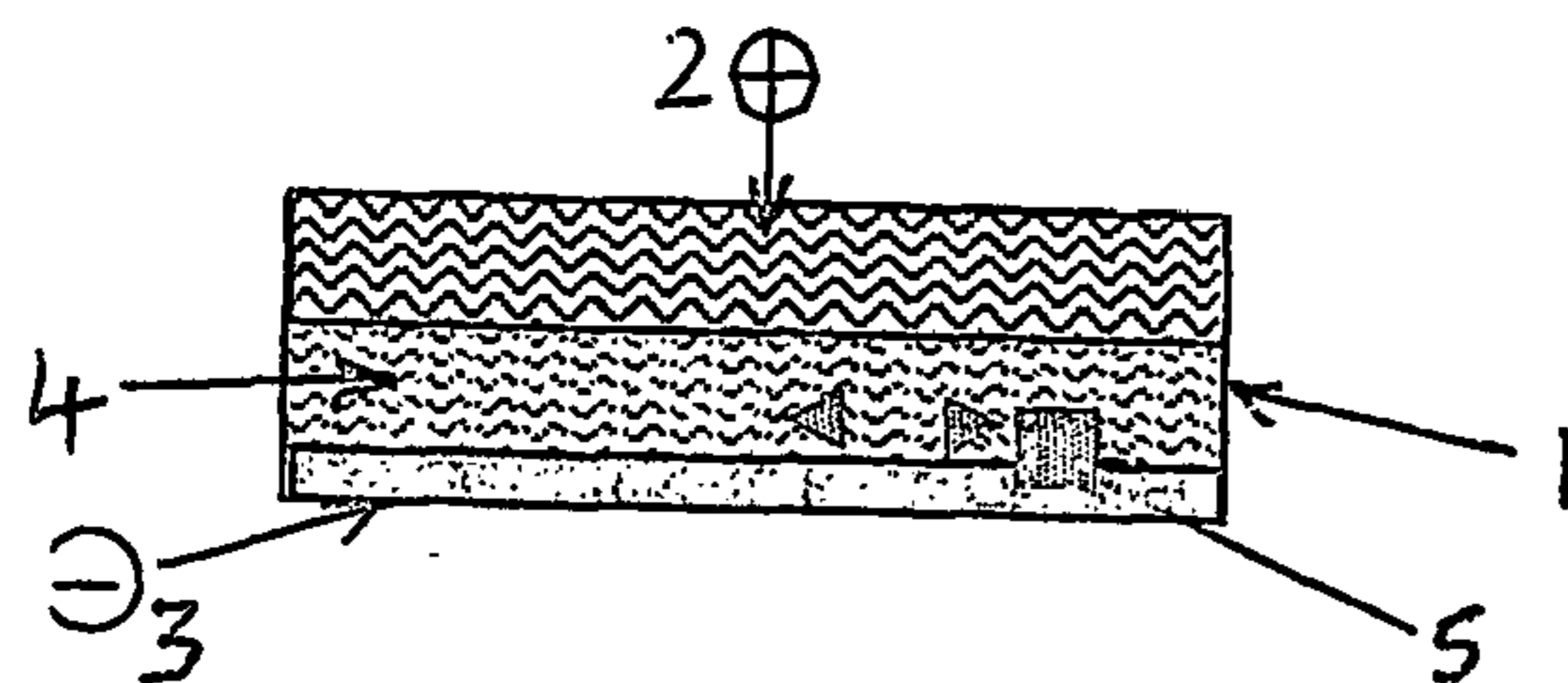
(21) Appl. No.: **10/547,813**

(22) PCT Filed: **Mar. 3, 2004**

(86) PCT No.: **PCT/GB04/00911**

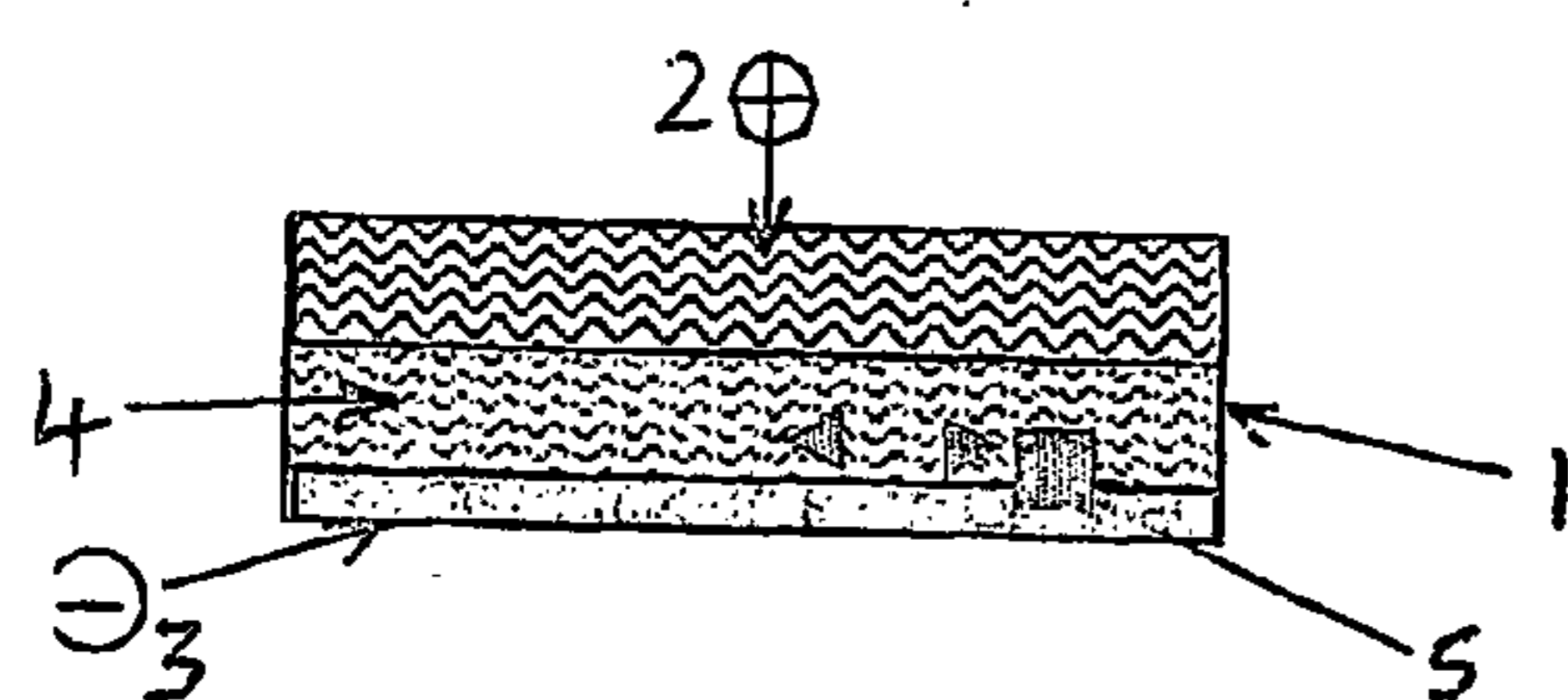
(30) **Foreign Application Priority Data**

Mar. 4, 2003 (GB) ..... 0304884.0



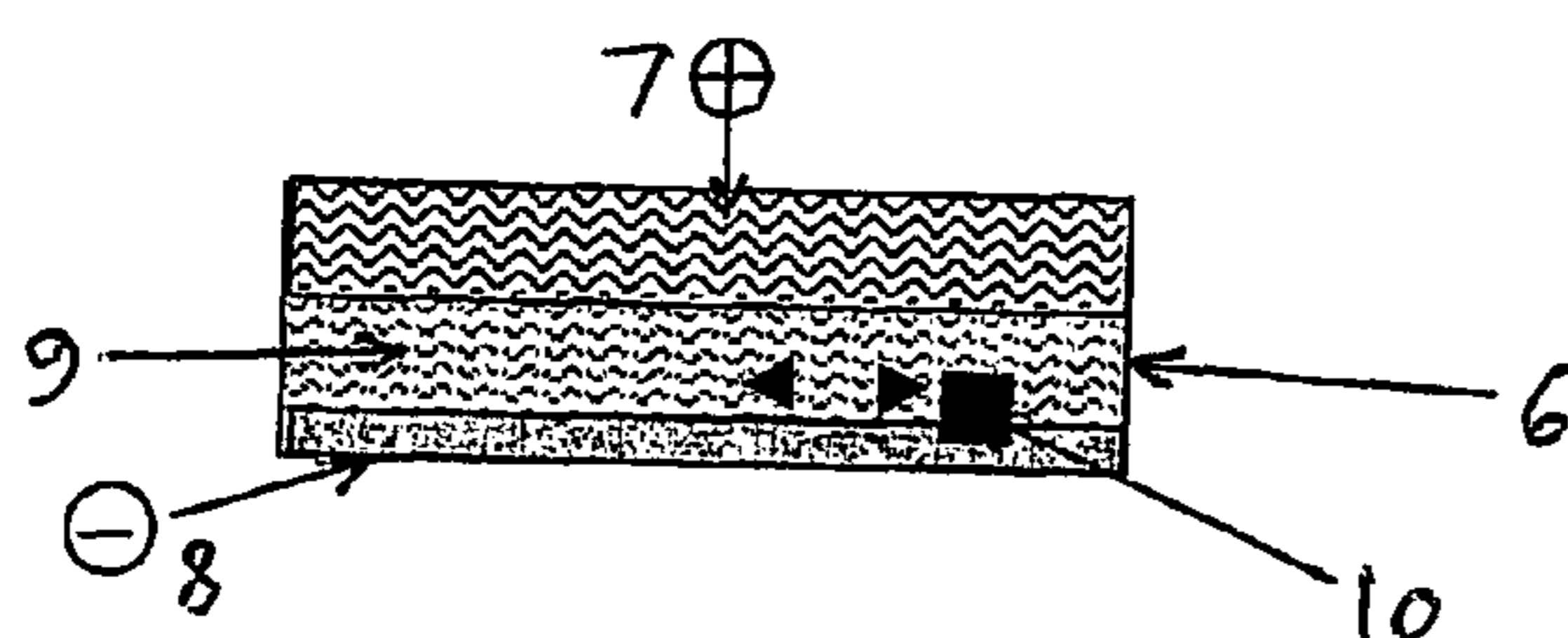
Vessel width	1 m
Vessel length	1 m
Vessel depth	0.1 m
Electrode width	1 m
Electrode length	1 m
Area of vessel base	1 m <sup>2</sup>
Volume of salt	0.1 m <sup>3</sup>

*Representation of crusting liquid cathode concept and approximate dimensions*



Vessel width	1 m
Vessel length	1 m
Vessel depth	0.1 m
Electrode width	1 m
Electrode length	1 m
Area of vessel base	1 m <sup>2</sup>
Volume of salt	0.1 m <sup>3</sup>

*Figure 1: Representation of crusting liquid cathode concept and approximate dimensions*



Vessel width	1 m
Vessel length	1 m
Vessel depth	0.1 m
Electrode width	1 m
Electrode length	1 m
Area of vessel base	1 m <sup>2</sup>
Volume of salt	0.1 m <sup>3</sup>

*Figure 2: Representation of cast cathode and approximate dimensions*

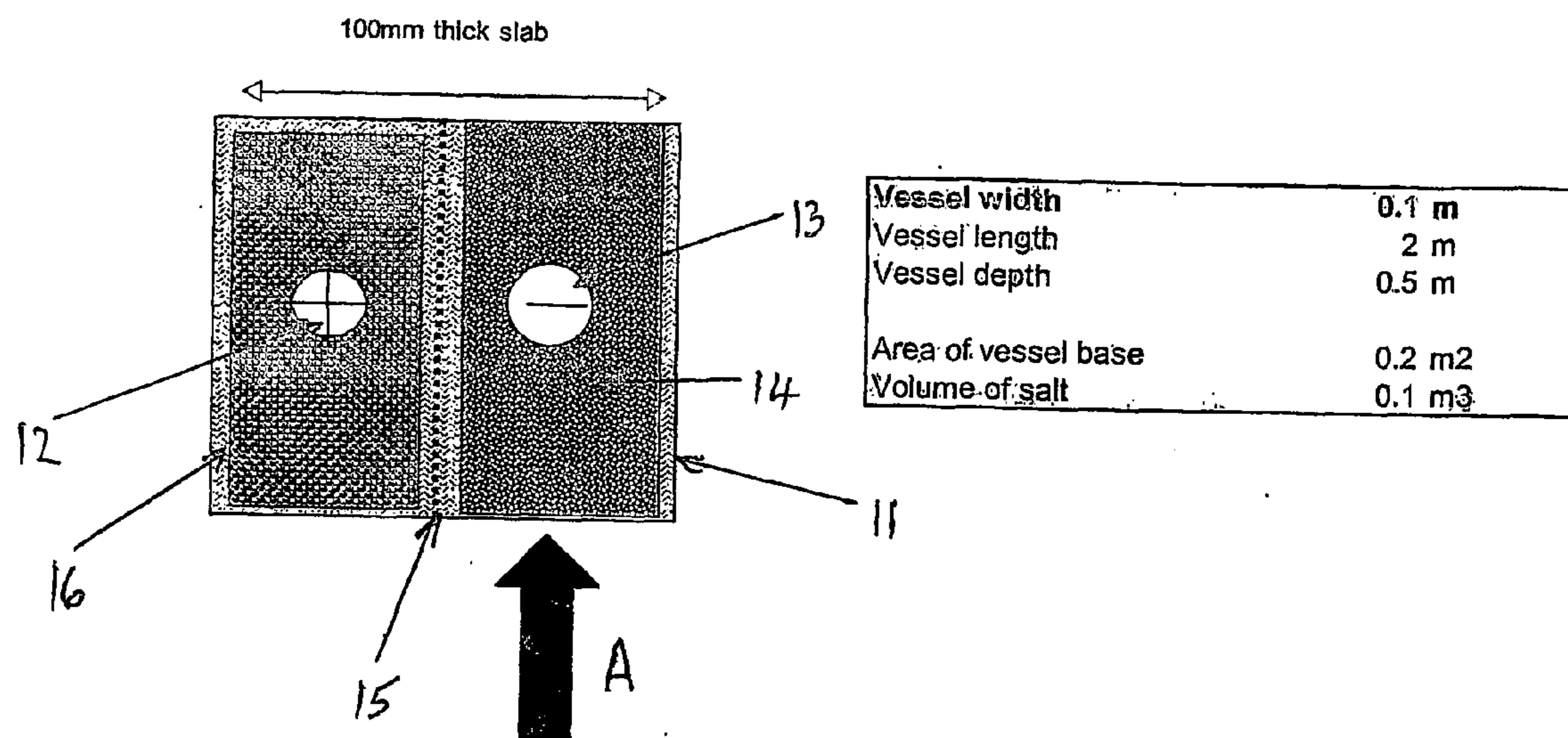


Figure 3: Representation of fluidised cell concept and approximate dimensions

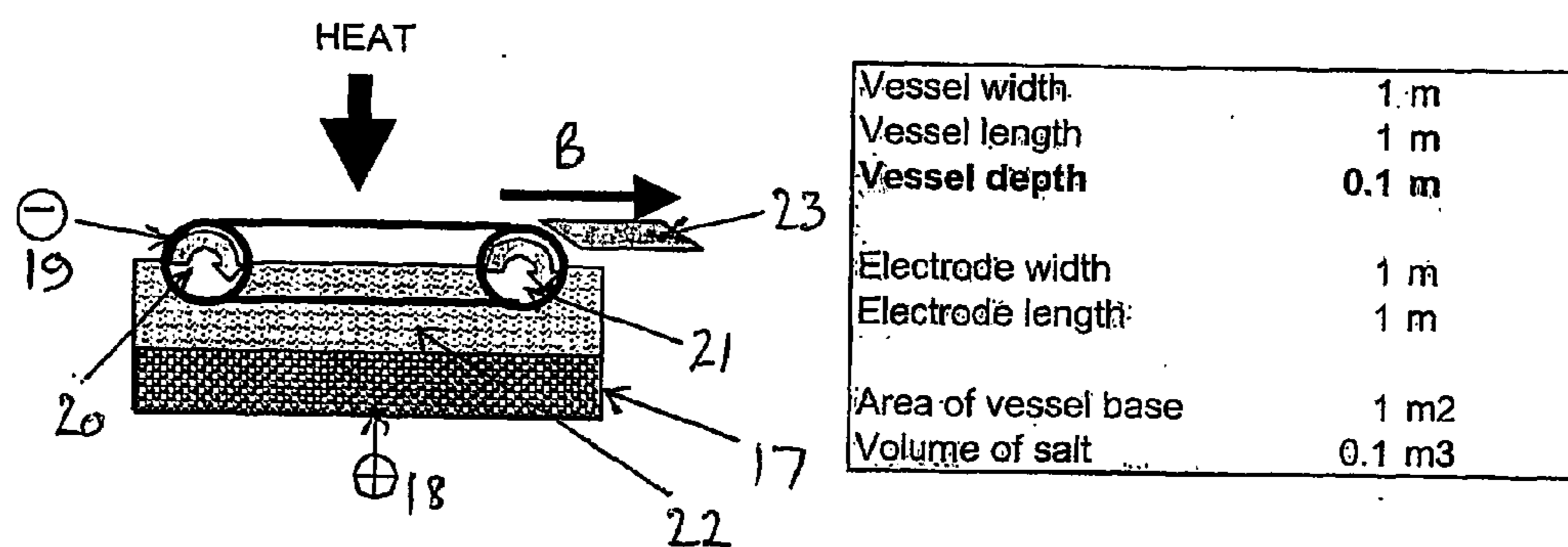


Figure 4: Representation of moving belt cathode concept and approximate dimensions

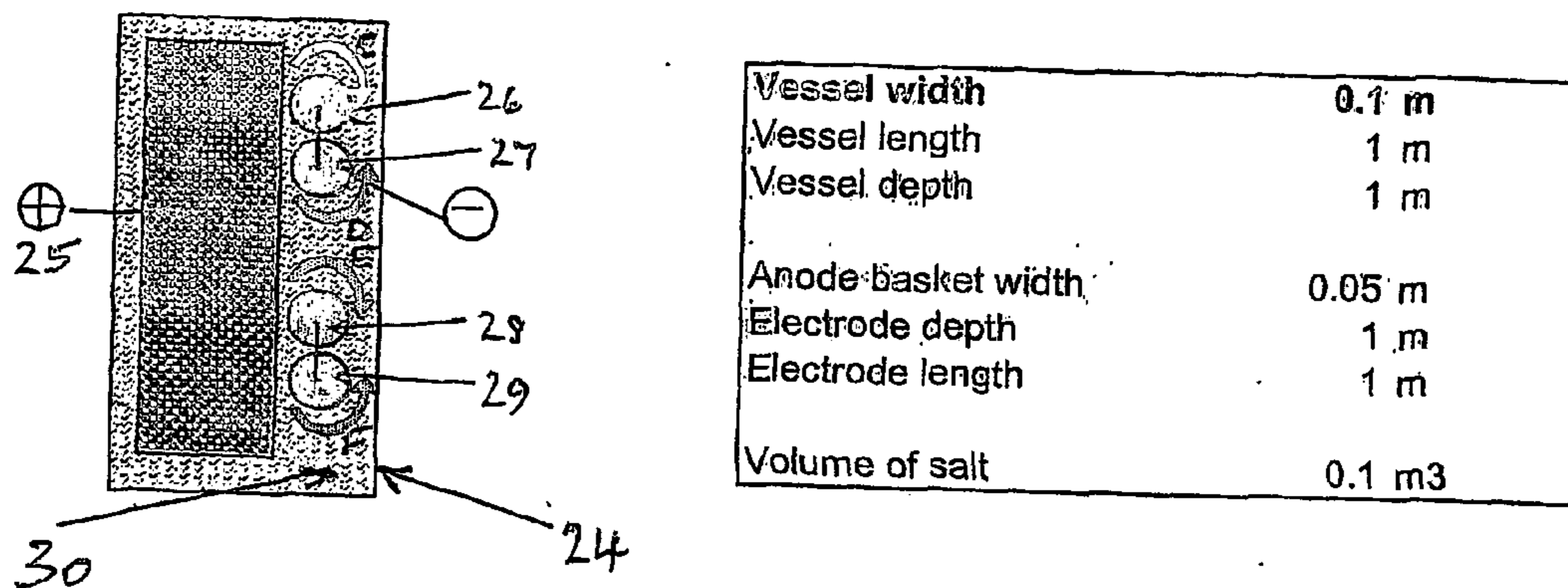


Figure 5: Representation of consolidating cathode concept and approximate dimensions

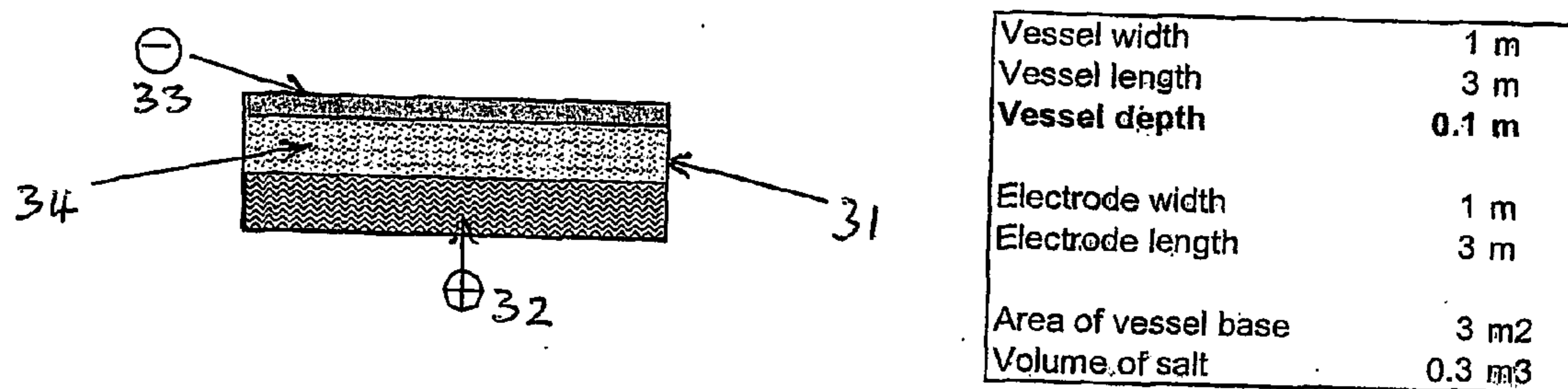


Figure 6: Representation of liquid anode/plate cathode concept and approximate dimensions

## PROCESS FOR SEPARATING METALS

### FIELD OF THE INVENTION

[0001] This invention relates to processes for the separation of metals from compositions containing metals. The invention includes processes for the treatment of spent nuclear fuel forming part of a process for reprocessing, conditioning and/or partitioning nuclear fuels. Reference will be made hereinafter mainly to nuclear fuels but it should be understood that the invention is not restricted to any particular type of material and has application outside the nuclear industry. The processes involve the purification of a substance which is liquid at its operating temperature and at this temperature is comprised wholly or largely of ionic species. Such substances generally fall within one of two main classes, ionic liquids and molten salts. Ionic liquids typically have a relatively low melting point and usually contain an organic cation, whereas molten salts are generally totally inorganic and most commonly have a melting point of at least several hundred degrees Centigrade. Molten salts typically comprise eutectic mixtures, the melting points of which can be significantly depressed from those of the individual components.

### BACKGROUND TO THE INVENTION

[0002] In the metals recovery and refining industry generally, the type of metal recoverable from a solvent is dependent upon the size of the electrochemical window of the solvent in which the metal is dissolved, and from which purification and recovery is taking place. In aqueous solutions, this is governed by the electrochemical window of water or supporting electrolyte. This limits the recovery, purification and electroplating of metals on to surfaces from aqueous solution to those metals whose electrode reduction potentials are more positive than the cathodic limit of the aqueous solution. In acidic aqueous solution, metal ions would not be recoverable where their electrode reduction potentials are more negative than that of the  $H_3O^+$  ion. Recovery of metals with electrode reduction potentials more negative than  $H_3O^+$ , means that non-aqueous (aprotic) solvents are required. There are a number of aprotic solvents which are used. These are often molten salts and, for instance, aluminium is industrially purified electrochemically by electrolysis of  $Al_2O_3$  dissolved in molten cryolite  $Na_3AlF_6$ . Other aprotic media include the organic solvents, such as acetonitrile, benzene and toluene.

[0003] Molten salts are often used as media in the nuclear industry. Such salts may be eutectic mixtures of salts and comprise chloride salts such as sodium or lithium chloride. These molten salts are typically liquid only at high temperatures. Alternatively, as previously noted, ionic liquids may be employed; the said term may refer to a salt, a mixture of salts, a mixture of components which produce a salt or salts which melts below or just above room temperature. (As used herein, the term "salt" means an entity comprising entirely of cationic and anionic species). The liquids are known as "ionic liquids" although this term is sometimes used for salts which melt at relatively high temperatures. In this specification, the term "ionic liquid" essentially refers to a salt which melts at a relatively low temperature. Ionic liquids free of molecular solvents were first disclosed by Hurley and Wier in a series of U.S. Pat. Nos. (2,446,331, 2,446,349, 2,446,350).

[0004] Common features of ionic liquids include a near zero vapour pressure at room temperature, a high solvation capacity and a large liquid range (for instance, of the order of  $300^\circ C.$ ). Known ionic liquids include aluminium(III) chloride in combination with an imidazolium halide, a pyridinium halide or a phosphonium halide. Examples include 1-ethyl-3-methylimidazolium chloride, N-butylpyridinium chloride and tetrabutylphosphonium chloride. An example of a known ionic liquid system is a mixture of 1-ethyl-3-methylimidazolium chloride and aluminium (III) chloride.

[0005] Internationally there are two well developed molten salts processes for the reprocessing/waste conditioning of irradiated nuclear fuel. A process developed by the Dimitrovgrad SSC—RIAR process uses high temperature (1000K) eutectic molten salt mixtures as solvents for the fuel and also as electrolyte systems. In this Russian system the solvent is typically an eutectic mixture of NaCl/KCl or CsCl/KCl. The process uses chemical oxidants (chlorine and oxygen gases) to react with powdered  $UO_2$  fuel, or mixtures of  $UO_2$  and  $PuO_2$ , to form higher oxidation state compounds such as  $UO_2Cl_2$  which are soluble in the molten salt. At the cathode the uranium and, if applicable, plutonium compounds are reduced to  $UO_2$ , or  $UO_2$ — $PuO_2$ , which form crystalline deposits. However, after a period of use the molten salt becomes loaded with fission products which not only begin to affect the quality of the product, but also result in too much heat generation within the salt. These fission products are commonly, but not exclusively, highly active lanthanide or actinide elements which may need to be isolated in a suitable form for immobilisation as a waste.

[0006] In the process developed by Argonne National Laboratory (ANL) in the USA, molten LiCl/KCl eutectic mixtures containing some  $UCl_3$  are generally used, rather than systems containing sodium or caesium salts, and a high temperature (around 773K) is again employed. However, single salts, such as LiCl, are suitable if higher temperatures are required, for example in the electrochemical reduction of fuel oxides. The process treats the spent nuclear fuel by flowing a current to oxidise a uranium anode and form uranium ions in the molten salt electrolyte. At the cathode the uranium is reduced and deposited as uranium metal. The ANL process is, unfortunately, a batch process, since the uranium is collected in a receptacle at the bottom of the apparatus, requiring that the process is interrupted in order that the receptacle may be withdrawn and the product recovered. In addition, the operation of the process is mechanically intense, involving the use of rotating anodes which are designed to scrape the product off the cathodes; difficulties are encountered on occasions due to the seizure of this mechanism.

[0007] 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 may be carried out chemically, using lithium metal in a LiCl or LiCl/KCl molten salt at  $500$  to  $700^\circ C.$  or, preferably, may be achieved by means of a direct electroreduction process. Alternatively, a salt transport process can be used involving a Cu—Mg—Ca alloy and molten  $CaCl_2$  salt. However, in these 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.

[0008] A disadvantage of the lithium reduction process for producing a metallic feed from an oxide is the production of  $\text{Li}_2\text{O}$  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.

[0009] EP-A-1055240 discloses a method for reprocessing spent nuclear fuel which comprises dissolving the spent fuel or constituent parts of the spent fuel in an ionic liquid to substantially separate fissile material from other components of irradiated fuel. Also disclosed is the subsequent treatment of the resulting ionic liquor, either by solvent extraction or electrochemical treatment to recover the dissolved uranium and plutonium. However, these processes for the clean up of the ionic liquid are disadvantageous from an economic point of view.

[0010] Furthermore, whilst the methods described in EP-A-1055240 are technically suitable for general use and, in particular, for use in nuclear fuel reprocessing, it has previously been thought that an electrorefining process, which avoids the need for an initial chemical dissolution step, requires the use of a high temperature molten salt electrolyte. If fuel is chemically oxidatively dissolved, there is less control over the species which are dissolved during this step. All those species which will be oxidised by the oxidising agent added will enter into the solution. Because the oxidising agents and conditions are aggressive, most species will dissolve, with the possible exception of species such as the noble metals.

[0011] EP-A-1212756 discloses a method for separating a metal from a composition including the said metal, the method comprising forming an electrolytic cell having an anode, a cathode and an electrolyte, wherein the anode comprises a composition including the metal and the electrolyte comprises an ionic liquid, and applying a sufficient potential difference between the anode and the cathode to cause the metal to transfer from the anode to the cathode and to be deposited thereon.

[0012] However, when this method is applied to a composition which comprises a metal or metal compound comprising a uranium or a transuranic element, problems of criticality may arise, since ionic liquids serve as moderators in such systems. In such circumstances, the difficulties may be obviated by placing a limit on the allowable dimensions of the electrochemical cell.

[0013] WO-A-02/066712 is concerned with the particular advantages that may be achieved by increasing the surface area per unit volume of the anode and cathode and reducing the electrode separation, thereby maximising the cell current. In addition, this document describes the benefits of providing high electrolyte velocities, which result in a scouring action, helping to remove dendritic growth on the cathode, and also provide turbulent flow, thus reducing the boundary layer and subsequently increasing the mass transfer coefficient. The advantages initially observed with uranium and transuranic elements were also applicable in the case of a wide range of other metals and metal compositions, and the process was found to be equally advantageous when using electrolytes comprising molten salts, rather than ionic liquids.

[0014] The provision of the metal in a form which exhibits a large surface area per unit volume facilitates increased

efficiency of the electrorefining process and enables the cell to be simply constructed, thereby leading to lower costs. The application of a suitable potential difference between the anode and the cathode results in electrochemical oxidation of the metal at the anode, causing it to enter into the liquid electrolyte medium. The soluble metal species is then electro-transported to the cathode where a reduction process occurs, which results in the deposition of the metal at the cathode.

[0015] The process may be applied to a variety of metal fuel feeds; typically the metal composition to be treated is irradiated nuclear fuel and the metal to be separated is uranium. Uranium or a uranium compound, and possibly other transuranic metals or compounds are deposited at the cathode in a purified form; the cathode generally comprises a solid cathode in the case of uranium, and a liquid cathode for mixtures of uranium, plutonium and other transuranics. Any fission products which are oxidised from the anode together with the uranium remain in the electrolyte. After the uranium electrorefining operation, and electrorecovery of transuranics, if desired, the electrolyte is subjected to further processing if fission product removal is required.

[0016] The process is analogous to the ANL process, wherein a metallic fuel feed is electrorefined and a uranium metal product is collected on a cathode. However, the process shows significant advantages over the earlier method in that it is free from the moving components, such as rotating anodes, which often cause problems with the ANL process. Nevertheless, although the system of WO-A-02/066712 also shows benefits over the ANL process in providing for semi-continuous operation, it is still essentially limited in applicability to batch electrorefiners. Additionally, it suffers from the disadvantage of limited size, and the geometry of the system can cause difficulty in achieving a uniform potential field. Consequently, the system is not well suited to scale-up.

[0017] The present invention, therefore, seeks to address these shortcomings in the prior art, and to provide a fully continuous process, which allows for maximised throughput, with the attendant economic advantages which thereby accrue.

[0018] EP-A-1240647 discloses 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.

[0019] The process thereby involves the use of 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 the cations (eg Ca ions) in the fused salt. Typically, the oxide comprises an actinide oxide, such as uranium oxide or irradiated uranium oxide.

[0020] WO-A-02/099815 provides a process for reducing to metallic form oxides of uranium, or metals more noble than uranium, present in spent nuclear fuel comprising a mixture of metal oxides, 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 metal from the cations present in the molten salt, and to ensure that reduction of metals other than uranium or metals more noble than uranium does not occur. The process is particularly applicable to the production of actinides, specifically uranium and metals more noble than uranium, from actinide oxides present in irradiated nuclear fuels. These methods are applicable to the treatment of irradiated fuels for producing actinides in metallic form suitable for use as feeds in subsequent electrorefining processes.

[0021] In the nuclear industry, it is often necessary to separate metals from a mixture of metal oxides such as occurs in spent nuclear fuel. Thus mixtures of uranium and plutonium oxides, together with the oxides of other actinide metals, may additionally be contaminated with oxides of other, chemically active, metals such as, for example, those associated with zircalloy cladding. The method of WO-A-02/099815 provides a method for the treatment of irradiated fuel which allows for the separation of uranium, and metals more noble than uranium, from such mixtures as found in spent nuclear fuel, and provides these metals in a form suitable for use as the feed in a molten salt electrorefining process, whilst ensuring that other, more electropositive, metals remain in the form of oxides.

[0022] The invention 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 the cations (eg Ca ions) in the fused salt, and also to ensure that, whilst reduction of uranium or metals more noble than uranium occurs smoothly, the less noble metals are not reduced and remain in the anode as oxides. Typically, the mixture of oxides includes an actinide oxide, such as uranium oxide or irradiated uranium oxide, or mixed uranium/plutonium oxides. The uranium oxide is commonly uranium dioxide.

[0023] After electrolysis the irradiated fuel is left in the form of a metal/metal oxide solid mixture at the cathode, with uranium and more noble metals having been reduced to the metallic form, whilst the less noble metals remain in the form of their oxides. This metallic/metal oxide product, which contains fission products, can be removed and 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.

[0024] In the electrorefining step, a potential is applied to the metal/metal oxide mixture at the anode such that only uranium metal enters the salt, whilst the less noble metals remain behind as oxides. Insufficient potential is applied to encourage the dissolution of metals more noble than uranium.

[0025] The advantage of the process is that it is effectively a single stage process. It is used for the treatment of irradiated mixed metal oxide nuclear fuel, possibly in the form of pellets and, most particularly, is applied to fuels which contain uranium oxide, and mixed uranium and plutonium fuels.

[0026] Whilst the technology of the prior art has found much success and wide applicability in the nuclear power

industry, however, the industry is always mindful of safety and environmental issues, and there are constant efforts to increase standards in these areas. An issue of particular concern is criticality, and improvements in criticality control continue to be sought. It is this aspect of the technology that is addressed by the present invention, which seeks to provide a method and apparatus for the geometrically safe electrochemical separation of uranium metal from spent nuclear fuel.

[0027] Criticality safety is concerned with the balance of neutrons produced by fission of fissile atoms, and the control of this balance, in order that both critical and supercritical states may be prevented, thus avoiding the possibility of a self-sustaining neutron chain reaction. One approach to criticality safety is asymmetric control, one dimension of the system is restricted, so that a critical mass of fissile material cannot be obtained. Thus, by adapting the geometry of the system, and limiting certain dimensions, it is possible to achieve criticality safety such that a critical mass of fissile material cannot be achieved. However, the known prior art does not provide a single example of metal electrorefiner or oxide electrolyser that displays such geometric safety and is capable of providing an industrial scale throughput. Hence, this is the problem addressed by the present invention, which seeks to provide this elusive combination of industrial scale viability and criticality safety.

[0028] Of the prior art previously discussed, only WO-A-02/066712 addresses the issue of criticality control. The application discloses that the electrorefiner is preferably designed to have significantly greater length and width than depth, providing a large, thin planar device which maximises the available surface area of the electrodes and is beneficial in delivering the criticality constraints imposed on the system. However, no further attention is paid to this matter, and no other options are considered. The present invention addresses this omission and proposes novel cell designs with geometric criticality control having particular application in the electrochemical separation of uranium metal from spent nuclear fuel.

#### STATEMENTS OF INVENTION

[0029] Thus, according to a first aspect of the present invention, there is provided an electrorefining apparatus, said apparatus being capable of operating in continuous mode, and including means for criticality control.

[0030] Said apparatus is capable of operating in fully continuous mode, rather than being restricted to operation in semi-continuous, or batchwise, mode as is the case with the apparatus of the prior art.

[0031] In order to facilitate efficient operation in continuous mode, it is preferred that said apparatus should additionally comprise means for the removal of deposited material from the apparatus, following operation. Said means for removal of deposited material may comprise, for example, sweeping means, conveyor means or means by which a section of the apparatus may be removed.

[0032] Preferably, said means for criticality control comprises means for geometric criticality control. Most preferably said means for geometric criticality control comprises means for control of the dimensions of said apparatus. It is desired that said means for geometric criticality control

should be fully compatible with other elements of the apparatus, in particular the means for removal of deposited material from the apparatus. Thus, for example, sweeping means should not be hindered by the specific dimensions of the apparatus.

[0033] Particularly preferred means for geometric criticality control comprise electrochemical cells having a large surface area per unit volume. Such means most preferably comprises a thin flat plate which may conveniently be horizontally or vertically disposed.

[0034] Said electrorefining apparatus may be utilised, for example, for the electrochemical separation of uranium metal from spent nuclear fuel. Alternatively, said electrorefining apparatus may be utilised for the reduction of a metal oxide fuel to a metallic form, with oxygen produced as the only by-product.

[0035] Typically, the apparatus according to the invention comprises an electrorefining cell having an anode and a cathode; in operation, an electrolyte is introduced into said electrorefining cell. Preferably, said electrolyte comprises a molten salt or an ionic liquid.

[0036] A second aspect of the present invention envisages a continuous process for the isolation of metals from spent nuclear fuels, said process comprising electrochemically treating said spent nuclear fuels in an apparatus according to the first aspect of the invention in the presence of an electrolyte.

[0037] Said continuous process preferably comprises the electrochemical separation of uranium metal from spent nuclear fuel, or the electrochemical reduction of a metal oxide fuel to a metallic form, with oxygen produced as the only by-product.

[0038] The application of a suitable potential difference between the anode and the cathode results in electrochemical oxidation of the metal at the anode, causing it to enter into the liquid electrolyte medium. The soluble metal species is then electro-transported to the cathode where a reduction process occurs, which results in the deposition of the metal at the cathode.

#### DETAILED DESCRIPTION OF THE INVENTION

[0039] A first embodiment of the apparatus according to the first aspect of the present invention comprises a crusting liquid cathode. Generally, said crusting liquid cathode is comprised in a horizontal thin slab configuration. Preferably, said crusting liquid cathode comprises a liquid metal cathode or liquid alloy cathode. During the electrochemical separation process for the separation of uranium metal from spent nuclear fuel, uranium metal is deposited on the cathode surface, and this metal deposit and residual amounts of cathode metal and molten salt are then removed from said cathode surface, for example by intermittent scraping or scooping. Initially, a high potential and current density may be employed in order to promote crusting of the molten metal surface by solid uranium. The metal deposit recovered at the conclusion of the process generally requires purification in order to remove contaminants, such as residual cathodic material. Typically, the anode in said apparatus comprises a basket containing spent fuel, which is adapted for use in a continuous process. Thus, for example, said

basket may form part of a conveyor belt of such baskets, which may be successively introduced into the apparatus in order to provide a continuous process.

[0040] A second embodiment of the apparatus according to the first aspect of the present invention comprises a cast cathode. Preferably, said cast cathode comprises a metal or alloy cathode with a lower melting point than uranium metal, the melted cathode being introduced to an electrorefiner cell as a liquid which is then frozen to form a solid metal or alloy cathode as a horizontal thin slab. In operation during the separation of uranium metal from spent nuclear fuel, uranium metal is deposited on the cathode surface, and the cathode is then melted and transferred out of the cell, transporting with it the uranium metal deposit as a slurry. The anode in said apparatus is adapted for use in a continuous process, and preferably comprises a horizontal basket containing spent fuel, which may be continuously fed and discharged transversely.

[0041] A third embodiment of the apparatus according to the first aspect of the present invention comprises a fluidised cell or pulsed bed. Preferably said fluidised cell or pulsed bed comprises cathode beads or particulates, preferably formed from graphite or uranium, and said electrorefiner cell is divided by a ceramic non-conducting membrane, forming a vertical thin slab. In operation during the separation of uranium metal from spent nuclear fuel, a charge is applied across the anode and cathode as though parallel plates and a molten salt containing dissolved uranium ions is pumped up through the cathode bed, resulting in the formation of uranium metal deposits on the bead or particulate surface. Typically, the anode in said apparatus comprises a basket containing spent fuel, which is adapted for use in a continuous process.

[0042] A fourth embodiment of the apparatus according to the first aspect of the present invention comprises a moving belt cathode. Preferably, said cathode comprises a refractory metal belt, forming a horizontal thin slab, conveying in and out of a molten salt and, in operation during the separation of uranium metal from spent nuclear fuel, the uranium metal deposits on the belt; once the belt is conveyed out of the salt, heat is applied to the uranium deposit to melt or soften it for scraping off the belt. Generally, the anode in said apparatus comprises a basket containing spent fuel or a liquid metal or alloy containing dissolved spent fuel, and adapted for use in a continuous process.

[0043] A fifth embodiment of the apparatus according to the first aspect of the present invention comprises a consolidating cathode. Preferably, said consolidating cathode comprises at least one pair of rotating cylinders, said cylinders being suspended vertically in a molten salt; in operation during the separation of uranium metal from spent nuclear fuel, uranium metal deposits on the cathode cylinder surface. Thereafter, rotation of the cylinders against each other causes the uranium deposit to compact and consolidate, thereby forming a plate of uranium metal. The cathode cylinders may then be scraped off line or scraped in situ to recover uranium metal; alternatively, the cylinders are formed from uranium metal and are melted down offline in order to facilitate removal of the salt and recovery of the cast uranium metal. Potentially, uranium deposits may break off and settle on the base of the vessel, and these deposits may be screw conveyed out of the apparatus for treatment. In



general, the anode in said apparatus comprises a basket containing spent fuel, adapted for use in a continuous process.

[0044] A sixth embodiment of the apparatus according to the first aspect of the present invention comprises a liquid anode and plate cathode. Preferably, said liquid anode comprises spent fuel pre-dissolved or slurried in liquid metal or alloy. Preferably, said plate cathode comprises a horizontal thin slab, and said plate cathode is positioned above said anode in parallel plate arrangement. Optionally, said cathode is comprised of uranium. In operation during the separation of uranium metal from spent nuclear fuel, uranium metal is electrodeposited on to the cathode plate and said cathode plate is removed periodically to allow for collection of said uranium metal or, preferably, said cathode plate is arranged in sections or modules, which may then conveniently be removed individually to allow for collection of the uranium metal in the context of the continuous electrorefining process.

[0045] In the process according to the second aspect of the invention, the spent nuclear fuel typically comprises a metal fuel assembly of fuel pins; alternatively, the spent nuclear fuel may comprise reduced metal oxides. Assemblies of fuel pins are firstly dismantled to single pins for feeding to an electrorefiner cell. Typically, said pins may then be cropped into small sections by means of a cropping machine, shredded using a bulk shredder, or ground to a small particle size. The sections of fuel, which should be as small as possible in order to allow the electrolyte to act on the composition, may then be loaded into an anode basket.

[0046] The electrolyte for use in the process according to the second aspect of the invention may comprise a molten salt or an ionic liquid. When the electrolyte comprises a molten salt, it may comprise any molten salt well known to those skilled in the art. Thus, for example, a LiCl/KCl molten salt eutectic mixture may be used, for example a LiCl/KCl eutectic melt comprising 41.5 mol. % KCl, with m.p. 361° C. If higher process temperatures, for example in the region of 600-700C, are required, such as in direct electrochemical reduction processes, LiCl alone may be employed as the molten salt electrolyte.

[0047] Alternatively, the electrolyte may comprise an ionic liquid, such as 1-ethyl-3-methylimidazolium chloride, or a mixture of two or more ionic liquids. In the case of electrolytes which comprise ionic liquids, the electrorefiner cell may be operated at lower temperatures, but the temperatures have to be kept sufficiently high to ensure that the liquid is maintained above its melting point; a suitable heating medium is employed for this purpose.

[0048] The process of the invention can be applied to a variety of metal fuel feeds. Uranium or a uranium compound, and possibly other transuranic metals or compounds, will be deposited at the cathode in a purified form. Any fission products and transuranics, including plutonium, which are oxidised from the anode together with the uranium, will remain in the electrolyte. After the uranium electrorefining operation has been carried out, the electrolyte is subjected to further processing if plutonium removal is required.

[0049] By contrast with a process involving chemical dissolution, in an electrochemical process there can be much

greater selectivity of the species to be dissolved. The potential at the anode can be controlled, such that metals which are more electropositive than uranium, and with larger negative Gibbs free energies associated with the species formed in solution, are the only metals which dissolve at the anode. This is the first separation step, as many of the more noble metals will remain behind in an anodic sludge. The electrolyte now contains a solution of metal ions including uranium and those of more electropositive species. A suitable potential is applied at the cathode, whereby uranium and metals less electropositive than uranium are electrodeposited. This should only include uranium, as those less electropositive metals have not been anodically dissolved.

[0050] The process of the present invention is analogous to the ANL process, wherein a metallic fuel feed is electrorefined and a uranium metal product is collected on a cathode. However, the process of the present invention shows significant advantages over this prior art method in that it is a continuous process, and is well suited to scale up as a consequence of the criticality safe nature of the apparatus of the invention. The present process also allows for the use of ionic liquids, as well as molten salts, in its operation.

#### DESCRIPTION OF THE DRAWINGS

[0051] The apparatus and method of the present invention will now be illustrated, though without limitation, by reference to the accompanying drawings, in which:

[0052] **FIG. 1** is a side elevation representation of a crusting liquid cathode according to the first embodiment of the first aspect the invention;

[0053] **FIG. 2** is a side elevation representation of a cast cathode according to the second embodiment of the first aspect of the invention;

[0054] **FIG. 3** is a side elevation representation of a fluidised cell according to the third embodiment of the first aspect of the invention;

[0055] **FIG. 4** is a side elevation representation of a moving belt cathode according to the fourth embodiment of the first aspect of the invention;

[0056] **FIG. 5** is a plan representation of a consolidating cathode according to the fifth embodiment of the first aspect of the invention; and

[0057] **FIG. 6** is a side elevation representation of a liquid anode/plate cathode according to the sixth embodiment of the first aspect of the invention.

[0058] Referring firstly to **FIG. 1**, there is seen an apparatus comprising a vessel **1** containing an anode **2** and a crusting liquid cathode **3**. In operation, an electrolyte **4** is introduced into the vessel **1**, and metal is deposited at the crusting liquid cathode **3**; this may be removed by the action of the scraper **5**, moving along the surface of the cathode. The vessel has a width and a length of 1 m, giving a base area of 1 m<sup>2</sup>; the depth of the vessel is 0.1 m. The electrodes have a length and width of 1 m. The volume of electrolyte employed is 0.1 m<sup>3</sup>.

[0059] Turning to **FIG. 2**, there is shown an apparatus comprising a vessel **6** containing an anode **7** and a cast cathode **8**. In operation, an electrolyte **9** is introduced into

the vessel 6, and metal is deposited at the cast cathode 8; this may be removed by the action of the scraper 10, moving along the surface of the cathode. The vessel has a width and a length of 1 m, giving a base area of 1 m<sup>2</sup>; the depth of the vessel is 0.1 m. The electrodes have a length and width of 1 m. The volume of electrolyte employed is 0.1 m<sup>3</sup>.

[0060] FIG. 3 shows an apparatus consisting of a fluidised cell comprising a vessel 11 including an anode 12 and a cathode 13 which comprises cathode beads or particulates 14. The vessel comprises sections separated by ceramic divider 15. In operation, electrolyte 16 is introduced in the direction of arrow A, and metal is deposited on the surfaces of the beads or particulates comprising the cathode 13. The vessel has a width of 0.1 m and a length of 2 m, giving a base area of 0.2 m<sup>2</sup>; the depth of the vessel is 0.5 m. The volume of electrolyte employed is 0.1 m<sup>3</sup>.

[0061] In FIG. 4, there is shown an apparatus comprising a vessel 17 including an anode 18 and a moving belt cathode 19 mounted on a pair of rollers 20, 21 and moving in the direction of arrow B. In operation, electrolyte 22 is introduced into the vessel and metal is deposited on the moving belt cathode 19. The metal is carried in the direction of arrow B and the application of heat facilitates its collection by the action of scraper 23. The vessel has a width and a length of 1 m, giving a base area of 1 m<sup>2</sup>; the depth of the vessel is 0.1 m. The electrodes have a length and width of 1 m. The volume of electrolyte employed is 0.1 m<sup>3</sup>.

[0062] In FIG. 5, there is seen an apparatus comprising a vessel 24 including an anode 25 and a cathode comprising two pairs of rotating cylinders 26, 27 and 28, 29. In operation, electrolyte 30 is introduced into the vessel, cathode cylinders 26, 27, 28 and 29 rotate in the directions of arrows C, D, B and F, respectively, and metal is deposited on the cathode cylinders. The vessel has a length and a depth of 1 m, and the width of the vessel is 0.1 m. The electrodes have a length and depth of 1 m, and the width of the anode basket is 0.05 m. The volume of electrolyte employed is 0.1 m<sup>3</sup>.

[0063] FIG. 6 shows an apparatus comprising a vessel 31 including a liquid anode 32 and a plate cathode 33, arranged in sections or modules. In operation, electrolyte 34 is introduced into the vessel and metal is deposited on the plate cathode 33, sections of which are removed and replaced periodically to allow for recovery of the metal. The vessel has a width of 1 m and a length of 3 m, giving a base area of 3 m<sup>2</sup>; the depth of the vessel is 0.1 m. The electrodes have a length of 3 m and a width of 1 m. The volume of electrolyte employed is 0.3 m<sup>3</sup>.

1. An electrorefining apparatus, the apparatus comprising an electrorefining cell having an anode and a cathode, wherein the apparatus is adapted for operation in continuous mode, and includes means for criticality control, the means for criticality control comprising electrochemical cells having a large surface area per unit volume.

2. An apparatus as claimed in claim 1 wherein the means for criticality control comprises a thin flat plate.

3. An apparatus as claimed in claim 2 wherein the thin flat plate is horizontally or vertically disposed.

4. An apparatus as claimed in claim 1 further comprising means for the removal of deposited material from the apparatus, following operation.

5. An apparatus as claimed in claim 4 wherein the means for removal of deposited material comprises sweeping means, conveyor means or means by which a section of the apparatus may be removed.

6. An apparatus as claimed in claim 1 further comprising a vessel, an anode and a crusting liquid cathode.

7. An apparatus as claimed in claim 6 wherein the crusting liquid cathode comprises a liquid metal cathode or liquid alloy cathode.

8-10. (canceled)

11. An apparatus as claimed in claim 1 further comprising a vessel, an anode and a cast cathode.

12. An apparatus as claimed in claim 11 wherein the cast cathode comprises a metal or alloy cathode with a lower melting point than uranium metal.

13. An apparatus as claimed in claim 12 wherein the cast cathode is introduced to an electrorefiner cell as a melted liquid cathode which is then frozen to form a solid metal or alloy cathode as a horizontal thin slab.

14-15. (canceled)

16. An apparatus as claimed in of claim 1 further comprising a fluidised cell or pulsed bed.

17. An apparatus as claimed in claim 16 wherein the fluidised cell or pulsed bed comprises a vessel including an anode and a cathode which comprises cathode beads or particulates.

18. An apparatus as claimed in claim 16 further comprising a ceramic divider.

19. An apparatus as claimed in claim 17 wherein the cathode beads or particulates are formed from graphite or uranium.

20. (canceled)

21. An apparatus as claimed in claim 1 which comprises a vessel, an anode and a moving belt cathode.

22. An apparatus as claimed in claim 21 wherein the moving belt cathode is mounted on a pair of rollers.

23. An apparatus as claimed in claim 21 wherein the moving belt cathode comprises a refractory metal belt.

24-25. (canceled)

26. An apparatus as claimed in claim 1 further comprising a vessel, an anode and a consolidating cathode.

27. An apparatus as claimed in claim 26 wherein the consolidating cathode comprises at least one pair of rotating cylinders, the cylinders being suspended vertically.

28. (canceled)

29. An apparatus as claimed in claim 27 wherein the cylinders are formed from uranium metal.

30. (canceled)

31. An apparatus as claimed in claim 1 further comprising a vessel, a liquid anode and a plate cathode.

32. An apparatus as claimed in claim 31 wherein the plate cathode is arranged in sections or modules.

33. An apparatus as claimed in claim 31 wherein the liquid anode comprises spent fuel pre-dissolved or slurried in liquid metal or alloy.

34. An apparatus as claimed in claim 31 wherein the plate cathode comprises a horizontal thin slab positioned above the anode in parallel plate arrangement.

35. An apparatus as claimed in claim 31 wherein the plate cathode is comprised of uranium.

36. A continuous process for the isolation of metals from spent nuclear fuels, the process comprising electrochemically treating the spent nuclear fuels in an apparatus according to claim 1.

**37.** A process as claimed in claim 36 further comprising the electrochemical separation of uranium metal from spent nuclear fuel, the spent nuclear fuel comprising reduced metal oxides.

**38-40.** (canceled)

**41.** A process as claimed in claim 36 wherein an electrolyte is introduced into the apparatus, the electrolyte comprising molten salt or an ionic liquid.

**42-46.** (canceled)

**47.** An apparatus as claimed in claim 5, wherein the sweeping means comprises a scraper.

**48.** An apparatus as claimed in claim 1, wherein the anode is adapted for use in a continuous process.

\* \* \* \* \*