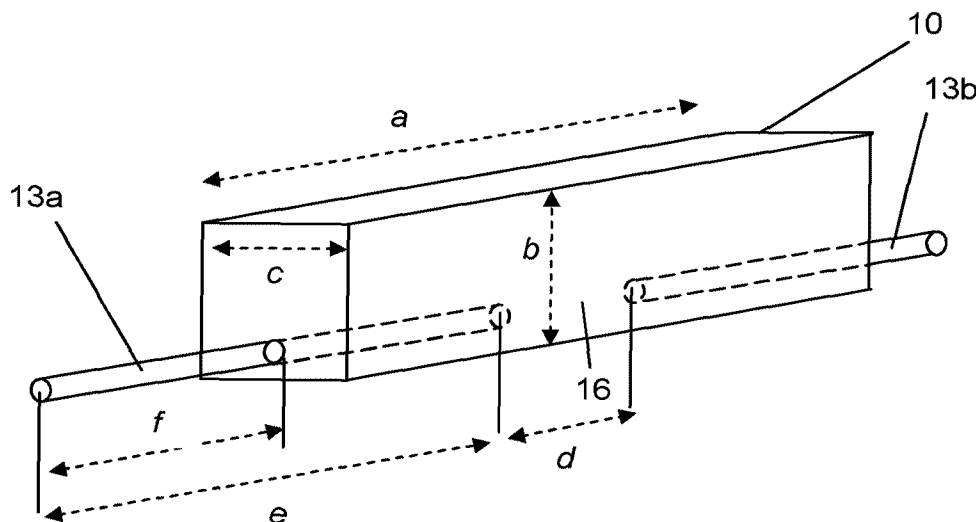




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(72) **Inventeurs/Inventors:**
JONQUA, BERNARD, AE;
ZAROUNI, ABDALLA, AE
(73) **Propriétaire/Owner:**
DUBAI ALUMINIUM PJSC, AE
(74) **Agent:** FASKEN MARTINEAU DUMOULIN LLP

(54) **Titre : BLOC DE CATHODE POUR CELLULE ELECTROLYTIQUE CONVENANT POUR LE PROCEDE HALL/HEROULT**
(54) **Title: CATHODE BLOCK FOR ELECTROLYTIC CELL SUITABLE FOR THE HALL-HEROULT PROCESS**



(57) **Abrégé/Abstract:**

Cathode element suitable for use in a Hall-Heroult electrolysis cell, comprising a cathode block (10) comprising a carbonaceous material, at least one metallic connection bar (13) made in copper or copper alloys, wherein said metallic connection bar (13) is fitted into a groove or bore in direct contact with a carbonaceous material, and wherein said carbonaceous material can be the carbonaceous material of said cathode block (10), or an intermediate carbonaceous material (17) that is in direct contact with the carbonaceous material of said cathode block (10).



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- (71) **Applicant:** DUBAI ALUMINIUM PJSC [AE/AE]; PO Box 3627, Dubai (AE).
- (72) **Inventors:** JONQUA, Bernard; Villa 30B, Street 27, Mirdiff, Dubai (AE). ZAROUNI, Abdalla; Villa 224, Street 24, Al Darari Area, Sharjah (AE).
- (74) **Agent:** SCHMIDT, Martin; Ixas Conseil, 15 rue Emile Zola, 69002 Lyon (FR).
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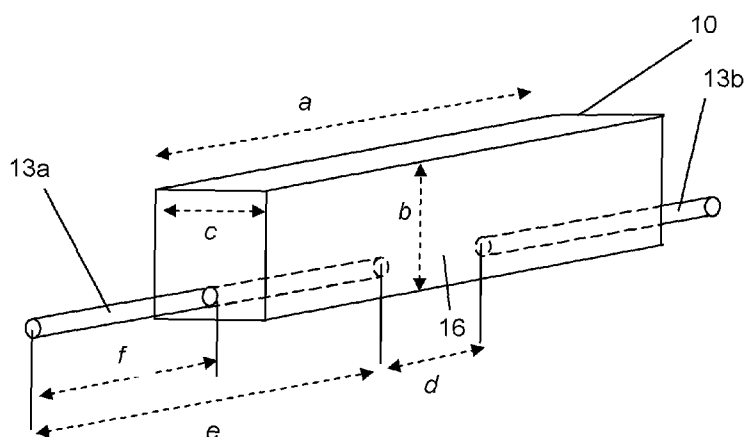


Figure 3

(57) **Abstract:** Cathode element suitable for use in a Hall-Heroult electrolysis cell, comprising a cathode block (10) comprising a carbonaceous material, at least one metallic connection bar (13) made in copper or copper alloys, wherein said metallic connection bar (13) is fitted into a groove or bore in direct contact with a carbonaceous material, and wherein said carbonaceous material can be the carbonaceous material of said cathode block (10), or an intermediate carbonaceous material (17) that is in direct contact with the carbonaceous material of said cathode block (10).

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Cathode block for electrolytic cell suitable for the Hall-Héroult process

Technical field of the invention

The invention relates to a cathode block for an electrolytic cell for producing aluminium by fused salt electrolysis using the Hall-Héroult-process. In particular, the invention relates to a cathode block in which the electrical contact between the cathode material and the busbar to which the cathode is connected involves a copper bar.

Prior art

The Hall-Héroult process is the only continuous industrial process for producing metallic aluminium from aluminium oxide. Aluminium oxide (Al_2O_3) is dissolved in molten cryolite (Na_3AlF_6), and the resulting mixture (typically at a temperature comprised between 940°C and 970°C) acts as a liquid electrolyte in an electrolytic cell. An electrolytic cell (also called "pot") used for the Hall-Héroult process typically comprises a steel shell, a lining (comprising refractory bricks protecting said cell against heat loss, and cathode blocks usually made from graphite, anthracite or a mixture of both, covering the whole bottom of the pot), a superstructure and a plurality of anodes (usually made from carbon) that plunge into the liquid electrolyte. Anodes and cathodes are connected to external busbars. An electrical current is passed through the cell (typically at a voltage between 3.5 V to 5 V) which electrochemically reduces the aluminium oxide, split by the electrolyte into aluminium ions and oxygen ions. The oxygen ions are reduced to oxygen at the anode, said oxygen reacting with the carbon of the anode. The aluminium ions move to the cathode where they accept electrons supplied by the cathode; the resulting metallic aluminium is not miscible with the liquid electrolyte, has a higher density than the liquid electrolyte and will thus accumulate as a liquid metal pad on the cathode surface from where it needs to be removed from time to time, usually by suction into a crucible.

The electrical energy is the main operational cost in the Hall-Héroult process. Capital cost is an important issue, too. Ever since the invention of the process at the end of the 19th century much effort has been undertaken to improve the energy efficiency (expressed in kW/h per kg or ton of aluminium), and there has also been a trend to increase the size of the pots and the current intensity at which they are operated in order to increase the plant productivity and bring down the capital cost per unit of aluminium produced in the plant.

Industrial electrolytic cells presently used for the Hall-Héroult process are rectangular and have a length usually comprised between 8 and 25 meters and a width usually comprised between 3 and 5 meters. Most newly installed pots operate at a current intensity comprised between about 400 kA and 600 kA. They are always operated in series of

several tens (up to more than a hundred) pots (such a series being also called a "potline"); within each series DC currents flow from one cell to the neighbouring cell. Much effort is still being made to optimise the process in order to increase its energy efficiency.

5 The passage of the enormous current intensities through the electrolytic cell leads to ohmic losses at various locations of the pot. Aluminium conductors are used for the busbar systems for both anodes and cathodes. However, aluminium cannot be used in direct contact with the cathode blocks due to its low melting point (about 660°C for pure aluminium). As a consequence, steel bars are conventionally used for ensuring electrical
10 contact with the cathode blocks; these so-called cathode bars are connected to cathodic busbars (made from aluminium) by welded and/or bolted connectors. Cathode bars are typically fitted into slots machined into the lower surface of the cathode block. Electrical contact between the steel bar and the carbon material of the cathode block can be direct, or the steel bar can be embedded in cast iron, as described in GB 663 763 (assigned to
15 Compagnie de Produits Chimiques et Electrometallurgiques Alais, Froges & Camargue).

During the past decades, much effort has been devoted to the decrease of ohmic losses in cathode bars. Most inventions reported in prior art patents focus on the intrinsic conductivity of the steel cathode bar, or on the contact resistance between the cathode
20 bar and the cathode block or between the cathode bar and the aluminium busbar.

The increase in the electrical conductivity of the cathode bars implies the use of a material having a higher electrical conductivity than steel bars. All reported solutions imply the use of inserts made from a material with a higher electrical conductivity into the cathode bar,
25 which is usually made from steel. The material with a higher electrical conductivity is usually copper. Typical solutions comprise a copper rod or bar that is inserted into a groove or slot machined into the steel cathode bar, over all or part of the length of said cathode bar. The basic concept of a copper insert fitted into a slot or groove machined in a steel cathode bar is described in WO 2001/63014 (Comalco), WO 2005/098093
30 (Aluminium Pechiney) and WO 2009/055855 (BHB Billington).

FR 1 161 632 (Pechiney) discloses a copper insert fitted into a groove machined in a carbon cathode block using cast iron as a sealing material. The composition of cast iron used for sealing cathode bars into the grooves of carbon cathodes is known to be critical
35 (see US 2,953,751 assigned to Pechiney), because the cast iron should not undergo any swelling due to structural transformations, as swelling could cause the carbon material to develop cracks.

A large number of more specific embodiments have been described for these copper inserts, such as:

- A copper bar with circular cross section fitted into a steel bar with outer rectangular cross section and an inner "U" section, the "U" section being closed by a block, see US 3,551,319 (Kaiser).
- A copper bar welded to a lateral face of a steel bar, see US 3,846,388 (Pechiney).
- A copper bar with rectangular cross section inserted into a steel tube with rectangular cross sections, see US 5,976,333 (Alcoa).
- A copper bar with circular cross section inserted into a steel tube with rectangular external cross section and a bore with circular cross section, see WO 2005/098093 (Aluminium Pechiney).

Several documents disclose the use of a joint material present between the cathode material and the steel bar: WO 2013/039893 (Alcoa) describes the use of a copper insert as a joint, WO 2007/071392 (SGL Carbon) describes the use of sheets made from expanded graphite, and RU 2285764 describes the use of a carbonaceous paste. Such a joint material may improve the electrical contact between the carbon block and the steel bar.

RU 2285754 proposes to secure the copper bar inserted into the slot of the steel bar by welded-on steel plates while allowing for a narrow cavity between the copper insert and the steel bar, i.e. the section of the copper insert is somewhat smaller than that of the groove into which it is fitted.

The opposite approach is taken by WO 2009/055844 describing the use of roll bonding or explosion bonding in order to obtain an excellent contact between the copper insert and the steel bar over the whole length of the insert.

Another problem addressed by many inventions is the connection between the copper insert and the steel cathode bar. This contact is critical for at least three reasons: the electrical contact between the copper insert and the cathode bar should be as good as possible; the thermal expansion coefficients of steel and copper are rather different and may lead to dimensional variations during the start-up of the pot; and the thermal conductivity of copper and steel is rather different, which needs to be taken into account for designing (and minimising) the heat transfer between the pot and the aluminium busbar.

For this reason, in some prior art embodiments the copper inserts do not extend along the whole length of the steel cathode bar, but a spacer section is provided at each end of the cathode bar into which the copper insert does not extend. Also, the copper bar can be made in two pieces separated in the centre of the cathode by a steel plug and/or an air gap. Such a structure is described in US 6,387,237 and US 6,231,745 (Alcoa).

The opposite approach is proposed by WO 2002/42525 (Servico), namely a cathode bar comprising a steel bar into which at each end a copper bar is inserted, the copper insert extending beyond the end of the steel bar and ensuring the electrical contact with the connection to the aluminium busbar.

The insertion of copper bars of complex shape into cathode bars has been used to fine-tune the current distribution over the length of the cathode bar; such an embodiment is described in WO 03/014434 (Alcoa). Other structures ensuring a variation of the electrical conductivity of the cathode bar along its length are described in WO 2004/059039 (SGL Carbon) and in WO 2008/062318 (Rio Tinto Alcan).

As can be seen, there has been a wealth of different designs of copper inserts in cathode bars. However, three potential problems with copper inserts have hardly ever been mentioned in the patent literature:

Firstly, as all these copper inserts are inlaid into grooves machined into a steel bar, it should be noted that the machining of steel is a rather difficult and expensive process which adds to the cost of the copper material.

Secondly, the melting point of copper (about 1080°C for pure copper) is rather close to the temperature of the liquid phases in the pot (around 950°C to 1000°C). Knowing that cathode blocks have a lifetime between typically 4 to 7 years, and knowing that copper readily forms a dense oxide layer on its surface, and knowing that the melting point of steel is much higher than that of copper, and knowing that spent cathodes usually show a significant deformation of the steel cathode bars, there can be some concern about the long-term behaviour of copper-inserted cathode bars in relation with their dimensional stability (related to possible local melting or at least creep) and contact resistance.

Thirdly, it is desirable to be able to separate the copper insert from the steel bar in spent cathode blocks completely and easily (i.e. without intensive labour). There are two reasons for this: copper is much more expensive than steel, and it is therefore desirable to recover the copper insert from the steel bar for recycling. Furthermore, if the steel bar is

recycled with the copper insert or with a significant amount of copper residues, not only the copper will be lost for separate recycling but also the copper may poison the steel batch into which the steel bar is recycled.

- 5 It is the objective of the present invention to come up with a new design of cathode bars that solves all of the abovementioned problems.

Figures

- 10 Figures 1 illustrates the prior art. Figure 1a shows a schematic perspective view of a cathode block 1 according to prior art. The steel bar 2 is fitted into groove at the bottom surface 5 of the cathode block 1. A copper bar insert 3 is fitted into a groove machined into the higher surface 6 of the steel bar 2.

Figure 1b shows a cross section of another prior art cathode block in which the steel bar 2 is fitted into the groove using cast iron 4; a copper bar 3 is fitted into the steel bar 2.

- 15 Figure 1c shows another variant of the prior art embodiment of figure 1a with two parallel cathode bars 2 made from steel with a copper insert 3.

Figures 2 to 5 illustrate embodiments of the cathode block according to the invention that will be discussed in more detail below.

20

Figures 6 and 7 show schematic perspective views of two examples of a connector (figure 6) or a connection plate (figure 7) used to connect the copper bar of the cathode block according to the invention to a busbar.

25

Object of the invention

According to the invention the problem is solved by using a cathode bar comprising a full copper bar over at least part of the length of said cathode block. That is to say that over at least part of the length of the cathode block the full section of said cathode bar is copper.

- 30 Unlike prior art cathode bars using copper inserts, the cathode bar according to the present invention does not use a copper bar that is inserted into a steel bar, but uses the copper bar in direct contact with the carbonaceous material of the cathode block or of an intermediate carbonaceous material that is in contact with the cathode block.

- 35 The first object of the invention is a cathode element suitable for use in a Hall-Héroult electrolysis cell, comprising a cathode block comprising a carbonaceous material, and at least one metallic connection bar made in copper or copper alloys, wherein said metallic connection bar is fitted into a groove or bore in direct contact with a carbonaceous

material, and wherein said carbonaceous material can be the carbonaceous material of said cathode block, or an intermediate carbonaceous material that is in direct contact with the carbonaceous material of said cathode block.

In an advantageous embodiment said cathode element does not comprise any other
5 metallic connection bar in direct contact with the carbonaceous material than connection bars made in copper or copper alloys.

Said intermediate carbonaceous material can be compressed expanded graphite and/or a cured carbonaceous seal. If a cured carbonaceous seal is used, a graphitized
10 carbonaceous seal is preferred. Said cured (and preferably graphitized) carbonaceous seal advantageously comprises graphite particles. In a specific embodiment the connection bar is in direct contact with compressed expanded graphite, and said expanded compressed graphite is in direct contact with a cured (and preferably graphitized) carbonaceous seal, said cured carbonaceous seal being in direct contact with
15 the carbonaceous material of the cathode block.

In specific embodiments, said metallic connection bar can have a round or a rectangular cross section. In a specific embodiment said metallic connection bar has a rectangular cross section, and an intermediate carbonaceous material is used in direct contact with
20 the metallic connection bar, said intermediate carbonaceous material being preferably compressed expanded graphite.

Another object of the invention is a process for manufacturing a cathode element suitable for use in Hall-Héroult electrolysis cell comprising the steps of:

- 25 - providing a cathode block comprising a carbonaceous material and at least one metallic contact bar made from copper or a copper alloy,
 - machining at least one groove or drilling at least one bore in a direction parallel to the length of said cathode block,
 - optionally covering at least part of the surface of said metallic bar with an
30 intermediate carbonaceous material,
 - fitting said metallic connection bar into each of said grooves or said bores,

wherein said metallic bar is fitted in such a way that direct contact between said carbonaceous material and the metallic bar is ensured, without the use of a metallic sealing material, said carbonaceous material in direct contact with said metallic contact
35 bar being either the cathode block itself or said intermediate carbonaceous material.

In a variant of this process, which is particularly suitable for rectangular metallic contact bars, said intermediate carbonaceous material may comprise a seal, preferable containing

graphite particles, said seal being applied onto said metallic contact bar and/or onto at least one face of said sheet of compressed expanded graphite.

5 Still another object of the invention is a process for producing aluminium in a Hall-Héroult electrolysis cell, wherein said electrolysis cell comprises one or more cathode elements according to the invention.

Description

10 The present invention applies to cathodes used in the Hall-Héroult process that form the bottom of an electrolytic cell, said cathodes being assembled from individual cathode blocks, each of which bears at least one cathode bar.

15 Said cathode blocks **10** are generally rectangular in shape and comprise an upper surface **50** (also called "hot surface") and a lower surface **15** (also called "cold surface"). They comprise at least one cathode bar. Said cathode bar is usually inserted into a groove machined into the cold surface **15** of the cathode block **10**.

20 According to the invention the problem is solved by using a cathode bar comprising a full copper bar **13** over at least part of the length of said cathode block **10**. That is to say that over at least part of the length of the cathode block the full section of said cathode bar is copper.

25 The present inventors have found that copper bars can be used directly as cathode bars, replacing the steel bars, instead of using them as inserts in steel bars. More precisely, the copper bar can be used in direct contact with a carbonaceous material. Said carbonaceous material can be the cathode block **10** itself, or an intermediate carbonaceous material **17** (shown on figure 4a) that is in direct contact with the metallic connection bar **13** made from copper or a copper alloy and also in direct contact with the carbon cathode block **10**. No metallic seal (such as steel or cast iron) is used.

30

The intermediate carbonaceous material **17** in direct contact with the metallic connection bar **13** must be somewhat deformable, such as to accommodate the higher thermal expansion of the metallic connection bar **13**, made from copper or a copper alloy, with respect to the material of the cathode block **10**. As an intermediate carbonaceous material **17** in direct contact with the copper bar **13** and the cathode block **10**, compressed expanded graphite (most conveniently in the form of a sheet) can be used, and/ or carbonaceous sealing paste.

35

Compressed expanded graphite is available in the form of sheet of different densities and thickness from several manufacturers and under different tradenames (such as Papyex™ manufactured by Mersen and Sigraflex™ manufactured by SGL).

5 Concerning the carbonaceous sealing paste, the sealing paste advantageously includes carbonaceous particles dispersed in a binder that has a high carbon yield after baking. Said carbonaceous particles can be graphite particles. Such sealing pastes are commercially available from different manufacturers and under various tradenames (Sealing paste HCF 80 from Carbone Savoie for example). The thickness of the sealing
10 paste is calculated according to the width of the collector bar, taking into consideration the differential of thermal expansions between the copper and the graphitized cathode block; a thickness comprised between 15 and 25 mm can be used.

Considering the very different thermal expansion coefficients for the copper and the
15 cathode block, if the copper bar 17 is sealed inside the cathode block groove, and for avoiding any mechanical stresses when starting the pot pre-heating, between the copper bar and the carbon material of the cathode block, the copper should be covered by a deformable intermediate carbonaceous material such as a sheet of compressed expanded graphite. It should be avoided to seal directly the copper bar inside the cathode
20 block groove.

The cathode blocks 10 are usually graphitized carbon blocks.

The expression "direct contact" means that there is direct contact between the copper bar
25 and the carbonaceous material (the carbonaceous material being the cathode block material itself, or an intermediate carbonaceous material such as graphite sheet or a carbonaceous sealing paste), without any intermediate metallic material (such as a steel bar or steel shell, or a metallic sealing material (for example cast iron)). The presence of the natural oxide layer on the copper bar is unavoidable and does not prevent "direct
30 contact".

According to one embodiment of the invention shown schematically in figure 2a, the copper bar 13 is directly inserted into a groove machined in the lower surface 15 of the cathode block 10; this surface is advantageously the bottom surface (cold surface) of the
35 cathode. The groove extends advantageously parallel to the length of the cathode block 10. In a first variant the groove extends over the whole length of the cathode block, and so does the cathode bar. In a second variant shown in figure 2d the groove is made on each end of the cathode block, and these two grooves are separated by a gap 16

centred at mid-length of the cathode block.

According to another embodiment of the invention shown on figures 2b and 2c, the copper bar is inserted into a hole drilled into the cathode block **10**. The hole extends parallel to the length of the cathode block. In a first variant of this embodiment (shown on figure 2b) a continuous hole is made in the cathode block, a continuous copper bar **13** is inserted. In another variant of this embodiment (shown on figure 2c), the hole is discontinuous, and two half copper bars **13a,13b** are inserted from each extremity of the cathode block **10**; inside the cathode block they are separated by a gap **16** centred at mid-length of the cathode block **10**. Said hole is closer to the bottom surface **15** of the cathode block **10** than to the upper (hot) surface.

The cathode bars **13, 13a, 13b** can be made with full cylindrical copper bars inserted into a cylindrical hole of corresponding section. They can also be made with full rectangular copper bars inserted into a rectangular groove of corresponding section that has been machined at the bottom or at the sides of the cathode bar. In that case the rectangular copper bar can be either directly in contact with the cathode block or the copper bars can be sealed inside the grooves using a carbonaceous sealing paste, or there can be another intermediate carbonaceous material such as a sheet of compressed expanded graphite. Other shapes of cross section of the copper bar and the corresponding groove or hole can be used, but are less preferred as a good surface contact between the cathode block and the copper bar is desirable. One cathode bar or two or more cathode bars can be used on each extremity of the cathode block. Figures 2d(1) and 2d(2) show embodiments with one rectangular bar **13a,13b** at each end of the cathode block **10** that is inserted into a groove machined at the bottom face **15** of the cathode block **10**; figure 2a(1) shows a continuous bar **13**, figure 2d(1) a discontinuous bar **13a,13b**. Figures 2a(3) and 2d(3) show corresponding embodiment with two rectangular bars at each end of the cathode block; figure 2a(3) represents continuous bars, figure 2d(3) discontinuous bars. Figures 2b(2) and 2c(2) show embodiments with one round bar inserted into a hole machined into the cathode block; figure 2b(2) represents a continuous bar, figure 2c(2) represents discontinuous bars. Figures 2b(3) and 2c(3) show embodiments with two round bars inserted into holes machined into the cathode block; figure 2b(3) represents continuous bars, figure 2c(3) represents discontinuous bars.

Figure 3 shows an example: two cylindrical copper bars **13a,13b** having a diameter of 90 mm and a length e of 1850 mm each are inserted in a hole made on both sides of the lower part of the cathode block **10**; the total length a of the cathode block was 3250 mm, the total height b was 425 mm, the total width c was 420 mm, and the cathode bar

extends out of the block by a length f of about 525 mm; the gap d between the two embedded ends of the copper bars was about 600 mm. The axis of the collector bars made with full copper cylindrical rod was located at 70 mm from the bottom (cold) face of the cathode block. Figure 3 corresponds to the embodiment schematically represented by figure 2c(2).

As the electrical conductivity of the copper ($1,68 \times 10^{-8} \Omega \text{ m}$) is about 6 times higher than that of steel ($10 \times 10^{-8} \Omega \text{ m}$), a given conductivity value of the cathode bar can be obtained with a copper bar having a smaller diameter or section for rectangular copper bars than the steel bar. As an example, to replace a steel bar with a cross section of about 221 cm^2 (width 170 mm, height 130 mm), a copper cross section of at least $37,14 \text{ cm}^2$ is needed, corresponding to a cylindrical bar of 68.77 mm in diameter.

Using copper bars **13** with larger cross section will lead to an increase in electrical conductivity. In the above example, the increase of the cathode bar section for the copper bar beyond 37.14 cm^2 will lead to a higher conductivity of the copper bar compared to the steel bar: the cylindrical copper bar with a diameter of 90 mm has a conductivity that has increased by about 71% compared to that of the steel bar (63.6 cm^2 compared to 37.14 cm^2 for the equivalent resistance using steel bars). This decrease in ohmic losses in the cell leads to a decrease in voltage drop across the cell. Such an embodiment is shown in figure 4b; this copper rod **13** is inserted into a hole drilled into the lower part of the cathode block **10**, parallel to its length.

For replacing a rectangular steel bar with a cross section of 221 cm^2 (width 170 mm, height 130 mm) by a rectangular copper bar, a copper cross section of 37.14 cm^2 would be sufficient; such a rectangular copper bar could have a cross section of approximately 60 mm by 65 mm.

For the case of using rectangular copper bar and to obtain the same increase of conductivity of 71%, the copper section would have to be about 69 cm^2 , which could be achieved by a rectangular copper rod of 70 by 100 mm. Such a rectangular copper bar should be installed horizontally inside the cathode block groove, meaning that the groove must have between 120 to 125 mm of width and between 72.5 and 75 mm of depth if a carbonaceous sealing material (sheet of compressed expanded graphite and carbonaceous sealing paste) is used.

Another consequence of the higher electrical conductivity of copper (and the smaller diameter of the copper bar with respect to the steel bar) is the possibility to increase the

depth of the copper bar in the cathode with respect of that of the steel bar, that is to say the spacing h between the upper surface **50** of the cathode block **10** that is in contact with the liquid aluminium and the upper surface **51** of the cathode bar **13**. In the above example, the full copper bar (cylindrical rod of 90 mm diameter, i.e. a cross section of 63.6 cm²) replaces a rectangular steel bar of much greater height (130 mm, width 170 mm, i.e. a cross section of 221 cm²), and the thickness of carbonaceous material in the cathode block is increased from $h = 275$ mm to $h = 310$ mm (see figure 4b), taking into account the additional thickness of the cast irons seal.

Figure 4b shows a cylindrical copper bar **13** installed on the bottom of the cathode block **10**. In this example, if cylindrical copper bars of 90 mm of diameter is used, the thickness h of carbonaceous material between the liquid aluminium and the upper surface of the copper bar can be increased from 275 mm to 310 mm. This increase of 35 mm (or 13 % more material) corresponds to about 8.4 months of wear for the cathode blocks, and therefore extends the life expectancy of the pot by 0.7 year.

In a variant of the rectangular copper rods, shown on figure 4a, a rectangular copper bar **13** with a width of 100 mm and an height of 70 mm (cross section = 70 cm²) has been inserted in a rectangular groove made in the bottom of the cathode block **10**. The total height b of the cathode block is 425 mm. In this case, the thickness h of carbon material above the copper bar (355 mm) is still higher than in the case of a cylindrical bar inserted into a hole: plus 45 mm. This increase of 80 mm (or 29 % more material) corresponds to about 1.6 years of wear for the cathode blocks, and therefore extends the life expectancy of the pot by 1.6 years. On the figure 4a, the intermediate carbonaceous material **17** is used between the rectangular copper bar **13** and the carbonaceous material of the cathode block **10**. This intermediate carbonaceous material might be avoided on the horizontal faces of the copper bar as very small amount of current is going through this top surface.

In a variant of the rectangular copper rod shown in figure 4c, the rectangular copper bar can be inserted directly in contact inside the groove made on the bottom of the cathode block, providing that the right adjustment is made for the copper rod inside the groove.

As there is a temperature gradient across the thickness of the cathode block, the copper cathode bar will heat less than the steel cathode bar. Moreover, due to the higher thermal conductivity of copper compared to steel, the copper cathode bar will transport more heat than a steel cathode bar of identical design.

Figure 5 shows a cross section across a Hall-Héroult electrolysis pot **20** according to the invention with cylindrical copper bars; the cross section is parallel to the width of the pot. The copper cathode bars **23a**, **23b** are discontinuous, with a gap **26** in the centre of the length of the cathode block **21**.

A possible problem related to the use of a full copper cathode bar is related to overheating of the cell. In modern Hall-Héroult cells the temperature of the liquid aluminium sheath **29** in contact with the upper surface **27** of the cathode blocks **21** is normally about 960°C to 965°C, and under these operating conditions the temperature in the centre of the cathode block can reach 950°C. However, in case of abnormal conditions the temperature of the aluminium sheath can increase to over 1000°C, typically up to 1080°C for short duration of up to 24 hours. Such overheating may occur especially when starting the pot. While modern potlines and sophisticated pot control can avoid and/or limit overheating (above 1080°C), this event cannot be fully excluded throughout the normal lifetime of an electrolysis pot (5 to 7 years).

Knowing that the melting point of pure copper is about 1084°C, it must be ruled out that in case of abnormal overheating the cathode bar **13** suffers irreversible damage. Increasing the carbon thickness h over the upper surface of the copper bar **13** will decrease the temperature seen by the copper bar **13** by a few degrees. Inserting the copper bar **13** in a groove at the bottom **15** of the cathode block **10** will further increase the carbon thickness h and gain a few degrees. In any case, using the cathode block according to the invention in a Hall-Héroult cell for the manufacture of aluminium requires a careful control of operating conditions in order to avoid overheating of the cell, or at least to limit it to small overheat and/or for short period periods of time.

In a preferred embodiment of the invention the copper cathode bars **13**, **23** are made from 99.99% copper that is oxygen free (OFE Copper grade).

In another embodiment copper alloys are used that have a higher melting point (by about 15°C to 35°C) than pure copper; however, such alloys will have a lower electrical conductivity.

Another potential problem related to the use of unsealed copper bars is the copper – carbon interface: copper oxidation or other changes in properties of the copper close to the carbon block may lead to higher electrical contact resistance. For this reason, and in case of rectangular copper bars, it is preferable to wrap the rectangular copper bars with

graphite sheet (graphite "paper") before sealing it inside the cathode block groove shown in figure 4a. This graphite sheet (representing an intermediate carbonaceous material) separates the copper bar from the cathode block material, which is advantageous considering the very different thermal expansion coefficients of copper and of the cathode
5 block material; the graphite foil can also act as a barrier preventing the oxidation of the copper surface.

When designing cathode blocks according to the invention in which steel cathode bars are replaced by copper cathode bars, another potential problem is related to the different
10 thermal expansion coefficient of steel and copper: about 16.6×10^{-6} /°C for copper, about 12×10^{-6} /°C for average steel used in cathode bars and cast iron used for sealing steel cathode bars. The thermal expansion coefficient for typical graphite (such as D grade from Carbone Savoie) is about 5.3×10^{-6} /°C The thermal expansion of copper is much higher than that of graphite, and higher than that of steel. This needs to be taken
15 into account when determining the width of the hole or groove made in the cathode to insert the copper bar.

The invention has numerous advantages. A gain in voltage drop of more than 100 mV can be reached in industrial potlines.

20

The increase in capital cost over prior art embodiments is not very significant. Copper is more expensive than steel, but this difference is partially offset because less copper is needed. While copper does add to the initial cost of the cathode bar according to the invention, part of this initial cost is recovered by copper recycling. Since no cast iron is
25 needed, the cost of cast iron and necessary man hours (and possibly the cost of the cast iron plant itself) is saved. On the other hand, the machining operation for the groove (and especially for the hole) is more expensive than for the groove according to prior art because the dimensional tolerance is a critical issue, while a steel bar can be sealed with cast iron into a groove with no special requirement of dimensional tolerance. Referring to
30 the rectangular copper bars, the groove to machine is not expensive as a gap is needed to seal the copper bars, the groove machining tolerance can be the same as the genuine one for steel bars: +/- 2 mm. Even for the cylindrical copper bars that need a very tight tolerance that may be difficult to achieve with some older machining equipment, the inventors have found that the total additional cost of the cathode block according to the
35 invention is offset by the higher energy efficiency of such a cell.

The cathode block according to the invention needs to be connected to the cathodic bus bar. Specific connectors **30** are needed to connect cylindrical copper bars **33** to the cathodic bus bar.

5 For the cylindrical copper bars **33**, an advantageous solution for connecting the copper bar extremities to the original cathode flex is shown in figure 6: to connect the copper tabs **34a**, **34b** connected to the aluminium flexes (not shown on the figure) to the cylindrical copper bar **33** extremities, two special copper plates **39a**, **39b** in contact with the copper cathode bar **33** are added: these copper plates **39a**, **39b** have a cylindrical recession on
10 one side (in contact with the copper bar **33**), the other side in contact with the genuine copper pads **34a**, **34b** being flat. A means of pressing the two copper tabs against the copper bar can be added (not shown on the figure). Advantageously the diameter of the cylindrical recess is about the same as that of the copper bar **33**; as an example, for a copper bar of diameter 90 mm a recess of diameter 90 mm is used.

15 Said copper tabs **34a**, **34b** can be connected to said aluminium flexes by any appropriate means. As an example, said copper tabs **34a**, **34b** can be part of (or can be in contact with the copper part of) a copper / aluminium transition joint (clad) or a copper / titanium / aluminium tri-metallic clad, said aluminium flexes being welded to the aluminium part of
20 said transition joint.

As shown in figure 7, another simple way to connect the cathode flexes (not shown) to the extremities **72** of the copper bar **33** is to add a metallic piece **70** to the extremities **72** of the copper bar **33**, preferably by welding. Said metallic piece **70** comprises a steel plate
25 providing a substantially vertical (preferably flat) contact surface **71** onto which the steel part of a tri-metallic clads (composed of aluminium, titanium and steel parts, not shown) can be welded. This solution is far less expensive than to add extra copper plates between copper tabs and copper bars, and, more importantly, the voltage drop, measured from the copper bar and the bus bar where the aluminium cathode flex is welded, will be
30 very low.

CLAIMS

1. Cathode element suitable for use in a Hall-Héroult electrolysis cell, comprising
 - a cathode block comprising a first carbonaceous material,
 - at least one metallic connection bar made in one of copper and copper alloys,wherein said at least one metallic connection bar is fitted into one of a groove and a bore in direct contact with a second carbonaceous material, wherein the at least one metallic connection bar extends from both extremities towards a centre length of the cathode block, leaving a gap in a centre of the cathode block, and wherein said second carbonaceous material is one of the first carbonaceous material of said cathode block, and an intermediate carbonaceous material that is in direct contact with the first carbonaceous material of said cathode block.
2. Cathode element according to claim 1, wherein said cathode element is free from any further metallic connection bar in direct contact with the second carbonaceous material other than the at least one metallic connection bar made in one of copper and copper alloys.
3. Cathode element according to claim 1 or 2, wherein said intermediate carbonaceous material comprises at least one of compressed expanded graphite and a cured carbonaceous seal.
4. Cathode element according to claim 3, wherein the cured carbonaceous seal comprises a graphitized carbonaceous seal.
5. Cathode element according to claim 3 or 4, wherein said the cured carbonaceous seal comprises graphite particles.
6. Cathode element according to any one of claims 3 to 5, wherein the at least one connection bar is in direct contact with the compressed expanded graphite, and wherein said expanded compressed graphite is in direct contact with the cured carbonaceous seal, said cured carbonaceous seal being in direct contact with the first carbonaceous material of the cathode block.

7. Cathode element according to any one of claims 1 to 6, wherein said at least one metallic connection bar has one of a round cross section and a rectangular cross section.
8. Cathode element according to any one of claims 1 to 6, wherein said at least one metallic connection bar has a rectangular cross section, and the intermediate carbonaceous material is used in direct contact with at least one the metallic connection bar.
9. Cathode element according to claim 8, wherein said intermediate carbonaceous material comprises compressed expanded graphite.
10. Cathode element according to any one of claims 1 to 9, further comprising a metallic piece that is fixed to the extremities of the at least one metallic connection bar, said metallic piece comprising a steel plate providing a substantially vertical contact surface.
11. Cathode element according to claim 10, wherein the metallic piece is fixed to the extremities by welding.
12. Cathode element according to claim 10 or 11, wherein the substantially vertical contact surface is flat.
13. Cathode element according to claim 10, wherein tri-metallic clads are welded onto said substantially vertical contact surface.
14. Cathode element according to claim 13, wherein the tri-metallic clads are electrically connected to a cathodic bus bar.
15. Cathode element according to claim 13 or 14, wherein said tri-metallic clads are aluminium – titanium – steel tri-metallic clads.
16. Process for manufacturing a cathode element suitable for use in Hall-Héroult electrolysis cell comprising the steps of:
 - providing a cathode block comprising a first carbonaceous material and at least one metallic contact bar made from one of copper and a copper alloy,

- one of machining at least one groove and drilling at least one bore in a direction parallel to a length of said cathode block, and
- fitting said at least one metallic connection bar into each of one of said at least one groove and said at least one bore,

wherein said at least one metallic bar is fitted in such a way that direct contact between a second carbonaceous material and the at least one metallic bar is ensured, without the use of a metallic sealing material.

17. Process according to claim 16, wherein said second carbonaceous material in direct contact with said at least one metallic contact bar is the first carbonaceous material of the cathode block.
18. Process according to claim 16, further comprising covering at least part of a surface of said at least one metallic bar with an intermediate carbonaceous material, said second carbonaceous material in direct contact with said at least one metallic contact bar being the intermediate carbonaceous material.
19. Process according to claim 18, wherein said intermediate carbonaceous material comprises a sheet of compressed expanded graphite.
20. Process according to claim 18 or 19, wherein said intermediate carbonaceous material comprises a seal, said seal being applied onto said at least one metallic contact bar.
21. Process according to claim 19, wherein said intermediate carbonaceous material comprises a seal, said seal being applied onto at least one of said at least one metallic contact bar and at least one face of said sheet of compressed expanded graphite.
22. Process according to claim 20 or 21, wherein the seal contains graphite particles.
23. Process according to any one of claims 18 to 22, wherein said intermediate carbonaceous material is used for rectangular metallic contact bars.
24. Process for producing aluminium in a Hall-Héroult electrolysis cell, wherein said electrolysis cell comprises one or more cathode elements according to any one of claims 1 to 15.

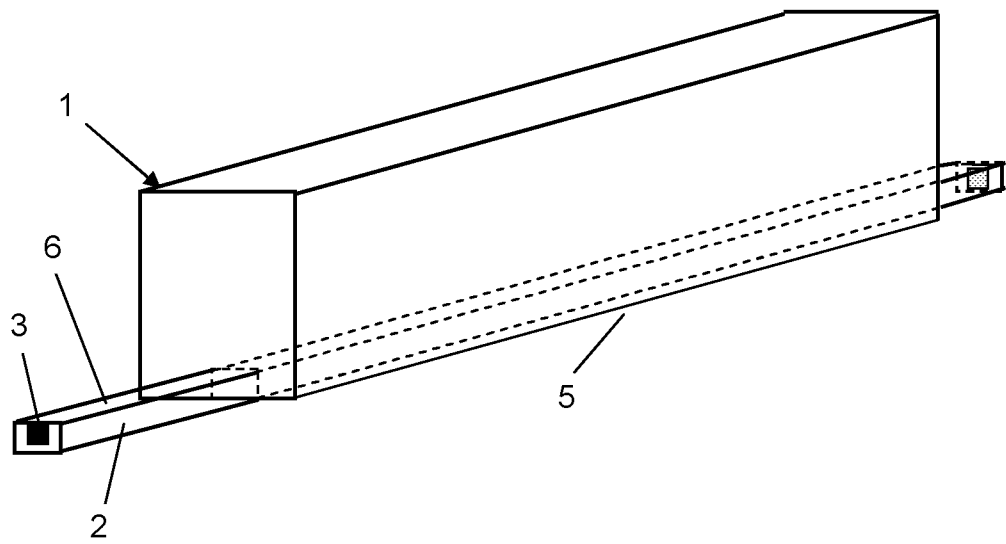


Figure 1a

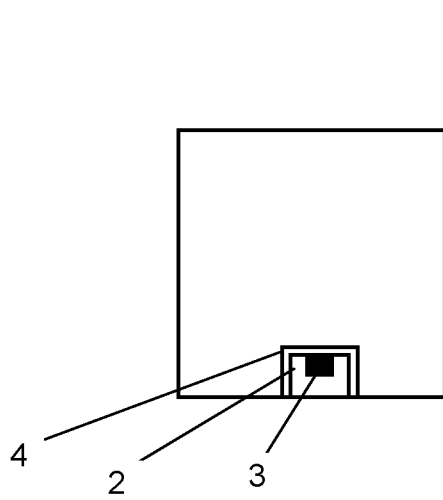


Figure 1b

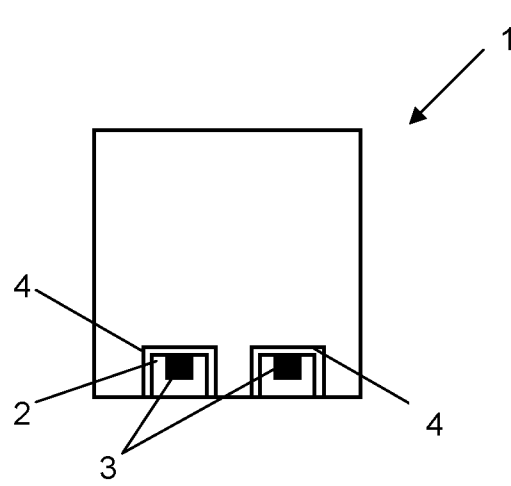


Figure 1c

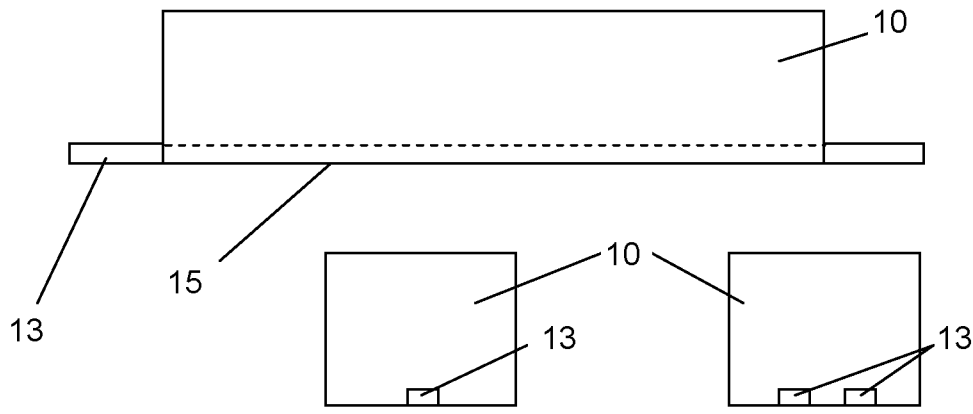


Figure 2a(1)

Figure 2a(2)

Figure 2a(3)

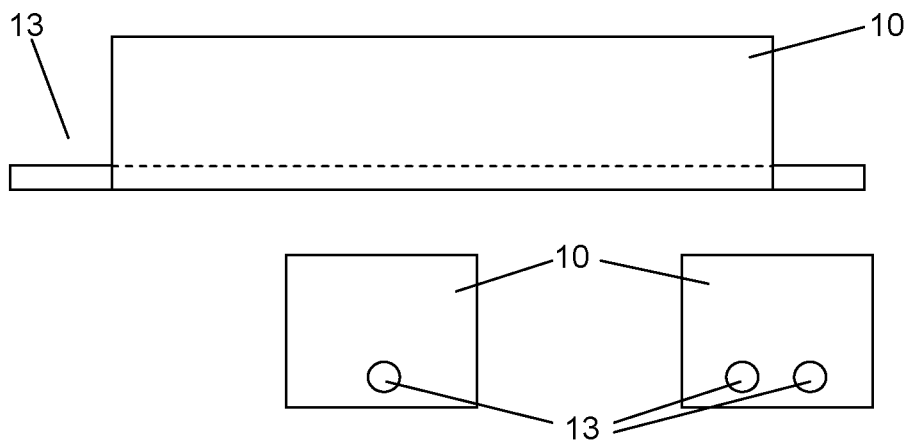


Figure 2b(1)

Figure 2b(2)

Figure 2b(3)

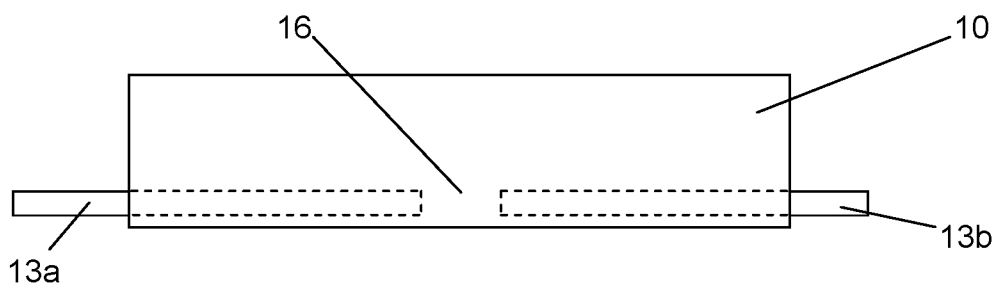


Figure 2c(1)

Figure 2c(2)

Figure 2c(3)

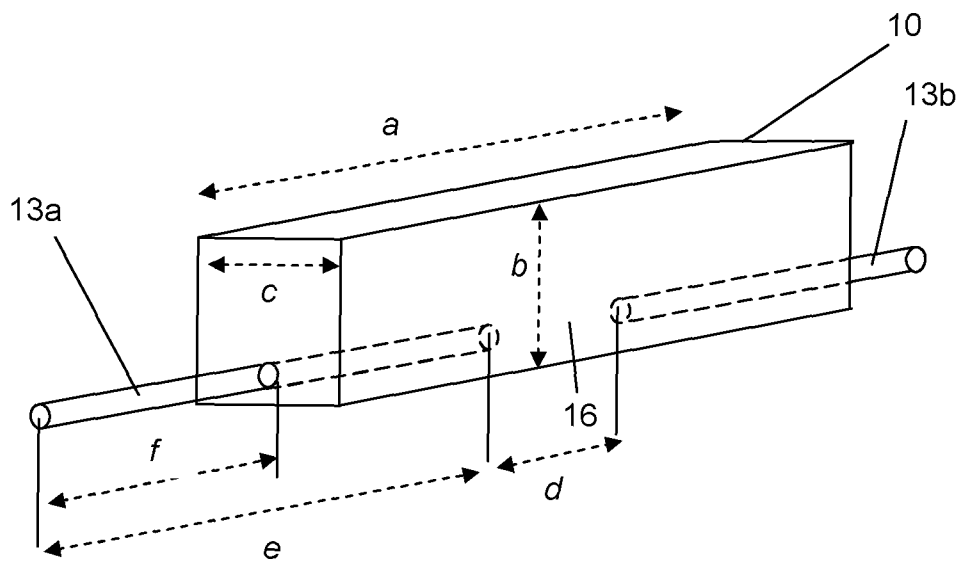
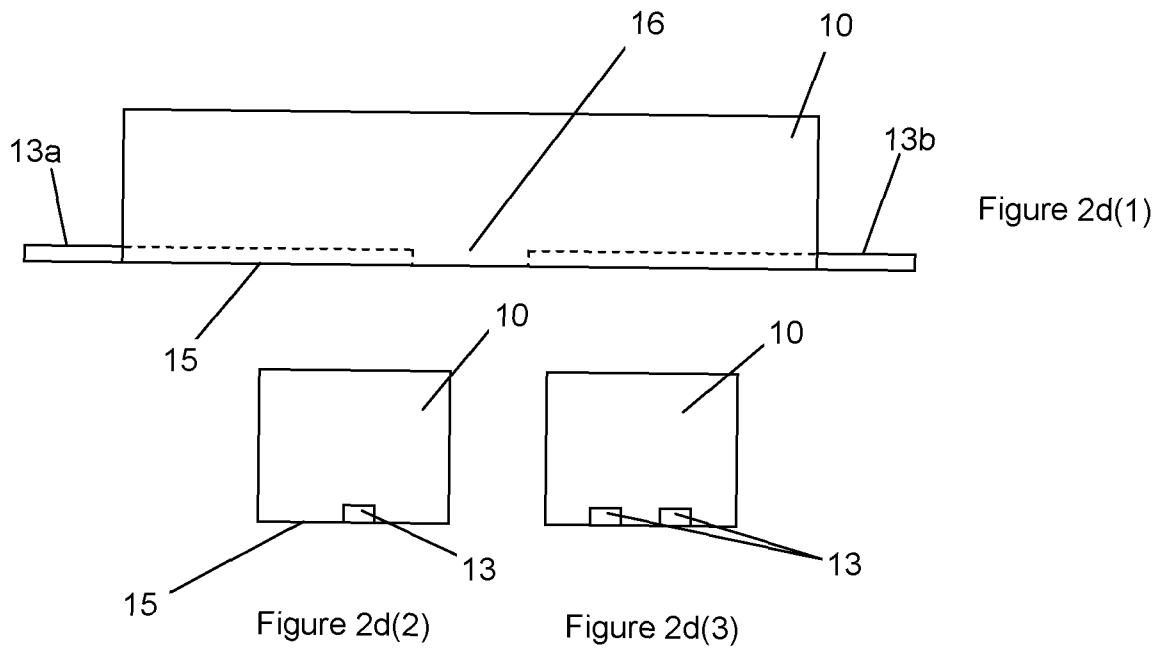


Figure 3

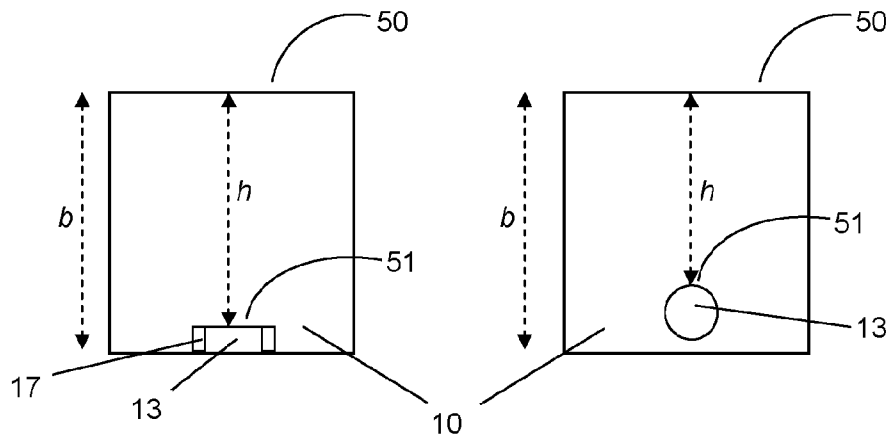


Figure 4a

Figure 4b

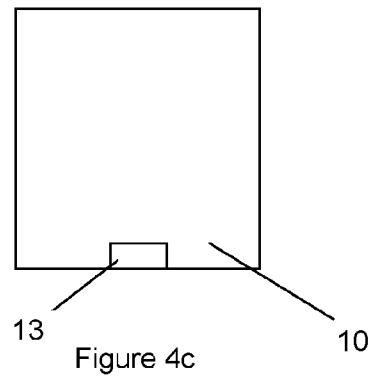


Figure 4c

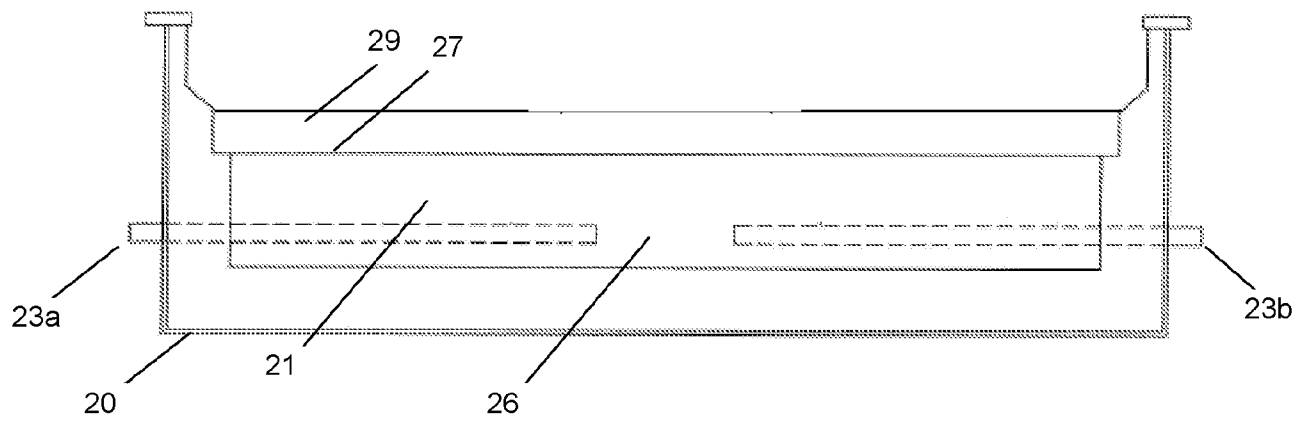


Figure 5

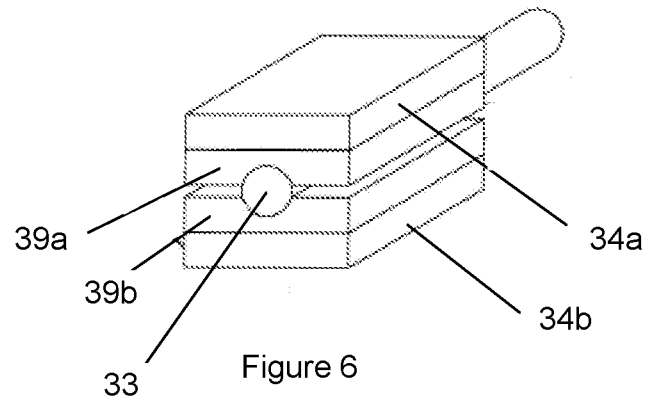


Figure 6

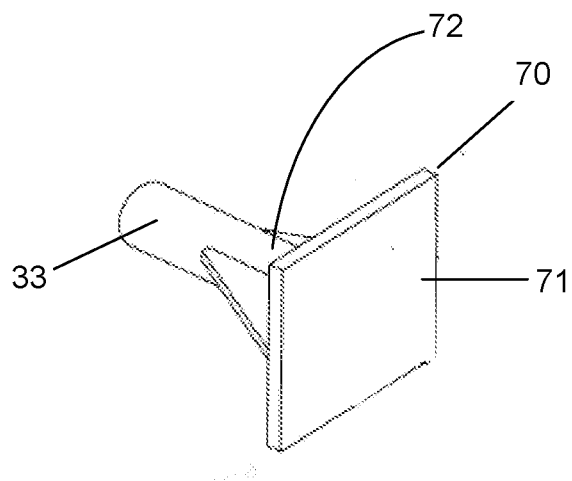


Figure 7

