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METAL RECOVERY PROCESS

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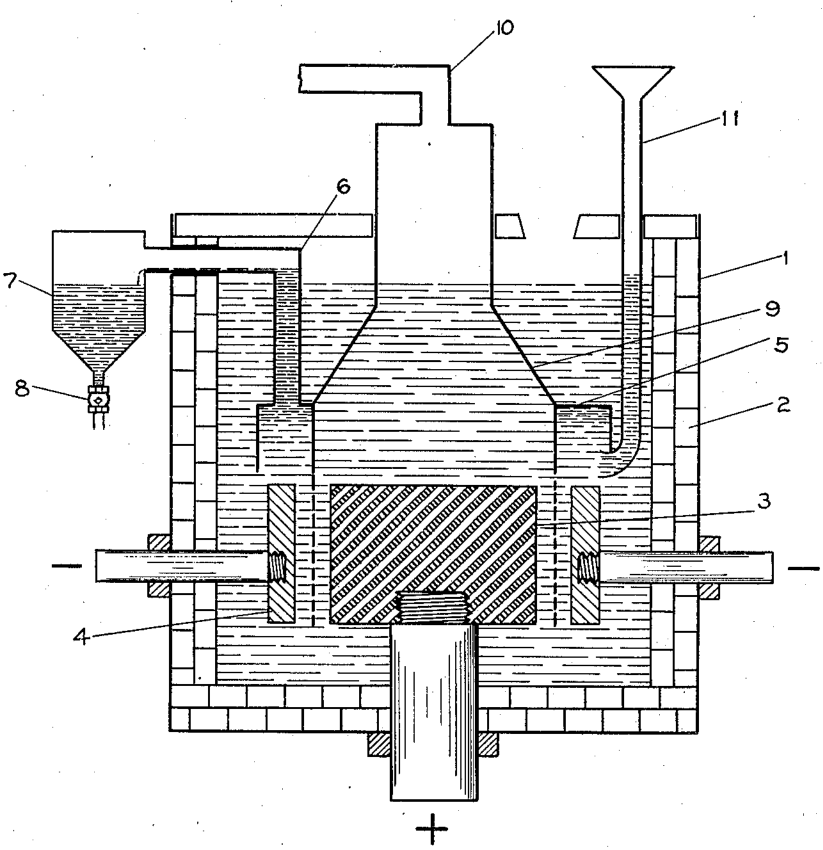

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METAL RECOVERY PROCESS

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This invention relates to the production of light metals by the electrolysis of fused salt mixtures and more particularly to the recovery or metals from mixtures produced by such electrolytic processes.

In the production of light metals by the electrolysis of fused salt, it is common practice to use a mixture of salts rather than a pure fused salt, chiefly in order to obtain a low-melting electrolyte. For example, in the production of sodium by the electrolysis of sodium chloride, one or more salts of other metals commonly are added. The salt which is added to a fused salt electrolyte for the purpose of lowering the melting point is known as a "fluxing ingredient". Thus, in the electrolysis of sodium chloride to produce sodium, calcium chloride is commonly added as the fluxing ingredient. As the electrolysis of a calcium chloride-sodium chloride mixture proceeds, a small amount of calcium is deposited at the cathode together with the sodium. This calcium is dissolved in the sodium and is removed from the cell along with the outgoing sodium. Therefore, the concentration of calcium chloride in the cell constantly decreases as electrolysis proceeds. In order to maintain the electrolyte at the desired maximum melting point, it is necessary to add small amounts of calcium chloride to the cell from time to time. Due to the hygroscopic nature of calcium chloride, this material must be carefully fused to remove all traces of water before the introduction to the fused electrolyte.

When a fused mixture of sodium chloride and calcium chloride is electrolyzed, the crude metal, as collected from the electrolytic cell, contains in addition to calcium, oxides and chlorides of these metals. Substantially pure sodium may be obtained by filtering the molten crude metal at a lowered temperature at which the calcium is substantially insoluble. The filter residue consists of the oxides and salts, together with large quantities of calcium and sodium. Such filter residues have little or no commercial value because of the difficulty of recovering metallic values therefrom; furthermore, they are highly reactive with air and moisture and therefore are hazardous to store or handle.

An object of the present invention is to provide a method of recovering metal values from filter residues resulting from the purification of electrolytic light metals by filtration. A further object is to provide an improved method for adding a hygroscopic fluxing ingredient to a fused salt electrolysis cell. Other objects will be hereinafter apparent.

The above objects are attained by feeding to a fused salt electrolysis cell the filter residue obtained by filtration of the molten crude cathodic product produced by such cell.

The appended drawing shows one type of apparatus suitable for use in practicing my invention. The drawing is a vertical section of a modified form of the electrolytic cell described in Downs, U. S. P. 1,501,756, hereinafter referred to as the "Downs cell". The cell consists of a cylindrical steel shell 1, lined with refractory ceramic material 2, to form a container for the electrolyte. In the center of this container is mounted a graphite anode 3, which extends through the floor of the cell. Surrounding the anode is an annular steel cathode 4, with connections extending through the side walls of the cell. Located directly above the cathode is an annular structure 5, in the nature of an inverted trough, denoted herein as the "collector ring" which serves to collect molten light metal rising from the cathode. Suspended from the inner edge of collector ring 5 is a cylindrical, foraminous diaphragm, separating the space between the electrodes into anode and cathode compartments. At one point, a vertical outlet pipe 6, is connected to the top of the collector ring 5, this pipe serving to carry out the metal collected in the collector ring 5. Pipe 6 leads into a receiver 7, which has an opening at the bottom, closed by a plug cock 8. At one side of the apparatus, at a point opposite the outlet pipe 6, is inserted a vertical pipe 11, the lower end of which opens into the lower part of collector ring 5.

One method of practicing my invention, utilizing the above described modified Downs cell, will be described. The cell is utilized to electrolyze a fused mixture of calcium chloride and sodium chloride, whereby metallic sodium, together with a small amount of calcium, is liberated at the cathode. The resulting product which is collected in the receiver thus contains certain amounts of calcium dissolved in the sodium, together with small amounts of electrolyte carried over and some oxide. This crude cathodic product is removed from the receiver, cooled and filtered to obtain a filtrate of substantially pure sodium, leaving a filter residue consisting of calcium, sodium and smaller amounts of calcium oxide and salts. In order to remove the maximum amount of calcium from the sodium, the filtration operation is conducted at a temperature slightly above the melting point of sodium, at which temperature calcium is relatively insoluble in sodium. At such filtration temperature, the filter residue is a semi-solid mass which may contain 65% to 72% of sodium, 18% to 27% of calcium, 2% to 10% of calcium oxide and/or sodium oxide and up to 3% of salt. The amount of oxide depends upon the amount of oxygen originally in the electrolyte and the care taken in handling the product during its removal from the cell and during the filtration process.

In accordance with my invention, the filter residue is fed into the modified Downs cell, preferably into the cathode compartment of the cell, for example by way of pipe 11 shown in the drawing. The residue may be transferred to the cell directly in the semi-solid or molten condition or it may first be cooled, e. g., by molding into bricks of suitable size, and the solid material fed into the cell. Upon coming into contact with the electrolyte in the cell, the calcium in the residue reacts with the sodium chloride of the fused electrolyte to liberate sodium and form calcium chloride. The sodium in the residue fed to the cell is at the same time separated and rises into the collector ring, together with the sodium liberated by the reaction of the calcium with the electrolyte. The oxide contained in the residue becomes disseminated throughout the bath and is eventually chlorinated by the chlorine evolved at the anode, to produce further amounts of calcium chloride. After the continual addition of relatively large amounts of the filter residue to the electrolytic cell, the calcium chloride content of the cell may be increasingly high. I prefer to feed to a single cell filter residue obtained from the products of a number of other cells until the electrolyte of the cell receiving the residue has reached a calcium chloride concentration somewhat higher than that normally used. Part of the cell bath then is removed and used to supply calcium chloride to the remaining cells, the portion removed being replaced by additional sodium chloride. However, if desired, the residue may be fed in equal amounts to each of the cells in the group. With either method, the calcium chloride which is removed from the electrolyte by electrolysis to calcium and chlorine is returned in the form of the metallic calcium in the filter residue and anhydrous calcium chloride need be added only to make up the small amount of calcium which may be lost by handling and/or by failure to remove all of the calcium from the sodium during the filtration process.

The filter residue may be added to the cell in any suitable manner or to any portion of the electrolyte in the electrolytic cell. I prefer to add the residue to the cell at some point within the cathode compartment or at such place that the metal liberated by separation or by reaction may rise into the metal-collecting means of the cell. I may also add the residue at another point in the cell beneath the surface of the electrolyte and arrange a separate collecting means for collecting only the metal released from the residue. In another method of practicing my invention, I feed the filter residue into the molten metal in the metal-collecting means of the cell, for example into the upper portion of the collector ring 5 of the above described Downs cell. By this method, the residue, on mixing with the molten crude metal in the collector ring, undergoes a separation, the salts and oxide settling out and descending into the electrolyte. The metal in the collecting means becomes saturated with the metal base of the fluxing ingredient (e. g., calcium in the above described Downs cell operation) with the result that further addition of filter residue causes this metal to precipitate and descend into the electrolyte and react therewith.

While I have described my invention with reference to the production of sodium and by means of a particular type of electrolytic cell, my invention is not restricted thereto as other well-known types of fused salt electrolytic cells may be utilized. Likewise, my invention is not restricted to the recovery of metal values from the filter residues obtained by the filtration of crude electrolytic sodium; my process obviously is applicable to the electrolytic production of other light metals where a crude cathodic product contains a plurality of metals from which a purified metal may be obtained by filtration.

An advantage of my invention is that it provides a simple, effective and inexpensive method of recovering metal values from the filter residues obtained by the filtration of crude electrolytic sodium or other light metals. A further advantage, especially in the electrolytic production of sodium, is that it avoids the waste of fluxing ingredient and eliminates the necessity of adding a hygroscopic fluxing ingredient in large amounts to the electrolytic cell.

I claim:

1. A process for recovery of metal values from a mixture of sodium, calcium and oxide comprising introducing said mixture into a fused mixture of sodium-chloride and calcium chloride undergoing electrolysis in an electrolytic cell.

2. A process for recovery of metal values from a mixture containing light metals comprising introducing said mixture into the electrolyte of an operating fused salt electrolytic cell at a point substantially directly below a metal collecting means in said cell, which means is located substantially directly above a cathode of said cell, said electrolyte having a specific gravity greater than that of said light metals.

3. A process for recovery of metal values from a mixture containing light metals comprising introducing said mixture into the electrolyte of an operating fused salt electrolytic cell at a point within the cathode compartment of said cell.

4. A process for recovery of metal values from a mixture comprising an alkali metal and an alkaline earth metal comprising introducing said mixture into the electrolyte of an operating fused salt electrolytic cell at a point within the cathode compartment of said cell.

5. A process for recovery of metal values from a mixture containing light metal and a metal oxide comprising introducing said mixture into the electrolyte of an operating fused salt electrolytic cell at a point within the cathode compartment of said cell.

6. A process for recovery of metal values from a mixture containing alkali metal and a metal oxide comprising introducing said mixture into the electrolyte of an operating fused salt electrolytic cell at a point within the cathode compartment of said cell.

7. A process for recovery of metal values from a mixture of sodium, calcium and oxide comprising introducing said mixture into a fused mixture of sodium chloride and calcium chloride undergoing electrolysis in an electrolytic cell at a point substantially directly below the metal collecting means of said cell, said collecting

means being located substantially directly above a cathode of said cell.

8. A process for recovery of metal values from a mixture of sodium, calcium and calcium oxide comprising introducing said mixture into a fused mixture of sodium chloride and calcium chloride undergoing electrolysis in an electrolytic cell at a point within the cathode compartment of said cell.

9. A process for recovery of metal values from a mixture of sodium, calcium and calcium oxide comprising introducing said mixture into a fused mixture of sodium chloride and calcium chloride undergoing electrolysis in an electrolytic cell at a point within the metal collecting means of said cell, said collecting means being located substantially directly above a cathode of said cell.

10. A process for the production of a light metal comprising electrolyzing a fused electrolyte, collecting an impure molten cathodic product, filtering said molten product to obtain a filtrate of purified metal and a filter residue containing a light metal and introducing said residue into said fused electrolyte at a point within the cathode compartment of the cell in which said electrolyte is being electrolyzed.

11. A process for the production of an alkali metal comprising electrolyzing a fused electrolyte, collecting an impure molten cathodic product, filtering said molten product to obtain a filtrate of purified alkali metal and a filter residue containing a light metal and introducing said residue into said fused electrolyte at a point within the cathode compartment of the cell in which said electrolyte is being electrolyzed.

12. A process for the production of an alkali metal comprising electrolyzing a fused electrolyte comprising a mixture of an alkali metal salt and at least one other metal salt, collecting an impure molten cathodic product, filtering said molten product to obtain a filtrate of purified alkali metal and a filter residue and contacting said residue containing a light metal with the aforesaid fused electrolyte at a point within the cathode compartment of the cell in which said electrolyte is being electrolyzed.

13. A process for the production of sodium comprising electrolyzing a fused electrolyte comprising a mixture of sodium chloride and calcium chloride, collecting an impure molten cathodic product containing sodium and calcium, cooling and filtering said molten product to obtain a filtrate of purified metal and a filter residue and contacting said residue with the aforesaid fused electrolyte.

14. A process for the production of an alkali metal comprising electrolyzing a fused electrolyte comprising a mixture of an alkali metal salt and at least one other metal salt, collecting an impure molten cathodic product containing alkali metal and at least one other metal, filtering said molten product to obtain a filtrate of purified alkali metal and a filter residue and contacting said residue with the aforesaid fused electrolyte whereby one of said metals in the residue reacts with said electrolyte to liberate alkali metal.

15. A process for the production of an alkali metal comprising electrolyzing a fused electrolyte comprising a mixture of an alkali metal salt and at least one other metal salt, collecting an impure molten cathodic product containing alkali metal and at least one other metal, filtering said molten product to obtain a filtrate of purified alkali metal and a filter residue, introducing said residue into the aforesaid fused electrolyte whereby one of said metals in the residue reacts with said electrolyte to liberate alkali metal and collecting said liberated metal.

16. A process for the production of sodium comprising electrolyzing a fused electrolyte comprising a mixture of sodium chloride and calcium chloride, collecting an impure molten cathodic product containing sodium and calcium, cooling and filtering said molten product to obtain a filtrate of purified metal and a filter residue, introducing said residue into the aforesaid fused electrolyte whereby calcium in the residue reacts with said electrolyte to liberate sodium and collecting said liberated sodium.

17. A process for recovery of metal values from a mixture containing light metal and a metal oxide comprising introducing said mixture into the electrolyte of an operating fused salt electrolytic cell at a point within the cathode compartment of said cell, in such manner that light metal is separated by gravity from said oxide and directly removing the separated light metal from said cell.

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