

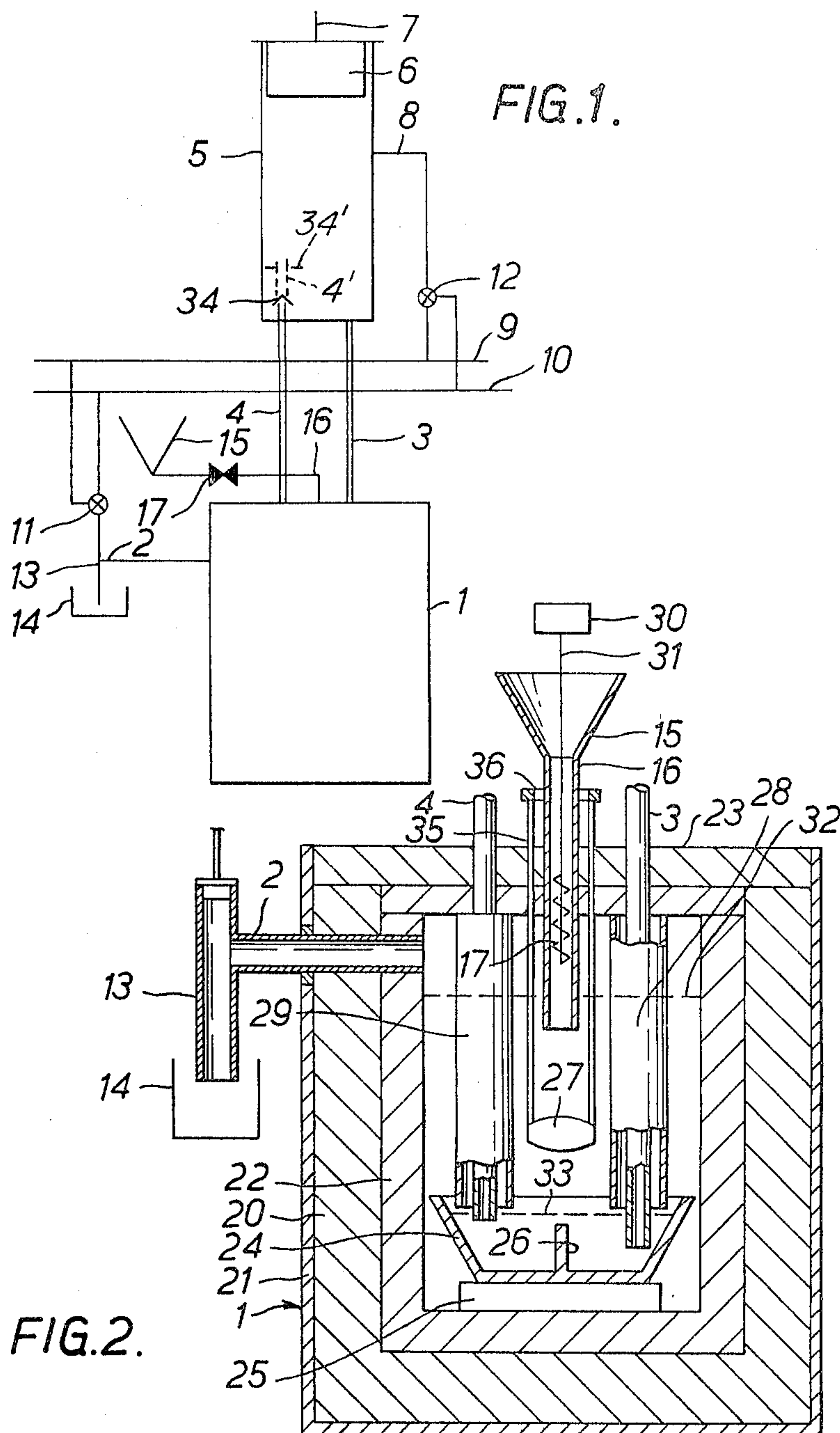
Nov. 8, 1966

A. R. GIBSON ET AL

3,284,325

PRODUCTION OF ALKALINE EARTH METALS

Filed Oct. 15, 1962





1

3,284,325

## PRODUCTION OF ALKALINE EARTH METALS

Allan Robert Gibson, Didcot, and Jan Zbigniew Lang, Aldershot, England, assignors to United Kingdom Atomic Energy Authority, London, England, and Elgar Trading Limited, Mytchett, Aldershot, Hampshire, England

Filed Oct. 15, 1962, Ser. No. 230,466

Claims priority, application Great Britain, Oct. 25, 1961, 38,188/61

9 Claims. (Cl. 204—69)

The present invention relates to the production of the alkaline earth metals calcium, strontium and barium from their salts.

It has previously been proposed, in British Patent 494,702, to prepare these alkaline earth metals by electrolyzing the sulphides in a fused chloride bath into a molten metal cathode pool.

It is an object of the present invention to provide a new or improved method and apparatus for producing these alkaline earth metals, as these metals have a wide use as reactant chemicals, in pyrotechnics and as getters.

According to the present invention there is provided a process for the production of alkaline earth metals, comprising dissolving the sulphide of such metals in a fused salt bath, electrolyzing such sulphide using a cathode formed by a molten alloy of the alkaline earth metal with copper, causing alloy enriched by the electrolysis to flow upwardly to a vacuum distillation apparatus where alkaline earth metal selected from the group of calcium, barium and strontium is removed therefrom, and causing such depleted alloy to return under gravity for further enrichment by electrolysis.

For the sake of convenience, the invention will be described solely with reference to the production of calcium, for the changes in conditions necessary to adapt the process to the other metals will be clear to those skilled in the art. Said electrolyte may conveniently comprise a mixture of calcium chloride and potassium chloride and is preferably the eutectic mixture containing 81% by weight of calcium chloride. The dissolved calcium sulphide may be present in amounts up to 4% by weight.

The calcium is removed from the copper-calcium alloy by vacuum distillation and, although the distillation may be effected batch-wise, the copper-calcium alloy is preferably continuously removed from the electrolytic cell by making use of the differing specific gravities of alloys containing differing proportions of calcium. Consequently the electrolyte is preferably continuously renewed by the continuous addition of calcium sulphide thereto. The sulphur liberated by the electrolysis will be in the vapour phase and may readily be removed.

The invention also includes apparatus for carrying the aforesaid method into effect.

Thus, according to a further aspect of the present invention, there is provided apparatus for the production of alkaline earth metals, such apparatus comprising an electrolytic cell having a molten alloy cathode pool at the lower part thereof, vacuum distillation apparatus located above said electrolytic cell, a flow pipe leading from the upper part of said pool to said distillation apparatus, a return pipe leading from a point in said distillation apparatus lower than the entry of said flow pipe and terminating in the lower part of said pool and means to maintain such a pressure differential between said electrolytic cell and said distillation apparatus that said pipes are maintained full of alloy.

The spacing of the still head (forming the distillation apparatus) from the electrolytic cell will depend on the temperatures of operation, vacuum differential and composition of the two copper-calcium alloys, but once these physical dimensions are fixed, a change in one of the operating conditions will cause a compensating change in the

2

other conditions. Thus, for example, a change in vacuum differential will cause a compensating change in the alloy composition. The preferred arrangement is described in detail hereinafter.

In order that the invention may more readily be understood, one embodiment of apparatus for effecting the same will now be described by way of example and by reference to the accompanying drawings, wherein:

FIG. 1 is a diagrammatic layout of the apparatus, and

FIG. 2 is a diagrammatic outline section through an electrolytic cell.

Referring now to FIG. 1 of the drawings which shows the plant in schematic form, an electrolytic cell 1 (shown in more detail in FIG. 2) is provided with a gas connection 2 and is also provided with alloy inlet (return) and outlet (flow) pipes 3 and 4.

The alloy pipes 3 and 4 are connected to a still head 5, this still head having a condenser 6 which is cooled by a gas line 7, while the still head itself has a gas connection 8. All parts of the apparatus are constructed so as to be gas-tight, for reasons which will appear, and unless otherwise specified may be made of mild steel or chrome iron.

Gas, e.g. argon, and vacuum pipe lines 9 and 10 respectively are provided and are connected to the gas connections 2 and 8 by three-way valves 11 and 12 respectively.

The gas connection 2 from the cell 1 acts as an air condenser for sulphur vapour and a branch line 13 runs to a sulphur well 14 in which molten sulphur seals the end of the line 13.

Fresh calcium sulphide for making up the electrolyte is admitted to the cell 1 from a hopper 15 through a pipe 16, this pipe having a valve 17.

The electrolytic cell 1 is shown in more detail in FIG. 2 and comprises a brickwork body 20, an alumina brick liner 22 and an outer mild steel shell 21. The cell has a gas-tight lid 23. The base of the cell supports a mild steel cathode cup 24 on an insulating spacer 25, this cup having a central weir 26. The anode is in the form of a graphite block 27 supported from the lid 23 of the cell by current carrying rods 35, these rods being joined at their upper ends by a terminal ring 36. The pipes 3 and 4 also enter the cell through the lid 23 and extend into the cup 24 and it will be seen that they terminate at different levels, the return pipe 3 extending to nearer the bottom of the cup. The pipes 3 and 4 are shrouded and effectively electrically insulated by alumina tubes 28, 29 respectively.

The calcium sulphide feed pipe 16 is also shown in more detail in FIG. 2 and it will be seen that the valve 17 is in the form of a screw-conveyor driven by a motor 30 on the end of a shaft 31.

In use, the cell is filled with electrolyte to the level 32, the electrolyte being a fused mixture of calcium chloride, potassium chloride and calcium sulphide. In order to operate the cell in the temperature range 700° C. to 800° C., the electrolyte is preferably a eutectic mixture of 81% by weight calcium chloride and 19% by weight potassium chloride and may conveniently contain approximately 4% by weight of calcium sulphide. The cathode cup 24 contains molten copper-calcium alloy to the level 33 and under the conditions chosen only the calcium sulphide is electrolysed, the calcium entering the alloy and the sulphur being discharged from the cell via the gas connection 2. The hopper 15, by the addition of calcium sulphide through the pipe 16 under the control of the valve 17, maintains the correct quantity and strength of electrolyte in the cell 1.

The mode of operation of the apparatus is to fill the cup 24 with copper-calcium alloy containing 30% by weight calcium (melting point 705° C.) and to fill the cell 1 with molten electrolyte. By operating the valve 11 the cell is



purged and filled with argon, and electrolysis may now begin using, for example, a voltage of 7.5 volts. After a period of electrolysis and due to the configuration of the cell 1, the upper layer of alloy in the cup 24 becomes enriched to 40% calcium (melting point 665° C.).

However, the specific gravity of the 40% alloy at 800° is approximately 2.9 while that of the 30% alloy is approximately 3.5. If, under these conditions, the still-head 5 is connected via the valve 12 to the vacuum line 10 (after a suitable purge with argon), the alloy will flow up the pipe 4 into the heated still-head 5, a proportion of its calcium content will be vaporised to be condensed on the condenser 6 and the depleted alloy will return down the pipe 3. Assuming that the cell 1 is at substantially atmospheric pressure and the still-head 5 at 0.1 mm. of mercury, the pipe 3 may be approximately 3 meters high and the pipe 4 approximately 3.5 meters. However, in practice the pipes will be slightly shorter to ensure that they are always filled with alloy and therefore a splash guard 34 should be provided over the pipe 4 as if it is considerably shorter, the alloy rising therein may splash on the condenser. With a cell volume of 16 liters, an anode pool of 4 liters and an electrical input of approximately 2.6 kwh., the production of calcium is at the rate of 130 g./hour, corresponding to 236 g./hour of calcium sulphide.

When a sufficient quantity of calcium has collected on the condenser 6, the vacuum to the still-head 5 is broken by admitting argon via the valve 12 so that all the alloy in the still-head drops down the pipe 3 into the cell 1. The condenser 6 may then be removed with the calcium thereon, a new condenser fitted and, after a purge, the distillation restarted. Alternatively a plurality of still-heads may be connected to a single cell by suitable valves or provision may be made for the continuous removal of calcium.

The cell 1 is conveniently operated at 700° C. to 800° C. and the still-head 5 at 800° C. to 850° C., and it is preferred to use electrical heating; the pipes 3 and 4 must also be heated. No details are given of the arrangement of the heaters or of the necessary temperature measuring and controlling circuits.

It has been shown that the theoretical difference in length between the pipes 3 and 4 is of the order of 0.5 meter and since the pipe 4 does not need to be so long, a splash guard is fitted. However, it may be convenient to use the full length of this pipe so that a heated plate (at about 900° C.) may be placed between the outlet of this pipe and the small alloy pool in the base of the still-head. The extended portion of the pipe and the heated plate are shown at 4' and 34' in FIG. 1 respectively. This modification will increase the rate of distillation of calcium and raise the mean specific gravity of the alloy in the still head so that a more rapid circulation of alloy is achieved.

It will be apparent that the invention provides a continuous electrolytic method of forming a copper-calcium alloy from calcium sulphide and a semi-continuous method of removing the calcium from the alloy. The starting material, calcium sulphide, may readily be made from calcium sulphate by reduction with town gas.

We claim:

1. A process for the production of alkaline earth metals comprising the steps of

(a) dissolving the sulphide of an alkaline earth metal selected from the group consisting of calcium, strontium and barium metal in a fused salt bath,

(b) electrolysing such sulphide using a cathode formed by molten alloy of the alkaline earth metal with copper,

(c) applying a vacuum to the alloy enriched by the electrolysis to cause the alloy to flow upwardly to a vacuum distillation apparatus where alkaline earth metal is distilled therefrom,

(d) causing alloy depleted in alkaline earth metal to return under gravity for further enrichment by electrolysis,

(e) and removing product alkaline earth metal from said distillation apparatus.

2. The process of claim 1, wherein said fused salt bath consists of 81% by weight of calcium chloride and 19% by weight of potassium chloride and said sulphide is calcium sulphide.

3. The process of claim 1, wherein the alkaline earth metal is calcium and wherein the conditions are selected so as to enrich the calcium content of the alloy from 30% to 40% by electrolysis and to deplete it by the same amount by distillation.

4. The process of claim 1, wherein the electrolysis is conducted continuously and the distillation is conducted semi-continuously.

5. Apparatus for the production of alkaline earth metals, comprising

(a) an electrolytic cell,

(b) a molten alloy cathode pool at the lower part of such cell,

(c) vacuum distillation apparatus located above said electrolytic cell,

(d) a flow pipe leading from the upper part of said pool to said distillation apparatus,

(e) a return pipe leading from a point in said distillation apparatus below the entry of said flow pipe and terminating in the lower part of said pool,

(f) a condenser for alkaline earth metal at the upper part of said distillation apparatus,

(g) and means for creating a vacuum in the said distillation apparatus to maintain a sufficient pressure differential between the electrolytic cell and the said distillation apparatus to maintain said pipes full of alloy.

6. The apparatus of claim 5, including means for providing continuous addition of alkaline earth metal sulphide directly to the electrolyte in the cell.

7. The apparatus of claim 6, including a pipe sealed by molten sulphur for the continuous removal of gaseous product sulphur from the cell.

8. The apparatus of claim 5, including, in the vacuum distillation apparatus, a plate capable of being heated and located so that alloy flows over it from the flow pipe.

9. The apparatus of claim 5, including a cathode pool container and a weir therein separating the alloy flow and return pipes.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

2,913,382	11/1959	Everts	204—69
3,119,664	1/1964	Szechtman	204—71

##### FOREIGN PATENTS

494,702	10/1938	Great Britain.
---------	---------	----------------

JOHN H. MACK, *Primary Examiner*.

H. S. WILLIAMS, *Assistant Examiner*.