

UNITED STATES PATENT OFFICE

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APPARATUS FOR THE PURIFICATION OF
CALCIUM

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1 Claim. (Cl. 266—19)

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This invention relates to improvements in the purification of calcium.

It has already been proposed to purify calcium and magnesium, and alloys thereof, by heating the said metal or alloy to cause its rapid vaporisation while subjected to an absolute pressure less than the vapour pressure of the metal or alloy at its melting point, and condensing the vapours in a suitable manner. Such a process has been described in British specification No. 270,060. Advantageously the pressure was not more than about 2 mm. of mercury, and the metallic product was condensed on two hemi-cylindrical sections of a removable liner placed in the condenser with its axis vertical. In distilling metal containing small amounts of sodium or other impurities more volatile than the metal or alloy, it was found that the deposit of metal which formed on the interior surface of the liner contained an upper portion relatively rich in the sodium or other impurity, while the lower portion was metal or alloy of high purity. By exposing the product to air a darkening of the surface of that portion rich in sodium occurred, and this served as an indication of the place to separate the pure metal from the impure. Such a process could normally be carried out in a metallic apparatus, conveniently an apparatus of iron or steel.

According to the present invention, a process for the purification of calcium containing an alkali metal as impurity comprises distilling the impure calcium in the presence of an inert gas at an absolute pressure not greater than 2 mm. of mercury, condensing substantially pure calcium on a condensing surface of iron or a ferrous alloy and condensing the alkali metal on a separate condensing surface, the two condensing surfaces being maintained at suitable temperatures by separate cooling means. Advantageously, in order to obtain substantially pure calcium in a readily divided form, the distillation of the calcium is effected at an absolute pressure between 0.5 and 2.0 mm. of mercury.

I have found that in distilling calcium in this manner, when using a condensing surface composed of iron or of certain ferrous alloys there is formed on the surface of the metal in contact with the condensing surface a thin layer or skin which contains a significant proportion of iron and which can readily be removed by mechanical means.

According to a further feature of the invention, therefore, the substantially pure calcium condensate is separated by mechanical means from an iron-containing layer formed on the surface thereof in contact with the ferrous condensing surface.

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A convenient apparatus for carrying out the production of high quality calcium from calcium containing an alkali metal as impurity by the process of the present invention comprises a still, means for maintaining therein an inert gas at a reduced pressure, means for vaporising metal which is in the lower part of said still, and condensing means in the upper part of the said still formed of two condensing surfaces, one above the other at a substantial vertical distance apart, the lower condensing surface extending across the major portion of the cross-section of the still but leaving a space between its periphery and the walls of the still through which vapour can ascend, means being provided for maintaining the lower of the two surfaces at a temperature at which calcium will condense thereon, and for maintaining the upper condensing surface at a temperature such that the alkali metal will condense thereon.

In use the lower condensing surface is maintained during the earlier part of the distillation at such a temperature that the calcium will condense thereon but not the alkali metal. Throughout the distillation this condensing surface should be maintained at a temperature which will ensure that the calcium is deposited in the desired readily divided form: thus the temperature of the calcium-covered surface on which further calcium is being deposited must not be allowed to rise to such an extent that fusion of the calcium takes place. Initially the ferrous condensing surface may be maintained at 450° C. to 500° C., but as distillation proceeds and the thickness of the condensed calcium increases, it may become necessary to cool the condensing surface further, so that the freshly formed surface of the calcium is kept at that temperature. For example, after the distillation has been proceeding for about an hour, the ferrous metal surface may be cooled to 250° C. to 300° C.

By using the process of the present invention for the distillation of calcium, I am able to effect a segregation of the alkali metal-containing impure product from the high purity calcium. It is thus much easier to obtain a high purity product free from alkali metal than has been the case with processes used hitherto, and moreover this can be done without subjecting the product to atmospheric oxidation which would necessarily entail the introduction of calcium oxide as impurity. Furthermore, when using an apparatus of the type described herein, I find that a much smaller condensing surface suffices to collect the calcium than in the apparatus used previously: this factor is particularly advantageous when the material of which the calcium condensing surface is com-

posed is such that an iron-containing layer is formed, since the fraction of the calcium which has to be rejected on this account is thereby reduced.

The formation of an iron-containing layer on the surface of the calcium in contact with the condensing surface depends upon the material of which this surface is composed. Thus if a condensing surface of iron or mild steel is used, the calcium in contact therewith absorbs a significant proportion of iron, forming a skin which must be removed after the completion of the distillation. However, when a stainless steel condensing surface is used, the iron absorption is so insignificant as to render this step of the process unnecessary. The iron-containing layer can readily be removed by mechanical means, as for example, by scraping; in many cases it can be prised off by merely inserting a chisel or the like under the skin. Thus by treating the condensed metal to remove such skin before grinding, milling or otherwise destroying the shape in which it is produced, a metal of correspondingly greater purity can be obtained.

In one form of the invention the apparatus comprises a stainless steel vessel adapted to contain the crude calcium in the lower portion while the upper portion has a cover which can be attached to the vessel in an air-tight manner and which carries a hollow member extending downwards into the upper portion of the vessel comprising the still, the bottom of the hollow member being a flat plate of mild steel, stainless steel, or other suitable ferrous metal extending over substantially the whole cross-section of the still but leaving a narrow space between its periphery and the walls of the still through which vapours not condensing thereon can rise to the upper condensing surface. This plate constitutes the surface on which the high purity calcium can be condensed. A suitable distance above this condenser plate, for example approximately halfway between the plate and the cover, a closed pipe or channel is attached to the hollow part depending from the cover, and means are provided for circulating water at high velocity through the pipe or channel. The interior of the hollow member is fitted, between the level of the condenser plate and the level of the pipe through which water can flow, with a number of radially disposed fins to increase the heat radiating surfaces of this condenser; means are also provided for circulating air or other suitable cooling medium over these radiating surfaces. The still is also provided with heating means for calcium in the lower part of the still, which is suitably a fused salt bath in which the still can be immersed to the level of the condenser plate. The upper part of the still is connected to a pump by which the still can be evacuated, means also being provided for measuring the pressure within the still and for supplying thereto an atmosphere or argon or other inert gas.

In using such an apparatus for the distillation of calcium I find that the physical nature of the calcium which is produced depends to a large extent upon the pressure which is maintained within the still during the distillation. If pressures much below 0.5 mm. absolute are maintained, the calcium is produced in the form of long, tough needles which are relatively difficult to break up subsequently if the calcium is required in a divided form. On the other hand, by maintaining within the still argon or other inert gas at an absolute pressure between 0.5 and 2

mm., the calcium is obtained in the form of small crystals which are joined loosely together and thus can be broken up in a mill to give high purity calcium in a divided form. In order that distillation may proceed in a suitable manner the lower part of the still should be at a temperature of the order of 850° C. to 950° C., say at 900° C. to 910° C., while the condensing surface for high purity calcium should be maintained initially at a temperature between 450° C. and 500° C. A much lower temperature, however, should be maintained in the region of the water-cooled pipe or channel, the temperature at this portion of the still being of the order of 30° C. to 60° C. By operating the still under these conditions to purify calcium containing small proportions of sodium and other impurities it is found that the calcium is deposited on the surface which is maintained at 450° C. to 500° C. in a state of relatively high purity which is readily broken up subsequently, whereas the product which is deposited in the neighbourhood of the water-cooled channel contains substantially all the sodium originally in the crude calcium. There will be substantially no product on the intermediate portions of the walls of the hollow member carrying the two condensing surfaces, and thus segregation of high purity calcium and impure sodium-containing material results. Not only can high quality calcium be obtained in this manner from technical quality calcium, which may contain of the order of 0.5% to 1% of sodium, but it can also be produced quite successfully from calcium containing as little as 0.2% or as much as 10% sodium. In addition it is possible to reduce to a matter of a few parts per million the amounts of iron, manganese and silicon which may be present in the crude material.

When distillation is complete the still is raised out of the fused salt bath and left until cold while maintaining the reduced pressure in the still; alternatively an atmosphere of argon may be introduced into the still. When the whole is quite cold and the vacuum has been broken, by introducing argon to a pressure of one atmosphere, the cover is lifted up, thus withdrawing the condensing surfaces with the product attached, and the high purity calcium is removed from the surface on which it has condensed by a hammer and chisel or like method. The product will then be in the form of a mass of glistering crystals which may have an iron-containing skin where it has adhered to the condensing surface. The skin, if present, is then removed by prising it off with a chisel or similar means. Instead of first detaching the product and then removing the skin in this way, it is possible to remove the majority of the calcium only from the condenser plate, leaving a narrow thickness of relatively pure calcium on the bottom of the condenser plate. The product removed by this method consists of high quality material, and the layer containing the iron is left on the condenser surface and can be removed separately before the still is used again.

One form of apparatus suitable for carrying out the process of the present invention is illustrated in the accompanying drawing in which the preferred type of still is shown diagrammatically.

Figure 1 is a vertical section and Figure 2 is a plan view taken on the line II—II of Figure 1.

In the drawing, a still comprising a stainless steel vessel 1, is supported in a fused salt bath 3 on feet 4. The top of the vessel is closed by a

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cover 5, which carries a hollow member 6 extending downwards into the upper part of the still and terminating in a flat steel plate 7 occupying almost the whole of the cross section of the still. A number of radially disposed metal fins 8 are situated in the interior of the hollow member 6, and a flat metal ring 9, fitted with a water cooling coil 10, is attached to the outside of said member about half-way between the cover 5 and the plate 7. A pipe 11 supplies compressed air to the fins 8 inside the hollow member, and a pipe 12, leading into the upper part of the still, and capable of being closed by a valve 13, is connected to a vacuum pump and pressure gauge and an inert gas supply, which are not shown in the drawing. Further water cooling coils are provided at 14, and thermocouple pockets at 15 and 16.

In carrying out the process by the preferred method using the apparatus illustrated in the drawing, the crude calcium in the form of an ingot, shown at 2, contaminated with sodium, is put into the still 1, and the cover 5 is attached in an air-tight manner. The still is then evacuated by means of the pump connected to the pipe 12, and a small amount of argon is introduced through the same pipe so that the absolute pressure within the vessel is between 0.5 and 2 mm. of mercury. As distillation proceeds some occluded gas may be evolved and it is therefore necessary to observe the pressure within the vessel from time to time and if necessary to pump out gas and to introduce an appropriate quantity of argon. The still 1 is lowered into the salt bath 3, maintained at a temperature of 900° C. to 950° C., so that the surface of the fused salt is level with the condenser plate 7. Cold water is then caused to flow through the cooling coils 10 and 14, and air is blown through the pipe 11 over the radiating fins 8. Distillation then proceeds, the high quality calcium collecting on the plate 7, which is maintained at a temperature of 450° C. to 500° C. by the air passing over the fins 8, while sodium condensed as a solid impure sodium-containing alloy on the water-cooled ring 9. As the thickness of the deposited calcium increases, the temperature of the plate 7 may be reduced as necessary by increasing the rate of flow of the compressed air.

When the distillation is complete, the still 1 is raised out of the fused salt bath and allowed to cool, and argon is introduced into the still until the pressure therein is equal to atmospheric pressure. The still is then opened, the condenser plate 7 withdrawn, and the deposited calcium removed therefrom, the iron-containing skin, if present, being subsequently removed from the product, which is then ground to give substantially pure calcium in the form of small crystals.

The following example illustrates but does not limit the invention, all proportions being by weight.

Example

The apparatus employed was similar to that described above with reference to the accompanying drawing. A calcium ingot was placed in the still, the calcium having the following composition:

Ca, percent	Na, percent	Cl, percent	Fe, p. p. m.	Mn, p. p. m.
95	0.8	0.65	3,010	310

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The distillation was carried out in the manner described above, the calcium being condensed on a mild steel plate, whose temperature was maintained initially at 500° C. and gradually reduced to 250° C.

After completion of the distillation, the still was cooled and the vacuum broken by introducing argon, the condenser plate was withdrawn and the calcium removed therefrom. The iron-containing skin, which had been formed on the surface of the calcium in contact with the mild steel plate, was scraped off the calcium mass, and the latter was then ground, giving a crystalline product of the following composition:

Ca, percent	Na, percent	Cl, percent	Fe, p. p. m.	Mn, p. p. m.
99.4	0.12	0.24	52	26

I claim:

An apparatus for use in the purification of calcium containing an alkali metal as an impurity which comprises a still, means for maintaining therein an inert gas at a reduced pressure, means for vaporising metal which is in the lower part of said still, a removable cover for said still, a tubular member carried by and extending downwards from said cover, a flat horizontal ferrous plate closing the lower end of said tubular member and occupying almost the whole cross section of the still but leaving a space between its periphery and the wall of the still through which vapour can ascend, said plate constituting a lower condensing surface, internal fins in said tubular member, means for circulating a cooling medium over said fins whereby said plate is maintained at a temperature at which calcium will condense thereon, a flat horizontal ring carried by said tubular member in the space between itself and the wall of said still, said ring constituting an upper condensing surface, a pipe coil on said ring, and means for circulating a cooling medium through said pipe coil whereby said ring is maintained at a temperature such that the alkali metal will condense thereon.

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