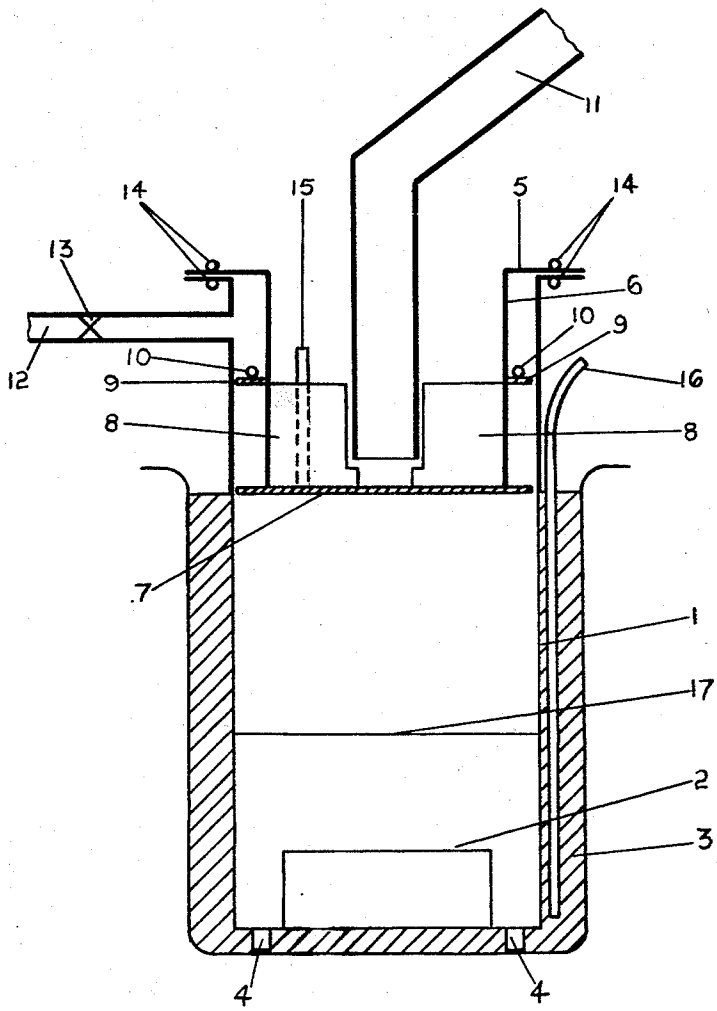
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DISTILLATION OF CALCIUM

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DISTILLATION OF CALCIUM

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This invention relates to improvements in the purification of calcium and magnesium.

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 hemicylindrical 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 said metal or its 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.

In copending application Ser. No. 686,959, filed July 29, 1946, now Patent No. 2,650,085, there is described a process for the purification of calcium containing an alkali metal as impurity, which 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. The present invention relates to improvements in the process of the above application.

I have now found that, in a process for the purification by distillation of calcium or magnesium containing a metal of higher vapour pressure at the melting point an improved separation of the latter metal from the calcium or magnesium is obtained by effecting the distillation in two stages, the first stage in the presence of an inert gas at an absolute pressure substantially greater than the vapour pressure of calcium or magnesium at the temperature employed but less than the vapour pressure at that temperature of the metallic impurity which it is desired to eliminate, and the second stage in the absence of an inert gas, the calcium or magnesium distilling under the pressure of its own vapour only.

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I have further found that a singular advantage is obtained by the use of a still in which a baffle plate is positioned above the crude calcium to be distilled. The presence of this plate serves to control the radiation of heat from the molten impure calcium to the lower condensing surface and thus stabilises the temperature conditions prevailing in the upper part of the apparatus. A particularly useful form of baffle comprises a stainless steel perforated plate having a highly polished upper surface. A convenient means of supporting the plate above the metal to be distilled is by means of legs resting on the base of the still.

While this invention is particularly applicable to the purification of calcium or magnesium containing alkali metals it is not applicable to the purification of calcium contaminated with lithium, since the vapour pressure of lithium is lower than that of calcium and consequently a two-stage separation process cannot be effected.

According to the present invention, therefore, a process for the purification of calcium or magnesium containing an alkali metal other than lithium as impurity comprises distilling the mixture in two stages, the first stage distillation being carried out in the presence of an inert gas at an absolute pressure substantially greater than the vapour pressure of calcium or magnesium at the temperature of distillation but less than the vapour pressure at that temperature of the said alkali metal so that the alkali metal is vapourised and condensed on an upper condensing surface and a second stage distillation being carried out in the absence of an inert gas so that the calcium or magnesium distils under its own vapour pressure only and condenses on a lower condensing surface.

The process of this invention may suitably be carried out in an apparatus similar to that described in copending application Ser. No. 686,959, filed July 29, 1946, now Patent No. 2,650,085, that is in a still provided in the upper part with two condensing surfaces separated from one another by a substantial vertical distance, the lower 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, separate cooling means

being provided for the two condensing surfaces.

According to a further modification of my invention there is also provided a stainless steel perforated baffle plate having a highly polished upper surface and positioned above the crude calcium or magnesium in the still. The baffle plate may contain any number of perforations of varying diameters but from 3000 to 4000 perforations are preferred each having a diameter of ¼ inch. Conveniently I employ a baffle plate of diameter 2 ft. 9 inches, the area occupied by the perforations being approximately 20% of the area of the plate. In general, I prefer that the perforations cover from 15 to 25% of the area of the plate but a coverage of even 5% would be suitable.

By carrying out the first stage of the distillation at an absolute pressure substantially greater than the vapour pressure of the calcium or magnesium at the temperature employed, the distillation of these metals is suppressed. However, the metallic impurities present in the calcium or magnesium distil, at first refluxing from the lower condensing surface, but eventually condensing on the upper condensing surface. When the first stage of the distillation has been completed, the metallic impurities all being deposited on the upper condensing surface, the external applied pressure in the still is reduced as low as possible, suitably to 0.001 to 0.01 mm. mercury and the calcium or magnesium then distils steadily under its own vapour pressure, collecting on the lower condensing surface. By distilling the alkali metal and the calcium or magnesium in two separate and clearly defined stages in this manner, a substantially complete separation of the two metals is effected.

In one method of carrying out the process of the invention for the separation of an alkali metal and calcium the still may be heated by immersion in a fused salt bath maintained at a temperature between 865° and 900° C. The lower condensing surface is cooled by any convenient means, suitably by air-blowing. When the salt bath has attained the desired temperature, for example 870° C., with the still immersed to the level of the lower condensing surface, the rate of cooling of the latter is adjusted to give a suitable condenser head temperature, for example 200–250° C., and this rate of cooling is maintained throughout the distillation. I have found that when temperatures of this order are employed the calcium condensate is coherent and adheres to the condenser plate during the second stage of the process. The distillation of the alkali metal proceeds steadily, the atmosphere in the still consisting of inert gas suitably at a pressure of 20 mm., and when all the alkali metal present has collected on the upper condensing surface, a sudden drop in the temperature of the lower condensing surface is observed due to the fact that no further condensation of the alkali metal is taking place thereon and hence no latent heat of vaporisation is being imparted thereto. When this drop in temperature occurs, the still is evacuated as completely as possible and the calcium distillation commences, the temperature of the lower condensing surface rising considerably above the original temperature of 200° C. to 250° C., for example 150° C. or more above this temperature. The condenser temperature falls gradually after the maximum has been attained, and finally falls rapidly, indicating that the calcium distillation is complete. Thus by maintaining the rate of cooling of the lower condensing surface constant, it is possible to follow the course of the distillation with great precision, simply by observing the fluctuations in temperature of the said condensing surface.

As previously stated the apparatus employed for carrying out the process of this invention may be similar to that described in copending application Ser. No. 686,959, filed July 29, 1946, now Patent No. 2,650,085. Thus in more detail and with reference to the diagram it may comprise a stainless steel vessel 1 adapted to contain the crude calcium or magnesium in the lower portion, while the upper portion has a cover 5 which can be detachably secured to the vessel in a gas-tight manner and which carries a hollow member 6 extending downwards into the upper portion of the vessel comprising the still, the bottom of the hollow member being a flat plate 7 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 subsequently referred to as the condenser plate constitutes the surface on which the calcium condenses, and is preferably composed of stainless steel in order that the amount of iron absorbed therefrom by the adjacent layer of condensed calcium shall be negligible. A suitable distance above this condenser plate, for example approximately half-way between the plate and the cover, a water-cooled flange 9 is attached to the hollow part depending from the cover, means being provided for circulating water at high velocity through a pipe 10 attached to the upper surface of the flange. The interior of the hollow member is fitted, between the level of the condenser plate and the level of the water-cooled flange, with a number of radially disposed fins 8 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 suitably heated by immersion in a fused salt bath 3 on feet 4, to the level of the condenser plate.

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 the preferred method of carrying out the invention using the apparatus described above there is also provided a stainless steel perforated plate 17 having a highly polished upper surface and positioned above the crude calcium in the still. In the preferred form the stainless steel perforated plate contains 3000–4000 perforations of diameter ¼ inch. Advantageously the fused salt bath is heated to 870° C. and the still, containing in the lower part an ingot of calcium containing sodium, is immersed therein up to the level of the condenser plate, the plate being cooled by the circulation of compressed air. The still is then evacuated completely, and argon is admitted to a pressure of approximately 20 mm. of mercury. The salt bath having cooled considerably as a result of the immersion of the cold still therein, a period of some hours may be required to restore the temperature of the salt bath to 870° C. When this temperature has been reached the salt bath level is finally ad-

justed. The sodium distils from the molten impure calcium, refluxing from the condenser plate and gradually condensing on the water-cooled flange. When a sudden drop in the temperature of the condenser plate indicates that the distillation of the sodium is completed, the air blowing on to the condenser plate is adjusted so that it reaches a steady temperature of 200–250° C. Under these conditions the still is again evacuated completely and the gas line is closed, no argon being present in the still during the second stage of the distillation. The calcium then begins to distil, and condenses on the condenser plate, the temperature of which rises to 350–450° C. When all the calcium has distilled, as indicated by a rapid fall in the condenser plate temperature, the still is withdrawn from the salt bath and allowed to cool while air is blown on to the condenser plate during the cooling. When the vessel is cold, argon is introduced into the still to a pressure of one atmosphere. The contaminated condenser is detached and withdrawn and freed from the inflammable sodium and the calcium is removed from the condenser plate in the form of crystals compactly aggregated together.

The improved process of the present invention when applied to the distillation of calcium containing sodium (or other alkali metal) enables the sodium to be substantially completely removed from the calcium. The process is also advantageous in that by its use it is possible to separate larger proportions of sodium from the calcium than has hitherto been the case, for example calcium containing up to 10% of sodium may be purified in this way. A further advantage of the process is to be found in the fact that, by maintaining a constant rate of cooling of the condenser plate, the progress of the distillation can be followed with great precision, a well defined break between the distillation of the sodium and the distillation of the calcium being clearly observed.

Moreover, the presence of the perforated steel plate between the molten charge and the condenser plate ensures that for a given salt bath temperature a standard quantity of heat is radiated to the condenser. As a consequence of this regulation of heat transfer condenser plate variations can be used satisfactorily to indicate the course of the distillation process.

A further advantage of the control of radiant heat is to be found in the quality of the calcium which is deposited and this is of primary importance when a homogeneous product is required.

It is found invariably in the absence of adequate temperature control that the distilled calcium consists of a mixture of its allotropic forms of difference crystalline structure. Usually the mixture contains as much as 20% of a hard product which is difficult to remove from the condensing surface and which is in a form quite unsuitable for convenient and efficient use in many chemical reactions.

The polished perforated steel plate overcomes this drawback and ensures a high yield of a homogeneous friable calcium product.

The following examples illustrate but do not limit the invention:

Example 1

A calcium ingot 100 lbs. in weight was contained in a stainless steel vessel which formed part of a distillation apparatus similar to that described in copending application Ser. No. 686,959, filed July 29, 1946, now Patent No. 2,650,085.

The apparatus consisted of a stainless steel vessel the lower portion containing the calcium ingot while the upper portion which held an air-tight cover carried a hollow member which extended downwards into the upper portion of the vessel comprising the still. The bottom of the hollow member was a flat condenser plate of stainless steel which extended over the entire cross-section of the still but left a narrow space between its periphery and the walls of the still through which vapour not condensing thereon could rise to the upper condensing surface.

Approximately half way between the condenser plate and the cover a water-cooled flange was attached to the hollow part depending from the cover, water being circulated through a pipe attached to the upper surface of the flange. Between the level of the condenser plate and the level of the water-cooled flange, the exterior of the hollow member was filled with fins radially disposed.

The still containing the calcium ingot was immersed in the fused salt bath up to the level of the condenser plate, the bath having been heated to a temperature of 870° C. and the condenser plate cooled continuously by the circulation of compressed air to a steady temperature of 250° C. The still was then evacuated completely and argon was admitted to a pressure of 20 mm. of mercury. Distillation was commenced with sodium volatilising from the molten impure calcium, refluxing from the condenser plate and gradually condensing on the water-cooled flange. A sudden drop in temperature on the condenser plate indicated that sodium distillation was complete. The air flowing on the condenser plate was adjusted and the temperature consequently maintained at 250° C. With this temperature steady the still was evacuated completely and the calcium distillation was allowed to take place and condensation of calcium on the condensation plate increased the temperature thereof to 400° C.

The completion of the calcium distillation after 2½ hours was indicated by a rapid fall in temperature of the condenser plate and the still was then withdrawn from the salt bath and allowed to cool. Argon was then admitted to the still to a pressure of one atmosphere and the calcium was removed in the form of crystals.

On analysis the crystals were found to have the following composition.

Ca, Percent	Na, Percent	Fe, p. p. m.	Cu, p. p. m.	Ni, p. p. m.	Mn, p. p. m.	Cr, p. p. m.	Cl, Percent
99.73	0.008	5	10	5.10	10.15	1	0.21

The yield of free calcium was 81 lbs. of which 56.5 lbs. were usable as friable material.

Example 2

A 100 lb. ingot of crude calcium was distilled acording to the process and in the apparatus described in Example 1 but the apparatus was provided with a stainless steel perforated baffle plate having a polished upper surface the plate being positioned above the crude calcium in the still. The plate contained 44 holes each of 2¼ inches' diameter arranged in concentric circles.

On completion of the process the calcium product contained 64.6 lbs. of friable calcium while 16.15 lbs. were found to be too hard to break up.

Example 3

A 100 lb. ingot of crude calcium was distilled according to the process and in the apparatus described in Example 1 but as in Example 2 with a stainless steel perforated plate having a polished upper surface positioned above the crude calcium in the still. The plate contained 3,500 holes each of ¼ inch diameter arranged in concentric circles.

On completion of the process the calcium product contained 70.72 lbs. of friable calcium while 4.03 lbs. were too hard to break up.

I claim:

1. A process for the purification of a metal selected from the group consisting of calcium and magnesium containing an alkali metal other than lithium as impurity which comprises distilling a batch of the mixture in two stages, the first stage distillation being carried out in the presence of an inert gas enclosed with the batch at an absolute pressure substantially greater than the vapour pressure of calcium or magnesium at the temperature of distillation but less than the vapour pressure at that temperature of the said alkali metal so that substantially only the alkali metal is vaporised and condensed on a condensing surface and a second stage distillation being carried out in the absence of an inert gas so that substantially only the calcium or magnesium distils under its own vapour pressure only and condenses in solid form on a lower condensing surface.

2. A process according to claim 1, in which distillation is effected by immersing a stainless steel vessel containing the alkali metal-contaminated calcium or magnesium in a fused salt bath maintained at a temperature of 870° C. approximately.

3. A process according to claim 1 in which the first stage distillation is continued until the condensing surface on which the alkali metal condenses indicates a sudden drop in temperature.

4. A process according to claim 1 in which the second stage distillation is continued until a rapid fall in temperature is indicated on the calcium or magnesium condensing surface.

5. A process for the purification of a metal selected from the group consisting of calcium and magnesium containing an alkali metal other than lithium as impurity which comprises distilling a batch of the mixture in two stages, the first stage distillation being carried out in the presence of an inert gas enclosed with the batch at an absolute pressure substantially greater than the vapour pressure of calcium or magnesium at the temperature of distillation but less than the vapour pressure at that temperature of the said alkali metal so that substantially only the alkali metal is vaporised and condensed on a plate maintained at a temperature of 250° C. approximately and a second stage distillation being carried out in the absence of an inert gas so that substantially only the calcium or magnesium distils under its own vapour pressure only and condenses in solid form on a lower condensing surface.

6. A process according to claim 1 wherein the quantity of heat radiated from the metal being distilled is in part prevented from reaching the condensing surface.

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