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METHOD OF SEPARATING THE RARE EARTHS TOGETHER WITH THORIUM, CERIUM, AND ZIRCONIUM BY ELECTROLYSIS.

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1,115,513. Patented Nov. 3, 1914.

Fig. 1

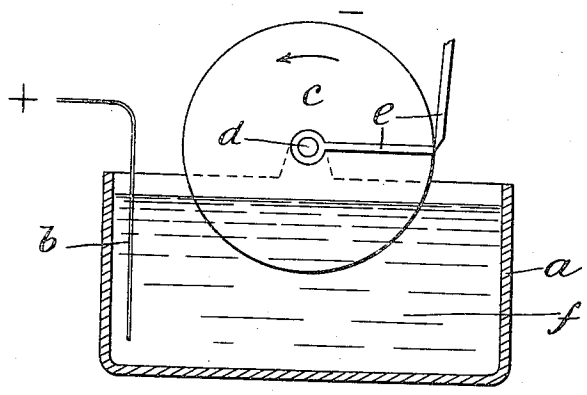
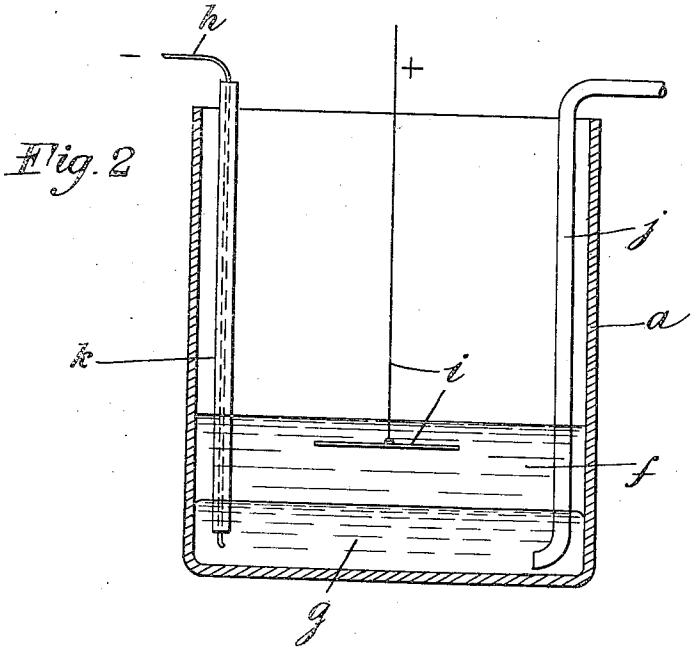


Fig. 2



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LOUIS M. DENNIS, OF ITHACA, NEW YORK.

METHOD OF SEPARATING THE RARE EARTHS, TOGETHER WITH THORIUM, CERIUM, AND ZIRCONIUM, BY ELECTROLYSIS.

1,115,513. Specification of Letters Patent. Patented Nov. 3, 1914.

Application filed September 18, 1913. Serial No. 790,413.

To all whom it may concern:

Be it known that I, LOUIS M. DENNIS, a citizen of the United States of America, and a resident of the city of Ithaca, Tompkins county, State of New York, have invented a new and useful Method of Separating the Rare Earths, together with Thorium, Cerium, and Zirconium, by Electrolysis.

My new method is based on a fractional electrolysis of solutions, emulsions or suspensions containing the elements to be separated, said elements being precipitated in the form of compounds, such as hydroxids for example, containing said elements or mixtures of them. Heretofore experiments have been made looking toward such method of separation but they have been failures because the compounds formed by the electrolysis have been precipitated or deposited upon or caused to adhere to the electrode in such manner as to so increase the internal resistance of the cell that appreciable or rapid separation was impossible. The reason for the failure of these earlier experiments was apparently due to the deposit on the fixed electrode used which greatly increased the resistance to the passage of the current and caused simultaneous separation of all of the elements referred to when the current pressure was raised sufficiently to overcome this resistance.

I have discovered that if the surface of the cathode be kept free from adhering deposits, the elements referred to may be fractionally separated in the form of compounds as described.

The cleaning of the cathode surface or the keeping it free from deposits may be accomplished in a variety of ways, mechanical or otherwise, and I shall describe two ways of doing this in order to illustrate a manner of practising my new method, it being understood that I do not confine myself to any particular way of accomplishing this result.

In the drawings Figure 1 is a sectional view partly diagrammatic and partly in elevation of a form of cell which may be used in practising my invention in which the deposit on the cathode is removed by a mechanical scraper, the scraper and the electrode being movable with relation to each other. Fig. 2 is a sectional view, partly diagrammatic and partly in elevation of another and at present the preferred form of cell in which mercury is made use of as the cathode and the surface thereof is broken up by air agitation.

Similar letters of reference indicate similar parts through the several views.

a indicates the cell proper which may be made of any suitable material which will not be attacked by the solution or any of the products of the electrolysis. I have found glass to be satisfactory.

b indicates the anode and *c* the cathode, here shown in the form of a disk carried by a shaft *d* supported in any suitable manner (not shown).

e indicates a scraper which is shown as adjacent the edge and sides of the cathode although in practice a scraper adjacent the edge only has given fair satisfaction. The cathode may be caused to rotate in any convenient manner (not shown). It is not essential that the cathode be the movable element as it is obvious that all which is necessary is a relative movement between cathode and scraper.

The electrolyte is indicated by *f*. It may be in the form of an aqueous or alcoholic or other suitable electrolyzable solution, an emulsion or a suspension, the essential feature being only that it be in such form that it may be electrolyzed. The temperature of the electrolyte may be varied by external or other means of heating as may be desirable. The electrodes may be of any suitable material which will not be affected by the electrolyte or the products of electrolysis. I have found a copper cathode and a platinum anode to give good results.

In Fig. 2 I have shown a cathode *g* of mercury. In this case the lead *h* to the electrode should be of any suitable material which will not form an alloy with mercury. I have found iron to be satisfactory. The anode *i* should be of any suitable material which will not be affected by the electrolyte or the products of electrolysis. I have found platinum to be useful for the purpose.

j indicates a pipe for conducting air or any suitable gas under pressure beneath the surface of the mercury to bubble up through the same and thus break up the surface of the mercury. These should be sufficient of pipes *j* or sufficient outlets from a single or more pipes in order to attain the result desired. If the lead to the cathode passes through the electrolyte it should be properly

insulated as by being passed through a glass tube *k*.

As an electrolyte I have used aqueous solutions of various salts of the rare earths, particularly the nitrates of these elements. In this form the products of electrolysis are the hydroxids of the rare earth elements and nitric acid and its decomposition products. Of course any soluble salt of the rare earths could be used instead of the nitrates, the necessary obvious changes being made in the material or arrangement of the electrodes to prevent them from being attacked by the products of electrolysis. In some cases it might be advisable to surround the anode with a porous diaphragm so that the electronegative products of electrolysis would not remain in the solution to react with the material liberated at the cathode or attack the cathode material.

In order to make my new method clear to those skilled in the art, I shall give one illustration of a means of carrying it out, not restricting myself to any of the details given as they are merely intended as illustrations of the general principles involved.

25 grams of the oxids of the yttrium group of the rare earths may be dissolved in nitric acid, the solution evaporated to dryness to remove the excess of acid; the resulting nitrates dissolved in 500 cc. of water and electrolyzed in the presence of a mercury cathode as shown in Fig. 2, maintaining the voltage approximately constant at 9 volts. At the end of about 6 hours a precipitate of rare earth hydroxid is formed in the cell. The current is then interrupted, this precipitate is removed by filtration and the filtrate is further electrolyzed under approximately the same conditions and voltage for a further period of six hours resulting in a second precipitation of hydroxid which is filtered off, and the process repeated for the number of fractions desired.

The determination of the mean atomic weight of the rare earths in each fractional precipitation and the absorption spectra of these earths show that a rapid and quite complete separation of yttrium from erbium is thus effected.

In the example just stated, the first precipitation is a fractional separation containing a higher cencentration of erbium hydroxid, and the second precipitation is a fractional separation containing a higher concentration of yttrium hydroxid.

In the claims where I use the term "rare earths" I mean to include the rare earth metals and thorium, cerium and zirconium, whether as elements or in the form of compounds, or mixtures of either; where I use the term "separating" I means to include separating them from each other or separating them in groups, or separating one of them from the remainder and either partially or completely and where I use the term "solutions" I mean to include any electrolyte whether in the form of solutions, emulsions or suspensions of the salts, compounds or mixtures of the elements referred to.

I do not restrict myself to the use of any particular type of cell or of solvent, nor to any particular salt, compound or mixture of the "rare earths" nor to the production of any particular compound as the end product of the electrolysis, nor to any particular electrodes or methods of keeping the same free from surface deposits, further than the scope of the appended claims demands.

What I claim and desire to secure by Letters Patent is:

1. An electrolytic method of separating the rare earths from solutions containing the same consisting in precipitating the same by subjecting a solution of the rare earths to the action of an electric current while maintaining the cathode surface substantially free from an adherent deposit.

2. An electrolytic method of separating the rare earths from solutions containing the same consisting in precipitating the same by subjecting a solution of the rare earths to the action of an electric current while maintaining the cathode surface substantially free from a covering of the electropositive products of the electrolysis.

3. An electrolytic method of fractionally separating the rare earths consisting in subjecting a solution of the rare earths to the action of an electric current and fractionally precipitating insoluble compounds of said rare earths from said solution while maintaining the cathode surface substantially free from a covering of the electropositive products of the electrolysis.

4. An electrolytic method of fractionally separating the rare earths consisting in subjecting a solution of the rare earths to the action of an electric current at and above the lowest decomposition voltage of the first product desired and fractionally precipitating insoluble compounds of said rare earths from said solution and repeating the steps as desired while maintaining the cathode surface substantially free from a covering of the electropositive products of the electrolysis.

5. An electrolytic method of separating the rare earths from solutions containing the same consisting in precipitating the same by subjecting an aqueous solution of the salts of the rare earths to the action of an electric current while maintaining the cathode surface substantially free from a covering of the electropositive products of the electrolysis.

6. An electrolytic method of separating the rare earths from solutions containing the same consisting in precipitating the same by

subjecting an aqueous solution of the nitrates of the rare earths to the action of an electric current while maintaining the cathode surface substantially free from a covering of the deposited rare earth hydroxid.

7. An electrolytic method of fractionally separating the rare earths consisting in subjecting a solution of the rare earths to the action of an electric current, precipitating a portion of said rare earths in the form of compounds insoluble in the electrolyte, removing the products of electrolysis desired from the solution, resubjecting the remainder to the action of the electric current and repeating the steps as desired while maintaining the cathode surface throughout the various steps substantially free from a covering of the electropositive products of the electrolysis.

8. An electrolytic method of fractionally separating the rare earths consisting in subjecting a solution of the rare earths to the action of an electric current at and above the decomposition voltage of the first product of electrolysis desired, precipitating a portion of said rare earths in the form of compounds insoluble in the electrolyte, removing said product from the solution, resubjecting the remainder to the action of the electric current, precipitating another portion of said rare earths in the form of compounds insoluble in the electrolyte, removing said last mentioned product of electrolysis from the solution and repeating the steps as desired, while maintaining the cathode surface throughout the various steps substantially free from a covering of the electropositive products of the electrolysis.

9. An electrolytic method of separating the rare earths from solutions containing the same consisting in precipitating the same by subjecting an aqueous solution of the nitrates of the rare earths to the action of an electric circuit in the presence of a mercury cathode and forcing air under pressure through the mercury to agitate the same and prevent the formation on the surface of the mercury of a deposit of the rare earth hydroxid produced.

In testimony whereof I have signed this specification in the presence of two subscribing witnesses.

LOUIS M. DENNIS.

Witnesses:
K. G. Le Ard,
Seabury C. Mastick.