THE PREPARATION AND PROPERTIES OF YTTRIUM MIXED METAL

BY

JOHN FREDERICK GROSS HICKS
B. S. University of Pennsylvania, 1906.
M. S. University of Illinois, 1916.

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1918
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY JOHN FREDERICK GROSS HICKS
ENTITLED THE PREPARATION AND PROPERTIES OF
YTTRIUM MIXED METAL
BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

A. F. M. Farland
In Charge of Thesis

W. A. Noyes
Head of Department

Recommendation concurred in*

S. Parr
Committee
on
Final Examination*

W. McPharm

*Required for doctor's degree but not for master's
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I. Introductory; Historical:

The isolation of metal by methods other than the decomposition of their oxides by carbon at elevated temperatures usually presents a problem somewhat difficult of solution. The usual methods for isolating such a metal are: (1) electrolysis of one of its fused salts; (2) decomposition of one of its salts by a more electropositive metal.

1) Wohler prepared a small quantity of metallic yttrium by decomposing the chloride with potassium; Popp reports a similar decomposition of yttrium ammonium chloride with metallic sodium; Humpidge and Burney report attempts to secure the metal by electrolysis of the fused chloride, and Minkler decomposed the oxide with finely-divided metallic magnesium. None of these investigators had the preparation of the metal for their main object; their results along that particular line are merely records incidental to their other results and no quantitative data of any sort are given. Preparations of materials and details of procedure are likewise omitted. All four workers agree that the product of such experiments as have been outlined is a powder, gray to black in color, although their accounts of its properties differ widely.

1). Pogg. Ann., 13 (1828) 577
4). Ber. 23 (1890) 787
instance, states that his powder did not decompose water; 5) the others state the exact opposite; Abegg gives two 6) other references by P. T. Cleve and by Cleve and Hoeglund, neither of which refer to the preparation of metal at all, but only to the preparation and analysis of new salts of yttrium and erbium.

II. Object and Reasons for the Investigation:

On account of the meagerness of the work done along this line, because the metal has never been obtained in other than the form of a powder, and because of the possibility of the metal or its alloys proving of more than mere scientific interest, the preparation of coherent "Yttrium Mixed Metal"* (analogous to the well known "Cerium Mixed Metal" which contains the several metals of the cerium group of rare earths) was undertaken. It was further intended to study the properties of the new "mixed metal" at length, and to alloy it with as many of the commoner metals as possible, up to, say five percent, studying its influence upon the properties of these metals. Owing to the high cost of production, the amount of yttrium mixed metal in any alloy could not be large, unless results of exceptional economic value were obtained.

5). Handbuch, 3 (1906) 329
6). Bull. Soc. Chim. 21 ii (1874) 344

* The name "Yttrio-Mischmetall" was originally proposed, but was changed to the present one at the instance of Dr. O. Balke, who pointed out that several controversies had arisen as to whether the term "mischmetall" (in the trade) meant pure cerium or an alloy of the metals of the cerium earths, and that the term "Cerium Mixed Metal" had been officially adopted as signifying the alloy. He thought it advisable to preserve the analogy here in case the new metal should prove of economic value.
III. Outline of Methods: Results Obtained:

Hydrated yttrium earth chlorides (RCl₃.6H₂O) were mixed with an excess of ammonium chloride and the temperature slowly raised to 115⁰ in an oven; this removed all but one molecule of water of hydration. The dehydration was completed in an atmosphere of dry hydrochloric acid gas at a temperature sufficient to volatilize ammonium chloride (350⁰-400⁰).

The anhydrous chloride was allowed to react with metallic sodium in sealed vessels under atmospheric pressure, but with indifferent results; in vacuo, however, this reaction proceeds to completion, and sodium chloride almost completely volatilizes out. Sodium vapors bubbled through fused anhydrous yttrium earth chlorides yielded worthless results; and but little better results were obtained by allowing sodium vapor to flow over the anhydrous chlorides in vacuo, there being surface action only.

Electrolyses were carried out upon the following baths: (1) fused anhydrous chlorides; (2) fused anhydrous fluorides; (3) oxides dissolved in fused anhydrous fluorides; (4) oxides dissolved in fused sodium chloride; (5) oxides dissolved in a mixture of one mol anhydrous fluoride and three mols sodium chloride; (6) oxides dissolved in fused cryolite. Only methods (1) and (6) produced results worthy of consideration. Method (1) is characterized by extremely heavy loss of chloride by volatilization, formation of carbide and basic salts, the
latter rendering the bath viscous and unfit for further electrolysis; method (6) to a large extent corrects the errors of (1). All electrolytic methods are disadvantageous in that the powdered metal and flux are extremely difficult to separate. Metallic electrodes and cathodes of carbon lined with refractory materials except for a small portion of the surface have a tendency to lessen the formation of carbide, although some carbide is formed if a carbon anode is employed.

Some alloys were prepared directly in the furnace by introducing some of the commoner metals into the fused flux before electrolysis commenced. These sank and after melting acted as a cathode, the metal produced in the course of electrolysis alloying with the introduced metal as fast as formed. Time did not permit of an extended study of this electrolytic preparation of alloys but the results obtained promise favorably. The concentration of rare earth metal in the common metal is of course regulated by the length of the electrolysis.

IV. Preparation of Materials:

(1) General: The raw material was oxide prepared from gadolinite. The mineral was ground to a coarse powder and mixed with concentrated hydrochloric acid to a thin paste, and allowed to remain in this condition for a week, with frequent stirring. Portions of this paste were heated over the steam bath for a week, the liquid lost by evaporation being replaced by fresh acid, then diluted
with an equal volume of water, and after vigorous agitation allowed to settle and the clear liquid siphoned off. The strongly acid residue was extracted with water until a small test-sample showed but slight precipitation with oxalic acid; as the concentration of acid in the extract was very low toward the end of the operation, more acid was added to prevent the hydrolysis of the earth chloride to difficultly soluble basic salts. The residue from the water extraction was again boiled with concentrated hydrochloric acid and the above process repeated; practically all of the earths could be extracted in this manner. The extracts were then evaporated to convenient volume and the rare earths (both cerium and yttrium groups) were precipitated from the solution of their chlorides by the addition of an excess of a hot saturated solution of oxalic acid. The liquid (acid with hydrochloric and oxalic acids) above the precipitated oxalates contained the complex oxalates of iron, beryllium, zirconium and thorium; it was evaporated to convenient volume and stored. The precipitated oxalates were then washed repeatedly by decantation, dried over the steam bath, then in an oven at 105°, and finally powdered. Determination of the atomic weight of the earth-metals in these mixed oxalates was made, using the method of Brauner and of Hopkins and Balke, that is, the ratio of oxide to oxalate. The following results were obtained:

104.14 mean

While these results are rough, they show that the material was very good considered as a starting point for yttrium earth materials.

The greater part of the cerium earths were then separated in the form of their difficultly soluble double sulphates with sodium, $R_2\left(SO_4\right)_3\cdot Na_2SO_4\cdot 8H_2O$, as follows:

The powdered oxalates were mixed with concentrated sulphuric acid to a thick paste and the temperature raised slowly to a dull red heat, maintaining these conditions until all of the sulphur trioxide had been expelled.

After cooling, the mass was powdered and dissolved in small quantities at a time in water containing ice ($30^\circ - 50^\circ$) and kept acid with sulphuric acid all the time to prevent hydrolysis of the sulphates to basic salts which are extremely difficult to get into solution. These sulphates are heavy, and it was found best to dissolve them by dropping them into a deep layer of water with constant stirring; such a condition rapidly brings about a saturated solution. (The sulphates of the rare earths are much more soluble in cold than in warm water, the hydrate $Ce_2\left(SO_4\right)_3\cdot 8H_2O$ being soluble to the extent of 19
per hundred grams of water at 0°, and 4 grams per 100 grams of water at 60°). Material not dissolved by above process (probably rendered basic by local overheating during the process of dehydration) was recovered by decantation of the supernatant solution, dried, re-sulphated as above, and again dissolved. The saturated solution of earth sulphates was then treated with an excess of solid sodium sulphate (calculated on the basis of \( R = 101 \) in the formula \( R_2(SO_4)_3Na_2SO_4.8H_2O \) introduced in small portions at a time with constant stirring; agitation was continued for several days. As a check on the removal of the cerium earths by this method, the appearance of the neodymium line 575 in the absorption-spectrum was adopted; addition of sodium sulphate caused complete elimination of this line, viewed through a layer of 12 cm. thickness. Although the most characteristic line in the absorption-spectrum of the cerium earths is the neodymium line 523, it was thought more advisable to use the line 575 as a check in view of the fact that solutions containing erbium (a yttrium earth) give a line very close to 523. How erbium, as one of the yttrium earths, will not at first be precipitated with the cerium earths as a double sulphate upon the addition of sodium sulphate to its solution, hence the erbium line near 575 will not be removed, and its persistence could easily lead to the allusion of


* Oral communication by E. W. Engle.
more and more sodium sulphate. James states that "The solubilities of the yttrium earth sulphates increase with the addition of sodium sulphate until the latter reaches a certain concentration, after which the former rapidly decrease." Prevention of this loss of yttrium earths, so readily possible if the line 532 were chosen as a check, is thus assured by the selection of the line 575. The solution containing the yttrium earths was tested for cerium and thorium by means of hydrogen peroxide and ammonium hydroxide; the precipitation of brown cerium dioxide was slight, and no white precipitate of Thorium dioxide was noticed. Atomic weight determination by Hopkins and Balke's method showed very good material for the present investigation. The results follow:

<table>
<thead>
<tr>
<th>No.</th>
<th>% CeO₂</th>
<th>% R₂O₃</th>
<th>At. Wt. R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.45</td>
<td>52.19</td>
<td>100.00</td>
</tr>
<tr>
<td>2</td>
<td>45.40</td>
<td>52.24</td>
<td>100.25</td>
</tr>
<tr>
<td>3</td>
<td>45.40</td>
<td>52.16</td>
<td>100.10</td>
</tr>
<tr>
<td>4</td>
<td>45.38</td>
<td>52.22</td>
<td>100.30</td>
</tr>
</tbody>
</table>

mean 100.16

(2) Anhydrous Chlorides: The double sodium sulphates of the yttrium earth metals were in the filtrate from the difficultly soluble double sodium sulphates of the cerium earths. To free the earths from alkali-metal, they were precipitated as the hydroxides by means of ammonium hydroxide, the precipitate washed repeatedly by decantation (hot water) and finally

dissolved in an excess of hydrochloric acid. The oxalates were precipitated from this solution as described in IV (1), and after drying, were roasted to oxides in a muffle furnace; the oxides were then dissolved in an excess of concentrated hydrochloric acid. The solution of yttrium earth chlorides was evaporated to a sirupy consistency over a steam bath, and then suddenly chilled; the mother-liquor was poured off from the crystals resulting from the above process, evaporated further and again chilled, the process being repeated until the whole had been reduced to a mass of crystals. These crystals were then powdered, dried for several days over the steam bath, re-powdered and the process of drying and powdering repeated until no tendency to lump together was noticed. The powdered chlorides were then mixed with their own weight of ammonium chloride (previously dried at 110°), and placed in an oven at 100°; the temperature of the oven was raised five degrees each 72 hours until a temperature of 115° was reached, which temperature was maintained for 72 hours. Hydrolysis of hydrated chlorides by their water of crystallization takes place between 115° and 120° although it is possible to dehydrate small quantities at 118°. The above process removes five of the six molecules of water of hydration; the removal of the sixth molecule is the cause of the greatest amount of hydrolysis*. The dry powder (monohydrate) was then transferred to the

* Oral communication, B. S. Hopkins.
drying-apparatus hereinafter described (V (9) Plate III), and the dehydration completed at a temperature somewhat above the dissociation-temperature of ammonium chloride (350° - 400°) in a rapid stream of dry hydrochloric acid gas. The anhydrous mixed yttrium earth chlorides form a pinkish yellow powder, melting at about 850° - 900°, (not sharply), to a clear amber colored liquid, afterward solidifying to a light gray mass. If properly prepared the liquid chlorides should show no suspended particles of white basic salt* and should not wet the walls of the fusion-vessel (in this case Jena glass); further, the anhydrous chlorides should dissolve in water with little or no turbidity, but with considerable evolution of heat. 13, 14).

C. Metignon states that the dehydration of yttrium chloride by the heating of a mixture of hydrated or partially dehydrated chloride with ammonium chloride is a matter of extreme difficulty, never yielding a material which is free from basic salts; he does not, however, mention the subsequent treatment with dry hydrochloric acid gas. This modification of his method has been repeatedly used by other workers in this laboratory with pronounced success.

* Oral communication, A. W. Owens: a very small quantity of basic salt may be present in a clear fusion. It does not interfere with electrolytic results, although damaging to atomic weight determinations such as Mr. Owens was making.
13). See note 12.
15). C. R., 134 (1902) 308
on the small scale of atomic weight determinations; although difficult to accomplish, it has been found to work successfully in large quantities. While the result of this investigation would tend to show the correctness of Matignon's statement as far as the contamination of normal chloride by basic salt is concerned, they are in opposition to his statement that "Yttrium chloride is not appreciably volatile at temperatures slightly above its melting point"; in fact, serious loss resulted in the course of some of the electrolysis, and the very sudden increase in atomic weight (see table, VI (2)a) of material used shows conclusively the elimination of the yttrium (lowest atomic weight) chloride by volatilization.

Hopkins and Balke in the purification of yttrium chloride state that "the volatility of yttrium chloride was a matter of some concern"; Engle and Kremers, working with dysprosium, Wichers with erbium, and Owens with samarium state distinctly that the chlorides of these elements are not volatile, confirming the writer's conclusion.

It is important that the anhydrous chlorides be free from basic salt as the electrolytic baths which contain them are poor conductors, decidedly viscous, and often show a marked tendency to "freeze"; higher temperature liquifies such a bath, as does also the addition of a little sodium chloride or fluoride, but more yttrium

16). See note 9
17). See note 12
*Thesis date, in course of publication.
chloride will be lost by volatilisation. It was also noted that the presence of this basic salt to a large extent prevented decomposition by metallic sodium. Such contamination of anhydrous cerium chloride seems to have no such ill effect.

3) Anhydrous fluoride: The aqueous solution of chlorides was treated with a slight excess of hydrofluoric acid, the precipitated chlorides washed repeatedly by decantation (hot water) and dried as completely as possible over the steam bath. The mass was powdered, and the process repeated until there was no tendency to lump together. The hydrolysis of these fluorides was very slight, as they contained but one-half mol of water of hydration per mol of fluoride; this should be an advantage. They are, however, so extremely gelatinous, that they cannot be filtered even with the aid of a Nelson vacuum-pump working for a number of hours.

4) "Mixed Fluoride Flux": One mol of anhydrous fluorides and three mols of dried sodium fluoride were sifted together several times, fused in a graphite crucible, poured and powdered. This flux contains the elements in the same proportions as they exist in cryolite (Na$_3$YF$_6$; Na$_3$AlF$_6$), and it was thought advisable to try such a material as a solvent for oxides in a manner analogous to the method for preparing aluminium by the Hall process.

(5) Recovery of earth materials from old fluxes.

(a) From partly electrolized anhydrous chloride and from fluxes containing earth oxides dissolved in fused sodium chloride: The recovery was precisely the same as for working up the original mineral (IV (1)) with the exception, of course, of the separation of the cerium and yttrium earth by means of sodium sulphate. This latter process, is, of course, unnecessary.

(b) From all fluxes containing fluorides: The flux was powdered, mixed with concentrated sulphuric acid into a thick paste, and slowly raised to a red heat. The cooled mass was powdered and treated precisely as were the yttrium earths double sodium sulphates in IV (1).

V. Description of Apparatus.

(1) Refractories resistant to metallic sodium: These must be basic in character in order to preclude corrosion by fused sodium. Crucibles of sintered magnesia and of sintered alumina proved too porous; the best results were obtained by lining a common fire-clay crucible with a paste made of 40% magnesia and 60% "aluminium cement". This lining is thoroughly air-dried, then dried several days in an oven up to 170° (raising the temperature slowly) and finally sintered together in an ordinary assay-muffle. It shrinks away from the walls of the crucible, and if a tendency to crack or flake off is shown (which is but seldom) it can be readily removed and a new lining put in
its place. A paste made from lime or magnesia and a concentrated solution of calcium or magnesium nitrate (as the case may be) works nearly as well as the first one, but shows a greater tendency to crack or flake off.

(2) Refractory lining for electrolytic cell: Alundum cement, put on as a thick paste, and treated as above, but with very slow annealing, answers well. It is not readily attacked by fluxes, and, by reducing cathode-surface greatly, reduces and even prevents the formation of carbides.

(3) The electrolytic cell: (See Plate I) Cathode. This consisted of a graphite crucible (A) (which acted as the cathode) made by cutting a piece seven inches in length from a six inch cylindrical electrode. It was bored to a depth of six inches, and the inside diameter was four inches. It was placed in a box of sheet steel, (B) twelve inches square and eight inches in height, the bottom of the box being lined with graphite boards one inch in thickness. The space between the crucible and the walls of the box was filled with sand (or better, "Sil-o-cel") rammed down tightly; contact was made between the bottom of the crucible and the graphite floor of the box by rubbing them together before packing as above stated. This packing served as a heat-insulator, hold the crucible in position, and prevented oxidation of the crucible by the air in the high temperature of the furnace. The cathode lead-block (C) was bolted securely to the outside of the box, and
both it and the leads proper were cooled by several turns of one-eighth inch copper tubing, (not shown in the drawing, being superseded by a simpler device) through which a rapid stream of water circulated. In the course of experimenting it was found that, in case of a "freeze-up", attempts to loosen the anode from the semi-liquid mass in the crucible almost always resulted in a shifting of the crucible and, although this shifting was slight, some of the packing sifted under the crucible, destroying contact quite readily, (since the maximum working voltage obtainable was but 14.5 volts) thereby causing much delay and inconvenience. To obviate this, a strap clamp of (3) three sixteenths inch boiler steel was bolted tightly about the lower portion of the crucible, (A), the longer and free portion of the strap being twisted so that its surface was at right angles to that of the crucible, and then bent upward and backward at right angles (see drawing) to accommodate the cathode lead block, (C), which was bolted to its extreme end. The cathode lead block (C) was coated thickly with a paste of alundum cement and water glass and finally with pitch to prevent electrolytic corrosion (the lead block was copper and the strap was iron) while the water was flowing over it for the purpose of keeping it cool. This change rendered the apparatus much more efficient than before, as a hot crucible could be lifted from position, the strap-clamp unbolted, quenched in water, and a new crucible installed in a few minutes. Spreading of the insulating material
Electrolytic cell
over the floor of the box made no difference in this case, as contact with the crucible was already established through the strap-clamp. As the strap-clamp was three inches in width and made to fit very tightly to the walls of the crucible, none of the insulating material found its way between the two, and good contact was thus insured at all times. The clamp being attached to the crucible as nearly as possible to the bottom, it could be efficiently protected from air-oxidation by the tightly-rammed insulation; one of the clamps lasted for a long time.

(4) The anode: (See Plate I) This consisted of graphite or hard carbon rods (E) square or circular in cross-section, and of the following dimensions:

Square: Graphite, 2" x 2" x 24"; 1" x 1" x 24"

Cylindrical: Graphite, 2" diam. x 24" length; 1" diam. x 24" length.

Some of the anodes were corrugated in order to increase their surface. The anode-leads were provided with a set of copper straps (I) two inches by sixteen inches and one sixteenth inch thick, four-ply, soldered into place so that the centers of the straps were at right angles to the extremity of the anode leads (J). They were bent downward into the form of a yoke (S) into which the upper end of the anode (E) could be inserted. The two brass water blocks (H,H) were then bolted into position, one on each side of the anode-head. This insured good contact and a firmly-setting joint, the whole being relatively light and very easy to handle. Through the top of the copper
anode-yoke (F) was thrust a common bolt (I) threaded full length; it passed through an eye at the end of a supporting arm (X) on a large retort-stand (L) and by means of a collar (M) and nuts (N) the anode could be raised and lowered at will. The collar (M) prevented sudden dropping, and the nut (N) provided with a handle (O) permitted any range of adjustment desired (see drawing). A guide (P) kept the anode plumb. Such a device was simple, quickly and easily adjusted, and could not get out of order.

(5) Electrode contact cooling devices: (See Plate I) The brass water blocks (H,H) above mentioned were fed by a rapid stream of water, and from their exit-pipes were leads to either the copper tube-coils (already spoken of) or else emptying directly upon the protected cathode lead-block (C) as described in V (3). This latter method of cooling was not only more efficient but saved a number of more or less troublesome small connections. The waste water escaped through a two inch pipe line which terminated in a large funnel (J) directly beneath the cathode-lead-block (C). The water-blocks were protected from corrosion by chlorine and other gases (notably hydrochloric acid and ammonium chloride) by first coating thoroughly with "Bakelite Protective Enamel" baked on, then by wrapping with several thicknesses of common "friction-tape", and coating this with the same enamel, also baked on; the ends of the copper anode-yoke were covered in the same manner. This was found to afford an excellent protection, the "Bakelite Protective
Diagram of Electrical Connections.

Key:
M - Motor
G - Generator
SW - Switch Board
F - Furnace
A - Shunt
A - Ammeter
V - Voltmeter
Enamel standing exposure to hot chlorine, hydrochloric acid or ammonium chloride for as long a period as six hours before breaking down. (shown by the green coating on the copper and brass).

(6) Auxiliary heating devices: These were of two types, (a) a common five inch Fletcher "solid flame" burner placed underneath the cathode-box in the larger scale operations. It was rarely found necessary to use it, as the charge could be melted up a little at a time by the heat of the furnace itself, and the insulating-packing was generally efficient enough to keep the molten charge in a perfectly fluid state; but few "freeze-ups" resulted.

(b) Electric heater: This was used only in small scale operations, and consisted of a simple alundum core, wound with nichrome wire, and capable of producing a temperature of 1000°C. It was used successfully with small carbon, nickel, and iron crucibles which were set inside it; for the latter two crucibles a four-way Bunsen or a large Meker burner were sometimes used.

(7) The source of current: A direct-current generator, Holtzer-Cabot, Type M, compound-wound, 10 kilowatt 12 volts, 835 amperes. A diagram of the set-up follows: Plate I I I.

(8) Gas-generators: These were for the purpose of preparing hydrochloric acid for the final dehydration of the yttrium-earth chlorides. (IV (2) ) and for flowing
Plate 2
over the surface of the molten bath in the furnace, and also for the preparation of nitrogen. The hydrochloric acid prevents hydrolysis of the chlorides by the water of crystallization during the process of dehydration, and both this gas and the nitrogen serve to exclude atmospheric moisture from contact with the surface of the molten furnace charge. Too long contact of this heated charge with the moisture from the air results in a partial hydrolysis of the fused chlorides, forming a difficultly fusible basic salt, which is insoluble in the fused chlorides. The effect of this basic salt has already been mentioned (IV (2) last paragraph; VI 2, (a)). The nitrogen was prepared by the deoxygenation of air, according to the method of Van Brunt; it was supplied by Dr. F. C. Anderegg of this laboratory, to whom the writer wishes to extend his thanks.

(9) Apparatus for the final dehydration of Yttrium-earth chlorides: (See Plate II). This consisted of a tube (A) of hard glass or quartz, two inches in diameter and about five feet in length, in which the chlorides (prepared as described under IV (2)) were placed. It was connected at one end with a battery of hydrochloric acid generators (with appropriate drying-apparatus) and at the other with a fume-absorption tube (B) and heated by means of an ordinary combustion furnace (C). The fume-absorption-tube was a glass tube of approximately the same length as the dehydrating-tube, but of smaller diameter

11. J. Am. Chem. Soc., 36 (1914) 1448
and provided with water inlets ($D, J$), so that a stream of running water flowed through it. By this means both hydrochloric acid gas and ammonium chloride vapors could be perfectly absorbed by the water and prevented from escaping into the atmosphere of the laboratory.

VI. Experimental Part:

(1) Decomposition of Anhydrous Chlorides by Metallic Sodium:

(a) In sealed vessels under atmospheric pressure:

A crucible (prepared as described in V (1)) was charged with previously-fused anhydrous chloride and slips of sodium equivalent to the chlorine* present plus five per cent excess; a small amount of previously-dried sodium chloride was sprinkled on top of the charge to act as a protective cover, and on top of this a little ammonium chloride (also previously dried) to serve as a means of expelling air from the crucible by its volatilization. A clay cover (containing a few small holes to serve as gas-exits) was luted on the crucible by means of alundum cement, and the whole allowed to dry for several hours in a desiccator over calcium chloride. After thoroughly drying, the crucible was transferred to a small "pot-furnace" and very slowly heated; a violent reaction resulted. The crucible was then allowed to cool somewhat, and transferred to the desiccator, and the cooling completed. It was found more advantageous to place all of the sodium in the bottom of the crucible

*Obtained by titration of chlorine in aqueous solution of chloride.
than to mix it with the charge. It could be more rapidly handled in this way, thereby involving less oxidation (and hence less tendency to form basic salts of yttrium earth), and farther, the sodium-vapors could be made to rise through the charge, thus causing a more complete and less violent reaction. Some reductions were carried out by means of "granulated sodium", prepared by melting the metal under anhydrous xylol or "coal-tar naphtha", but this caused a reaction so violent as to cause its abandonment as unsafe. The result of the more successful decomposition with sodium performed as above stated (with the sodium in the bottom of the crucible) was a fine light-grey powder, much like zinc-dust in appearance; under the lens, however, it appeared to be made up of a dark-grey powder mixed with a rather large quantity of white particles. It had but little action on water, although some evolution of gas was noticed with warm water; dilute hydrochloric acid gave a violent evolution of hydrogen in the cold. The following analytical results were obtained:

<table>
<thead>
<tr>
<th>No.</th>
<th>% CaCO₃</th>
<th>% Ca₂(CO₃)₂</th>
<th>At. Wt. R.</th>
<th>At. Wt. Orig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>43.70</td>
<td>50.03</td>
<td>99.64</td>
<td>100.16</td>
</tr>
<tr>
<td>2</td>
<td>43.73</td>
<td>49.96</td>
<td>99.26</td>
<td>100.16</td>
</tr>
<tr>
<td>Av.</td>
<td>43.74</td>
<td>49.99</td>
<td>99.45</td>
<td></td>
</tr>
</tbody>
</table>

(b) Passing sodium vapors into fused anhydrous chlorides:

It was thought that passing sodium vapors through

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21. Levy and Anderocci, Ber. 21 (1888), 1464
fused anhydrous chloride (exactly as metals are precipitated by bubbling some other gas through their solutions) might prove more efficient, in that too great an excess of sodium could be avoided as well as the possibility of the formation of sodium-yttrium alloys. The calculated amount (plus ten per cent excess) of sodium was placed in a small iron "Skidmore" crucible, provided with a copper delivery-tube, bent at right angles, but not sharply, so as to prevent clogging. The fused chloride was contained in a small crucible lined as already described, and covered with a close-fitting clay lid through which the copper delivery-tube passed; it reached nearly to the bottom of the crucible, so as to give the sodium vapors an opportunity to pass upward through the charge.

Two runs were made, both of which were highly unsatisfactory, because of the incompleteness of the reaction as well as the formation of a large quantity of basic salt.

This method has several mechanical disadvantages, for instance the tendency of the delivery tube to clog regardless of the temperature, and the difficulty in securing a suitable gasket for the Skidmore crucible. The clogging of the delivery-tube caused the sodium-vapors to blow out the gasket, and it was further found that they
attacked the material of the gasket itself, e.g., with copper gaskets a brittle alloy is formed, and the attacked gasket "blows out". "Garlock #900" packing carbonizes and burns loose, also "blowing out". Lead gaskets are, of course, impossible owing to the low melting-point; asbestos packing was found to be worthless. The same gray powder as before described, resulted; it was, however, lighter in color and smaller in quantity. Analysis gave the following results:

Analysis.

<table>
<thead>
<tr>
<th>No.</th>
<th>Cu₂O₃</th>
<th>Fe₂O₃</th>
<th>At. Wt. R.</th>
<th>At. Wt. Orig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39.85</td>
<td>47.04</td>
<td>103.50</td>
<td>100.16</td>
</tr>
<tr>
<td>2</td>
<td>39.82</td>
<td>47.02</td>
<td>103.55</td>
<td>100.16</td>
</tr>
<tr>
<td>Av.</td>
<td>39.83</td>
<td>47.03</td>
<td>103.53</td>
<td></td>
</tr>
</tbody>
</table>

Owing to the fact that there is a considerable quantity of basic chloride mixed with the reduced metal, it is evident that atomic weight determinations are worthless as a means of indicating the purity of the product, for this basic salt dissolves in acids along with the metal; this means that atomic weight determinations must refer to the total earth-metal present, rather than to the reduced metal only. The rather close checks between the atomic weights of the reduced and original material, both for this method and the one immediately preceding, are therefore to be expected. It is quite evident that these methods of decomposition are of no value; they were abandoned.

(c) Decomposition of anhydrous chlorides by
metallic sodium in vacuo:

The anhydrous chlorides were mixed with the calculated quantity of freshly cut slips of sodium (plus one per cent excess) in sheet iron or nickel boats, which were then placed in two-inch seamless steel tubes about four feet in length. One end of a tube of this type was closed by a steel plate welded into position and the other with a heavy rubber stopper provided with a glass stop-cock which had been inserted hot into the rubber to insure a gas-tight joint. The tube was then connected with a Nelson vacuum-pump, exhausted to 3-1 mm., and, after disconnecting from the pump, the reaction was started by quickly inserting the tube into a muffle-furnace which had been heated to a temperature somewhat above 1100° C. The reaction took place almost at once, as was shown by the fact that the tube frequently became red hot up to a point within about eight inches of the rubber stopper, although only about fifteen inches of it could be inserted in the furnace. Some experiments were tried with the sodium in one boat and the crushed anhydrous chloride in another boat immediately in front of the first one (with the idea of preventing the formation of sodium alloys) but the results by this method were decidedly unsatisfactory in that very little reduction took place; no residual sodium was found in the boats when either method was used. This method was adopted as the best means of carrying out the sodium reduction for three reasons:

(1) oxidation of yttrium metal was almost impossible and
oxidation of sodium was reduced to a minimum. (2) The temperature of the operation is considerably above the melting point of the NaCl formed as the result of the reaction. As NaCl is decidedly volatile under atmospheric pressure at temperatures but little above its melting-point, it should be all the more rapidly so at this temperature in vacuo. Since, also, there is an excess of sodium vapor, the method concerns itself with the partial pressure of the NaCl vapor. All this tends toward the rapid and complete removal of NaCl; it was found, however, that a little undecomposed yttrium chloride did remain behind. This was removed by shaking with anhydrous bromoform or ethylene bromide, with anhydrous chloroform as a regulative diluent in the usual way, using a Harada separatory funnel. (3) This method is more rapid than any of the others tried, the time of weighing, charging, reduction, and cooling totaling about 30 minutes per tube; each run yielded about 30 - 35 gms. of metal. The tubes were cooled by placing them under running water; this treatment did not result in so much corrosion of the tube as might be expected under the circumstances.

The resulting metal was a black powder in every way analogous to that described by Winkler. It did not show any tendency to alloy with the iron of the boat. Analytical results on the mixed material from three runs gave the following:
Complete analysis of the material produced yielded the following results:

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal</td>
<td>95.68</td>
</tr>
<tr>
<td></td>
<td>Iron</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td>RCl₃</td>
<td>2.33</td>
</tr>
<tr>
<td>C (by difference)</td>
<td>0.13</td>
<td>0.34</td>
</tr>
</tbody>
</table>

(2) Electrolytic methods:

(a) General method of procedure; description.

The usual method recommended for starting electrolysis of this sort is to insert a small graphite or carbon "pencil" between the end of the anode and the bottom of the crucible (thereby giving increased current-density at this point), and pile a small quantity of the charge about it, after which the current is turned on; this portion is fused by the heat occasioned by the resistance of the pencil. When fusion commences, more of the charge
is added, a little at a time, until the bottom of the crucible is covered with a layer of fused material; the anode is then raised, the "starting pencil" quickly removed, the anode lowered into position, and the electrolysis allowed to proceed in the usual manner. While such procedure is not what might be termed a poor one, it has certain disadvantages, viz., the starting-pencil often breaks, and is not always easily removed, and good contact is not always obtained. Some of these difficulties can be overcome by boring a small hole in the end of the anode and a similar one in the bottom of the crucible-cathode, the two holes acting as a socket for the starting-pencil. This insures good contact, but does not prevent the pencil from breaking; in fact it seems to snap off more easily, especially if, in raising the anode to remove the pencil, the anode swings a trifle. Another serious disadvantage of this procedure lies in the fact that, since the starting-pencil must be removed quickly, it must not fit tightly in the socket. This gives an opportunity to the fused charge to flow in between the pencil and the walls of the borings, and, if the current suddenly lowers or is interrupted (as is frequently the case on this line) freezing of the charge results, and the time to make necessary re-adjustments is unwarrantedly long. The best procedure was found to be that of sawing off the end of the anode in such a manner that the cut surface was a plane inclined in two directions, thus giving one corner of the
(square) anode which was lower than any of the others; if
the anode-leads were suspended above it, their weight could
be used to press this corner of the anode firmly against
the bottom of the empty crucible. Under these conditions
the current could be turned on, and the anode rubbed back
and forth a few times against the bottom of the crucible,
when contact was at once established, and no interruption
of the current thereafter observed. The charge was slowly
fed in after the crucible and anode were red-hot. This
method has the advantage of simplicity, speed, ease of
adjustment, impossibility of break-down, and introducing
no loose pieces of carbon into the bath. No failures to
start the furnace under these conditions were ever noticed,
even under so low a pressure as 10 volts.

Attempts to pour a charge after electrolysis
resulted in burning the metal produced; it is deposited
in the form of a fine powder on the bottom of the crucible
(as later experiments showed) and, when the hot liquid was
poured, the material remaining in the crucible burned
quickly with a bright flash, resembling magnesia. In
order to discharge the furnace, then, the anode was raised,
the current interrupted, the mass in the crucible allowed
to cool and the cold charge removed. It was found that
the mass shrank together quite a little on cooling, and
that it could be easily removed after loosening or by
splitting with a chisel. The deposited material could
be easily brushed out of the crucible.
There was not much tendency for any of the charges to freeze during the course of electrolysis, except in the case of the electrolysis of anhydrous chlorides which showed a decided tendency to freeze when an appreciable amount of basic salt had been formed in the bath. A bath which has "gone basic" always gives worthless results; it could be liquified by the addition of sodium chloride, sodium fluoride or calcium fluoride in small quantities, which apparently cause the basic chloride to dissolve, but no good deposits were ever obtained after the bath once showed an increased viscosity from the formation of basic salt. The only thing to do in such a case seemed to be to discard the run and start afresh.

"Metal fog" was very appreciable in all cases; but there did not appear to be any remedy for it, although the addition of sodium chloride, sodium fluoride, calcium fluoride, cryolite, etc. was repeatedly tried with this object in view.

The "anode effect" was also quite noticeable, and this invariably resulted in worthless runs. Sometimes the evolution of halogen would start after having once been interrupted, but this evolution when once interrupted, was always thereafter intermittent. When this "anode effect" was once noticed, the run was discontinued, and a fresh start made; there appeared to be no other remedy.

Formation of carbide was frequently noticed; in the case of the bath of fused chloride, this could only
have been Yttrium carbide, but it could have been sodium carbide in the case of baths containing sodium, and in fact, was always more noticeable in such cases except in the cryolite bath. The formation of carbide could be detected in that the odor of hydrocarbon was very apparent as the bath cooled down; it is assumed that this is due to the action of atmospheric moisture. The fact that the "carbide" odor was never noticed during a run or when the bath was very hot, but always when it was cold or nearly so, leads one to the conclusion that the temperature of decomposition of this carbide is below the melting point of the bath, and that it is formed as the bath cools. Sudden chilling (if practical) might serve to remedy this. However, as has been stated, lining the crucible with a refractory apparently cuts down the formation of carbide even when sodium is present. The surface of C-cathode exposed, then, also appears to be a determining factor in the formation of carbide. Later experiments (on a small scale) would indicate that a carbon anode also induces the formation of carbides.

(b) Electrolysis of fused anhydrous chlorides: Theoretically this should be a very good method, as well as very simple, but there are many practical difficulties aside from those attendant upon the preparation of the anhydrous chlorides. It does not require a very great amount of basic chlorid to render a bath worthless; apparently the basic salt is suspended in the fused normal
(as can be seen). This bath is a mobile liquid (unless there is a large amount of basic salt) and conducts the current, but no chlorine is given off under widely-varying limits of temperature and electrolytic conditions. It is admissible, however, that this may be likewise "anode effect" on the fused normal chloride, independent of basic material in the bath. It is to be noted that this basic chlorid is in no way a drawback in the production of cerium by this method. (See footnotes 19 and 20).

Another and quite serious drawback to this method is the volatility of Yttrium chloride (see IV (2)); this resulted in serious losses of material. It was always noticed that after the recovery of material from several runs, the atomic weight of the earths contained showed a marked increase, thus indicating a steady diminution in Yttrium-content (Yttrium having the lowest atomic weight of these earths.) Some of the volatilized material was collected and examined; it will be referred to later. If the temperature is kept down to prevent volatilization, the bath becomes pasty and the electrolysis takes place but little, and often not at all; again, if the temperature is too high, the "anode effect" is very marked. Smaller units might prove more efficient in preventing volatilization by overheating. It was also noted that electrolysis did not commence until the bath had been in a molten condition for some time, thus increasing the possibility of loss by volatilization, and giving time for the leads
to heat up; this is not true for smaller units. There is also a tendency for the fused chloride to "go basic" at the surface; this is shown by the gradual separation of solid particles, which slowly sink, with the result that the bath becomes pasty in time, and later shows a tendency to "freeze". Such a run as has been described is always worthless; it is thought that this formation of basic salt is due to the action of atmospheric moisture. A stream of hydrochloric acid or nitrogen played over the surface of the melted bath is of material assistance in this case.

A tabulation of the results of the electrolysis of fused yttrium earth chlorides follows:
<table>
<thead>
<tr>
<th>Run no.</th>
<th>wt. of charge (F.)</th>
<th>Time of run (min.)</th>
<th>Average voltage (v.)</th>
<th>Current density (amps/cm²)</th>
<th>Yield in grams</th>
<th>nature of yield</th>
<th>insoluble (%)</th>
<th>wt. starting</th>
<th>H-equiv. (soluble portion)</th>
<th>H-equiv. (total mass product)</th>
<th>Direct. Ret.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>500</td>
<td>7.5</td>
<td>10.3</td>
<td>355</td>
<td>7.0</td>
<td>gray powder</td>
<td>12.75</td>
<td>100.16</td>
<td>43.2</td>
<td>149.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>500</td>
<td>7.0</td>
<td>11.2</td>
<td>350</td>
<td>6.9</td>
<td>gray powder</td>
<td>33.59</td>
<td>100.16</td>
<td>41.3</td>
<td>186.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>500</td>
<td>6.5</td>
<td>12.7</td>
<td>500</td>
<td>9.3</td>
<td>black powder</td>
<td>36.12</td>
<td>100.16</td>
<td>32.0</td>
<td>50.2 1000°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>500</td>
<td>6.0</td>
<td>12.5</td>
<td>470</td>
<td>9.3</td>
<td>gray powder</td>
<td>27.19</td>
<td>100.16</td>
<td>36.5</td>
<td>50.0 1000°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>500</td>
<td>5.0</td>
<td>13.2</td>
<td>400</td>
<td>7.8</td>
<td>black powder</td>
<td>56.79</td>
<td>100.16</td>
<td>71.4</td>
<td>111.4 1000°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>500</td>
<td>3.5</td>
<td>10.7</td>
<td>460</td>
<td>9.1</td>
<td>gray powder</td>
<td>35.34</td>
<td>100.16</td>
<td>133.0</td>
<td>207.0 1100°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>300</td>
<td>3.0</td>
<td>12.6</td>
<td>300</td>
<td>5.9</td>
<td>gray powder</td>
<td>26.15</td>
<td>114.5</td>
<td>77.4</td>
<td>104.8 1100°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>300</td>
<td>3.0</td>
<td>11.9</td>
<td>367</td>
<td>7.1</td>
<td>gray powder</td>
<td>33.39</td>
<td>114.5</td>
<td>142.0</td>
<td>212.0 300°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>300</td>
<td>7.5</td>
<td>12.1</td>
<td>375</td>
<td>7.4</td>
<td>gray powder</td>
<td>37.73</td>
<td>114.5</td>
<td>124.0</td>
<td>193.4 900°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>300</td>
<td>5.0</td>
<td>12.5</td>
<td>320</td>
<td>6.3</td>
<td>gray powder</td>
<td>30.79</td>
<td>114.5</td>
<td>118.0</td>
<td>171.0 1100°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>300</td>
<td>6.0</td>
<td>13.7</td>
<td>430</td>
<td>8.1</td>
<td>gray powder</td>
<td>30.42</td>
<td>114.5</td>
<td>109.5</td>
<td>157.5 1100°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>300</td>
<td>5.0</td>
<td>13.3</td>
<td>350</td>
<td>6.9</td>
<td>gray powder</td>
<td>40.76</td>
<td>114.5</td>
<td>58.3</td>
<td>120.0 1100°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>300</td>
<td>4.0</td>
<td>12.8</td>
<td>350</td>
<td>6.9</td>
<td>magnetic globules</td>
<td>** 124.2</td>
<td>** 120°</td>
<td>** 120°</td>
<td>** 120°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>300</td>
<td>3.5</td>
<td>13.3</td>
<td>393</td>
<td>7.4</td>
<td>magnetic globules</td>
<td>** 124.2</td>
<td>** 120°</td>
<td>** 120°</td>
<td>** 120°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>100</td>
<td>5.25</td>
<td>13.0</td>
<td>317</td>
<td>6.1</td>
<td>black powder</td>
<td>** 101.5</td>
<td>** 101°</td>
<td>** 101°</td>
<td>** 101°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*2" x 2" anode. ** Not determined, since globules contained no Yt. *** Not determined; very slight.
The severe loss entailed by volatilization of Yttrium chloride during electrolysis can be best shown by considering that the original amount of material (anhydrous chloride) was a trifle over 3 kg. and that 3 kg. were used for the first six runs. The recovered material, ready for electrolysis (anhydrous chloride) weighed 1960 g. and six runs each using 370 g. were made; the recovered anhydrous chloride from this weighed 1265 g. and, when two more runs (each using 300 g.) had been made with unsatisfactory results, it was decided to prevent further waste of valuable and tediously recovered material by trying less volatile electrolytes.

Some of the volatilized earth chloride was condensed upon a sheet of asbestos (glazed with sodium silicate to prevent contamination of sublimed chloride with asbestos) held above the crucible. Analytical results showed the following, and proved the volatility of earth-chlorides:

<table>
<thead>
<tr>
<th>No.</th>
<th>%SiO₂</th>
<th>%MgO</th>
<th>At. Mt. R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39.54</td>
<td>41.37</td>
<td>52.75</td>
</tr>
<tr>
<td>2</td>
<td>39.26</td>
<td>41.33</td>
<td>52.60</td>
</tr>
<tr>
<td>Av.</td>
<td>39.25</td>
<td>41.35</td>
<td>52.67</td>
</tr>
</tbody>
</table>

The material contained a small quantity of iron.

Analytical results upon the material produced in the last electrolysis of fused chlorides (See No. 15, table) were as follows:

<table>
<thead>
<tr>
<th>No.</th>
<th>%SiO₂</th>
<th>%MgO</th>
<th>At. Mt. R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.21</td>
<td>54.99</td>
<td>120.10</td>
</tr>
<tr>
<td>2</td>
<td>41.19</td>
<td>54.93</td>
<td>120.05</td>
</tr>
<tr>
<td>3</td>
<td>41.24</td>
<td>54.90</td>
<td>119.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>120.00</strong></td>
</tr>
</tbody>
</table>
Complete analysis of material yielded the following results:

<table>
<thead>
<tr>
<th></th>
<th>original</th>
<th>final</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td>94.10</td>
<td>93.99</td>
</tr>
<tr>
<td>Iron</td>
<td>1.20</td>
<td>1.16</td>
</tr>
<tr>
<td>HCl₂</td>
<td>0.79</td>
<td>0.85</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>3.91</td>
<td>3.98</td>
</tr>
</tbody>
</table>

(c) Electrolysis of fused anhydrous fluorides:
These should prove much easier of dehydration, as they contain but one half mol of water of hydration per mol of fluoride as against six mols of water of hydration per mol of chloride. It was found that the mixed fluorides readily fused to a clear yellow liquid, which was free from solid particles, and this would tend to indicate that heating involved little or no hydrolysis. The melting-point of these mixed fluorides was decidedly higher \((1000^°)\) than that of the chlorides, but there was no tendency to volatilize; it was noted, however, that they offered a decidedly greater resistance to the current than the chlorides. Three runs were made, using the unused material remaining from the last chloride run, viz., about 665 grams as follows:

<table>
<thead>
<tr>
<th>Run</th>
<th>wt.</th>
<th>hrs.</th>
<th>amp.</th>
<th>volts</th>
<th>yield</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200g</td>
<td>4</td>
<td>200</td>
<td>12.5</td>
<td>31.0</td>
<td>none</td>
</tr>
<tr>
<td>2</td>
<td>200g</td>
<td>6</td>
<td>315</td>
<td>13.6</td>
<td>48.8</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>200g</td>
<td>8</td>
<td>250</td>
<td>12.8</td>
<td>40.0</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

(1" x 1" anode. (Original material apparently unchanged (except for the addition (of carbon, disseminated (through mass of the (flux. No gas evolved (upon treatment with (dil. HCl. Temperature (molten bath = 1200°.}
This method is unsatisfactory owing to the high melting point of the bath and the high resistance, as far as is shown by these results. An auxiliary heating device was necessary in order to keep the mass in a fluid condition.

(a) Electrolysis of oxides dissolved in fused fluorides:

A mixture of 150 grams of anhydrous fluorides (from the runs in (c) powdered) and 50 grams of oxide from a sample furnished by Dr. E. J. Hopkins and Mr. L. E. Yntema (atomic weight of metal = 104.6) was used as a bath for three electrolyses; the same amount of material and in the same proportions were used in each bath. This bath had a high melting point and was unsatisfactory in that much of the oxide apparently failed to dissolve, at least there was a considerable quantity of solid material suspended in the fused bath. The resistance of this bath was about as high as that of the previous one and no evolution of gas (it should be CO) was noted. The cooled flux was apparently unchanged, except, of course, for the addition of the disseminated carbon already noted in run (c). Treatment with dilute hydrochloric acid yielded no gas whatever. An auxiliary heater was also necessary here. The anode used had a cross section of one square inch. The results follow:
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Hrs.</th>
<th>Amp.</th>
<th>Volts</th>
<th>Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>215</td>
<td>12.3</td>
<td>43.3</td>
<td>none</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>300</td>
<td>13.0</td>
<td>46.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>300</td>
<td>13.1</td>
<td>46.5</td>
<td></td>
</tr>
</tbody>
</table>

(e) Electrolysis of oxides dissolved in fused sodium chloride:

Fifty grams of the oxides (atomic weight of metal = 104.6) were dissolved in 250 grams of fused sodium chloride. This mixture melted at about 850° and was a much better conductor than the other electrolytes; if the temperature was allowed to rise much above 900°, sodium chloride volatilized out to quite an extent, and more had to be added to prevent the mass becoming pasty, although the deflagration was too violent to permit of the addition of other than small quantities of sodium chloride at a time, rendering the operation slow. The oxides dissolved slowly in the fused sodium chloride but never completely; chlorine was evolved instead of carbon monoxide, hence it was apparent that the solvent was being electrolyzed rather than the solute. As the melt cooled down after a run a strong odor, similar to that given off when commercial calcium carbide is hydrolyzed, was noted. This odor was most noticeable after the cold melt had stood for some time in contact with the air, and it is assumed that it was due to some action between a metallic carbide in the flux and the moisture of the air. The odor above described will hereinafter be termed "carbide odor"
for the sake of brevity. It was always more noticeable in fluxes containing sodium salts with the exception of the cryolite flux. Two trials were made on a flux such as has been described, but as the results were exactly alike in both cases, the method was abandoned. The results follow:

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Hrs.</th>
<th>Av. Amp</th>
<th>Av. Volts</th>
<th>Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>300</td>
<td>12.5</td>
<td>46.5</td>
<td>none (1&quot; x 1&quot; anode (Black fused mass in (the crucible, but no (powder. 40 gr. flux (HCl give only .4 cc (gas. Temperature above (bath = 900°</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>300</td>
<td>12.5</td>
<td>46.5</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

(f) Electrolysis of oxides dissolved in "Mixed Flux":

A mixture of fifty grams of oxide (atomic weight of metal = 104.5) and 250 grams of mixed flux prepared as in IV (4) was electrolyzed in the usual manner. It proved a better conductor than either baths (c) or (d), although it melted rather high, 950°. A very small quantity of metal was produced by this method, but it could not be separated from the flux, hence no quantitative data are available. An auxiliary heater was necessary in this case. The usual 1" x 1" anode was employed. The results follow:

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Hrs.</th>
<th>Av. Amp</th>
<th>Av. Volts</th>
<th>Yield</th>
<th>Nature of Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>300</td>
<td>10.6</td>
<td>46.5</td>
<td>poor light gray (50 g. of powder (flux + HCl</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>320</td>
<td>10.5</td>
<td>50.0</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>360</td>
<td>13.1</td>
<td>55.0</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

(bath = 1000°.
(g) Electrolysis of oxides dissolved in fused cryolite:

A mixture of 50 grams of oxide (atomic weight of metal = 104.6) and 250 grams of cryolite was electrolized in the usual way. It was thought possible that some aluminium might be deposited by electrolysis of the fused cryolite, and to ascertain the facts two runs were made on 500 grams lots of the powdered cryolite with the following results:

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Hrs. Run</th>
<th>Av. Amp</th>
<th>Volts</th>
<th>Qn in cm²</th>
<th>Yield</th>
<th>Nature of Product</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>350</td>
<td>12.1</td>
<td>54.3</td>
<td>none</td>
<td>unchanged</td>
<td>(Some carbon dissolved in flux.</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>350</td>
<td>12.7</td>
<td>54.3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>(Treatment with HCl or boiling in NaOH solution (yielded no H.</td>
</tr>
</tbody>
</table>

From the above results it was concluded that cryolite was a safe solvent for oxides, that is, there was no danger of contamination by means of aluminium. The cryolite apparently dissolves the oxides completely, but the solution is quite slow. This flux is better than any of the preceding ones in that its melting point is lower than the four immediately preceding, and there is no volatilization of metallic chloride possible; as a conductor it is inferior to well prepared chlorides. During the electrolysis carbon monoxide was evolved slowly; a great deal of "metal-fog" was formed. The metal did not separate out in the form of a powder so well as it did in the case of the fused chlorides, although
it could be separated from the flux by the same process.
In general the yields from this method are only fair. The
same apparatus was used as for the electrolysis of cryolite.

The results follow:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>350</td>
<td>13.5</td>
<td>Fair</td>
<td>light gray (1&quot;xl&quot; powder)</td>
<td>anode</td>
</tr>
<tr>
<td>2</td>
<td>12.5</td>
<td>425</td>
<td>13.5</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>8.5</td>
<td>332</td>
<td>13.5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Analytical results upon the products of this electrolysis were as follows:

\[ \begin{array}{ccc}
\text{At. Wt.} & \text{At. Wt.} & \text{At. Wt.} \\
40.09 & 52.90 & 118.5 \\
40.11 & 52.86 & 118.4 \\
40.09 & 52.94 & 118.6 \\
\end{array} \]

Metal = 61.54%
Iron = 0.68%
Insoluble = 36.44%

(g) Electrolysis where both electrodes were not carbon:

The special object of this portion of the investigation was to ascertain whether carbon anode or cathode was chiefly responsible for the formation of metallic carbide during electrolysis.

These electrolyses were carried out in a small iron or nickel crucible (about 200 cc capacity) which
served as a cathode. Two types of anode were used, a common 3/8" cylindrical "hard carbon" rod, such as is used for the arc-lamp of stereopticons, and also a bar of "Illium Alloy", 1" x 3/8" in cross-section. An iron rod 1/2" in diameter was also tried, but it corroded very rapidly and was not tried further.

Each charge consisted of 100 grams of fused anhydrous chloride, to which in some runs were added 5-10 grams of sodium or potassium chloride, to lower the melting-point. A current of 6-7 amperes at 110 volts was allowed to act from two to three hours after fusion, electrolytic conditions being regulated by outside resistance. The results of these electrolyses may be summarized as follows:

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Wt. Grs.</th>
<th>Time Hrs.</th>
<th>Volts</th>
<th>Amps</th>
<th>Amps cm</th>
<th>Electrode</th>
<th>Yield grs</th>
<th>Nature of Product</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>2</td>
<td>6-7</td>
<td>2.67</td>
<td>1.5-Fe</td>
<td>I(^+)-Fe(^-)</td>
<td>10</td>
<td>dk-gray practically no odor pwd.</td>
<td>Anode not attacked.</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>2</td>
<td>6-7</td>
<td>2.67</td>
<td>1.5-Fe</td>
<td>I(^+)-Fe(^-)</td>
<td>8</td>
<td>&quot; &quot;</td>
<td>Same as 1</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>3</td>
<td>6-7</td>
<td>2.67</td>
<td>1.5-Ni</td>
<td>C(^+)-Ni(^-)</td>
<td>21</td>
<td>&quot; &quot;</td>
<td>Distinct carbide odor</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>110</td>
<td>6</td>
<td>2.67</td>
<td>1.5-Fe</td>
<td>Fe(^+)-Fe(^-)</td>
<td>&quot; &quot;</td>
<td>Fe corroded rapidly; run stopped; no result</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>3</td>
<td>6-7</td>
<td>2.67</td>
<td>1.5-Ni</td>
<td>I(^+)-Ni(^-)</td>
<td>14</td>
<td>&quot; &quot;</td>
<td>Same as 1 and 2</td>
</tr>
</tbody>
</table>

*Key: I\(^+\)= Illium alloy anode, C\(^+\)= hard carbon anode, Fe\(^+\)= iron anode, Fe\(^-\)= iron cathode, Ni\(^-\)= nickel cathode.
These results tend to show that a carbon anode is at least partly responsible for the formation of metallic carbides; they do not, of course, indicate to what extent a carbon cathode influences this carbide formation. This has, however, been discussed in a previous section (V (2); VI, (2), (a)). It is also of interest to note that the anode made of "illium Alloy" was apparently unattacked during the course of an electrolysis. This may be due to the fact that it is not a good conductor, and hence the chlorine would of necessity be evolved slowly and in small quantities at a time. Volatilization of Yttrium chloride was noticeable during these runs as well as during those on the large scale, but it did not take place so rapidly.

The metal produced under the above conditions did not differ essentially from that produced by the other methods recorded. Time did not permit of an extended study of this branch of the research, the work done being rather of the nature of a preliminary test-run. The outlook, however, appears to be promising for small units.

VII. Properties of Yttrium Mixed Metal:

The metal, after separating as completely as possible from foreign matter in the manner already described, was placed in a crucible of fused magnesia and sintered together in a vacuum furnace of the Arsem type. Several lots of the metal were burnt by reason of the furnace springing sudden leaks, or were damaged by gases occluded by the carbon heating-element. However, a few small
sintered masses were obtained which could be studied, although imperfectly. Attempts to protect the metal by a layer of fluorite or cryolite resulted in the partial slagging of the crucible; the metal did not appear to attack the crucible when heated in it alone, i.e., without flux.

Accurate pyrometric data were not obtainable for the furnace used; a radiation pyrometer would not be reliable under the conditions owing to the fact that there is a continual variation in the intensity of the light within the furnace, as well as a series of intermittent flashes across the carbon helix which served as a heating element. Slight discharges of vapor from time to time were also noted which would tend to render the intensity of the light within the furnace still less dependable as a means for measuring temperature. Some idea of the melting point of the metal may be gathered by noting that the furnace operated under a power of 12,000 watts for twenty minutes, afterwards raised to 14,000 watts for twenty-five minutes, failed to completely melt a 200-gram charge of it; the same furnace will keep a 600-gram charge of pure iron melted for an indefinite period when operating under a power of 10,800 watts. It may be safely inferred then, that the melting point of Yttrium mixed metal is considerably higher than iron; the actual melting point was closely approached, however, as some sintering resulted. Higher temperatures could not be obtained under the conditions.
The sintered metal was bluish-grey in color, not of a very high luster, although it was capable of taking a good polish; it soon tarnished in contact with the air. The sample examined contained 0.32 per cent carbon, and had a specific gravity of 5.508 at 15°/15°. The powdered metal burned in the air with a bright flash much resembling magnesium, and leaving a residue of light brown oxide; it is slowly oxidized in moist air. It blows when heated in hydrogen, nitrogen, and carbon dioxide; when heated in carbon dioxide carbon monoxide is evolved, and the oxide of the metal is formed. The product from heating in hydrogen is a pale yellow powder, and that from heating in nitrogen somewhat of the same color, although lighter, and is readily hydrolized. Neither the powdered metal nor the sintered material shows any tendency to amalgamate with mercury, both the powder and the sintered metal give off a decided odor, much like that of impure acetylene, although somewhat suggestive of phosgene. The odor is more powerful with the sintered metal than with the powdered (that is, material which has not been sintered as distinguished from sintered metal which has disintegrated by standing in the air); in some instances no odor was noticeable in the powdered metal, as has already been noted. It is thought that the odor is due to the hydrolysis-products of small traces of carbide in the metal.

The metal decomposes water at ordinary temperatures and this action is quite rapid if the water is heated.
Dilute acids react violently with the powdered metal, and also attack the sintered material vigorously; a solution of 0.5 cc glacial acetic acid in 25 cc of 95% alcohol will attack the sintered material sufficiently for the etching of metallographic specimens in ten seconds. Solutions of bases have no other action than that of water upon sintered material or powdered.

The metal obtained after heating in the vacuum furnace was not completely fused; it was merely sintered together, and fell to pieces in time (even disintegrating to a powder) especially if exposed to the air. Grinding and rough-polishing seemed to accelerate this breaking up, most of the specimens undergoing preparation for microscopic study behaving in this way; only two were obtained which could be studied, and these were very unsatisfactory. Hardness tests were not attempted, owing to the ease with which the sintered mass broke up and to the small size of the pieces obtained. The metal is scratched with a file with difficulty, and is pyrophoric, although not highly so, certainly not nearly so highly pyrophoric as cerium mixed metal or the so-called "pyrophoric alloys".

It was found quite difficult to polish the sintered metal, owing to the ease with which small pieces were chipped out; the polished surface also scratched very easily and "dragged" quite readily. In view of the difficulty of preparing specimens for microscopic study the photo-micrographs obtained can scarcely be said to be
satisfactory; the rapidity with which the metal tarnished in the qir also tends to prevent good definition in the taking of photo-micrographs.

In general the field is divided into two portions: first, the dark portion, some parts of which have the appearance of a eutectic under the microscope; second, the lighter portion, which shows a complex structure of interlocked crystals, although not sharply defined. Unetched specimens did not yield photo-micrographs, owing to the tendency of the surface to "drape" under polishing.

For the sake of comparison photo-micrographs of cerium mixed metal* (containing 0.25 per cent silicon)** and of sintered tungsten are shown. The resemblance between the structures of the two mixed metals is at once apparent, although it must be borne in mind that the cerium mixed metal has been completely fused while the yttrium mixed metal has not. The darker component of the yttrium mixed metal is the softer, the other crystalline material showing in relief when the specimen is polished. Change of magnification in either direction revealed nothing worthy of note; a single magnification (x 185) was therefore adhered to as yielding the best results.

* Purchased in the open market
** Oral communication by C. W. Balke.
Yttrium Mixed Metal x 185
Etched 10 seconds with 0.2 cc glacial acetic acid in 25 cc 95% alcohol.

Cerium Mixed Metal x 185
Etched 10 seconds with 0.2 cc glacial acetic acid in 25 cc 95% alcohol.

Tungsten. Sintered bar, x 500 perpendicular to long axis.
Etched 2 minutes in boiling hydrogen-peroxide, 3%.
(Courtesy of Dr. C. W. Balke)

Tungsten. Sintered bar x 175, perpendicular to long axis, near end. Etched 2 seconds in nitro-hydrofluoric acid.
(Courtesy of Dr. C. W. Balke)
IX. Summary:

1. The research here recorded partakes somewhat of the nature of pioneer work. No claims are made for it beyond the fact that it is a preliminary study of the conditions necessary to obtain a mixture of the metals of the Yttrium earths, analogous to cerium mixed metal.

2. The method of preparing the anhydrous chlorides of the Yttrium earths, already employed in atomic-weight researches, has been extended so as to apply to the preparation of these chlorides in large quantities.

3. Yttrium mixed metal has been prepared in the form of a powder by the decomposition of the anhydrous chlorides with metallic sodium in vacuo, and also by electrolysis of these chlorides in the fused condition.

4. Various other electrolytes have been studied. In general, however, they are inefficient with the exception of that consisting of oxides of Yttrium earth metals dissolved in fused cryolite.

5. Loss of Yttrium chloride by volatilization during the course of electrolysis has been demonstrated; this is a serious drawback to what would otherwise be the most efficient electrolytic process studied.

6. Yttrium mixed metal has been obtained in the coherent form for the first time by partial fusion in vacuo. The resulting mass tends to disintegrate while metallographic specimens are being prepared from it, and upon exposure to the air.
7. Some of the properties of the powdered and sintered metal have been recorded.

8. Further work on preparation of the metal in large quantities and the study of its alloys is contemplated.
Acknowledgment:

The writer gratefully acknowledges his indebtedness and extends his thanks to the following gentlemen:

Dr. David F. McFarland, under whose direction the research was carried to a successful completion; for very material assistance in the preparation of metallographic specimens and in the taking of microphotographs, and for his advice and interest throughout the work.

Dr. Clarence W. Balke, for several suggestions as to process and furnace-construction, and for his continued interest in the work.

Dr. B. Smith Hopkins and Mr. Leonard P. Yntema, for supplying sufficient new Yttrium earth materials at a time when losses by volatilization had rendered further work impossible.

Mr. Ralph H. Hufferd, for a suggestion markedly improving the absorption of hydrochloric acid gas and ammonium chloride in the dehydration process.

Prof. Ellery B. Peine and Mr. William A. Lyon, of the Department of Electrical Engineering: the former for permission to use the electric furnace laboratory, and the latter for his hearty co-operation in setting up and running the vacuum furnace, often under much difficulty.
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   Compt. Rend. 134 (1902) 1308-1310

   Trans. Amer. Electrochemical Soc. 20 (1911) 57-102

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   J. Amer. Chem. Soc., 34 (1914) 1448-1450
AII. Vita:

The writer was born in Philadelphia, August 31, 1884. He received his early training in the lower schools of Philadelphia, later in the Central High School of that city and entered the University of Pennsylvania, receiving therefrom the degree of Bachelor of Science in Chemistry, 1906. Since that time he has held the following positions:


Instructor in Chemistry, Villanova College, 1907-1908. Second semester, 1907; held this and the above position.

Associate Professor in Chemistry, Villanova College, 1906-1909.

Professor of Chemistry, Villanova College, 1909-1910.

Assistant Chemist in charge of Naphthaline Division Barrett Manufacturing Company, 1910-1912.


Associate Professor in Chemistry, Oklahoma Agricultural and Mechanical College, Stillwater, Okla., 1914-1915.

Assistant in Chemistry, University of Illinois, 1915-1918. (Master of Science in Chemistry, University of Illinois, 1916.)