Yttrium Mixed Metal*

A Preliminary Study in the Production and the Properties of the Rare Earth Mixed Metals

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OBJECT OF AND REASONS FOR THE INVESTIGATION.

ON account of the meagerness of the work done, because the metal has never been obtained in other than powder form, and because of the possibility of commercial application of the metal or its alloys, the preparation of coherent "Yttrium Mixed Metal" (analogous to the well-known "Cerium Mixed Metal") was undertaken. It was further intended to make a detailed study of the properties of the metal and of its alloys with the common metals. Depending on the source of material, such a metallic product should vary in composition and "atomic weight."

II. PREPARATION OF MATERIALS.

Powdered gadolinite was decomposed by boiling conc. hydrochloric acid, and the mixed cerium and yttrium earths precipitated from the filtered solution by excess of oxalic acid. The "atomic weight" of these mixed earths (by oxide-oxalate ratio¹) was 104.14. The cerium earths were almost completely removed as difficulty soluble double sulfates with sodium, $R_2(SO_4)_2 \cdot Na_2SO_4 \cdot 8H_2O$, yielding mixed yttrium earths of "atomic weight" = 100.16. It should be noted that the term "atomic weight" here signifies an indication of relative purity of material for starting, or of product, on a basis of $Y = 89$; the numerical values are used in analytical calculations of metal content of product, the components of the mixture not being separable by ordinary analytical methods.

The soluble yttrium-earth sodium sulfates were converted to chlorides, and the crystallized chlorides mixed with an equal weight of ammonium chloride and partly dehydrated at 115°. Five of the 6 molecules of water of hydration were thus removed; the removal of the sixth causes hydrolysis.² Complete dehydration was effected in an atmosphere of dry hydrochloric acid gas at 350-400°. The product was a pinkish yellow powder, melting at 850-900° to a clear amber-colored liquid, which solidified to a gray mass.

C. Matignon³ makes note of the difficulty of preparation of anhydrous yttrium chloride free from basic salt, but says nothing of the dehydration in hydrochloric acid gas. This modification of his method has been repeatedly used with success by workers in this laboratory on a small scale for atomic-weight determinations; although difficult, it can be worked successfully for large amounts. While the writer's results are in harmony with Matignon's as to the contamination of normal chloride by basic salt, they are in opposition to his finding that "Yttrium chloride is not appreciably volatile at temperatures slightly above its melting point;" in fact, serious loss resulted from this cause during some of the electrolyses. Hopkins and Balke⁴ state, in connection with the purification of yttrium chloride, that its volatility "was a matter of some concern."

Rare earth material was recovered from wastes precisely as has been described for working up gadolinite, with the exception of the separation of the cerium earths from the yttrium earths.

III. DESCRIPTION OF APPARATUS.

The final form of electrolytic cell is shown in the diagram. The cathode was made by cutting a 7-inch piece from a 6-inch cylindrical graphite electrode, and boring it to a depth of 6 inches, the inside diameter being 4 inches. In service it was lined with a thick paste of "alundum cement," which covered the inner walls completely, leaving the bottom of the cell available as cathode. This decreasing of carbon surface reduced very materially the formation of metallic car-

bides. The refractory lining was not attacked by the bath. Radiation was reduced by packing "Sil-o-cel" or sand tightly around the crucible. The anode was a graphite rod, two inches square and about two feet long, suspended and adjusted as shown. Such a device is very unlikely to fail in service, and has the additional advantage of capability of adapting new electrodes without waiting for the furnace to cool. In case of the necessity for auxiliary heating, a common Fletcher 5-inch "solid flame" burner placed beneath the cathode box answered well.

The apparatus for the final dehydration of the earth chlorides consisted of a tube of hard glass or quartz, in which the partly dehydrated chlorides were placed, connected at one end with a hydrochloric acid generator and at the other with a fume absorber. This latter was a glass tube provided with water inlets, and it efficiently prevented both hydrochloric acid gas and ammonium chloride vapors from escaping into the air.

IV. EXPERIMENTAL PART.

The decomposition of the anhydrous chlorides by metallic sodium was first attempted by slowly heating

Final form of cell used in electrolysis of yttrium mixed metal

a mixture of the two in small crucibles lined with a paste of "alundum cement" and magnesia. The results were [not] very satisfactory, owing to incomplete reaction; passing sodium vapors through fused anhydrous chlorides was even less so. The product of some of the best runs by the former method was a powder somewhat resembling zinc dust in appearance, which the lens showed to be made up of a dark gray powder mixed with white particles. The entire mass was readily soluble in acids, and the usual "atomic-weight" determinations were therefore valueless, referring to total earth metal rather than to that liberated by the reaction. These methods were abandoned.

When the decomposition was carried out *in vacuo*, the reaction mixture was placed in iron or nickel boats, and these into seamless steel tubes. After exhausting to 3-1 mm., the charged tubes were inserted in a muffle previously heated to 1,100°; the reaction took place quickly and quietly. This method was adopted as the best chemical means for decomposing the chlorides because: (1) oxidation was reduced to a minimum; (2) by-products efficiently removed; (3) ease and rapidity of manipulation. Admixed material was removed by shaking with anhydrous bromoform in a Harada separatory funnel, using anhydrous chloroform as a regulative diluent. This applies also to metal produced by electrolytic methods.

The resulting metal was a black powder, of "atomic weight" = 122.4 (original material = 104.3), and showed upon analysis:

	Per cent.
Metal ($R = 122.4$)	95.70
Iron	1.66
Undecomposed RCl	2.30
Oxygen (by difference)	0.34

The results indicate a simple and easy method for preparing such a "mixed metal" on a large scale and of relatively high purity.

In the electrolytic methods, the anhydrous chlorides (300-500 g.) were charged into the crucible cathode, and the temperature slowly raised to complete fusion, after which the electrolysis was carried out in the usual manner. During both fusion and electrolysis a stream of dry hydrochloric acid was allowed to enter the crucible; this prevented hydrolysis by atmospheric mois-

ture. The basic chlorides produced by such hydrolysis dissolve but slightly in the fused normal chlorides, as is shown by the formation of solid particles at the surface of the fused mass. These soon afterward sink, and it takes but a small quantity to render a bath viscous and unfit for further electrolysis. The addition of small quantities of common salt causes these particles to dissolve, and the bath relieves, but no good results were ever obtained after the pasty stage had once been observed. The corresponding phenomenon for cerium chloride seems not to have this ill effect.⁵

"Metal fog" was very noticeable in all electrolyses. The addition of salt, fluorspar, or calcium chloride had no remedial effect.

The "anode effect" was of quite frequent occurrence during the earlier experiments; runs in which it occurred were always worthless. Sometimes the evolution of halogen would recommence after interruption, but it was always thereafter intermittent.

Formation of carbides was also frequently noticed, until the matter of lining the crucible (except at the bottom) was worked out. In the case of baths of pure fused chloride, the carbide could only have been that of an earth metal, yet in the case where sodium or calcium salts had been added it could have been carbides of these metals. Indeed, it was always more noticeable in baths known to contain sodium, except the cryolite bath. The formation of carbides could be detected by the pungent "hydrocarbon" odor,⁶ which was very noticeable as the bath cooled down; it is thought this is due to hydrolysis of carbides by atmospheric moisture. The absence of the odor during a run or when the bath was very hot, and the presence of it when the bath had been cooling for some time, might prove that the carbides decompose at a temperature below the melting point of the bath, and that they are formed as it cools, although it could with equal propriety be concluded that they are formed at the higher temperature but not hydrolyzed until the temperature becomes low enough to permit of the action of atmospheric moisture.

A series of small scale experiments was made with the object of determining which carbon electrode caused the formation of carbides. It was found that with carbon anode and iron or nickel cathode no "carbide odor" was noticed; with a carbon anode and either metallic cathode carbide odor was frequently noticed. This shows that a carbon anode is at least partly responsible for the formation of carbides during the course of an electrolysis.

Electrolyses were carried out using a current density of 6 to 10 amperes per sq. cm. at 10 to 13 volts; the temperature varied from 900° to 1,100°, the best runs being made at about 1,000°. The yield of such runs was a black powder, exactly like that produced by the chemical method above described; the average "atomic weight" was 120, and analysis showed:

	Per cent.
Metal ($R = 120$)	94.05
Iron	1.19
RCl (undecomposed)	0.82
Oxygen (by difference)	3.94

It is thus obvious that electrolytic methods will produce a material of the sort under discussion of equal purity with chemical methods, and perhaps of lower content of undecomposed material. The disadvantage of a higher percentage of oxide (doubtless due to the high temperature and much slower cooling) is apparent; this oxide may prevent coalescence when attempts at fusion are made. Loss by volatilization of yttrium chloride at this temperature (the crucible is open) has also been referred to as a disadvantage. It was estimated that about 1,700 g. of chloride was lost by volatilization; the loss by recovery processes is very slight—less than one per cent. Some of the volatile material was condensed on a piece of glazed asbestos held over the crucible during a run; it was a yellow powder, reacting positively for rare earths, and faintly positive for iron. An "atomic-weight" determination yielded the value 52.7 for the earth present.

Another series of electrolyses was made using a solution of 50 g. of yttrium earth oxides (atomic weight (Continued on page 144))

¹Hirsch, *Proc. Am. Electrochem. Soc.*, 1911, 20, 57; Thompson, *Met. Chem. Eng.*, 1918, 17, 213.

²A strong odor similar to that given off when commercial calcium carbide is hydrolyzed. It will hereafter be termed "carbide odor" for the sake of brevity.

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³Other investigators mention isolation of yttrium (pure metal), but only as incidental to other studies. Their accounts are, in the main, conflicting. See Wohler, *Pogg. Ann.*, 1828, 15, 577; Pöpp, *Inaug. Diss. (Göttingen)*, *Pogg. Ann.*, 1864, 131, 186; Humpidge & Burnay, *Jour. Chem. Soc. (Lond.)*, 1879, 35, 115; Winkler, *Ber.*, 1890, 23, 787.

⁴The name "Yttrio-mischmetall" was originally proposed, but at the instance of Dr. C. W. Balke, it was changed to the present one, for the sake of analogy. Dr. Balke further pointed out that the term "Cerium Mixed Metal" officially means the alloy of cerium with the other cerium earth metals, as distinguished from pure cerium, and that the older term "Mischmetall" had been used to mean both, thereby resulting in confusion.

⁵*Z. anorg. Chem.*, 1905, 47, 464; *Jour. Amer. Chem. Soc.*, 1916, 38, 2338.

⁶Oral communication by B. S. Hopkins.

⁷*Compt. rend.*, 1902, 134, 308.

⁸*Jour. Amer. Chem. Soc.*, 1916, 38, 2338.