

PREPARATIONS OF THE METALS OF THE
RARE EARTH GROUP

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The extreme electropositive character of the rare earths renders the preparation of the metals a difficult one. Their isolation is rendered still more difficult by the fact that the separation of the individual members from each other is no mean task. The rare earth ores are fairly abundant, especially those in which the cerium group predominates. In fact, in the incandescent mantle industry thousands of tons of cerium group material are annually thrown away after the extraction of thorium from monazite sand. This enormous waste of rare earth material has been a great stimulus for research on the preparation of the metals.

There are in general two methods of attack in the isolation of the metals: Reduction chemically by metals more electropositive in character and electrolysis of fused salts.

The only metals which have been used more or less successfully for reduction chemically are sodium and potassium. The method has been partially successful and that only in the case of the less positive of the rare earths, namely the yttrium group. The method usually used¹ was to mix the anhydrous chloride of the rare earths with the equivalent amount of granulated sodium, placing the mixture in an iron or nickel boat in an iron tube and allowing the reaction to take place under a high vacuum. The metal obtained as a fine powder is lixiviated with a large amount of water to dissolve away the sodium chloride, undecomposed chlorides and unused sodium. The metal powder can then be fused into a coherent state in a vacuum furnace. This method would, of course, hardly be applicable in a commercial way since it would be far too expensive and slow, but it has been the means of making a study of some of the physical and chemical properties of the rare earth metals. Perhaps the greatest drawback to the method is the fact that the

1. Hicks. Jour. Am. Chem. Soc. 40, 1619.

reaction of sodium and a rare earth chloride is a reversible one, and that metallic sodium can very easily be prepared by the interaction of a rare earth metal and sodium chloride.

Electrolysis of the fused salts of the rare earths has been in commercial use for several years. This has, of course, only been applied to the production of cerium group metal or "misch metal". Several tons of misch metal have been made annually in this country alone during the late war. Considerable use of this metal was made in igniters for hand grenades, tracer bullets and trench lighters. The raw material in the production of misch metal has always been the double sodium cerium group sulfates obtained as a by-product in the incandescent mantle processes. The waste liquors after the extraction of Thorium are simply acidified with sulfuric acid, and upon the addition of NaCl the double sodium cerium group sulfates will precipitate out. The double sulfates are then converted to the rare earth hydroxides by treatment with strong hot sodium hydroxide solution and the soluble sodium salts filtered off. The hydroxides are then converted to neutral chlorides, filtered to remove any rare earth phosphates that may have formed and dehydrated. The anhydrous chlorides are electrolyzed, using a cast iron pot as cathode and a graphite rod as anode. The melting point of the bath is usually sufficiently high to melt the misch metal as fast as it is formed. The melting point of misch metal is about 750°C , well below that of the melting point of the anhydrous chloride, the latter being about 950°C . It is thus evident that in the electrolysis of the fused chlorides of the cerium group or in general any of its members, the melting point of the metal being below or near that of its anhydrous chloride, the metal is easily obtained in a coherent state. Excessively high temperatures of the bath are not necessary and there is very little volatilization of the latter. Considerable interest has been shown in the use of misch metal as a deoxidizer for cast iron,¹ steel and other alloys requiring a scavenger to clean the

1. Maldenke. *Iron Age* 105, 324 (1920).

molten metal of its dissolved oxygen. Misch metal has properties which make it quite desirable for this purpose: melting point 750°C , heat of oxidation 1740 calories per gram, and alloys with most metals are readily formed.

With respect to the yttrium group, considerably more difficulty is encountered in the isolation of the mixed metal or any of its individual members. The metals are less electropositive, it is true, but their melting points are very much higher. Yttrium is reported as melting at 1250°C , Erbium 1250°C and ytterbium as high as 1800°C , although there is some doubt with respect to the last named. These high melting points are not the greatest evil to be overcome. Most of the anhydrous chlorides of the yttrium group have low melting points as compared with those of the cerium group. Yttrium chloride melts at 680°C , dysprosium chloride at 700°C , and ytterbium chloride at 880°C . Thus in the electrolysis of the fused chlorides of this group it is impossible to obtain the metal in the fused state, and since the temperature of the bath must be maintained in the neighborhood of 1000°C there is a large loss of salt due to volatilization. It has been found that yttrium chloride is quite volatile slightly above its melting point.

Since the metals of the yttrium group are less electropositive than the cerium group and are also slightly less positive than aluminium, it has been possible to prepare the mixed metals of this group by a solution of the oxides in a molten bath of cryolite and subjecting them to electrolysis similar to that of the production of aluminium.² It is also possible to use the double fluorides of the yttrium group instead of the cryolite. By these methods there is very little loss of any material due to volatilization.

It is quite probable that most of the rare earth metals as individuals will not command a great commercial use since the isolation of their salts is a very difficult matter.

2. Hicks. Loc. cit.

In summation then there are perhaps four metals of the rare earths which will find commercial use:

Cerium, which can be separated from the cerium group with considerable ease and has already been prepared and exhaustively studied.¹

Cerium free misch metal, for which a demand will be created in time. The element cerium having two stages of oxidation is at times undesirable as a metal, and cerium free misch metal would meet this difficulty.

Cerium group metal, or misch metal which has found considerable use in pyphoric alloys as deoxidizers.

Yttrium group metal, slightly less electropositive in character but having a much higher melting point.

1. Hirsch. Trans. Am. Elec. Soc. 22, 57.